Short Communications

J. Synchrotron Rad. (1998). 5, 1317–1320

Multiple solutions in data fitting: a trap in EXAFS structural analysis and some ideas to avoid it

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(*Received 2 January 1997; accepted 16 February 1998*)

A possible source of error on interatomic distance determination in EXAFS multishell data analysis is described on the basis of fitting a simulated signal for a cluster of Rh atoms with an interaction of O atoms; a fit of an experimental signal is also presented. The origin of this type of mistake is briefly discussed.

Keywords: EXAFS data analysis.

1. Introduction

During the last decade a number of articles have been published in the field of EXAFS applied to catalysis which report exceptionally long metal—oxygen (M—O) distances (Martens *et al.*, 1988; Vaarkamp *et al.*, 1993; Purnell *et al.*, 1994; Kawi *et al.*, 1994; Koningsberger & Vaarkamp, 1995; Muñoz-Paez & Koningsberger, 1995; Zhao & Gates, 1996).

In all of these papers a series of compounds were studied and normal M—O distances were found (2–2.2 Å), except in some special cases where the determined distances were as long as 2.70 Å. In a few of the cited papers a mixing of the two kinds of M—O distances are refined together; all the EXAFS fits presented in these papers were made by using the Fourier filtering method with experimental phases and amplitudes extracted from reference samples.

We have found a very curious behaviour in these papers: each time the E_0 values are reported and a long M—O distance is found, there is a very important difference in shift of E_0 between the shell with the long M—O bond and that with the short one. The difference between the two E_0 values is in the range 10–20 eV.

There are other papers where these distances are reported (see, for instance, Miller *et al.*, 1993; Triantafillou & Gates, 1994) but the fitted E_0 values are not quoted.

Since this exceptional distance was discussed in terms of chemical properties of the catalytic systems, it is important to address the issue. Some aspects of this problem have already been discussed in EXAFS and catalysis meetings (Joyner, 1990, 1992, and references therein) and it was quoted that the above results could not be obtained by any other group working in the same field. However, the question is still open since, up to now, to our knowledge, nobody has proposed a simple explanation of these unusual results.

The purpose of this short contribution is to describe as carefully as possible one of the traps that may lead to unrealistic distance and E_0 values with apparently good fits. Although one could find this trap trivial and easy to avoid, the fact that some important EXAFS papers exhibit strange R and E_0 values stimulated us to study the issue in order to alert EXAFS users, especially the new ones.

This problem has also been briefly discussed during the data analysis session of the XAFS IX Conference, Grenoble, in August 1996, where the necessity to obtain more insight into the problem was envisaged.

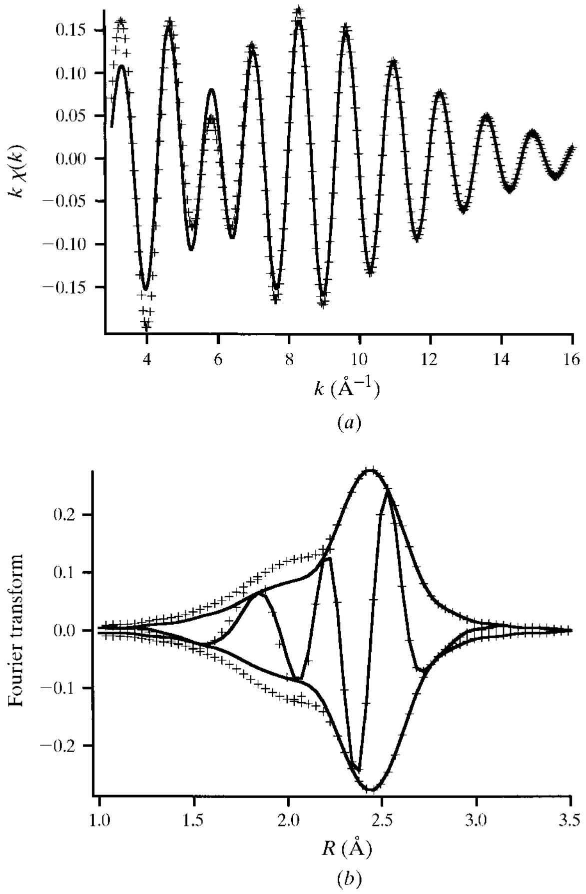
Table 1
Parameters used for the simulation.

