Quantitative analysis of XANES spectra of disordered systems based on molecular dynamics

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A general procedure which computes X-ray absorption near-edge structure (XANES) spectra starting from the individual configurations obtained from molecular dynamics (MD) simulations has been developed. This method allows one to perform a quantitative analysis of the XANES spectra of disordered systems and to estimate the effect of disorder on the low-energy region of the X-ray absorption spectra. As a test case, a Ni^{2+} aqueous solution has been investigated. The configurational averaged XANES theoretical spectrum obtained from the MD configurations compares well with the experimental data. This confirms simultaneously the reliability of the procedure and of the structural results obtained from the MD simulation.

Keywords: XANES; molecular dynamics; water solutions.

1. Introduction

X-ray absorption spectroscopy (XAS) has become an increasingly important tool for probing the local environment of atoms in both solids and liquids. Over the last years a large number of investigations have been devoted to elucidate the local structure in solid systems, while the applications of the XAS technique to the study of condensed matter lacking long-range order, such as solutions or biological systems, has been less frequent. A theoretical approach which uses pair distribution functions to model the extended X-ray absorption fine-structure (EXAFS) signal has been recently developed and successfully applied to the quantitative structural investigation of liquid systems (D'Angelo et al., 1994; D'Angelo, Barone et al., 2002). Conversely, owing to the lack of suitable theoretical tools, the modeling of the X-ray absorption near-edge structure (XANES) spectra of disordered systems has been quite crude or sometimes completely impossible.

Recently a new method (MXAN) of extracting the metrical and angular structural information available in XANES spectra has been developed (Benfatto & Della Longa, 2001). MXAN employs the full multiple-scattering (MS) theoretical approach to a description of the rising absorption edge up to about 200 eV. An iterative fitting procedure extracts information about both the geometry and the bond metrics of the nearest neighbors of the absorbing atom. This method has been successfully applied to the analysis of several systems, both in the solid and liquid state, allowing a quantitative extraction of the relevant geometrical information about the absorbing site (Benfatto & Della Longa, 2001; Benfatto et al., 2003; D'Angelo, Benfatto et al., 2002). However, all the investigated systems were characterized by the presence of short-range order, and disorder effects were essentially due to the thermal motion.

The quantitative analysis of the XANES energy range of truly disordered systems is, up to now, hampered by the lack of a suitable computational scheme which is capable of performing a reliable full-MS treatment of the low-energy range of the spectrum. A possible strategy to overcome this problem is to calculate the configurational averaged spectrum directly from the geometrical configurations generated from molecular dynamics (MD) simulations. This approach has been extensively used for the analysis of the EXAFS energy region while only qualitative applications have been performed, up to now, for the XANES spectra (Merkling et al., 2002).

The aim of this paper is to perform a quantitative treatment of disorder effects on the XANES spectra. To this end an iterative procedure which uses MXAN and MD simulations to generate a configurational averaged XANES spectrum has been developed and applied to the investigation of Ni^{2+} in aqueous solution, as a test case.

The possibility of performing a quantitative analysis of the XANES region of disordered systems is particularly stimulating as it may provide useful structural and geometrical information not accessible by other means. The success of this procedure paves the route for the XANES analysis of systems ranging from solutions to biological media.

bioXAS and metallogenomics

2. Experimental data

A 0.2 M Ni^{2+} aqueous solution was obtained by dissolving the appropriate amount of $Ni(NO_3)_2$ in water. XAS spectra at the Ni K edge were recorded in transmission mode with use of the EMBL spectrometer at DESY (Hermes *et al.*, 1984). Measurements were performed at room temperature with a Si(111) double-crystal monochromator and 50% harmonic rejection achieved by slightly detuning the two crystals from parallel alignment. Three spectra were recorded and averaged after performing an absolute energy calibration (Pettifer & Hermes, 1985, 1986). The DORIS III storage ring was running at an energy of 4.4 GeV with positron currents between 70 and 40 mA. The solution was kept in cell with Kapton film windows and Teflon spacers of 1 mm.

3. MD details

The Ni^{2+} water potential has been obtained from an *ab initio* procedure developed by Chillemi *et al.* (2002) and it has been included in the *GROMACS* package version 1.51 (Berendsen *et al.*, 1995). The simulated system consisted of one Ni^{2+} ion and 819 SPC/E water molecules. A cut-off of 12 Å was used for the pair interactions, updating the neighboring pair list every ten steps. The temperature was kept fixed at 300 K by weak coupling to an external temperature bath with a coupling constant of 0.1 ps (Berendsen *et al.*, 1984). The system was equilibrated for 50 ps and simulated for 1 ns with a time step of 2 fs. The trajectory was saved every 25 time steps for analysis, which was carried out using in-house-written codes.

