EXAFS and molecular dynamics studies of ionic solutions

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This paper focuses on recent advances in the X-ray absorption spectroscopy (XAS) analysis of ionic solutions. The asymmetry of radial distribution functions $g(r)$ associated with the solvent molecules surrounding the ions has to be taken into account to perform a reliable structural analysis. Molecular dynamics (MD) simulations provide reliable $g(r)$'s which can be used as starting models in the XAS data analysis. The combined MD-XAS investigation reduces meaningfully the indetermination of the structural parameters, especially for coordination numbers and Debye–Waller factors. Double-electron excitation channels can be present in the XAS spectra of ionic solutions and they have to be accounted for in the background extraction. The ability of the XAS technique to probe three-body correlation functions in ionic solutions with the aid of MD $g(r_1, r_2, \theta)$ has been shown. The analysis of the low-k region of the spectra allows the detection of a weak but significant hydrogen structural signal. The XAS technique is especially well suited to determine the detailed shape of the nearest-neighbor peak in the atom–atom pair correlation functions of disordered systems. The information that they contain about the short-range atom–atom pairwise interactions can be very helpful for specifying and properly modifying model potentials used in MD simulations.

1. Introduction

Solvation is important for many chemical properties of ions in solution and nowadays it is well recognized that a correct description of ionic solutions requires a precise knowledge of their geometrical structure. Several classical methods, such as X-ray and neutron diffraction, have been applied to the investigation of ion solvation (Magini *et al.*, 1988; Ohtaki & Radnai, 1993) but there remains considerable confusion in the detailed understanding of the structure of solvated ionic species – in principle as a result of the wide scatter in established results in the literature and a general lack of direct information relating to static and dynamic properties of solvent molecules when they coordinate ions.

The increasing interest in characterizing disordered systems has stimulated the development of complementary techniques. Among these, XAS has acquired a central role due to its atomic selectivity. In fact, for an N-component system, the radial distribution function $g(r)$ extracted from the XAS signal contains the overlap of N independent pair distribution functions, against the $N(N + 1)/2$ correlation functions overlapped in the X-ray diffraction data. Moreover, samples with a low photoabsorber concentration can be studied using the XAS technique and a good discrimination of the atomic species can be performed when the scattering amplitudes and phases of the surrounding species are different. Extended X-ray absorption fine structure (EXAFS) displays a good resolution in detecting the near-neighbor environment, but suffers by the lack of low-k data. In disordered systems, owing to the broad correlation functions towards the large distances and to the mean free path of the photoelectron, the information concerning long-range order is dropped from EXAFS spectra. This limits the accessible k range which is essentially insensitive to the second shell that is lessened, relative to the first, much faster as k increases. If the pair distribution function is Gaussian, the loss of low-k data does not affect the accuracy of the structural parameters but it can cause errors for asymmetric distributions (Crozier *et al.*, 1988). In the case of ionic solutions, the radial distribution functions associated with the solvent molecules are not Gaussian in form and the neglect of this asymmetry in EXAFS data analysis leads to unreliable results, *i.e.* interatomic distances and coordination numbers are underestimated (Crozier *et al.*, 1988; D'Angelo *et al.*, 1994).

Recent reviews have pointed out the remaining major problems in XAS analysis of liquid systems: the need to account for asymmetric distributions, the extraction of the XAS $\chi(k)$ signal from the absorption background, the availability of a narrow k range, the presence of multiple scattering (MS) effects in the spectra (Crozier, 1995, 1997). In this paper we will address these problems and we will describe recent developments in the XAS investigation of ionic solutions.

2. MD model-dependent XAS analysis

In the standard EXAFS analysis the coordination of the photoabsorber is usually defined, in the small disorder limit or harmonic approximation, by means of Gaussian shells. This is a valid approximation for solids and liquids in which a high degree of local order is preserved by covalent bonding or strong ion–ion interactions. In general, amorphous and liquid systems are expected to possess moderate to large disorder and the application of this procedure can produce significant errors in the determination of the structural parameters (Crozier *et al.*, 1988). However, by careful modeling of the assumed radial distribution functions, the final results of an EXAFS analysis of complex fluids can be very detailed owing to its atomic selectivity.