Neighbour	N	R (Å)	σ (Å)	ΔE_0 (eV)
Rh	6	2.70	0.07	0
O	2	2.50	0.07	0

2. Methods and discussion

For this study we have chosen to simulate an EXAFS signal due to a cluster of rhodium atoms in which each central Rh atom is surrounded by six Rh neighbours at a distance of 2.7 Å and two O neighbours at a distance of 2.5 Å.

We have used the standard EXAFS formula (Teo, 1981)



(*a*)

(*b*)

Figure 1
(*a*) Simulated EXAFS signal for the Rh—Rh contribution (continuous line) and the total Rh—Rh + Rh—O EXAFS signal (crosses); (*b*) the corresponding k^1 weighted Fourier transforms (moduli and imaginary parts).

Table 2
Fitting results for the simulation.

	First 'false solution'	True solution	Second 'false solution'
N	1.9	2.0	2.3
σ (Å)	0.119	0.07	0.069
R (Å)	2.13	2.50	2.78
ΔE_0 (eV)	20.0	0.0	−23.0
ρ	5.91×10^{-3}	0	2.7×10^{-3}

$$k\chi(k) = \textstyle\sum_i (N_i/R_i^2)\exp(-2\sigma_i^2k^2)\exp[-2R_i/\lambda(k)] \\ \times |f_i(k,R_i)|\sin[2kR_i + \Phi(k,R_i)].$$

The structural parameters of the simulated curve are listed in Table 1. $|f_i(k, R_i)|$ and $\Phi_i(k, R_i)$ were taken from spherical-wave theoretical amplitude and phase functions for the Rh—Rh and Rh—O shells (McKale *et al.*, 1988). The mean free path, $\lambda(k)$, was taken to be $\lambda(k) = k/\Gamma$ (Teo, 1981) with $\Gamma = 1$ Å^{-2}.

The corresponding signal is shown in Fig. 1(*a*), together with the single Rh—Rh shell contribution. The Fourier transforms of the signals were calculated in the interval 3–16 Å. Before calculating the Fourier transform, $\chi(k)$ data were multiplied by k and a Kaiser–Bessel apodization window (smoothness parameter τ = 2.5). The moduli and imaginary parts of the Fourier transforms are shown in Fig. 1(*b*).

