

Full-potential XANES analysis for 3D local structure investigation of isocyanide Ni complex

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Abstract

A novel technique of 3D local structure refinement using full-potential X-ray Absorption Near Edge Structure (XANES) analysis is proposed and demonstrated in application to planar Ni complex (tetrakis-*tert*-phenyl isocyanide Ni(II) perchlorate). It can be applied to determine local structure also in other cases (like nanoclusters or nanotubes) where the muffin-tin (MT) approximation for the potential fails. The method is based on multidimensional interpolation of the XANES spectra as a function of structural parameters and ab initio full-potential calculations of XANES using finite difference method. The possibility to extract information on bond angles in addition to those accessible to standard EXAFS is demonstrated and it opens new perspectives of quantitative XANES analysis as a 3D local structure probe having nanoscale resolution.

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1. Introduction

X-ray absorption near edge structure (XANES) is a well-known technique, which can be used to probe bond lengths and angles. Only few methods for the extraction of structural parameters from XANES were developed. In particular, XANES fitting using full multiple scattering (FMS) calculations based on the muffin-tin (MT) approximation for the potential was recently applied using the MXAN [1] and FitIt [2,3] codes. Alternatively, simultaneous analysis of EXAFS and XANES taking into account limited number of multiple scattering paths sometimes gives angular-sensitive data [4]. In this paper, we present a method for local structure determination from quantitative XANES fitting on the basis of full-potential approach, which can be applied in those cases where the MT approximation used in most FMS schemes fails.

As a system for the application of the method we have selected planar complex of Ni: (tetrakis(*tert*-pentyl iso-

cyanide) Ni(II) perchlorate) Ni-isoCN. Non-MT effects could be important for the systems with large interstitial regions [5,6] or with strong covalent bonds. Considered Ni-isoCN is a system where one can expect the second type of non-muffin-tin effects due to short CN bond.

2. Method of calculation

The proposed method of local structure determination is based on quantitative XANES fitting using multidimensional interpolation approach [2] and full-potential calculations of XANES on the basis of the finite difference method [7]. The main idea is to minimize the number of required time-consuming FDM calculations using the following expansion of the spectrum as a function of structural parameters:

$$\begin{aligned} \mu_i(E, p_1 + \delta p_1, p_2 + \delta p_2, \dots, p_n + \delta p_n) \\ = \mu(E, p_1, p_2, \dots, p_n) + \sum_n A_n(E) \delta p_n + \sum_{m,n} B_{nm}(E) \delta p_m \delta p_n + \dots \end{aligned}$$

Here, $\mu_i(E)$ is the interpolated X-ray absorption coefficient, whereas $\mu(E)$ is the absorption coefficient calculated

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via FDM, (p_1, p_2, \dots, p_n) is a starting set of structural parameters, and δp_n is a deviation of parameter p_n from the starting value. The energy-dependent coefficients $A_n(E)$, $B_{mn}(E), \dots$ are deduced from the results of FDM calculations. A general description of the multidimensional interpolation and finite difference method can be found in [2,3,7], respectively. For comparative purposes, FMS calculations were also performed using FEFF8.4 code [8].

3. Results and discussion

In order to check the influence of non-MT effects on the theoretical XANES results, we have performed calculations of spectra for the same local geometry using MT FMS approach and non-MT FDM method. As one can see from comparison of curves shown in Fig. 1 both MS and FDM methods can reproduce all spectral features. Slight differences in the energy positions and relative peak intensities of the spectra, calculated using FDMNES and FEFF codes can be due to the use of alternative schemes for the construction of the potential or spectra broadening. Nevertheless, the relative intensity of C and C₁ features is also different in MS and FDM spectra obtained using the same code FDMNES (curves 3 and 4), parameters of potential and broadening factor. This difference between spectra can be due to the deviation of the potential from the MT form. Therefore for quantitative analysis of the near edge region (including first 10–15 eV of the spectrum) it is better to use full-potential scheme. Another type of non-MT effects related with non-constant potential in the interstitial region can influence more significantly on the theoretical spectra of metalloorganic compounds, but it is important for other types of systems with such regions very close to the absorbing atom, for example Ni(acac)₂ [6].