A method to analyze EXAFS spectra of liquid systems by fitting $g(r)$ models obtained from MD simulations has been recently applied to the investigation of several aqueous and non-aqueous ionic solutions (D'Angelo *et al.*, 1994, 1995; D'Angelo, Nolting & Pavel, 1996; D'Angelo, Pavel *et al.*, 1996). The EXAFS data analysis has been performed using the *GNXAS* program (Filipponi *et al.*, 1995; Filipponi & Di Cicco, 1995). MD has been used to generate partial pair distributions, $g(r)$'s, from which a model $\chi(k)$ is constructed. Note that the $g(r)$'s are obtained on a time scale that is large enough to provide an ensemble average. In an iterative process a modified gamma distribution is then used to refine the small r region of the $g(r)$ first peak to improve the agreement with the experimental $\chi(k)$. Initial asymmetric distribution functions are obtained by splitting the MD $g(r)$'s into an asymmetric first peak and a long-distance tail. This peak is modeled with a gamma-like distribution function which depends on four parameters, namely the coordination number N, the average distance R, the distance mean-square variation σ^2 and the skewness β (β is the third cumulant divided by σ^3). With respect to the usual fitting procedure within the Gaussian approximation, the use of asymmetric peaks implies one additional parameter to be fitted for each peak. This increment is largely compensated by the shape correctness of the first $g(r)$ rise. Note that MD $g(r)$'s provide realistic starting models on which trial $g(r)$ functions can be refined. When MD simulations are not wide of the mark, the fitting process is similar to a minimization with constrained parameters. These conditions

reduce meaningfully the indetermination on the structural parameters, especially for coordination numbers and mean-square variations which cannot be determined with sufficient accuracy if the asymmetry of the pair distributions is not taken into account. An exhaustive discussion on the effect of the Gaussian approximation on the accuracy on the structural parameters and a comparison with the results obtained with asymmetric peaks are reported by D'Angelo, Di Nola *et al.* (1996). With the aid of MD $g(r)$ models the average distance values of a nearest-neighbor shell can be obtained with an accuracy of 0.01 Å, while the error on the first-shell coordination number is less than 1.

It is important to stress that the EXAFS information on the distance range beyond the first peak of the radial distribution function is negligible and, therefore, the reliability of the final model $g(r)$ in the long-distance range is strongly dependent on the original model. Instead, the short-range shape of the $g(r)$ can be accurately probed and refined by the EXAFS data.

The symbiosis MD-EXAFS becomes extremely useful when complex systems containing several pair distribution functions are investigated or when MS contributions are present in the spectra. In these cases, $g(r)$ models obtained from MD simulations can represent an essential starting point for the EXAFS analysis.

Examples of applications to ionic solutions will be given in the following sections.

3. Background removal

The full X-ray absorption contains two main contributions: the structural signal, which is composed of harmonic components, and the multielectron excitation signal, which is composed of distinct absorption features such as resonances and absorption edges. While the former contribution can be properly calculated, the latter is not predictable with comparable precision. The presence of multielectron transitions influences the EXAFS analysis by introducing spurious peaks at low-distance values in the Fourier transform (FT) of the spectrum, and modifying its intensity. As a consequence, the final structural results are affected by systematic errors whose magnitude depends on the particular experiment and on the amplitude and frequency of the EXAFS oscillations. The atomic background distortions associated with the opening of multielectron excitation channels are more evident for k smaller than about 4 Å^{-1}. Yet, in the case of solutions, it is important to extract $\chi(k)$ to lower k-values to maximize the spatial resolution, to better analyze asymmetric distributions, to gain structural information on small atomic number backscatterers and to detect the presence of MS contributions associated with triangular and higher body correlation functions.

