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G Smolentsev[1], **A V Soldatov**[1], **F D'Acapito**[2], **G Polzonetti**[3] **and I Fratoddi**[4]

[1] Faculty of Physics, Rostov State University, Rostov-on-Don, 344090, Russia
[2] INFM—OGG c/o ESRF-GILDA CRG, Grenoble, France
[3] Department of Physics, University of Rome 'Roma Tre', Rome, Italy
[4] Department of Chemistry, University of Rome 'La Sapienza', Rome, Italy

E-mail: soldatov@rsu.ru

Abstract
A new method of advanced quantitative analysis of x-ray absorption near edge structure (XANES) is described. The method is based on the fitting of experimental XANES data using multidimensional interpolation of the spectra as a function of the structural parameters and full multiple scattering calculations. Such an approach has several advantages in comparison with schemes that existed before, in particular a very small number of *ab initio* calculations, significant reduction of required computational time, and the possibility to see immediately the spectrum that corresponds to any set of structural parameters. A first application of the method to determine the parameters of the local geometry of a real system, namely Pd-diethynylbiphenyl, is reported. The procedure of polynomial construction is described in detail for this complex of palladium. The best-fit three-dimensional geometry obtained has the following bond distances: Pd–P 2.36 ± 0.02 Å, Pd–C 2.06 ± 0.02 Å and C–C 1.1 ± 0.03 Å, in agreement with results of previous EXAFS studies.

1. Introduction

The problem of quantitative determination of the local structure parameters from x-ray absorption near edge structure (XANES) has recently excited a great interest in the scientific community. The importance of multiple scattering (MS) contributions makes the analysis of these spectra more difficult in comparison with extended x-ray absorption fine structure (EXAFS), but more informative. In many cases XANES is very sensitive not only to bond

lengths (as is EXAFS), but also to the bond angles for the atoms, which are at distances up to 4.5–6 Å from the x-ray absorbing atom. Thus it can be used to study three-dimensional (3D) geometry, not only the radial distribution of atoms like in EXAFS. A few attempts to use analysis of XANES in the way related to EXAFS fitting have been performed and it was proposed to use a limited number of MS paths during the fitting of absorption spectra (both EXAFS and XANES starting from $k = 0$) [1]. Sometimes for crystalline compounds and minerals consisting of low-z elements it is possible to apply a Fourier filtration of XANES to extract the first coordination number and bond lengths [2]. A first approach for quantitative analysis of XANES, which uses full multiple scattering algorithms, has been proposed recently and was realized in the MXAN procedure [3]. It is based on the fitting of XANES in the space of a few structural parameters. To calculate the theoretical spectrum for given sets of structural parameters, a full multiple scattering algorithm is used. Thus, the number of such time-consuming calculations is equal to the number of points in the space of structural parameters which are necessary to minimize the difference between theoretical and experimental spectra (generally this value is about 1000 or even more). Recently we have proposed an alternative approach [4] that is realized in the 'FitIt' code.

The method was applied in the determination of the local structure around the Pd atom in thin films of poly[(4,4′-bis-ethynyldiphenyl)-*trans*-bis(tributylphosphine)-palladium(II)] metal poly-yne, Pd-DEBP, deposited onto a chromium substrate. The interest in organometalic polymers has increased recently due to their different redox, magnetic, optical, and electronic properties with respect to purely organic polymers combined with outstanding mechanical properties of classical polymers [5]. The synthesis and characterization of *rigid-rod* organometallic polymers containing diethynyl π-conjugated organic spacers σ-bonded to square planar Pd(II) or Pt(II) centres (metal poly-ynes) has been developed in recent years [5]. By following the building block approach, i.e. changing the organic spacer or the nature, geometry and oxidation state of the transition metal, a fine tuning and enhancement of their physical properties is achieved [6]. By this way metal poly-ynes become materials suitable for technological applications such as molecular sensing, optoelectronics or catalysis. Recently, the formation of molecular architectures at the nanometric scale was studied, leading to an enhanced sensitivity of the device [7, 8]. Moreover, the metal poly-yne Pd-DEBP was used recently as a membrane in surface acoustic wave sensors [8].

