# An extended x-ray absorption fine structure study of aqueous solutions by employing molecular dynamics simulations

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(Received 19 July 1993; accepted 21 September 1993)

Bromine-oxygen radial distribution functions [g(r)] have been calculated by means of molecular dynamics simulations for aqueous solutions of rubidium bromide, 2-bromopropane and bromoethane. X-ray absorption spectra at the bromine K edge have been recorded for these solutions. The water contribution to the extended x-ray absorption fine structure spectra has been calculated starting from the  $g_{Br,O}(r)$  distribution function. Fits of the x-ray absorption spectra have been performed directly on the raw experimental data, allowing the reliability of the g(r) distribution functions to be verified. The agreement between theoretical and experimental spectra is satisfactory. A procedure to improve model g(r) functions on the basis of the short-range structural information provided by extended x-ray absorption fine structure data is proposed.

## **I. INTRODUCTION**

Structural investigation of solid and liquid disordered systems are of paramount importance for the knowledge of their properties. The main techniques involved in the study of the structure of disordered systems are x-ray diffraction (XRD), neutron diffraction, and x-ray absorption spectroscopy (XAS), which provide complementary structural information. From the extended x-ray absorption fine structure (EXAFS) region, which starts about 50 eV above the absorption threshold, the local structure around the photoabsorber atom can be determined with a good approximation for crystalline and disordered systems.<sup>1,2</sup>

In the case of crystalline samples, the analysis is usually done by describing the coordination of the photoabsorber atom with a set of Gaussian shells. In several accurate studies, anharmonic vibrations have been accounted for by considering asymmetric peak profiles and a generalization of the Debye-Waller damping in the framework of the cumulant expansion method has been seldom applied.<sup>2-4</sup> Due to the local sensitivity of the EXAFS technique the Gaussian and the asymmetric peaks have been also widely used to describe the local coordination in liquids providing, however, only a coarse description of the local disordered environment around the excited atom. The appropriate description of disordered systems in the real space is performed in terms of the radial distribution function g(r). For multicomponent systems with N different atoms, the EXAFS technique is more selective than x-ray or neutron diffraction, since the partial g(r) around each type of atom can be obtained separately. In fact, for an N-component system, N(N+1)/2 independent partial correlation functions are overlapped in the XRD data, against N correlation functions corresponding to the

photoabsorber atom studied by the XAS technique. Moreover, samples with a low photoabsorber concentration can be studied with the XAS technique and a better discrimination of the atomic species can be done when the scattering amplitudes and phases of the surrounding species are different. However, in disordered systems, the partial correlation functions are usually broad and asymmetric towards the large distances. This occurrence, together with the photoelectron mean-free path (about 5–10 Å), are the main factors giving rise to the lack of information at large distances. Several examples of EXAFS applications in disordered systems are known in literature.<sup>2,5,6</sup>

The aid of other structural techniques may be essential to define the interval of variation of the parameters used to model the g(r) functions. Molecular dynamics (MD) simulation technique has widely developed during the last years. It can be useful in the prediction of structural aspects of liquids and solutions.<sup>7,8</sup> Its results are generally compared with experimental data obtained by NMR and conventional structural techniques such as x-ray and neutron diffraction. In particular, several MD and Monte Carlo simulations on aqueous salt solutions have been performed<sup>9-13</sup> and have been compared with XRD<sup>14</sup> and neutron diffraction experiments.<sup>15</sup> The comparison between computer structural simulations and EXAFS experiments has been rarely performed; some examples exist related to the non-Gaussian cumulant expansion analysis in hightemperature or high-pressure crystalline solids.<sup>3,5</sup> A promising algorithm that allows the fit of g(r) functions generating a three-dimensional structural model compatible with the experimental data is the reverse Monte Carlo procedure<sup>16</sup> that has been also applied to the EXAFS case.<sup>17</sup>

0021-9606/94/100(2)/985/10/\$6.00

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The analysis of EXAFS data of aqueous solutions of ions or molecules is usually performed within the Gaussian approximation obtaining average coordination number, distance, and variance for the first hydration shell. However, the experimental data contain a wider structural information that can be extracted with a more sophisticated procedure and is particularly interesting for structural investigations of complex fluids. Data analysis of ions or molecules in solution can derive strong benefit from the pair partial correlation functions obtained from theoretical simulations which can be used as relevant models in the EXAFS fitting procedure. The results presented in this paper are intended to represent an advance along this line of research. In particular the EXAFS spectra of rubidium bromide, 2-bromopropane (IPB) and bromoethane (ETB) aqueous solutions have been analyzed with the aid of the g(r) obtained from MD simulations.