The experimental determination of multielectron excitations can be easily performed for noble gases (Bernieri & Burattini, 1992; Deslattes *et al.*, 1983; Deutsch & Kizler, 1992), while in the case of bound atoms the structural oscillations often mask the small multielectron excitation contributions, which are usually only a few percent of the single-electron transitions. In disordered systems, where multielectron background features may be of comparable intensity to the weak structural oscillations, the standard background subtraction is totally inadequate and these are ideal systems to investigate multielectron transition effects, which are visible in the raw data (Ito *et al.*, 1995).

MD radial distribution functions have been used as relevant models in the calculation of the EXAFS structural signal of Br$^-$, Rb$^+$, Sr^{2+} and Ba^{2+} water solutions (D'Angelo *et al.*, 1994, 1995; D'Angelo, Nolting & Pavel, 1996; D'Angelo, Pavel *et al.*, 1996). Removal of the EXAFS structural contributions from the absorption spectra allowed

the isolation of multielectron transition features and the identification of their positions. For example, this method has been applied to the investigation of an Sr^{2+} aqueous solution (D'Angelo, Nolting & Pavel, 1996; D'Angelo, Pavel *et al.*, 1996).

Fig. 1 shows the comparison between the $\chi(k)$ theoretical signal calculated from the MD Sr–water radial distribution functions and the experimental K-edge spectrum extracted with a conventional three-region polynomial spline. The agreement between the two curves is not satisfactory, especially in the low-k region, and the residual curve shows a pattern with a marked cusp at 3.4 Å^{-1} and two step-shaped thresholds around 6.4 and 8.9 Å^{-1}. The energy positions of these three features correspond to the onset energies of the $1s4s$, $1s3d$ and $1s4p$ edges, respectively. Similar results have been obtained for the K-edge spectra of Br$^-$ and Rb$^+$ and for the L_1, L_2 and L_3 edges of Ba^{2+} water solutions (D'Angelo *et al.*, 1994, 1995; D'Angelo, Pavel *et al.*, 1996). In the latter case it was possible to identify the presence of multielectron resonances only starting from $g(r)$ models obtained from MD simulations and performing a combined L-edge analysis.

In the case of solutions it is crucial to develop a data analysis method which allows multielectron transitions to be properly accounted for. A new improved method, which uses a background empirical model to account for double-electron excitations, has been successfully employed in the EXAFS analysis of several systems (D'Angelo *et al.*, 1993; D'Angelo, Nolting & Pavel, 1996; D'Angelo, Pavel *et al.*, 1996). Several other methods have appeared in the literature (Li *et al.*, 1992; Frenkel *et al.*, 1993). With these different approaches, extracting experimental $\chi(k)$ that are reliable to $k = 2.5$ Å^{-1} is now feasible. It has been shown that for ionic solutions a reliable determination of the structural parameters is possible only if double-excitation edges are taken into account. The exclusion of these effects results in systematic errors in the structural parameters and, in particular, in a severe underestimation of the coordination numbers (D'Angelo, Nolting & Pavel, 1996; D'Angelo, Pavel *et al.*, 1996).
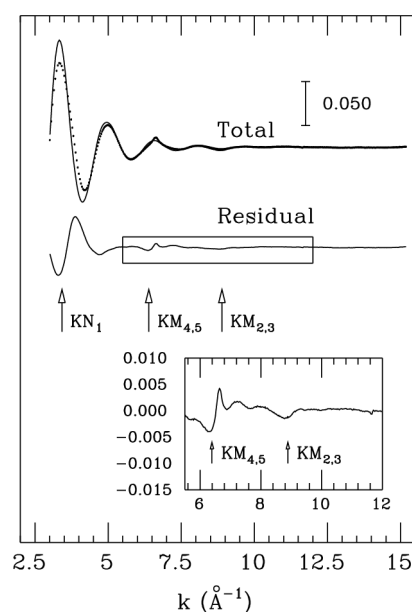

Figure 1
Comparison of the total theoretical curve of an Sr^{2+} aqueous solution calculated from the MD $g(r)$'s (solid line) with the $\chi(k)$ experimental spectrum (dots) extracted without the inclusion of the double-excitation edges.