To test the sensitivity of XANES spectrum to structural parameters, we have calculated the spectra varying only one parameter (distance or angle). In this case, the trends observed in the positions of peaks and their intensities do not depend on the values of other structural parameters. As it is clearly seen from Fig. 2, all considered types of distortions influence on the spectrum. It is well known that due to the focusing effect it is necessary to consider multiple scattering paths for collinear chains such as Ni–C–N in the EXAFS analysis. Therefore, in principle, determination of Ni–C–N angle is possible from the EXAFS. Nevertheless, determination of other angles, for example C–Ni–C from the EXAFS is impossible. As one can see from Fig. 2, XANES is sensitive to the angle between the chains C–Ni–C. The effect of its variation disappears for the energies beyond 35 eV above the edge. Therefore, XANES region contains additional information on bond angles, which is almost not available in EXAFS region.

To investigate the local atomic structure on the basis of comparison of theoretical and experimental spectra, it is necessary to calculate XANES for different sets of structural parameters. If the computation method is time

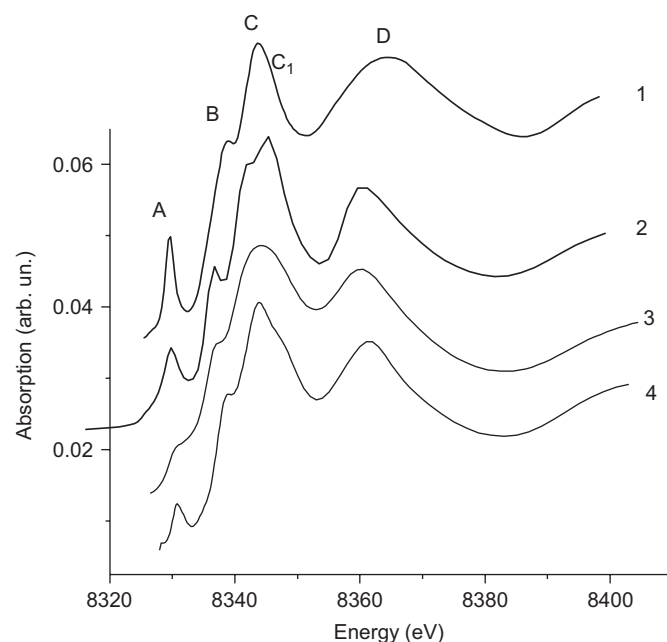


Fig. 1. Comparison of experimental (line 1), theoretical muffin-tin FMS (FEFF8.2 code) (line 2), muffin-tin FMS (FDMNES code) (line 3), and non-muffin-tin FDM (FDMNES code) (line 4) Ni K-edge XANES of Ni-isoCN for the same set of structural parameters.

consuming, as it is in the case of full-potential FDM approach, the minimization of number of such calculations is essentially important. For this purpose, we propose for the first time to combine full-potential FDM approach and multidimensional interpolation of spectra as a function of structural parameters. Such approach allows to calculate spectrum for any set of structural parameters within selected limits on the basis of a few FDM calculations for specific sets of parameters. Using strategy of interpolation polynomial construction described previously [2], we have found that polynomial with 9 interpolation nodes is sufficient to reproduce correctly theoretical results for variation within 0.1 Å variation limit for distances and 25° for angle. The following polynomial was obtained:

$$\begin{aligned} \mu_i(E, p_1 + \delta p_1, p_2 + \delta p_2, p_3 + \delta p_3) \\ = \mu(E, p_1, p_2, p_3) + \sum_{n=1}^2 A_n(E) \delta p_n + A_3(E) \delta p_3^2 \\ + B_3(E) \delta p_3^4 + C_{12}(E) \delta p_1 \delta p_2 + C_{13}(E) \delta p_1 \delta p_3^2 \\ + C_{23}(E) \delta p_2 \delta p_3^2 + D_{123}(E) \delta p_1 \delta p_2 p_3^2. \end{aligned}$$

As one can see from Fig. 3, the agreement between calculated using FDM and interpolated spectra corresponding to different random sets of parameters is quite good and all the trends are well reproduced. It demonstrates the efficiency of multidimensional interpolation approximation and opens new possibilities for quantitative XANES analysis using full-potential approaches.

