

Impact of the number of fitted Debye-Waller factors on EXAFS fitting

K Provost¹, E C Beret², D Muller¹, E Sanchez Marcos² and A Michalowicz¹

¹ Equipe SAX, ICMPE UMR7182 CNRS-UPEC, Thiais, 94320, France

² Departamento de Quimica Fisica, Universidad de Sevilla, Sevilla, 41012, Spain

E-mail: provost@u-pec.fr

Abstract. EXAFS fit applied to asymmetric systems may imply the fit of parameters for many scattering paths. We illustrate on some examples how fitting too many independent DWs may lead to incorrect distances and mask some structural details. We question the physical meaning of the fitted DW values and we propose some ideas to avoid this problem.

1. Introduction

EXAFS applied to systems with asymmetric coordination spheres may imply the fit of parameters for many scattering paths. In such a situation raises the question of how to deal with the Debye-Waller factors (DWs) in the fit procedure. A usual approach consists in fitting a first DW for single scattering in the first coordination sphere and a second one for all the other scattering paths. Less usual is the fit of a unique DW for all scattering paths, which leads to a potential overestimation of amplitudes beyond the first coordination sphere [1]. In the hope to improve the fit, and in absence of external information, it stands tempting to fit as many DWs as many shells introduced in the fit procedure.

It is well-known that, in EXAFS fit procedure, amplitude parameters are highly correlated. It can be a source of unrealistic error bars or fitted values. When working on a Nitrile Hydratase model complex (FL1O2) and on platinum based anticancer drugs (figure 1), we observed that, when we fitted too many DWs, we had troubles in the structure determination [2]. The aim of this paper is to illustrate some drawbacks of a large number of fitted DWs, and to question the physical meaning of such fitted DWs in a case where the actual distance distributions are known *a priori*: the fit of average spectra issued from a molecular dynamics trajectory [3,4].

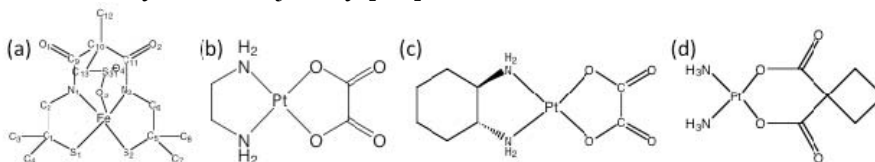


Figure 1. Structures of FL1O2(a), Edo-Pt (b), oxaliplatin (c) and carboplatin (d).

2. Experiments

2.1. Nitrile hydratase model complex FL1O2.

Pellets of FL1O2 [5] were prepared as a homogeneous mixture of pure product and cellulose. XAS spectra were recorded in transmission mode on the EXAFS13 spectrometer, at LURE-DCI, at the Fe K-edge, using a Si(111) channel-cut monochromator. EXAFS spectra were extracted using standard

procedure available in MAX [6], and fitted using phases and amplitudes calculated with FEFF [7] on the basis of the crystal structure [5] with RoundMidnight. Because of difficulties to obtain the 1st coordination sphere distances, we tested 108 fits conditions. The criteria for fit acceptance were: a fitted distance differing from the crystallographic one by less than 0.03Å, a 0.02-0.15Å range for DWs, and error bars lower or equal to the value. The detailed study will be published elsewhere.