The availability of low-k data is extremely important in the case of aqueous and organic solutions where the amplitude of the back-scatterer atoms is usually small and the structural signal is rapidly lessened as k increases. As will be shown in the following sections, with improvements to background removal procedures it is possible to investigate small amplitude contributions which are associated with three-body correlations and to the presence of H atoms.

4. Multiple scattering

The inclusion of MS contributions in the EXAFS analysis of crystalline compounds is nowadays a standard procedure. As far as disordered systems are concerned, the possibility of extracting higher-order correlation functions from the XAS data has been shown only recently. The presence of three-body contributions in the XAS spectra of elemental liquids such as Hg, Ga and Sn (Ottaviano *et al.*, 1993; Di Cicco & Filipponi, 1994; Di Cicco, 1996) and the importance of accounting for MS contributions for transition-metal ion aqueous solutions has been pointed out in several studies (Benfatto *et al.*, 1986; Filipponi *et al.*, 1994; D'Angelo *et al.*, 1997, 1998). In the latter case, highly stable regular or distorted octahedral hydration complexes are present in solution and the MS effects are associated with the first hydration shell. For example, the hydration shell of the Cu^{2+} ion (Filipponi *et al.*, 1994) has an elongated octahedral structure with four equatorial O atoms at a close distance and two axial O atoms at a slightly longer distance. The two in-plane quasilinear O–Cu–O configurations give rise to a strong MS contribution. This is due to the focusing effect, which enhances the amplitude of the three-body signals associated with linear configurations. On the contrary, the MS signals associated with the four orthogonal O–Cu–O triangles of the equatorial plane and with the quasilinear configuration which involves the axial O atoms are negligible. A detailed EXAFS data analysis including MS effects produced quantitative information on the chlorocuprate complexes in aqueous solutions of $CuCl_2$ with increasing Cl^-/Cu^{2+} ratio (D'Angelo *et al.*, 1997). The degree of complex formation between Cu^{2+} and Cl^- ions increases with increasing chloride concentration.
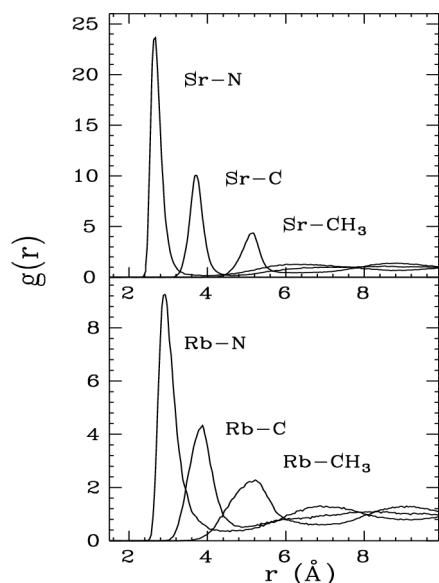
At high Cl^- concentration the anion occupies both the equatorial and the axial sites.

MS effects can be easily identified in atomic liquids and ions with strong and regular ion–solvent coordination. A more challenging goal is the detection of three-body correlation functions in the XAS spectra of ions which give rise to non-regular coordination in solution. To better understand if three-body correlation functions can be present in short-lived molecular associations, such as ionic solutions, EXAFS spectra of Rb^+ and Sr^{2+} in acetonitrile (ACN) have been investigated (D'Angelo & Pavel, 1999). Owing to the linearity of the ACN molecules, well defined three-body distributions associated with the first and second ion coordination shells may be present. MD simulations have been performed and both two- and three-body distribution functions have been determined. The Sr^{2+}-ACN $g(r)$'s show sharp and well separated first peaks while the Rb^+-ACN distribution functions are partially superimposed, owing to the less tightly packing of the solvent molecules around the ion. This is due both to the presence of a single charge and to the bigger ionic radius of the Rb^+ ion (see Fig. 2). Ion–N–C and N–ion–N three-dimensional arrangements of the linear acetonitrile molecules have been determined on the basis of the MD calculations. The analysis of the $g(r_1, r_2, \theta)$ three-body distributions shows the presence of well defined peaks in the triangular configurations. Integration of these peaks allows the number of triangular configurations contributing to the distribution to be estimated. A three-dimensional representation of the $Sr–N–C$ distribution function is reported in Fig. 3, as an example. The best-fit analysis of the Sr^{2+} acetonitrile EXAFS spectrum is shown in Fig. 4. As expected, the strongest MS contribution is associated with the $Sr–N–C$ three-body distribution, while the $N–Sr–N$ signal is very weak. A similar investigation has been carried out for Rb^+ in acetonitrile. The results of this study have clearly shown that the XAS technique, in combination with MD simulations, provides structural information on three-body correlation functions present in ionic solutions.