2. Method of calculation

The main idea of the proposed approach is to limit significantly the number of time-consuming '*ab initio*' calculations (for example, full multiple-scattering calculations of XANES) using the interpolation of the spectrum as a function of structural parameters. To fit a XANES spectrum in the space of structural parameters we first construct an energy-dependent interpolation polynomial which reproduces the theoretical spectrum for all values of parameters within some given physical limits and then we minimize the difference between the interpolated and the experimental spectra by varying the structural parameters. To construct the polynomial we use the following expansion:

$$\mu_i(E, p_1 + \delta p_1, p_2 + \delta p_2, \ldots, p_n + \delta p_n) = \mu(E, p_1, p_2, \ldots, p_n) + \sum_n A_n(E)\delta p_n$$

$$+ \sum_{m,n} B_{mn}(E)\delta p_m \delta p_n + \cdots.$$

Here $\mu_i(E)$ is the interpolated x-ray absorption coefficient, whereas $\mu(E)$ is the absorption coefficient calculated via MS. $\vec{p}^0 = (p_1, p_2, \ldots, p_n)$ is a starting set of structural parameters

and δp_n is a deviation of parameter p_n from the starting value. In many cases a small number of terms are necessary since relatively small changes of the structural parameters do not change the shape of XANES significantly. The energy-dependent coefficients $A_n(E)$, $B_{mn}(E)\ldots$ can be deduced from the results of multiple scattering calculations for certain sets of structural parameters solving a system of linear equations: $\mu_i(E, \vec{p}^k) = \mu(E, \vec{p}^k)$. In this formula $\vec{p}^k$ is the set of structural parameters which we will call interpolation node number k. The interpolated spectra $\mu_i(E, \vec{p}^k)$ contain coefficients, which have to be determined. MS calculations of spectra $\mu(E, \vec{p}^k)$ have to be performed at this stage. Interpolation is very fast in comparison with MS calculations, therefore the most time-consuming step is the determination of minimal polynomial, which is necessary to obtain good agreement between interpolated and MS calculated spectra in the whole range of structural parameter variations.

The procedure of polynomial construction consists of step-by-step testing and correction of the polynomial. Starting with the simplest polynomial, discrepancies between the interpolated and MS calculated spectra are checked for certain sets of structural parameters, which we will call 'control points'. They are selected so that the influence of the tested term of the polynomial is maximal for this set of parameters. If the modulus of maximal discrepancy between interpolated and MS calculated spectra exceeds 10% of the difference between the MS calculations for the control point and the spectrum calculated for the initial set of parameters ($\delta p_i = 0$ ($i = 1\ldots n$)), then one has to include the corresponding term into the constructed interpolation polynomial. To calculate the energy-dependent coefficient for this term a new equation corresponding to this control point is added into the system. In what follows, this control point and corresponding spectrum form an interpolation node of the polynomial. The next control points are tested using this improved polynomial. If it is found that any term is negligible in the polynomial then it is possible to reduce the number of more complex terms which have to be tested on subsequent steps, and thus reduce the number of control points that correspond with the required number of MS calculations. In particular, higher-order cross terms are negligible if they are the product of any previously neglected term and another one. A general description of the procedure of polynomial construction and tests of the method on model molecules can be found elsewhere [4].

3. Experimental details

The samples were obtained by dehydrohalogenation reaction in normal conditions [8] starting from *trans*-[Pd(PBu$_3$)Cl$_2$] as precursor complex and diethynylbiphenyl as organic spacer in equimolecular ratio. The traditional spectroscopic characterizations confirmed the formation of the metal poly-yne [9]. Details of the sample deposition procedure can be found in [10]. Experimental x-ray absorption spectra at the Pd K-edge were measured at the GILDA CRG beamline (BM08) [11] of the European Synchrotron Radiation Facility (ESRF). The monochromator was equipped with a pair of Si(311) crystals and was run in the dynamical focusing mode [12]. The harmonic rejection was achieved by using a pair of Pt-coated mirrors working at 3 mrad (cutoff energy $\approx$27 keV). Data were collected in total reflection mode in order to minimize the signal from the substrate.

