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3D local structure refinement using full-potential XANES analysis

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A new technique of 3D local structure refinement is proposed and demonstrated by applying it to the metal complex $\text{Ni}(\text{acacR})_2$. The method is based on the fitting of experimental XANES using a multidimensional interpolation of spectra and ab-initio full potential calculations of XANES. The low number of ab-initio calculations required is the main advantage of the method, which allows a computationally time-expensive method using a non-muffin-tin potential to be applied. The possibility to determine bond angles in addition to bond-lengths accessible to EXAFS opens new perspectives of XANES as a 3D structure probe.

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One of the most extensively used techniques of local structure determination of materials without long-range order is Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. It allows the extraction of precise information about bond lengths and coordination numbers, but it is insensitive to the bond angles. At the same time X-ray

Absorption Near Edge Structure (XANES) can in principle be used to probe bond angles. But quantitative theoretical analysis of these spectra is much more complicated than EXAFS fitting and it has only recently become possible to develop methods for the extraction of structural parameters from XANES. 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 MXAN¹ and FitIt^{2,3} codes. Alternatively simultaneous analysis of EXAFS and XANES taking into account a limited number of multiple scattering paths sometimes gives information about angles in addition to distances⁴.

For many important applications like nanomaterials, porous solids, nanotubes, fullerenes, diluted soft matter, and biological substances, it was found important to go beyond the MT approximation for the potential. First full-potential calculations of XANES for diatomic molecule were performed by Foulis et al⁵. Recently some full-potential approaches based on band structure methods^{6 7 8}, the full-potential FMS theory⁹, and the finite difference method (FDM)¹⁰ were proposed. As band structure approaches are not well suited for 3D geometry fitting of molecules since they work in reciprocal space and require translational symmetry and non MT FMS methods are still at an early stage of development, we have used the FDM scheme for the present research.

In this Letter we present the first example of local structure determination from quantitative XANES fitting on the base 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 a complex of Ni with acetylacetonate (acacR, where R is a para-tertiarybutylbenzyl group attached to the acetylacetonate in the 3-position). It was shown recently that non-MT effects could be important for the systems with large holes or interstitial regions⁷ between atoms and sometimes in planar molecules⁹. Thus considered Ni(acacR)₂ is a system where one can expect the non-MT effects to be important ones. On the other hand the local structure of a metal complex, especially in solution, or around the metal in a metalloprotein, which is a related problem, is of broad interest since application of X-ray crystallography in this field is very limited and only X-ray absorption spectroscopy can be expected to give valuable additional and more accurate structural information based on the experimental measurements.

The proposed method of local structure determination is based on combination of quantitative XANES fitting using multidimensional interpolation approach² and *ab-initio* calculations of XANES on the basis of the finite difference method⁹. The main idea is to minimize the number of required time-consuming *ab-initio* calculations using the following expansion of the spectrum as a function of structural parameters

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

Here $\mu_i(E)$ is the interpolated X-ray absorption coefficient, whereas $\mu(E)$ is the absorption coefficient calculated 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 $A_n(E), B_{mn}(E)...$ are deduced from the results of ab-initio calculations. A general description of the multidimensional interpolation and finite difference method can be found in Ref [2-3] and [9], respectively.

The finite difference calculations were performed at order 4 with square grid and inter point distance equal to 0.25 Å. Within the small areas around atoms (with radius $r=0.65$ Å) the spherical wave expansion was used up to $l=l_{\max}+1$; $kr = \sqrt{l_{\max}(l_{\max} + 1)}$ where k is a photoelectron wave vector. In outer sphere expansion was performed up to $l=l_{\max}+5$, where l_{\max} calculated in the same way, but r is a radius of the outer sphere (4.6 Å). The convergence of spectrum as a function of cluster size was tested and it was found that after this radius the spectrum does not change. The potential was constructed on the base of simple superposition of atomic densities calculated self-consistently. The energy dependant exchange-correlation potential is obtain following the Hedin and Lundqvist approach. During FDM calculations only real part of the potential was taken into account and the spectra were then broadened using Lorentzian function with energy-dependent width. Non spin-polarized potential was used since Ni atom is in low spin state. The method was tested for related model compounds with well known structure and very good agreement between theory and experiment was obtained¹¹.

In order to demonstrate the sensitivity of the method to the bond lengths and angles we present in Figure 1 theoretical calculations of XANES based on the full potential method for different sets of structural parameters schematically shown in Fig 2.

The values of parameters are listed in Table 1. As one can see from the comparison of calculations 1 and 2, the energy separation between the maxima A and B and the intensity of shoulder C have a strong angular dependence.