2.2. Platinum complexes.

Experimental XAS spectra were obtained for a 10mg/ml solution of oxaliplatin, at the Pt L_{III} edge, at ELETTRA, as described in ref. [4]. They were extracted using MAX [6]. EdoPt simulated spectra were calculated on the basis of a Car-Parrinello trajectory (CP-MD) of Edo-Pt in water [3,4]. Both experimental and simulated spectra were fitted in the same conditions using RoundMidnight [6], on the basis of a 7-shell model including: 1st coordination sphere single scattering (SS) (4PtN/O), 2nd coordination sphere SS (2PtC_{oxalate}, 2PtC_{ethylenediamine}), single and multiple scattering (MS) of oxalate (2PtO, 4PtCO, 2PtCOC) and MS through platinum (4PtNPtO). We tested different amplitude parameters and different constraints on distances and DWs. In all cases, a unique distance and a unique DW are used for oxalate. We reduced the number of fitted distances from 5 to 4 or 3 by using distance shifts constraints (cf. §3.2). We tested three empirical choices for DWs fitting: (i) a unique DW for all scattering paths (1DW); a first DW for 1st coordination sphere SS and a second one for all other signals (2DW); a first DW for the 1st coordination sphere SS, a second one for 2nd coordination sphere SS, a 3rd one for oxalate, using a ratio of 2 between the 1st DW and DW for MS in the 1st coordination sphere [8] (3DW); two more choices are based on the use of CP-MD DWs (MDV: no DW fitted, MDR: one DW fitted). The detailed study will be published elsewhere.

For reaction of carboplatin and oxaliplatin with methionine, experimental XAS spectra were obtained and treated as described in ref. [1].

3. Results and discussion

3.1. Nitrile hydratase model complex

The theoretical signal calculated on the basis of the crystallographic structure [5] fits well the experimental signal (figure 2a): the fit of a global DW and an E₀ shift, without any structural rearrangement, leads to a QF=1.66 ($\sigma^2=56(3)\cdot 10^{-4}\text{\AA}^2$, $\Delta E=0.7(2)\text{eV}$). However, when the distances were fitted, among the 108 tested fit conditions, only few gave fitted distances in agreement with crystallography: 33 fits presented incorrect distances and incorrect amplitude parameters, 45 incorrect distances and correct amplitude parameters, 1 correct distances and incorrect amplitude parameters, and only 29 presented all parameters correct. When fitting a unique DW for first coordination sphere, 44% of fits were correct (100% with fitting conditions reducing the signal weight at low k), while for three DWs, 0% were correct.

Table1. Example of fit parameters for 1DW or 3DW, all other fit conditions identical

	1DW	3DW	Cryst.
R _S (Å)	2.23(1)	2.23(1)	2.22(1)
σ_S^2 (Å ²)	22(6)10 ⁻⁴	26(8)10 ⁻⁴	
R _N (Å)	1.94(1)	2.00(2)	1.95(1)
σ_N^2 (Å ²)	22(6)10 ⁻⁴	0(324)10 ⁻⁴	
R _O (Å)	1.99(2)	1.87(2)	2.00(1)
σ_O^2 (Å ²)	22(6)10 ⁻⁴	11(45)10 ⁻⁴	
QF	1.66	1.55	

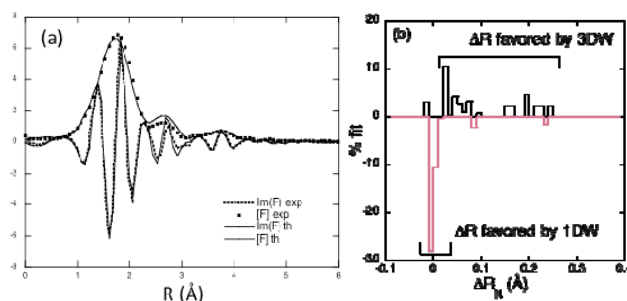


Figure 2. (a) Global fit of FL102 spectra: Fourier transform of the experimental signal and of the theoretical signal based on the crystal structure, with a global DW and a global ΔE .

(b) Histogram of distance difference $\Delta R = R_{\text{fit}} - R_{\text{crystal}}$ for FeN scattering path: $\% \text{fits}_{3\text{DW}} - \% \text{fits}_{1\text{DW}}$ as a function of ΔR .