Even if the analysis of triangular correlations were possible only with the aid of MD simulations, the existence of an experimental technique capable of probing three-body correlations in liquid systems is extremely important.
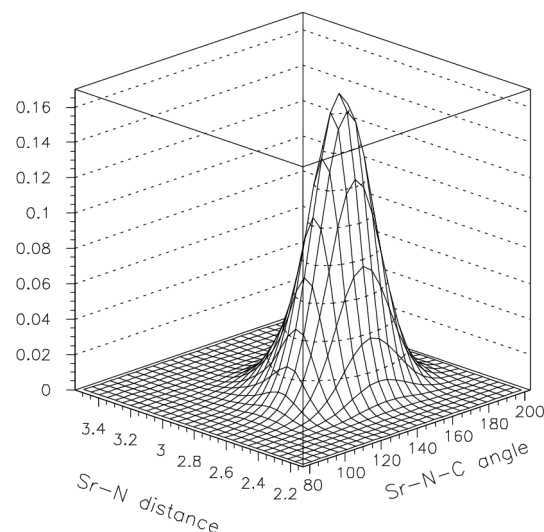

Figure 2
Sr–N, Sr–C and Sr–CH$_3$ (upper panel) and Rb–N, Rb–C and Rb–CH$_3$ (lower panel) pair distribution functions derived from MD simulations.

Figure 3
Representation of the three-body distribution functions of the Sr–N–C triangles of an Sr^{2+} acetonitrile solution derived from MD simulations.

5. Hydrogen contribution

The effect of H atoms is usually neglected in EXAFS theoretical calculations and data analysis. A first example where the presence of H atoms has been taken into account is in the case of Ni and Cr hydrides (Lengeler, 1984). Owing to the focusing effect, radial and angular information on the lattice sites occupied by H atoms has been obtained.

With the improvements to the background-removal procedures, a weak Br—H structural signal has been evidenced in gaseous HBr (D'Angelo *et al.*, 1993). The XAS data analysis provided a Br—H distance in excellent agreement with the known value.

The effect of H atoms on the X-ray absorption near-edge structure (XANES) spectra of water solutions has been recently investigated (Benfatto *et al.*, 1997). A detailed XANES analysis of Ni^{2+} and Co^{2+} aqueous solutions has been performed and it has been found that the inclusion of H atoms significantly improves the agreement between the theoretical and experimental data.