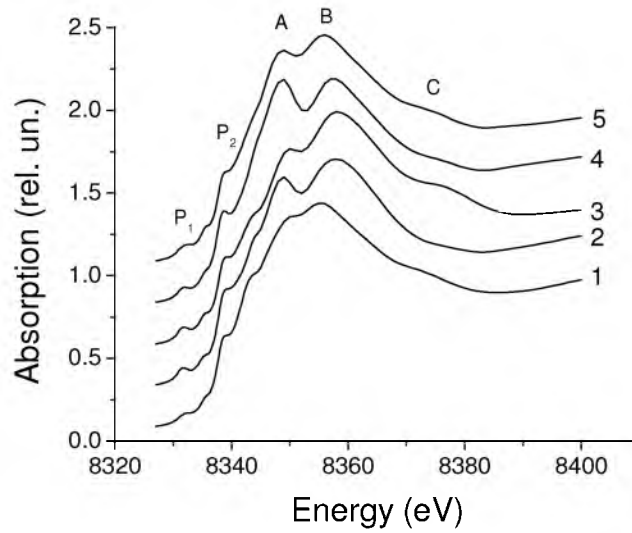


FIG. 1. Theoretical Ni K edge XANES of Ni(acacR)₂ calculated for the different structural models. The trace numbering corresponds to the sets of parameters in Table 1.

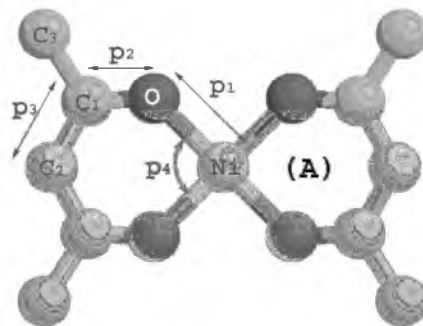


FIG. 2. Structural model of Ni(acacR)₂ used for XANES fitting.

TABLE 1. Sets of structural parameters that correspond to the calculations presented in Figure 1. Distances in Å, angles in degrees.

Set of parameters	p_1 (Ni-O)	p_2 (O-C ₁)	p_3 (C ₁ -C ₂)	p_4 (O-Ni-O)
1	1.84	1.30	1.38	80
2	1.84	1.30	1.38	100
3	1.76	1.30	1.38	90
4	1.84	1.22	1.38	90
5	1.84	1.30	1.46	90

The shape of the spectrum is also quite sensitive to the bond lengths (compare curves 3-5). The observed high sensitivity of XANES to small variations of structural parameters confirms that XANES really contains information on the full three-dimensional geometry around the absorbing atom in the X-ray spectroscopic experiment.

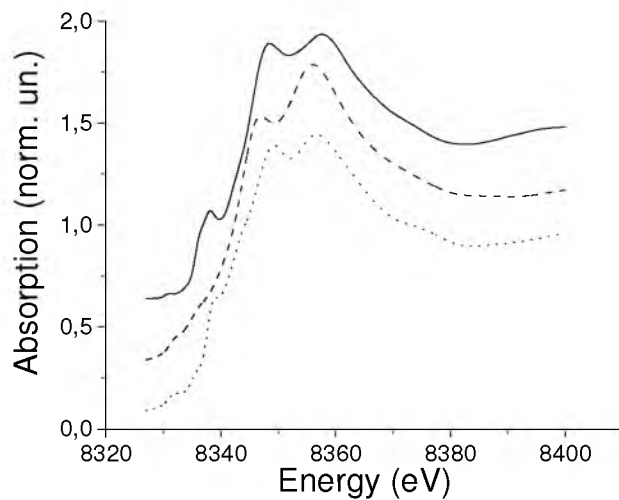


FIG. 3. Comparison of the experimental Ni K edge XANES (solid line) with theoretical MT FMS (dashed line) and non-MT FDM calculations (dotted line) spectra for the same set of structural parameters.

The comparison of MT FMS and non-MT FDM calculations (see Fig. 3) clearly demonstrates the importance of non-MT effects in the XANES of monomeric Ni(acacR)₂. This is due to the presence of large interstitial regions inside the rings (marked as A in Fig. 2) in which the molecule potential cannot be considered as a constant any more - thus one has to go beyond the MT approximation. During subsequent fitting, the structural parameters were varied within the following limits: Ni-O distance 1.76-1.92 Å, O-C₁ distance 1.22-1.38 Å, C₁-C₂ distance 1.30-1.46 Å, and O-Ni-O angle 80⁰-100⁰. The C₁-C₃ distance and the O-C₁-C₃ and O-C₁-C₂ angles were fixed to 1.49 Å, 120⁰, and 120⁰ respectively. Using the strategy of interpolation polynomial construction described elsewhere² we have found that only 21 spectra need to be calculated ab-initio to reproduce results of FDM calculations for any considered geometry.