4. Results and discussion

4.1. Structural model and interpolation polynomial

In Pd-DEBP polymer the metal atom is surrounded by two butylphosphine groups in trans configuration and two chains C–C–C. A cluster of 15 atoms nearest to the Pd was chosen using the criterion of spectrum convergence as a function of cluster size. Schematically this cluster
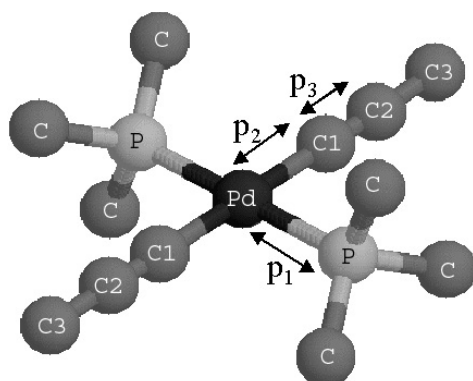
Figure 1. Pictorial view of Pd-DEBP cluster used during XANES fitting and varied structural parameters.

is shown in figure 1. To calculate XANES spectra, FEFF 8.2 package has been used [13]. Self-consistency of the muffin-tin potential has been performed for 14 atoms nearest to the Pd (but in the present case even 5 atomic cluster around Pd ion was found to give correct values of phase shifts for the photoelectron) with the Hedin–Lunqvist exchange potential. Dirac–Hara exchange was also tested, but the absorption threshold is significantly shifted from the main maximum of absorption to the low energy part (the disagreement between experimental and theoretical values is 6–7 eV, and cannot be significantly reduced by varying local structure parameters). Therefore we conclude that the Hedin–Lunqvist potential is much more accurate in the case considered. To take into account thermal and possible structural disorder, a Debye–Waller factor equal to 0.0033 Å^2 was used (this value corresponds to the average value of this parameter obtained by EXAFS for the pellet Pd-DEBP sample [10]). The influence of this parameter on the spectrum in the XANES region is very weak and the same values of determined structural parameters can be obtained without consideration of such disordering. Overlapping of muffin-tin radii was 15%. In principle this parameter can be varied, starting from the touching spheres, and it can slightly affect the results of geometry optimization. This aspect will be discussed below.

The influence of different structural distortions, the distances Pd–P, Pd–C1, C1–C2, C2–C3, and angles P–Pd–C1, Pd–C1–C2, C1–C2–C3, was tested (see figure 1). It has been found that only three parameters strongly influence the spectrum, namely p_1–Pd–P, p_2–Pd–C$_1$ and p_3–C$_1$–C$_2$ distances. These parameters were varied within the following limits based on existing crystallo-chemical information: 2.22–2.42 1.88–2.08 and 1.04–1.24 Å, correspondingly. The initial structure was constructed on the basis of x-ray diffraction data obtained for the related molecular crystal named 1c in [14].

In order to check the existence of correlations between structural parameters and the reliability of the structural parameter determination from XANES we used a recently described method [15]. It is based on the evaluation of the conditioning number $Z_q = q_1/q_3$, where q_i are the eigenvalues of the matrix Q_{ij} listed in order of decreasing magnitude. In our notation Q_{ij} can be written as

$$Q_{ij} = \sum_k A_i(E_k)A_j(E_k),$$

where the index k corresponds to the different energy points of the spectrum. The obtained eigenvalues are 0.21, 0.11 and 0.02, which corresponds to $Z_q = 10$, and therefore the considered model has significance under this criterion.

To construct an energy-dependent polynomial for interpolation of the spectra we have calculated four MS spectra for the following sets of parameters: (0, 0, 0), (1, 0, 0), (0, 1, 0) and (0, 0, 1). Here and below we use relative units for deviations of parameters: (0, 0, 0) corresponds to the structure with minimal values for all parameters; (1, 0, 0) corresponds to the maximal value for the first parameter, i.e. Pd–P distance -2.42 Å, etc. As a first approximation we interpolated the spectrum with the following linear function:

$$\mu_i(E, p_1 + \delta p_1, p_2 + \delta p_2, p_3 + \delta p_3) = \mu(E, p_1, p_2, p_3) + \sum_{n=1}^{3} A_n(E)\delta p_n.$$