MD simulations of Br^- in methanol have shown that six methanol molecules are coordinated with the halogen anion. The Br—H, Br—O and Br—methyl pair distribution functions are sharp and well separated. Owing to the well ordered structure of the solvent molecules, it was possible to identify, for the first time, the contribution of the H atoms of the solvent to the X-ray absorption cross section (D'Angelo, Di Nola *et al.*, 1996). Starting from the $g(r)$'s obtained from MD simulations, the parameters of three asymmetric peaks have been determined and used in the EXAFS analysis. The upper panel of Fig. 5 shows the Br—H, Br—O and Br—methyl theoretical signals, the comparison between the total $\chi(k)$ signal and the experimental spectrum, and the residuals. This analysis has been performed without including MS effects. The total signal is dominated by the ion–oxygen contribution, while the ion–hydrogen signal is weaker and mainly affects the low-k region of the spectrum. However, the inclusion of the latter contribution has been found to be essential to reproduce properly the experimental spectrum in the low-k region. This has been proved by performing a minimization without including the Br—H signal. The results of this analysis are shown in the lower panel of Fig. 5. The residual curve contains a low-frequency oscillation which is due neither to the oxygen nor to the methyl coordina-
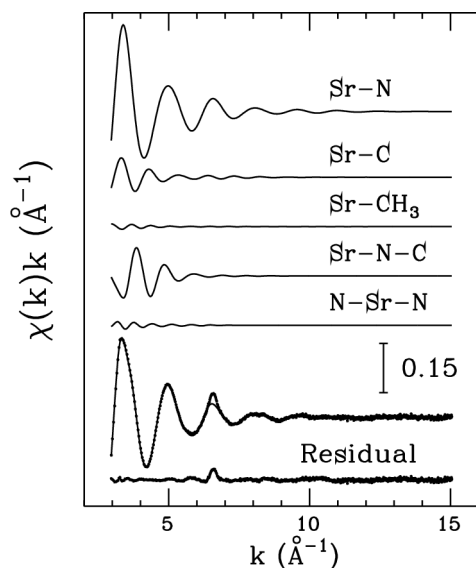
tion shells. When the hydrogen shell is not included, an increase of about 18% and 6% can be observed for the oxygen and methyl coordination numbers, respectively. It is important to stress that the analysis of the low-k region of the spectra allows the detection of the hydrogen structural signal which cannot be studied by X-ray diffraction. Moreover, a reliable analysis of MS or second-shell contributions can be performed only if the hydrogen signal is included in the analysis as the amplitudes of all these contributions are similar.

The first hydration shell of cations usually contains six to nine water molecules. The ion–O and ion–H pair distribution functions present tight and not overlapped first peaks in the case of double-charged ions such as alkaline-earth or transition-metal ions. On the contrary, much broader and less defined first peaks can be observed in the radial distribution functions of alkaline metal ions, due to the presence of a single charge. In the former case, where the hydrogen shells are sharp and well separated from other coordination spheres, the hydrogen contribution to the XAS spectra is not negligible. For example, the ion–H signal has been detected in the XAS spectra of Sr^{2+} and Ba^{2+} in water and Sr^{2+} in methanol (D'Angelo, Nolting & Pavel, 1996; D'Angelo, Pavel *et al.*, 1996; Roccatano *et al.*, 1998). On the contrary, a negligible ion–H signal has been found in the case of Rb^+ in water (D'Angelo *et al.*, 1995) and methanol.

6. MD potentials

MD is a powerful tool in the analysis of the chemical and physical properties of molecular systems but the structural and dynamic results depend on the validity of the intermolecular potential models used in the simulations. The parameters describing the atomic interaction functions used in MD calculations are usually derived
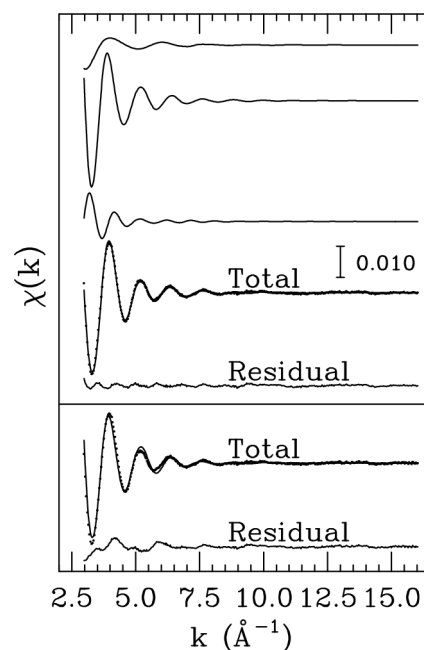
Figure 5
Fit of the experimental spectrum of the Br^- ion in methanol, performed with asymmetric shells. Upper panel: from top to bottom, the $\chi_{BrH}(k)$, $\chi_{BrO}(k)$ and $\chi_{BrC}(k)$ asymmetric peak contributions, their sum compared with the experimental spectrum, and the residual are shown. Lower panel: fit performed without including the $\chi_{BrH}(k)$ signal. From top to bottom, the total theoretical signal compared with the experimental spectrum, and the residual are shown.