The final step of the XANES fitting is the minimization of the discrepancy between experimental and interpolated spectra. The measurements were performed at BM26 DUBBLE CRG beamline of ESRF (Grenoble, France) at room temperature in transmission mode as described earlier¹². To compare spectra a standard mean-square deviation criterion was used. Interpolated and FDM calculated spectra for the best-fit geometry as well as experimental curve are shown in Figure 4 and the agreement between them is quite good. The slight overestimation of the intensity of the pre-edge peak is

systematic and cannot be reduced by variation of the local structure. One of the possible reasons for small differences between experimental and theoretical curves that still exist is that interaction between core hole and photoelectron is not described with necessary accuracy at nowadays status of XANES calculations¹³. The discrepancy between interpolated and FDM calculated spectra, due to uncertainties typical for a multidimensional interpolation approximation, is very small and it does not affect the results of the geometry determination. The values of the best-fit structural parameters are summarized in Table 2. The use of non-MT approach is essential to find physically-reasonable values of structural parameters. Trying to fit the spectrum within MT approximation we have found that minimum of discrepancy between theoretical and experimental spectra is situated out of the limits of variations for 2 parameters (Ni-O distance is more than 1.92 Å and O-Ni-O angle is more than 100⁰). It is due to the fact that the structural parameters variations attempts to compensate the difference between experiment and theory, which is due to non-MT effects.

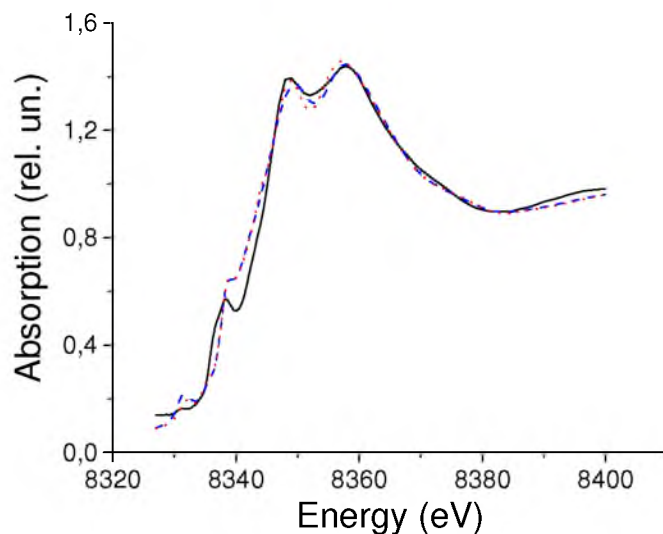


FIG. 4. Comparison of the experimental Ni K edge XANES (solid line), interpolated (dashed blue line) and FDM calculated (dotted red line) spectra for the best fit of parameters (color on line).

TABLE 2. Structural parameters obtained by different methods. Distances in Å, angles in degrees

	p_1 (Ni-O)	p_2 (O-C ₁)	p_3 (C ₁ -C ₂)	p_4 (O-Ni-O)	Ni-C ₁
XANES	1.83 ± 0.02	1.28 ± 0.02	1.39 ± 0.035	$93 \pm 1.$	2.82
DFT	1.84	1.30	1.39	95	2.81
EXAFS	1.83	-	-	-	2.78

To validate the results obtained by XANES fitting we compare them in Table 2 with EXAFS results¹⁰ as well as with results of theoretical optimization of the structure of the full Ni(acacR)₂ molecule using an all-electron DFT approach¹⁴ implemented into the ADF2005.1 code. X-ray crystallographic data for related Ni complex¹⁵ also show similar

structural parameters: Ni-O distance 1.84 Å, O-C₁ - 1.31 Å, C₁-C₂ 1.39 Å and O-Ni-O angle 94°. In DFT calculations the electronic configuration of the molecule was described by an uncontracted double- ζ basis set of Slater-type orbitals. Energies were calculated using Perdew¹⁶ and Vosko, Wilk and Nusair's¹⁷ exchange correlation potential. As one can see from Table 2 the values of bond lengths (obtained by both EXAFS and DFT methods) and angles (obtained by DFT approach), correlate well with XANES fitting results.

In conclusion, for the first time we have demonstrated quantitative determination of local structural parameters on the basis of full-potential XANES calculations. The field of future applications of the method is not limited by the metalloorganic compounds and includes various systems without long range and low-dimensional objects like nanoclusters, surfaces, nanotubes and various diluted materials, for example metalloproteins. Most such systems have large interstitial regions between the atoms and therefore consideration of non-muffin-tin effects is crucial for correct determination of structural properties from XANES. The possible limitation of the method is a huge amount of required memory (RAM) and CPU time (up to 3-4Gb of memory and 500 hours of calculations of each spectrum for cluster of 5-6 Å with 30-40 atoms without any symmetry; each symmetry operation reduce both parameters to 8 times), but it will be overcome soon with development of high-performance computers. The advantage of this spectroscopic technique in comparison with EXAFS is that it is very sensitive to the bond angles and therefore it opens a possibility for reconstruction of the 3D local geometry with high spatial resolution.

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