Table 1 presents an example of fitted parameters when going from 1 to 3 DWs fitted: fitting 3DWs induces a 0.06Å increase of FeN distance and a 0.12Å decrease of FeO distance. When considering all fitting conditions, it is possible to calculate, for each shell (2 FeS, 2 FeN or 1 FeO), and each distance difference $\Delta R=R_{\text{fit}}-R_{\text{crystal}}$ value, the corresponding percentage of fits, for 1 DW and for 3DW, and to calculate the difference: $\%fit_{3DW}-\%fit_{1DW}$. Figure 2b presents the results obtained for FeN distance. Fitting 1 DW favors perfect agreement with crystallography ($\Delta R \approx 0\text{\AA}$) for all shells, while fitting 3 DW favors $|\Delta R|$ larger than 0.1Å especially for FeN and FeO distances. Thus, for FL1O2 compound, fitting three independent DWs impairs the structure determination.

3.2. Oxaliplatin and EdoPt: systematic study

Figure 3 presents the percentage of good and physically unacceptable fits for all distances constraints (a), and the percentage of fits presenting at least one incorrect distance when all distances are fitted (b), as function of the DW constraints. As long as we fit no more than two independent DWs, all percentages stand stable. But fitting three independent DWs induces a huge decrease for good fits, and an increase for unacceptable ones and fits presenting at least one incorrect distance.

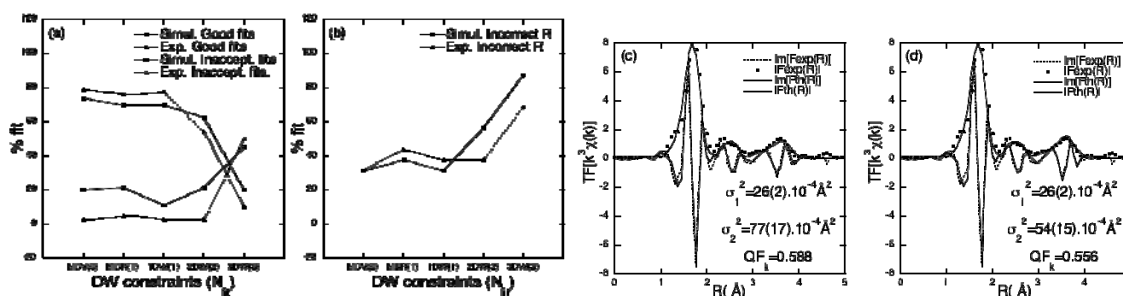


Figure 3. (a)-(b) % of good fits, physically unacceptable ones (a) and fits with incorrect distances (b) for a simulated spectrum and an experimental one. N_{fit} is the number of fitted DWs. (c)-(d): Compensation of interference effect by a 2nd DW fitted: (c) 0Å distance shifts; (d) 0.1Å distance shift.

A way to decrease the risk of obtaining wrong distances beyond the 1st shell is to apply ΔR distance shifts constraints: it is possible to fit $\text{PtC}_{\text{oxalate}}$ distance, and to set $\text{PtC}_{\text{ethylenediamine}}$ one to $\text{PtC}_{\text{oxalate}} + \Delta R$, where ΔR is fixed. A similar distance shift can be applied between the whole oxalate signal and MS through platinum. We tested two distance shifts: $\Delta R=0\text{\AA}$ corresponding to distance equality, and $\Delta R=0.1\text{\AA}$ close to the distance shifts observed in oxaliplatin crystal structure [9] and EdoPt optimized one [3]. Significant fit improvements are tested by the QF ratio $QF_{\text{max}}/QF_{\text{min}}$ which should be much greater than 1. When the systematic errors are minimized, the 0.1Å distance shift always presents a lower QF than 0Å distance shift with significant QF ratios (1.43-2.08), provided that no more than a unique DW is fitted. When 2 independent DWs are fitted, the QF ratios are much less significant (1.16-1.22). Figure 3c and 3d present the experimental and theoretical Fourier transform for a simulated spectrum, fitted with 2 DWs and distance shifts of 0Å (figure 3c) or 0.1Å (figure 3d). Changes in interference effects, between 0Å and 0.1Å distance shifts, are compensated by the 2nd DW fitted: it becomes impossible to distinguish the two structural models on the basis of EXAFS fit.