4. The *MXAN* code

MXAN is a new software procedure capable of performing a quantitative analysis of the XANES data (Benfatto & Della Longa, 2001). The X-ray-absorption cross section is calculated in the framework of full MS scheme with the muffin-tin approximation for the shape of the potential; in particular, the exchange and correlation part of the potential is determined on the basis of the local density approximation of the self energy. The real part of self energy is calculated by using the Hedin–Lundqvist (HL) energy-dependent potential while all inelastic processes are accounted for by convolution with a broadening Lorentzian function having an energy-dependent width of the form $\Gamma(E) = \Gamma_c + \Gamma_{mfp}(E)$. The constant part Γ_c accounts for both the core-hole lifetime and the experimental resolution, while the energy-dependent term represents all the intrinsic and extrinsic inelastic processes (Benfatto *et al.*, 2003).

Twelve H atoms have been included as scatterer atoms in the calculations using the geometry and the orientation of each MD snapshot. The potential has been calculated using muffin-tin radii of 0.2 Å, 0.9 Å and 1.2 Å, for hydrogen, oxygen and nickel, respectively.

5. Computational procedure

In order to obtain the proper configurational average of the Ni^{2+} first-hydration-shell X-ray absorption cross section, several theoretical XANES spectra have been generated from distinct MD snapshots. At this stage only the real part of the HL potential has been used, *i.e.* theoretical spectra do not account for any intrinsic and extrinsic inelastic processes. The proper configurational average has been derived afterwards by summing all the spectra and dividing by the total number of MD snapshots used. The damping associated with the inelastic processes has to be included in the calculation in order to perform a comparison with the experimental data. To this purpose we have modified the *MXAN* program in order to read an external theoretical spectrum (the configurational averaged calculated data) and to perform a minimization in the non-structural parameter space only.

In the first step of the analysis a trajectory containing only the nickel ion and its first hydration shell has been extracted from the total MD trajectory. Each snapshot has been used to generate the correct input for *MXAN* that calculates the theoretical XANES spectrum associated with each instantaneous geometry. An iterative procedure has been implemented in order to perform an incremental average of the XANES spectra which provides the final configurational averaged theoretical spectrum.

An IBM SP3 (16× PW111@375 MHz) parallel machine has been used and the execution time for a single *MXAN* calculation was 60 s. We exploited the embarrassing parallel characteristic of the procedure to independently perform 16 *MXAN* calculations contemporaneously. The total calculation time for 9680 XANES spectra was then reduced to about 10 h. A flow diagram of this procedure is shown in Fig. 1.

6. Results

The inner hydration shell of Ni^{2+} is well known to have an octahedral structure with six tightly bound water molecules. The structural disorder within the first hydration shell is derivable from fluctuations of the water molecules around the absorber atom as determined from the MD simulations. This microscopic description of the solution enables an *a priori* estimation of the damping associated with the structural disorder which is typically expressed through the Debye–Waller factor.

An important question when dealing with the computation of spectra from MD simulations is to determine the total sampling length that is necessary to have a statistically significant average. To this end we performed an over-sampled average using 9680 configurations.