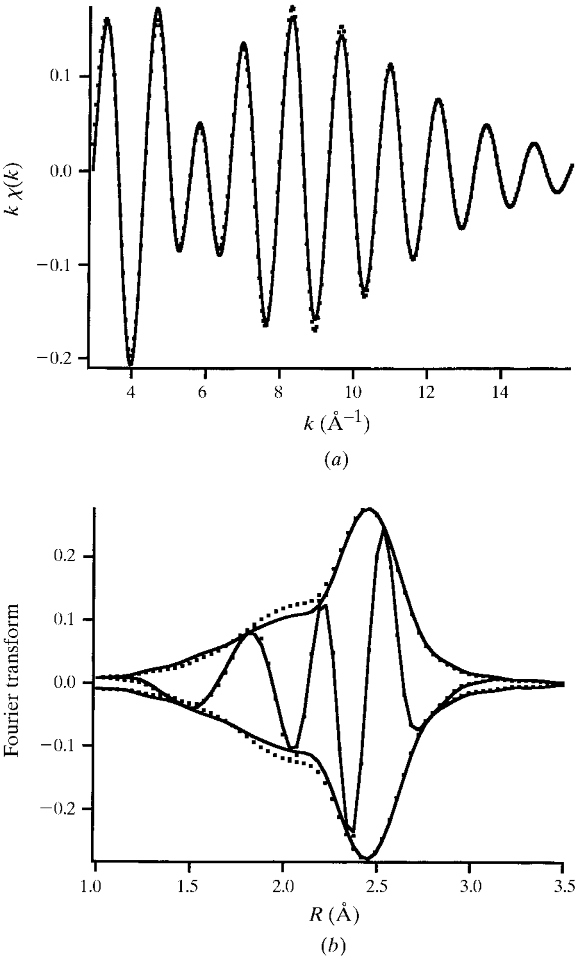


Figure 2
(*a*) Simulated EXAFS signal (dots) and fit (continuous line) with the short Rh—O distance; (*b*) the corresponding k^1 weighted Fourier transforms (moduli and imaginary parts).

The oxygen contribution is clearly visible as the shoulder on the left-hand side of the Fourier transform peak. Although this light-atom contribution is not negligible, the signal is largely dominated by Rh.

The fitting procedure was performed on the original theoretical signal (without any Fourier transform or filtering). The original theoretical curve will be called 'simulation' ($\chi_{\rm sim}$) and the curve fitted with varying parameters will hereafter be called 'fitting' ($\chi_{\rm fit}$). We used *Round Midnight*, the fitting program of the *EXAFS pour le Mac* package (Michalowicz, 1991). The Rh contribution parameters were kept fixed at the initial values while the O parameters (N, σ, R and ΔE_0) were allowed to vary. Since the present problem is not directly connected with the statistical analysis of the error bars (the simulation is purely theoretical and free from experimental noise), we used the residual ρ, where

$$\rho = \textstyle\sum k[\chi_{\rm sim}(k) - \chi_{\rm fit}(k)]^2 / \sum k\chi_{\rm sim}(k)^2,$$

as the 'best-fit' criterion.

If the starting point of the fitted parameters is chosen not too far from the theoretical solution, obviously the residual falls directly into the expected true minimum, and its value is exactly at ρ(minimum) = 0. Now, if we choose a starting point sufficiently far from this true solution, two different minima are reached, depending on the chosen starting point. The corresponding values of these fits are listed in Table 2 and the corresponding curves are

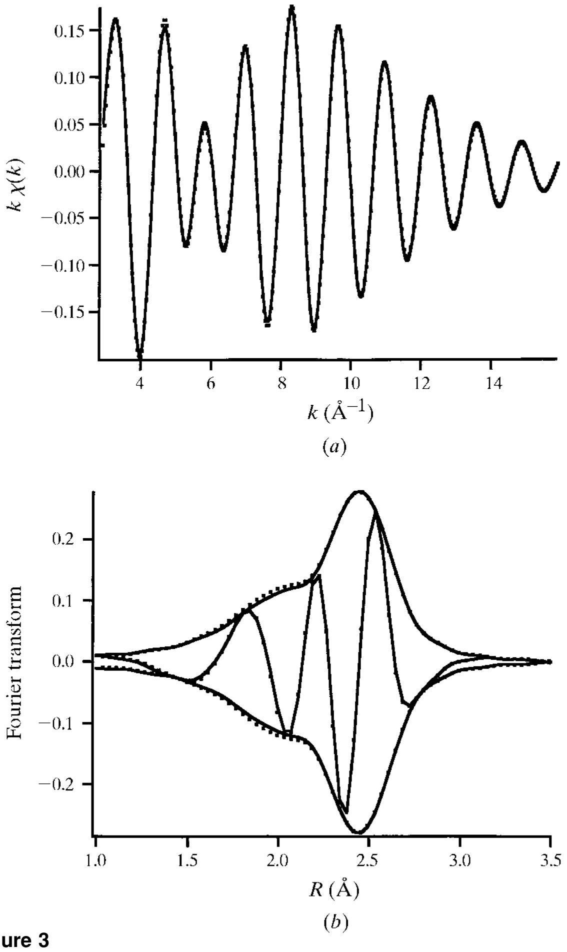


Figure 3
(*a*) Simulated EXAFS signal (dots) and fit (continuous line) with the long Rh—O distance; (*b*) the corresponding k^1 weighted Fourier transforms (moduli and imaginary parts).