Then we tested the influence of square terms for interpolations with one variable. For this purpose the following control sets of parameters were used: (0.5, 0, 0), (0, 0.5, 0) and (0, 0, 0.5). It was found that square terms slightly improve the interpolation for all the parameters, and inclusion of these terms is enough to obtain very precise polynomial. To test second-order cross terms (i.e. terms depending on more than one parameter), spectra for the sets of parameters (1, 1, 0), (1, 0, 1) and (0, 1, 1) were calculated. It was found that only the cross term between variables p_1 and p_3 is negligible. From a physical point of view this means that the contribution into XANES of photoelectron multiple scattering paths passing through Pd–P and C1–C2 legs is very weak. Therefore higher-order terms with the two parameters p_1, p_3 were not considered during subsequent analysis. Trajectories, which include couples of bonds Pd–P, Pd–C$_1$ and Pd–C$_1$, C$_1$–C$_2$, are important, and therefore the corresponding cross terms are non-zero. Thus as a second approximation we used the following polynomial:

$$\mu_i(E, p_1 + \delta p_1, p_2 + \delta p_2, p_3 + \delta p_3) = \mu(E, p_1, p_2, p_3) + \sum_{n=1}^{3} A_n(E)\delta p_n$$

$$+ \sum_{n=1}^{3} B_n(E)\delta p_n^2 + C_{12}(E)\delta p_1 \delta p_2 + C_{23}(E)\delta p_2 \delta p_3.$$

The next terms which were tested are the products of one parameter and square of another parameter. Their influence is maximal in the following points: (1, 0.5, 0), (0.5, 1, 0), (0, 1, 0.5) and (0, 0.5, 1). From the comparison of interpolated and MS calculated spectra we have concluded that such terms are important only for the two parameters p_2, p_3. Therefore we have included contributions from $\delta p_2^2 \delta p_3$, $\delta p_2 \delta p_3^2$ and tested the fourth-order term $\delta p_2^2 \delta p_3^2$ using the set of parameters (0, 0.5, 0.5). The analogous term for p_1 and p_2 was not considered since third-order terms are negligible. Finally, we obtained an interpolation polynomial, which allows us to reproduce the spectrum correctly within the selected limits of parameter variations:

$$\mu_i(E, p_1 + \delta p_1, p_2 + \delta p_2, p_3 + \delta p_3) = \mu(E, p_1, p_2, p_3) + \sum_{n=1}^{3} A_n(E)\delta p_n + \sum_{n=1}^{3} B_n(E)\delta p_n^2$$

$$+ C_{12}(E)\delta p_1 \delta p_2 + C_{23}(E)\delta p_2 \delta p_3 + D_{23}(E)\delta p_2^2 \delta p_3 + D_{32}(E)\delta p_3^2 \delta p_2.$$

4.2. Fitting of XANES

The next step of the analysis is variation of parameters and minimization of the difference between the interpolated and experimental spectra. We used the standard mean-square criterion of spectra comparison:

$$\frac{1}{E_2 - E_1} \int_{E_1}^{E_2} (\mu_i(E) - \mu_{\exp}(E))^2 \, dE$$
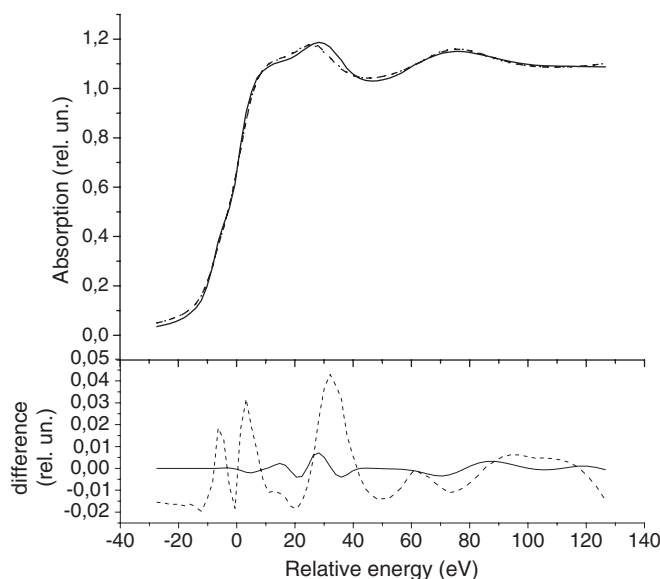
Figure 2. Top: comparison of experimental (solid), interpolated (dash) and MS calculated (dot) spectra for the best-fit set of parameters. The dot and dash curves are so close that it is difficult to resolve them by eye. Bottom: difference between experimental and MS calculated spectra (dash) and difference between interpolated and MS calculated spectra (solid).