In Fig. 2 the averaged XANES spectrum is represented in comparison with an individual spectrum computed from a symmetrical first-shell cluster with Ni—O distances of 2.03 Å. The interesting fact derived from this figure is that the structural disorder has a small effect on the XANES spectrum and differences are only evident in the energy range above 25 eV in agreement with the exponential trend of the thermal
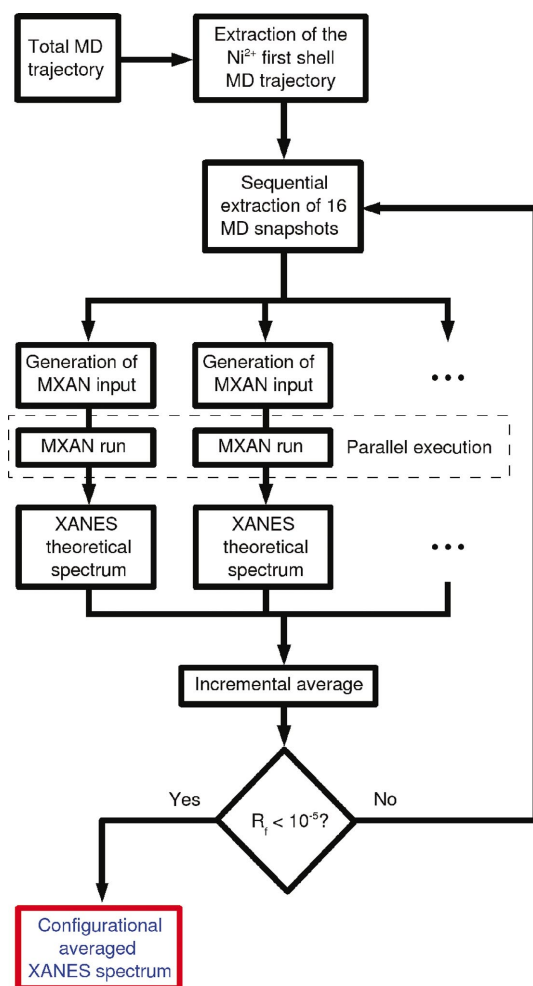
Figure 1
Flow diagram of the parallel computational procedure used to obtain the configurational averaged XANES spectrum from MD simulations.
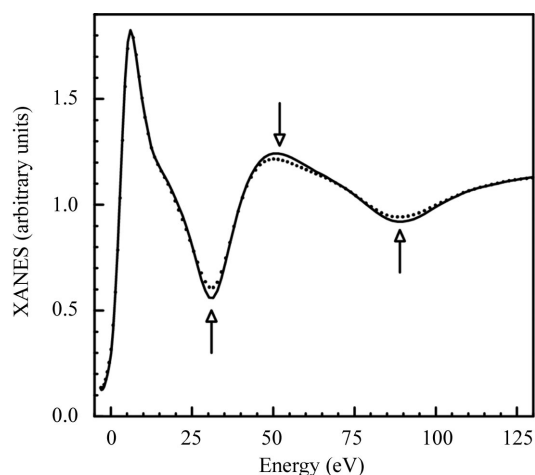

Figure 2
Comparison of the theoretical XANES spectrum (dotted line) obtained from the MD average and a single theoretical spectrum computed from a symmetrical first-shell cluster (solid line).
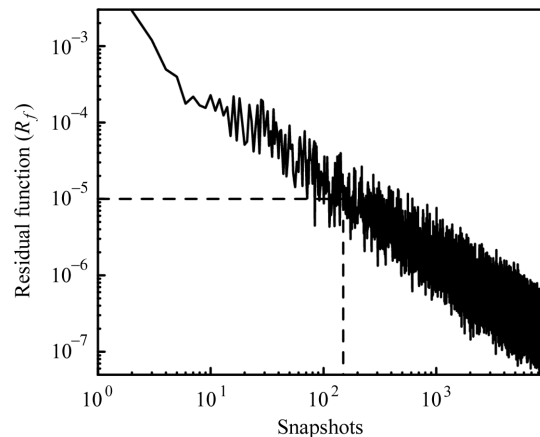
Figure 3
Residual function $R_f(N)$ of the XANES averaged spectra as a function of the number of DM snapshots.

damping factor. This result is not surprising as the Ni^{2+} ion forms a quite stable hydration complex and fluctuations of the first-shell water molecules are due to the thermal motion only. In the case of alkali metal ion aqueous solutions, where the mean-residence time of water molecules in the first hydration shell is very short, the hydration sphere is highly diffuse and poorly defined, and the corresponding damping effect is expected to be much stronger.

In order to determine the minimum number of MD configurations which are necessary to provide a correct sampling, we have carried out a statistical treatment of the data. In particular we have calculated a residual function defined as

$$R_f(N) = \left\{ \sum_i \left[\alpha^N(E_i) - \alpha^{N-1}(E_i) \right]^2 \right\}^{1/2}, \qquad (1)$$

where $\alpha^N(E_i)$ is the theoretical spectrum averaged over N snapshots and the sum is extended over all the energy points E_i.

When the $R_f(N)$ value is smaller than 10^{-5}, the corresponding averaged XANES spectrum is practically coincident with the spectrum averaged over 9680 configurations. Thus, for this system, 130 configurations is the lower limit that is necessary to have a statistically significant average (see Fig. 3). The determination of the actual number of DM configurations which are necessary to have a correct sampling is very important when a bigger number of atoms are used in the XANES calculations.

In Fig. 4, XANES spectra of two individual instantaneous structures of the simulations are compared with the averaged spectrum. The corresponding geometries of the Ni^{2+} hydration clusters are shown in the upper part of the figure. It is interesting to observe that the small distortions of the complex due to the thermal motion give rise to small differences in the XANES spectra. It is important to outline that, when the second hydration shell contribution is included in the calculation, the differences are expected to be more important.