displayed in Figs. 2(*a*), 2(*b*) and Figs. 3(*a*), 3(*b*). Although these two fits are obviously worse than the true theoretical solution, they look fairly good 'by eye'. The false solution with the long Rh—O distance (R = 2.78 Å) seems better than that with the short Rh—O distance. Both could be accepted as the 'true solution' prior to any discussion.

At this point it is important to understand why it is possible to find several residual minima, including the true one, and also two false solutions which are 'not so bad'.

During the fit the value of the energy threshold (E_0) was allowed to vary together with the parameters involving oxygen. We recall that this procedure is absolutely necessary while fitting real experimental signals because the experimental E_0 must always be corrected. A variation of E_0 can be understood as a phase shift of the fitted signal. One should remember that both simulation and fitting are damped sine-wave functions. Obviously the fit is perfect if the phase shift is exactly zero. If this phase shift corresponds to $\pm 2\pi$, again a good match between the simulation and the fitted curves is obtained. The values $\pm 2\pi$ correspond exactly to ΔE_0 = +20 and −23 eV found in the false fits of Table 2.

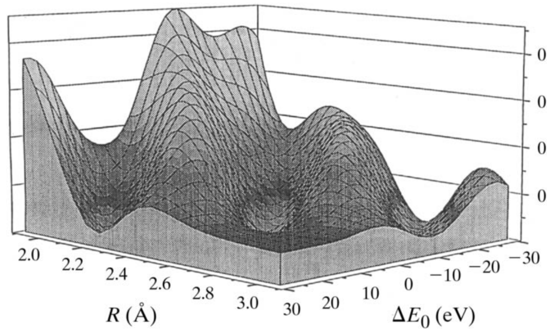
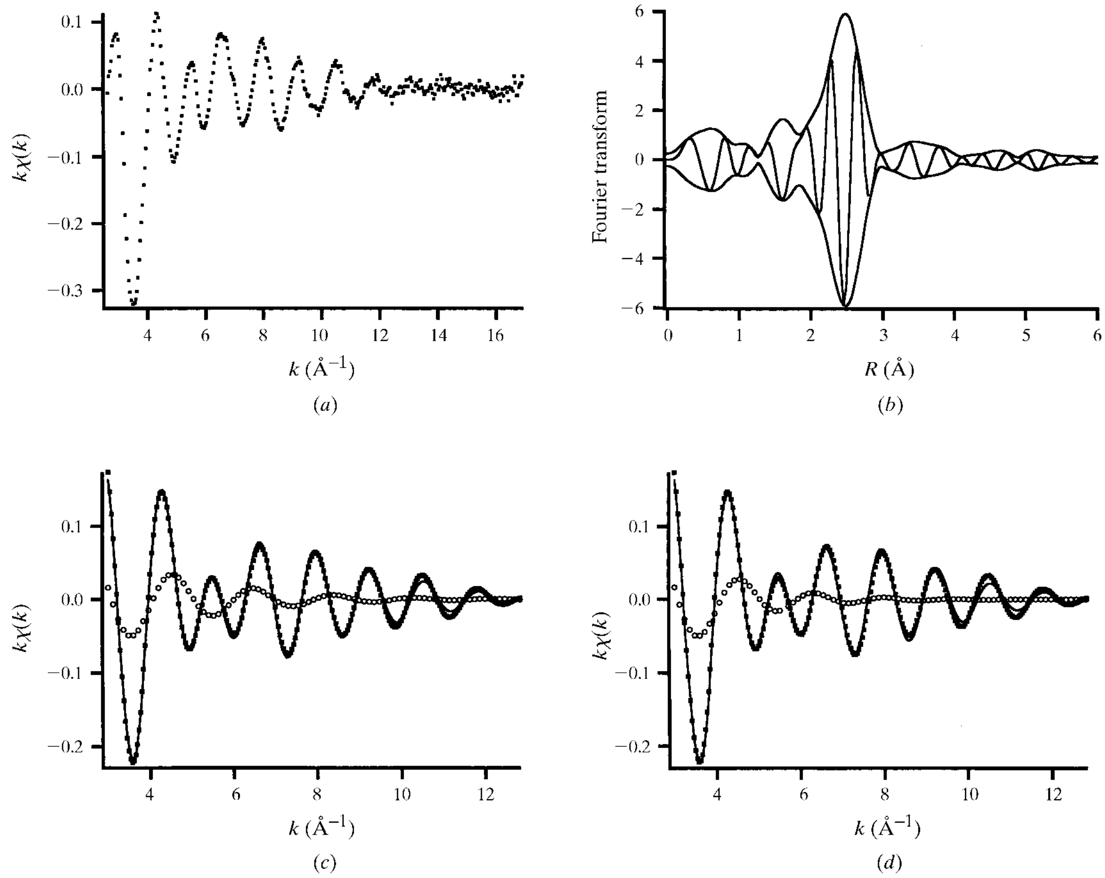