3.3. Platinum anticancer drugs degradation products by methionine.

Reaction of carboplatin and oxaliplatin with an excess of methionine leads to degradation products with PtN_2S_2 or PtN_3S first coordination sphere [1]. From the complete modeling, fitting a unique DW, we concluded that carboplatin and oxaliplatin degradation products were *cis*-Pt(Met)₂ and Pt(Dach)(Met), respectively, in agreement with other experimental and theoretical studies [1]. Table 2 presents the quality factors obtained for all the models tested. When a second DW is fitted, most fits present unacceptable distances. The QF ratios are decreased for carboplatin, and, for oxaliplatin, the fit would bring to conclude on the most chemically unlikely model: Pt(Dach)(S-Met)₂.

Table 2. QF values obtained for 1DW and 2DW. ⁽¹⁾ S-monodentate fixation of methionine; in all other cases S,N-bidentate fixation. ⁽²⁾ Fits with unacceptable distances.

		Pt(NH ₃) ₂ (Met) ₂	<i>cis</i> -Pt(Met) ₂	<i>trans</i> -Pt(Met) ₂	Pt(Dach)(Met)	Pt(Dach)(Met) ₂
CarboPt	1DW	1.82 ⁽¹⁾	0.70	0.93		
	2DW	0.61 ⁽¹⁾	0.50 ⁽²⁾	0.66 ⁽²⁾		
OxaliPt	1DW		1.32	1.34	1.03	1.38 ⁽¹⁾
	2DW		0.71 ⁽²⁾	0.70 ⁽²⁾	0.80 ⁽²⁾	0.59 ^(1,2)

3.4. Validity of the fitted DW values

When working on CP-MD based spectra, the actual distance distributions are known and it is possible to check whether the fitting procedure reconstitute the right DW values or not. Using EdoPt simulated spectra we applied this strategy. Table 3 presents the CP-MD DW values and the fitted ones. DW error bars are large for scattering paths beyond the first coordination sphere. For 3DW, they are larger than the values difference. Comparison CP-MD and fit results shows that neither 2DW nor 3DW succeed in reconstituting the right values. Lower QF values can be explained by the compensation of systematic errors by the introduction of other systematic errors.

Table 3. CP-MD and fitted DW values for an EdoPt simulated spectrum.

	CP-MD		2DW		3DW	
	σ_i^2 (Å ²)	σ_i^2/σ_1^2	σ_i^2 (Å ²)	σ_i^2/σ_1^2	σ_i^2 (Å ²)	σ_i^2/σ_1^2
1: PtN/O	0.0024	1	0.0027(5)	1	0.0026(4)	1
2-3: PtC	0.0035	1.46	0.0068(23)	2.5(6)	0.0056(16)	2.1(6)
4-5-6: oxalate signal	0.0033	1.37	0.0068(23)	2.5(6)	0.0063(17)	2.4(4)
7: MS through Pt	0.0044	1.83	0.0068(23)	2.5(6)	0.0052	2

4. Conclusion

In EXAFS fit of complexes with asymmetric coordination spheres, correlations between distances and DWs are not negligible. They may cause instabilities in the fit process resulting in physically unreasonable distances. It may happen as well in the first coordination sphere as well as beyond. In all cases tested, 3DW led to bad results. Structural interference effects related to the presence of many similar scattering paths with different distances may be compensated when a second DW is fitted. Thus fitting many DW may mask some structural details. At least, the fit procedure applied to CP-MD based spectra proves that the fit of many DW does not give a more accurate description of the system physical reality. Thus the number of independent DWs should be reduced as much as possible. Introducing theoretical external information should be a solution to reach this aim.

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