In order to compare the MD averaged XANES spectrum with the experimental data, all inelastic processes have to be accounted for. To this end the theoretical averaged spectrum has been convoluted with a broadening Lorentzian function
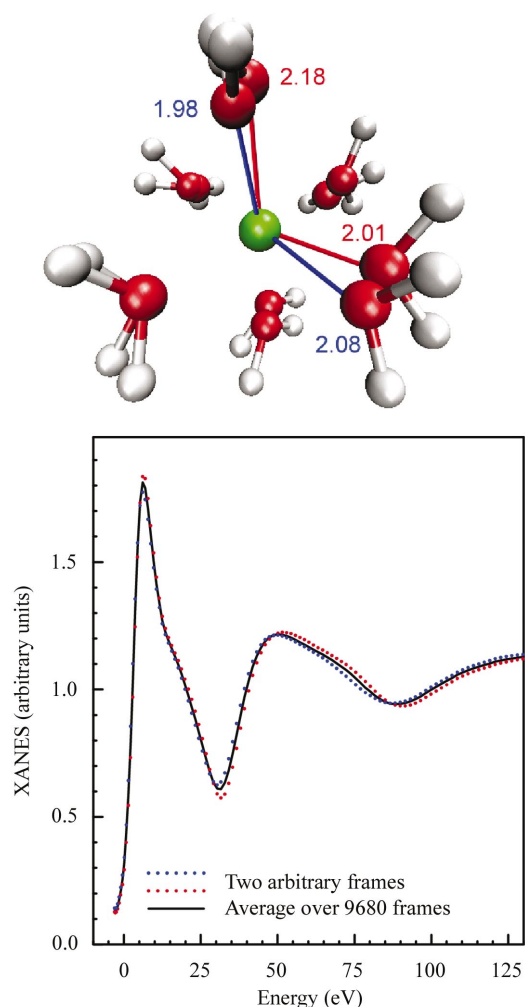
Figure 5
Comparison between the average theoretical XANES spectrum (solid line) and the experimental data (dotted line) of Ni^{2+} in water solution.

The very good agreement between the experimental and theoretical data show that both the structural configurations obtained from the MD simulations and the theoretical scheme implemented are reliable.

7. Conclusions

We have developed a general procedure to calculate a configurational averaged XANES spectrum directly from the geometrical configurations generated from MD simulations. Theoretical XANES spectra have been calculated with the *MXAN* code and the procedure has been applied to a Ni^{2+} aqueous solution. A parallel execution of *MXAN* has been performed allowing a substantial reduction of the calculation time. The averaged XANES theoretical spectrum reproduced perfectly the experimental data confirming simultaneously the reliability of the procedure and of the structural results obtained from the MD simulation. The effect of disorder on the amplitude of the XANES region of the absorption spectra has been quantitatively determined. Our procedure allows the analysis of the XANES spectra of disordered systems ranging from liquids to biological media. For biological and complex systems, where the number of atoms is expected to be big, this procedure becomes very computationally demanding and the parallel procedure is mandatory.

Figure 4
Individual XANES spectra (dotted blue and red lines) computed from different snapshots compared with the averaged spectrum (solid black line). In the upper part, the hydration complex geometries of the corresponding snapshots are shown.

and the non-structural parameters have been optimized. The resulting averaged XANES theoretical spectrum is compared with the experimental data in Fig. 5. The overall agreement of the two spectra is excellent even if the first rising peak of the theoretical spectrum is slightly over-damped as compared with the experimental data. Moreover, the shape of the hump at about 20 eV is not completely reproduced. The origin of these discrepancies has been investigated and it has been found to arise both from the shape of the potential used in the calculations and from the exclusion of the second hydration shell.

Recent EXAFS studies on metal transition ions in aqueous solutions have indicated that there is a small but measurable scattering contribution from nearby H atoms (D'Angelo, Barone *et al.*, 2002). Moreover, it has been shown that the exclusion of the H atoms affects the quantitative analysis of the XANES region resulting in shorter first-shell distance values (D'Angelo, Benfatto *et al.*, 2002). In this analysis the inclusion of the hydrogen contribution has been found to be important to correctly reproduce the experimental spectrum.
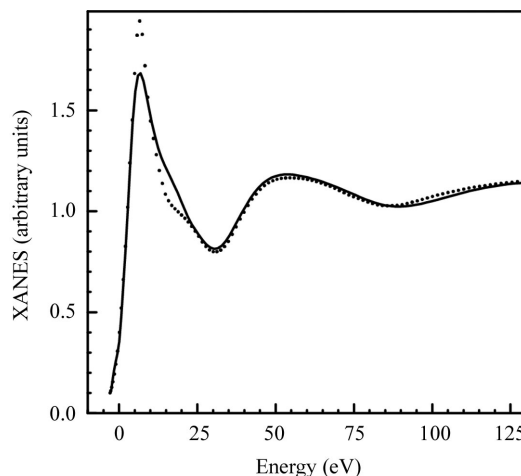
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