Figure 4
Plot of the residual surface $\rho(R, \Delta E_0)$.

Another way to show the position of these minima is represented by the analysis of the hypersurface $\rho(N, \sigma, R, \Delta E_0)$. We show in Fig. 4 the surface $\rho(R, \Delta E_0)$, where the values of N and σ for the O atoms are kept constant (N = 2, σ = 0.07 Å). In spite of this restriction the resulting figure is very convincing: the three minima described above are evident. Using this figure it is easy to understand that the final result depends on the starting point chosen by the user.

Quite obvious for a theoretical simulation, the 'multiple minima' trap can also be observed in true experimental spectra. The following analysis refers to an $RhCl_3$/MgO (4%wt Rh) catalyst. The sample was impregnated, calcined and only partially reduced under hydrogen. The data presented in this paper were collected at the ESRF (GILDA beamline) at the K edge of rhodium. As the reduction was only partial, this sample is a good example of an EXAFS signal containing Rh—Rh and Rh—O contributions.

We present the unfiltered EXAFS spectrum in Fig. 5(*a*) and its $k^3\chi(k)$ Fourier transform in Fig. 5(*b*). Fits on the filtered (1.27–3.00 Å region) spectrum were performed by using experimental



(*a*) (*b*)

(*c*) (*d*)

Figure 5
$RhCl_3$/MgO sample, partially reduced: (*a*) experimental EXAFS signal; (*b*) the corresponding k^3 weighted Fourier transform (modulus and imaginary part); (*c*) filtered signal (dots) and total fit (continuous line) with the Rh—O short distance (open circles show the oxygen contribution); (*d*) filtered signal (dots) and total fit (continuous line) with the Rh—O long distance (open circles show the oxygen contribution).

Table 3

Fitting results for the $RhCl_3$/MgO partially reduced sample.

	First fit	Second fit
Rh—Rh contribution		
N	7.7	7.8
R (Å)	2.74	2.74
σ (Å)	0.114	0.115
ΔE_0 (eV)	−3.5	−3.5
Rh—O contribution		
N	1.0	2.0
R (Å)	2.07	2.44
σ (Å)	0.094	0.131
ΔE_0 (eV)	3.7	−18.3
ρ	4.27×10^{-3}	8.21×10^{-3}

phases and amplitudes functions deduced from reference compounds, *i.e.* metallic Rh foil (for the Rh—Rh contribution) and Rh_2O_3 powder (for the Rh—O contribution); all the structural parameters (N, R and σ) and ΔE_0 were free to vary during the fit.