The paper is organized as follows: in Sec. II the MD computational procedure for the three systems under investigation will be presented, in Sec. III the experimental details, in Sec. IV the EXAFS simulation performed on the basis of the MD g(r) distribution function and its comparison with the experimental spectra will be described, and finally in Sec. V the description of a procedure to improve the short-range distance of model g(r) functions by means of the EXAFS analysis will be provided.

# II. MOLECULAR DYNAMICS COMPUTATIONAL PROCEDURE

The molecular dynamics simulations were performed using an isothermal-isobaric simulation algorithm.<sup>18</sup> Weak coupling to an external temperature bath of 300 K with a coupling time constant of 0.1 ps, and to an external pressure bath of  $1.0 \times 10^5$  Pa with a coupling time constant of 0.5 ps was used to maintain constant temperature and pressure in the simulations. The solute molecules were immersed in rectangular boxes consisting of the molecules and 250 water molecules, subjected to periodic boundary conditions. The simulations were performed with programs from the Groningen molecular simulation system (GROMOS) software package.<sup>19</sup> The applied empirical force field contains terms representing covalent bond stretching. bond angle bending, harmonic dihedral angle bending (out-of-plane, out-of-tetrahedral configuration), sinusoidal dihedral angle torsion, van der Waals and electrostatic interactions.<sup>20</sup> The Lennard-Jones parameters used for the Br were taken to be different for Br<sup>-</sup> and covalent bonded Br, to account for the larger size of ion with respect to the covalent bonded Br. This choice is analogous to that of Keirstead et al. for Cl<sup>9</sup> and is due to the fact that it is impossible to obtain simulated distribution functions in agreement with the experimental ones by the use of a unique Lennard-Jones function. The function used in the present study for Br<sup>-</sup> has been reported by Straatsma and Berendsen.<sup>11</sup> For the covalent bonded Br, the Br-Br parameters have been given by Pavel, Quagliata, and Scarcelli,<sup>21</sup> and the Buckingham potential function has been transformed into a Lennard-Jones 12-6 one. The obtained parameters are  $\sigma = 3.34$  Å and  $\epsilon/k_B = 107.7$  K. The Br-O



FIG. 1. Br-O partial radial distribution functions as derived from the MD simulations for  $Br^-$ , IPB, and ETB water solutions from top-tobottom, respectively. The curves are shifted downwards one unit on the ordinate scale for legibility.

parameters were obtained by geometric mean of the Br–Br and O–O parameters.<sup>19</sup> The SHAKE algorithm was used to constrain bond lengths.

Charges of the solute molecules were calculated using the method developed by Gasteiger and Marsili.<sup>22</sup> They resulted: 0.013, 0.068, and -0.181 for CH<sub>3</sub>, CH<sub>2</sub>, and Br in ETB respectively; 0.013, 0.057, and -0.083 for CH<sub>3</sub>, CH, and Br in IPB, respectively.

A dielectric permittivity,  $\epsilon = 1$ , was used. The cut-off radius for the nonbonded interactions was 9 Å. The model potential for the water is the simple point charge (SPC) model.<sup>23</sup> A time step of 0.002 ps was used in the simulation.

All atoms were given an initial velocity obtained from a Maxwellian distribution at the desired initial temperature. After the initial energy minimization of the water molecules, the MD simulations were performed. The first 30 ps were used for equilibration; they were followed by 100 ps that were used for analysis. The trajectories were saved every 50 fs.

The partial  $g_{Br,O}(r)$  radial distribution function for Br<sup>-</sup>, IPB, and ETB are shown from top to bottom in Fig. 1.