Figure 4
EXAFS experimental structural signal of Sr^{2+} in acetonitrile (dots) compared with the $\chi(k)$ theoretical signal derived from MD simulations.

from experimental methods and the validity of the MD results can be assessed by comparison with experimental data. In particular, the XAS technique can be employed to assess the reliability of the interatomic potential functions (IFP) used in the simulations. Comparison of short-range pair distribution functions derived by EXAFS and results of the MD simulations provide a strict test of the reliability and accuracy of the theoretical models used in the simulations. Application of EXAFS is particularly interesting for simple systems such as ions in solutions. In this case the small number of interaction functions required in the simulations allows each function to be checked and modified on the basis EXAFS experimental data, if necessary. A detailed investigation of Sr^{2+} in methanol solution has been carried out combining MD simulations with EXAFS experimental results (Roccatano *et al.*, 1998). Different Sr^{2+} potential functions and methanol models have been combined and radial distribution functions have been calculated at the end of each MD simulation. In particular, three Sr^{2+} Lennard Jones parameter sets (namely CHARM22, Palmer and Åqvist) and four methanol models (namely OPLS, HFM1, OM2 and GROMOS) have been used. Sr—O, Sr—H and Sr—C $\chi(k)$ signals have been calculated from MD $g(r)$ models. Comparison of the theoretical and experimental $\chi(k)$ signals has allowed the reliability of the $g(r)$'s, and consequently of the Sr^{2+} and methanol models in the simulations, to be checked.

In Fig. 6 the comparison between the EXAFS experimental signals and the theoretical contributions calculated using the Åqvist, Palmer and CHARM22 IFP is reported. From these results it is clear that MD simulations performed using the Åqvist Sr^{2+} IFP provide a good description of the solvent structure around the ion. Sr—O $g(r)$'s obtained from simulations performed with the Palmer and CHARM22 IFP's have been found shifted towards larger distances with respect to the results of the EXAFS analysis.

As far as different methanol models are concerned, the OPLS and HFM1 models have been found to give the best agreement with the EXAFS experimental data, while the GROMOS and OM2 methanol models have shown larger deviations in the shape and position of the pair correlation functions.

From the results of this investigation it is clear that the EXAFS data are especially well suited to determine the detailed shape of the nearest-neighbor peak in the atom–atom pair correlation functions of disordered systems. The information that they contain about the short-range atom–atom pairwise interactions can be very helpful for specifying and properly modifying model potentials used in MD simulations.

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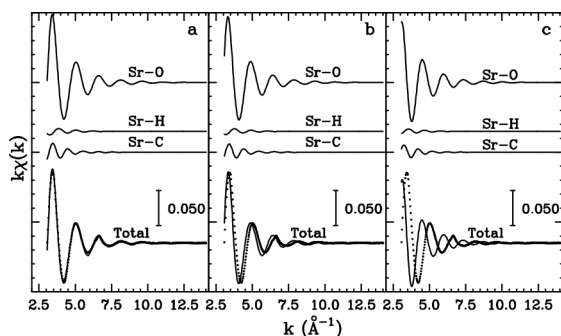Roccatano, D., Berendsen, H. J. C. & D'Angelo, P. (1998). *J. Chem. Phys.* **108**, 9487–9497.

Figure 6
EXAFS experimental structural signal (dots) of Sr^{2+} in methanol compared with the $\chi(k)$ theoretical signals calculated using MD $g(r)$'s obtained from the Åqvist, Palmer and CHARM22 interatomic potential functions (left, middle and right panels, respectively).