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Determination of two- and three-body correlation functions in ionic solutions by means of MD and EXAFS investigations

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The solvation structure of Sr^{2+} ions in acetonitrile has been studied by x-ray absorption spectroscopy (XAS) and molecular dynamics (MD) simulations. The extended x-ray absorption fine structure (EXAFS) above the Sr K-edge has been interpreted in the framework of the multiple scattering (MS) formalism and, for the first time, clear evidence of MS contributions has been found for non-complexing ions in solution. Molecular dynamics has been used to generate the partial pair $g(r)$ and the three-body $g(r_1, r_2, \theta)$ distribution functions from which a model χ(k) has been constructed. An excellent agreement has been found between the theoretical and experimental data. This result demonstrates the ability of the XAS technique in probing three-body correlation functions in solutions.

Keywords: Sr^{2+} ion EXAFS, three-body correlations, multiple scattering, disordered systems, acetonitrile.

1. Introduction

The local structure of ions dissolved in aqueous and non-aqueous solutions has been extensively studied by means of x-ray absorption spectroscopy (D'Angelo *et al.*, 1996a, 1996b, 1996c, 1997, Filipponi *et al.*, 1994, Roccatano *et al.*, 1998). This technique offers the unique opportunity to probe the local coordination of ions in solution. Whereas pair correlation functions can also be obtained by x-ray and neutron diffraction, information on higher order correlation functions can only be extracted from the XAS data. The presence of these contributions appears in the XAS spectra as multiple-scattering effects whose quantitative analysis allows the presence of angular correlation in the solvent to be investigated. The importance of accounting for the MS effects in XAS spectra of transition metal ions in aqueous solution has been pointed out in several papers (Benfatto *et al.*, 1986, D'Angelo *et al.*, 1997, Filipponi *et al.*, 1994). In this case highly stable octahedral or tetrahedral hydration complexes are present in solution and the MS effects are associated with the first hydration shell.

Alkaline and alkaline earth ions give rise to a non-regular coordination in aqueous and non-aqueous solutions (D'Angelo *et al.*,1996b, 1996c, Roccatano *et al.*, 1998). Nevertheless, in some cases the presence of three-body correlation functions can still be detected. Here we present an extended x-ray absorption fine structure study of a dilute Sr^{2+}-acetonitrile solution with the aim of determining the presence of MS contributions. Due to the linearity of the acetonitrile molecules three-body distribution associated with the first and the second Sr^{2+} coordination shells may be present in solution. Sr^{2+}-acetonitrile pair and three-body distribution functions obtained from molecular dynamics simulations have been used as relevant models in the calculation of the total χ(k) signal which has been compared to the EXAFS experimental data. This procedure has allowed us to determine from the EXAFS data the three-body correlation functions describing the molecular associations existing in the solution.

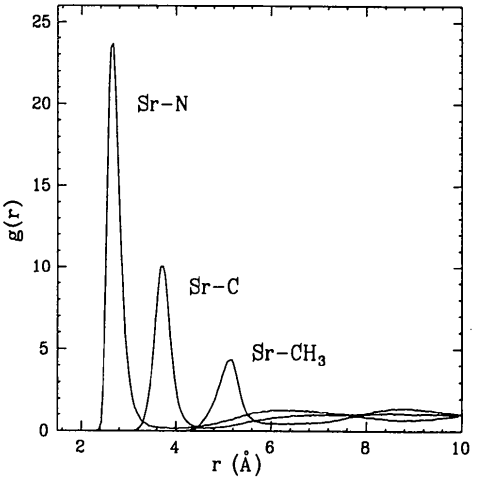

Figure 1
Sr-N, Sr-C and Sr-CH_3 radial distribution functions as derived from MD calculations.

2. Experimental details

2.1. EXAFS measurements

A 60 mM Sr^{2+} acetonitrile solution was obtained by dissolving the strontium trifluoro methansulfonate, prepared as described by Hedwing *et al.* (1974), in acetonitrile. EXAFS spectra at the Sr K edge were recorded in transmission mode using the EMBL spectrometer at HASYLAB (Hermes *et al.*, 1984). Measurements were performed at room temperature with a Si(220) double-crystal monochromator (Pettifer *et al.*, 1986). Three spectra were recorded and averaged after performing an absolute energy calibration (Pettifer *et al.*, 1985). 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 a cell with a 7 mm Teflon spacer and Kapton film windows.