The calculations were performed on the IBM 3090 of the University of Rome.



FIG. 2. Br K-edge spectra of  $Br^-$ , IPB, and ETB water solutions from top to bottom, respectively. The solid line represents a fit of the edge region performed by summing a Lorentzian peak and an arctangent step function all convoluted with a Gaussian.

## **III. EXPERIMENTAL DETAILS**

Aqueous solutions of rubidium bromide, IPB, and ETB have been prepared using commercial products (Fluka purum). IPB and ETB have been distilled and the sample concentrations were 150, 60, and 80 mM for the RbBr, IPB, and ETB solution, respectively.

The EXAFS spectra above the bromine K edge have been recorded in the transmission mode at room temperature on the x-ray BX1 beam line of the PWA laboratory (wiggler source, Adone storage ring, Frascati), equipped with a Si(220) channel-cut monochromator. The ionization chambers were filled with krypton gas. The ring was operating at 1.5 GeV with ring currents between 10 and 85 mA. The data have been calibrated to the Au  $L_{\rm II}$  edge.

The experimental spectra for RbBr, IPB, and ETB are shown in Fig. 2. The solid line in the edge region represents a fit performed by adding a Lorentzian peak to an arctangent step function, accounting for the pre-edge resonance and continuum threshold respectively, with the known core-hole full width at half-maximum (FWHM) of 2.52 eV. The resulting model signals have been convolved with a Gaussian representing the experimental resolution, which resulted in 1.5 eV for RbBr, 1.4 eV for IPB, and 1.3 eV for ETB, depending on the crystal monochromator used in the experiments.

#### **IV. XAS CALCULATIONS**

In order to perform a reliable calculation for the x-ray absorption spectra of brominated molecules in aqueous solution at the Br K edge, both intermolecular and intramolecular contributions have to be taken into account. While the EXAFS oscillations of the RbBr diluted aqueous solution spectra are essentially due to the Br–O pair correlation function, in the case of the brominated hydrocarbons the intramolecular contacts give rise to a strong contribution with two Br–C shells at about 1.94 and 2.84 Å. In addition, noticeable multiple scattering (MS) contribution from the triplets Br–C–C occurs that has to be considered in any accurate calculation. In a previous paper all details regarding the XAS analysis of these brominated hydrocarbons in gaseous phase have been described.<sup>24</sup>

Unlike the intramolecular contribution, the intermolecular one originates from a disordered phase having a broad distribution of distances around the photoabsorber atom. In particular, in the case of an ion such as Br<sup>-</sup>, the solvent nearest-neighbor distribution is expected to be sharper than in the case of brominated hydrocarbons as shown by the MD simulations (see Fig. 1). Each water molecule mainly contributes to the absorption cross section with the oxygen atom scattering since the hydrogen contribution can be neglected. The average distribution of oxygen atoms around Br is described by the  $g_{Br,O}(r)$  distribution function that has been calculated by means of MD simulations as described in the previous section. Each oxygen atom contributes to the total  $\chi(k)$  signal with an oscillating signal, as a function of the photoelectron wave vector k, of the type:

$$\chi(k) = A(k,r)\sin[2kr + \phi(k,r)]$$
(1)

with amplitude A(k,r) and phase  $\phi(k,r)$  functions.<sup>1</sup> A distribution of oxygen atoms described by the appropriate distribution function  $g_{Br,O}(r)$  will provide an average signal given by

$$\chi_{\text{water}}(k) = \int_0^\infty dr \, 4\pi \rho r^2 g_{\text{Br,O}}(r) A(k,r) \sin[2kr + \phi(k,r)].$$
(2)

This equation is well established in the EXAFS field<sup>2</sup> and has been often applied in the study of disordered systems. In the present investigation for the first time it is used in conjunction with MD simulations to calculate the water contribution to the spectra of molecules in solution.