and normalization of the spectra:

$$\frac{1}{E_2 - E_1} \int_{E_1}^{E_2} \mu^2(E)\, \mathrm{d}E = 1.$$

To find all best-fit structures we used a gradient search of minima from 20 random points within a volume of the selected parameter space. Interpolation is very fast and therefore optimization of the strategy for multidimensional minima search is not very important. The best-fit geometry was found with the following distances: Pd–P 2.36 Å, Pd–C_1 2.06 Å and C_1–C_2 1.1 Å; experimental, interpolated and MS calculated spectra for this set of parameters and differences between them are shown in figure 2.

As one can see from figure 2, the difference between interpolated and MS calculated spectra is very small and significantly less than the discrepancy between the theoretical and experimental spectra. This validates the use of interpolation during XANES fitting. As has been mentioned in section 4.1, the choice of the muffin-tin radii can slightly influence the results of the geometry determination. To test this effect all steps of the fitting were performed on the basis of calculations with 0% overlapping. This way we consider the lowest limit of MT spheres overlapping—touching spheres. For such a choice of MT radii rather close best-fit geometry with the following parameters was obtained: Pd–P 2.34 Å, Pd–C_1 2.06 Å and C_1–C_2 1.07 Å. Therefore uncertainties and corresponding error bars in interatomic distances between Pd atom and its neighbours (P or C atoms) can be estimated as up to 0.02 Å, while for other types of atoms (namely C_1–C_2) it can be up to 0.03 Å. The discrepancy between theoretical and experimental spectra is much less when the overlapping of muffin-tin spheres is 15% (0.015 in contrast to the 0.023) and therefore we suppose that the corresponding structural parameters (namely: Pd–P 2.36 ± 0.02 Å, Pd–C 2.06 ± 0.02 Å and C–C 1.1 ± 0.03 Å) are favourable. The distances found by the present XANES fitting well agree with the results of

EXAFS fitting: Pd–P 2.32 ± 0.02 Å, Pd–C_1 1.99 ± 0.02 Å and C_1–C_2 1.14 ± 0.05 Å, published previously [5].

As is clear from the analysis described above, the multidimensional interpolation of XANES spectra as a function of structural parameters allows performing XANES fitting on the basis of a very small number of MS calculations. To construct the polynomial we have calculated 15 spectra using MS theory. Only 11 of them were included as interpolation nodes in the final polynomial. This is the main advantage of the method, because it leads to a significant reduction of overall computational time in comparison with MXAN procedure [3] in which time-consuming MS calculations of the spectra need to be done at each step of the minimum search. The multidimensional interpolation approximation is quite accurate within physical limits of the structural parameters that are reasonable in this case. Calculations of the spectra within this approach are very fast and can be performed in real time; therefore one can immediately see the shape of the spectrum calculated for any set of structural parameters, using a visual interface, which is realized in FitIt software [4].

In summary, for the first time we have shown that multidimensional interpolation of XANES spectra can be used to obtain a quantitative determination of local structural parameters. A rather small number of MS calculations and a visual control of the fitting procedures are the main advantages of the present approach. The field of future applications of the method is not limited to metallo-organic compounds, and tests of other types of condensed matter systems are now in progress. The proposed interpolation approach is rather universal and can be applied not only to the XANES but also to the other spectroscopic methods to fit structural parameters. It is important that the method can also be combined with any scheme of XANES calculations, in particular with time-consuming non-muffin-tin algorithms [16], because the number of required *ab initio* calculations is very small.

Acknowledgments

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