2.2. Molecular dynamics computational procedure

The MD simulations have been carried out using a three-site acetonitrile model (Edwards *et al.*, 1984). MD simulations have been performed using an isothermal-isocoric simulation algorithm (Berendsen *et al.*, 1984). The system consisted of a Sr^{2+} ion surrounded by 215 acetonitrile molecules in a cubic box 26.4 Å side length with periodic boundary conditions. The box dimensions were chosen to reproduce the density of the liquid acetonitrile. The Lennard-Jones parameters used in the present paper for Sr^{2+} were reported by Åqvist (1990). All the MD runs were performed using the program package GROMACS (van der Spoel *et al.*, 1994). The SHAKE algorithm was used to constrain bond lengths of the acetonitrile model. After the initial minimization of the system, the MD simulations were performed. The first 100 ps were used for equilibration; they were followed by 1 ns that was used for the analysis. The time step used was 2 fs. The temperature was kept constant at 300 K by weak coupling to an external temperature bath with a coupling constant of 0.1 ps. The

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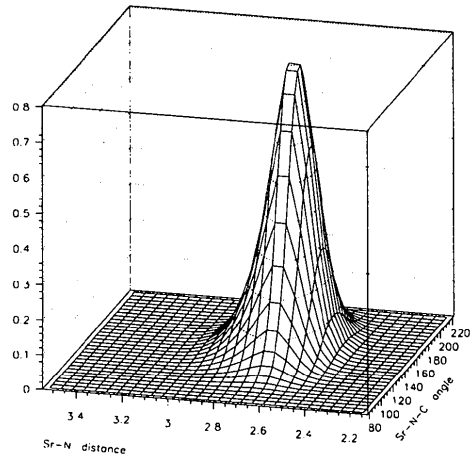

Figure 2
Representation of the three-body probability distribution of the Sr-N-C triangles as derived from MD calculations.

Sr^{2+}-acetonitrile pair distribution functions $g(r)$ were averaged over 1 ns after the equilibration of the simulation. The Sr-N, Sr-C and Sr-CH_3 radial distribution functions are reported in Fig. 1. They show very sharp and well defined first peaks. The sharpness of the peaks indicates the presence of a well organized first solvation shell. The first maxima of the Sr-N, Sr-C and Sr-CH_3 radial distribution functions are at 2.65, 3.70 and 5.12 Å, respectively. The number of acetonitrile molecules in the first solvation shell has been found to be 9.0. The three-dimensional arrangement of the linear acetonitrile molecules around the Sr^{2+} ion has been determined on the basis of the MD calculations. The analysis of the three-body distributions has been carried out on 20000 configurations which were taken from the trajectory every 0.1 ps. The orientation of the acetonitrile molecules has been obtained from the analysis of the Sr-N-C and N-Sr-N triangular configurations with a w=$1/r_1 r_2 sin\theta$ weight. Three-dimensional representations of the Sr-N-C and N-Sr-N distribution curves are reported in Figs. 2 and 3, respectively. In the former case only the Sr-N distance R_{Sr-N} and the Sr-N-C angle θ are shown as the N-C distance is equal to the N-C acetonitrile bond length (1.17 Å). The distribution curve shows a well defined peak with a maximum at $\theta = 163°$ and R_{Sr-N}=2.65 Å. In the latter case the N-Sr-N angle θ and one of the two symmetric Sr-N distances are reported. In this case the distribution curve shows two peaks with maxima at $\theta = 73°$ and 138° and R_{Sr-N}=2.65 Å.

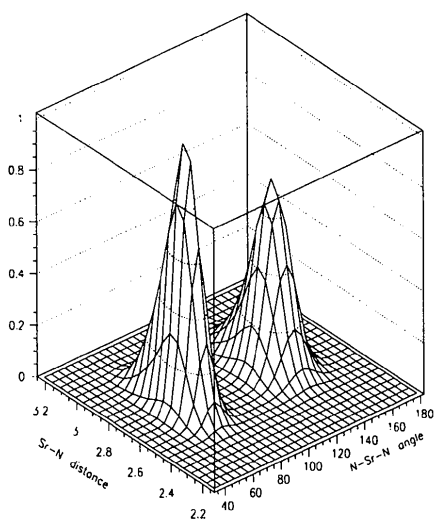

Figure 3
Representation of the three-body probability distribution of the N-Sr-N triangles as derived from MD calculations.

3. Results and discussion

A method which uses MD radial distribution functions as relevant models in the calculation of the EXAFS structural signal of disordered systems has been employed to study the solvation shells of several ions in solution (D'Angelo *et al.*, 1994, 1996a, 1996b, 1996c, Roccatano *et al.*, 1998).

It has been shown that a thorough insight into the interpretation of the EXAFS from liquid matter can be obtained by this method. The first step of the analysis involved the calculation of the χ(k) theoretical signal starting from the Sr-N, Sr-C and Sr-CH_3 pair distribution functions obtained from the MD simulations, only. A fitting procedure has been applied to optimize the agreement between the experimental and theoretical data. The fit analysis of the EXAFS spectrum performed in the range k=2.9-15.0 $Å^{-1}$ is shown in Fig. 4. Note that the presence of double-electron excitations in the Sr absorption background has been accounted for in the extraction of the χ(k) experimental spectrum (D'Angelo *et al.*, 1996b). The agreement between the theoretical and the experimental signals is not satisfactory, especially in the low-k region of the spectrum. The amplitude of the residual curve is very large and above the noise level of the experimental data, with a leading frequency which corresponds to a path length of about 3.8 Å. The origin of the residual signal has to be ascribed to the presence of three-body (or higher) correlation functions describing the short lived association existing in the Sr^{2+}-acetonitrile solution. Proof of the importance of the three-body contributions has been obtained by applying a fitting procedure to the experimental spectrum, including the MS contributions.