In Figs. 5(*c*) and 5(*d*) and in Table 3 we present the results of two different fits of the Rh—Rh and Rh—O contributions. The differences between the two fits lie in the starting values of the Rh—O parameters. Correlations between Rh—Rh and Rh—O fitting parameters are low: while the Rh—O results of the two fits are dramatically different, the Rh—Rh parameters are identical.

We notice that the Rh—O distance is found to be 2.07 Å or 2.44 Å and the ΔE_0 value is 3.7 eV and −18.3 eV, respectively. The variations between the two sets of values are of the same order as those obtained in our simulated spectrum (Table 2) and also very similar to the numbers found in the papers cited in the introduction.

Fig. 6 illustrates why it may be easy to fall into the 'false' minimum and why a simple visual inspection of the fits is insufficient to escape from this trap: in this figure we have plotted together the filtered experimental curve, the Rh—O contribution with the short (2.07 Å) distance and the long Rh—O contribution (2.44 Å). It appears clearly that the important difference in distances is almost compensated by the large difference in ΔE_0 in the 3–7 $Å^{-1}$ range. On the other hand, the two Rh—O signals are strongly shifted in the 7–13 $Å^{-1}$ range, but then these contributions are largely hidden by the strong Rh—Rh signal.

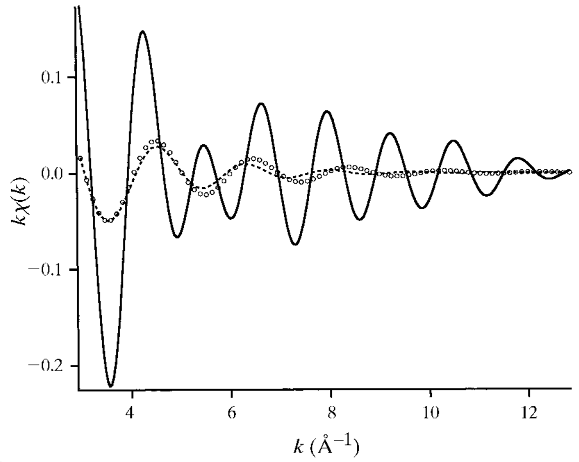


Figure 6

$RhCl_3$/MgO sample, partially reduced; filtered signal (continuous line); oxygen contribution to the total fit at the short (open circles) and long (dashed line) distance, respectively.

3. Conclusions

We should emphasize that the first part of this analysis was performed on a pure noise-free signal. Moreover, in the theoretical simulation case we have simplified the problem by allowing only the parameters describing one of the two studied shells to vary, and the ρ surface was studied only for two correlated parameters.

For the true experimental signal presented in this work we have obtained the same kind of result: the possibility to fall into a false solution is clear.

Fortunately, it is possible to follow some simple rules in order to avoid this trap.

(i) Even if theoretical phases and amplitudes functions are used in the fitted model, it is necessary to use at least one model compound in order to estimate a reasonable ΔE_0 value. In a multishell analysis, different ΔE_0 values could be used for each type of scatterer, but this should be tested on a model compound. The use of different ΔE_0 for two shells of the same absorber–scatterer pair seems to us a dangerous choice.

(ii) E_0 of the unknown compound can be varied, but only in a reasonably limited range, never 15 eV.

(iii) In the case of finding an 'exotic' absorber–scatterer distance far from known values obtained from crystal structure analysis, it is useful to explore the ρ or χ^2 surface before claiming that this distance has a chemical meaning.

In this paper we do not want to discuss if a long metal—oxygen distance could have a chemical meaning. Our opinion is that the energy shift value should be taken as the crucial criterion to decide which fit is chemically reasonable.

We do not suggest that the authors cited in our introduction are systematically wrong, but we think that their results should be reexamined taking into account our remarks.

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