In conclusion, for the first time we have demonstrated the application of multidimensional interpolation of spectra in combination with full-potential XANES

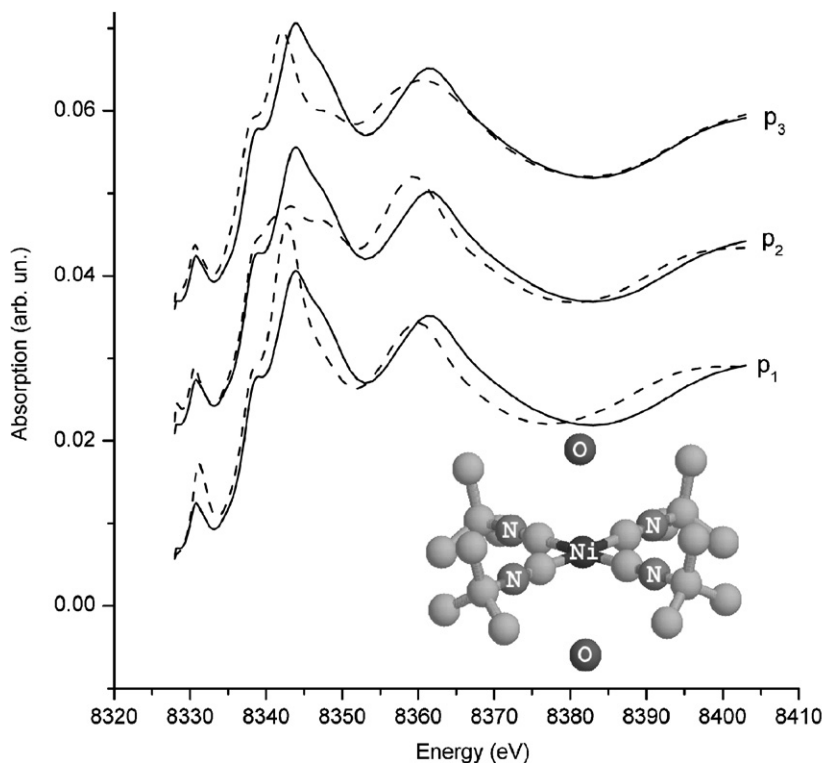


Fig. 2. Comparison of the theoretical non-muffin-tin FDM spectra calculated for initial local geometry (solid curves) and with 0.1 Å elongated Ni–C distances (p_1 , dashed curve), C–N distances (p_2 , dashed curve), and with 25° increase of C–Ni–C angles (p_3 , dashed curve). Inset: Structural model of Ni-isoCN. Only Ni, O, and N atoms are marked, other atoms are carbon.

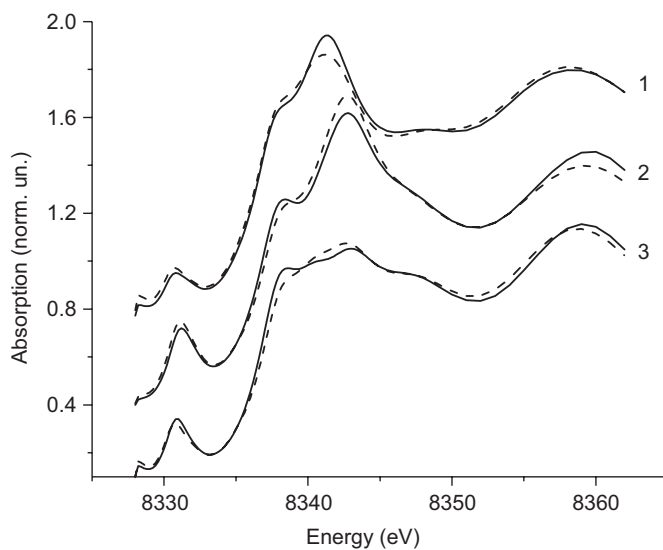


Fig. 3. Comparison of the theoretical FDM (solid lines) and interpolated (dashed lines) spectra calculated for the following sets of parameters: Ni–C, C–N distances, and C–Ni–C angles are 1.890 Å, 1.225 Å and 112.5° (lines 1), 1.955 Å, 1.175 Å and 92.5° (lines 2), and 2.000 Å, 1.235 Å and 95.0° (lines 3).

calculations, which can be applied to investigate 3D local atomic structure. The field of future applications of the method is not limited to organometallic compounds since non-MT effects can be important for different materials with large interstitial regions between the atoms and strong covalent bonds, such as for example nanoclusters, nanotubes, zeolites, and biological molecules. Consideration of non-MT effects in these systems is crucial for correct

determination of structural properties from XANES analysis.

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