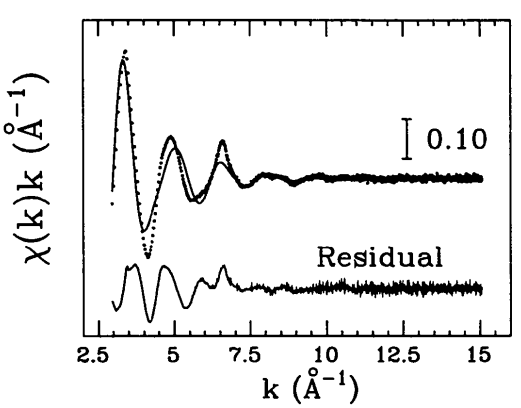

Figure 4
EXAFS experimental spectrum of Sr^{2+} in acetonitrile (dots) compared with the χ(k) theoretical signal (line) not including the MS contributions.

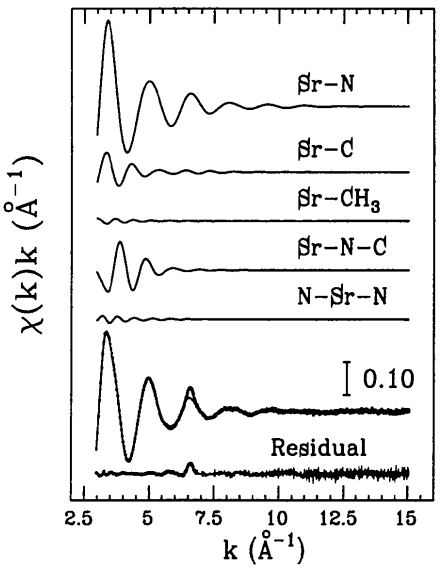

Figure 5
EXAFS experimental structural signal of Sr^{2+} in acetonitrile (dots) compared with the $\chi(k)$ theoretical signals derived from the MD simulations. From top to bottom the following curves are reported: Sr-N, Sr-C and Sr-CH_3 two-body signals, Sr-N-C and N-Sr-N three-body signals, sum of the above curves compared with the experimental data and residual curve.

The three-body signals associated with the Sr-N-C and N-Sr-N triangular configurations have been calculated by means of the GNXAS program (Filipponi *et al.*, 1995). Least-squares fits of the experimental spectrum have been performed starting from the results of the MD simulations and refining the two-body distribution average distances and the distances, angles and vibrational amplitudes of the three-body configurations. Moreover, two empirical parameters have been refined: S_0^2 which accounts for an overall intensity rescaling and E_0 which alignes the experimental and theoretical energy scales. The results of the fitting procedure including the MS contributions are shown in Fig. 5. The first five curves from the top correspond to the Sr-N, Sr-C and Sr-CH_3 two body-signals, and to the Sr-N-C and N-Sr-N three-body contributions calculated from the MD distributions. The lower part of the figure shows the total theoretical contribution compared with the experimental data and the resulting residual. The agreement between the experimental data and the theoretical signal is excellent and the residual curve contains experimental noise only. From Fig. 5 it is evident that the Sr-CH_3 and N-Sr-N signals are very small, even if they are both above the noise level of the spectrum. However, the inclusion of these two additional signals in the minimization procedure provides a significant improvement, as deduced from the statistical F test. It is important to stress that the stronger MS contribution is associated with the Sr-N-C three-body distribution while the N-Sr-N MS signal is very weak and is due to the peak centered at $\theta = 138°$ (see Fig. 3).

Note that the residual curve of Fig. 4 contains a frequency component which is similar to the Sr-N-C MS signal, even if the amplitudes of the oscillations are slightly different. This discrepancy is mainly associated with a different extraction of the $\chi(k)$ experimental signal.

From the results of this analysis it is clear that the inclusion of the MS signals is essential to properly reproduce the experimental data. The three-body contributions are particularly important in the k region < 4.5 Å^{-1}. This is the first direct experimental evidence of the presence of triangular configurations involving the first and second coordination shells in ionic solutions.

This study demonstrates that the combined use of MD simulations and EXAFS experimental data allows the detection of the local arrangement of the linear acetonitrile molecules around the Sr^{2+} ion. The results of the present investigation provide a guideline for the correct structural analysis of the three-body correlation functions present in ionic solutions.

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