Although the integral in Eq. (2) formally extends to infinity, it is well known that there is a natural cutoff distance due to the photoelectron mean-free path. The cutoff is provided by an exponential function of the type  $\exp[-r/\lambda(k)]$ , where  $\lambda(k)$  is the photoelectron mean-free path, hidden in the amplitude function A(k,r) yielding an effective upper integration limit of about 6-8 Å. Similarly the A(k,r) function accounts for the monochromator resolution, that provides an effective additional damping especially in the low-k region.

Thus the XAS signal is expected to be sensitive only to the very short range of the  $g_{Br,O}(r)$  function while it is completely insensitive to the medium- and long-range atomic distributions. This characteristic of short range sensitivity has been for a long time considered a strong limitation of the EXAFS technique because it hampers the experimental determination of the g(r) in the whole range and in particular towards its asymptotic behavior  $\lim_{r \to \infty} g(r) = 1$ . On the other hand the XAS signal is extremely sensitive to the short-distance features of the g(r) and in particular to the shape of its first rise. In the present paper we shall fully exploit the characteristic of the XAS signal.

Phase shifts have been calculated in the muffin-tin approximation starting from overlapped spherically averaged relativistic atomic charge densities. In the case of Br<sup>-</sup> one of the molecular distributions obtained from the MD simulations has been used to calculate the phase shifts. The muffin-tin radii  $(R_{\rm MT})$  were 1.58 and 1.34 Å for the Br<sup>-</sup> and the oxygen atoms, respectively, on the basis of the criteria given by Norman.<sup>25</sup> For the IPB- and ETB-water clusters,  $R_{\rm MT}$  values were chosen to be 1.14 Å for Br and 0.74 Å for all the carbons, the overlap between the spheres not exceeding 2% in all cases. The oxygen phase shifts have been calculated based on one of the configurations obtained from the MD simulations and an  $R_{\rm MT} = 1.06$  Å has been used both for the IPB and ETB case. It has been verified that different configurations gave the same result. An energy-dependent complex self-energy for the photoelectron effective potential was calculated in the Hedin-Lundqvist approximation.<sup>26</sup> The imaginary part, which takes intrinsically account of the photoelectron inelastic loss, included also a constant factor accounting for the known core-hole width.

In the case of dilute RbBr aqueous solutions, by neglecting the hydrogen atoms, the bromine nearestneighbors are only oxygen atoms and the total  $\chi(k)$  theoretical signal may be properly calculated by means of Eq. (2). In the calculation the  $g_{Br,O}(r)$  obtained from the MD simulations has been utilized. The IPB and ETB intramolecular signals have been calculated with the GNXAS program<sup>27</sup> in the same way as described for the gaseous molecules in a previous paper.<sup>24</sup> The theoretical  $\chi(k)$  signal associated with the water contribution has been calculated by means of Eq. (2) starting from the  $g_{Br,O}(r)$  functions obtained from the MD simulations.

Fits of the XAS spectra have been performed directly on the raw data using the FITHEO program.<sup>27</sup> The background spectra have been modeled accounting for the double-excitation edges using step-shaped functions as previously described.<sup>24</sup> The KN,  $KM_{4,5}$ , and  $KM_{2,3}$  edges have been evidenced in the XAS spectrum of the Br<sup>-</sup> solution, with energy onset values equal to those found for gaseous HBr within the reported<sup>28</sup> errors. In the case of IPB and ETB the KN edge was out of the low-k range used in the minimization and, therefore, has not been included. The  $KM_{4.5}$  edge parameters used in the calculation of the background were the same as those determined for the gaseous molecules within the reported<sup>24</sup> errors.

Let us now examine the results of the fits in the three cases considered in this work. In Fig. 3 the comparison between the theoretical  $\chi(k)$  signal and the experimental

8 10 2 6  $k (Å^{-1})$ 

FIG. 3. Fit of the Br<sup>-</sup> aqueous solution experimental spectrum. Upper curves:  $\gamma(k)$  experimental spectrum (dots) compared with the theoretical one (solid line), calculated on the basis of the MD  $g_{Br,O}(r)$  function, lower curve: residual.

spectrum of the Br<sup>-</sup> sample is shown together with the residuals. The fit has been performed in the range k=2.0-9.7 Å<sup>-1</sup>. A single nonstructural parameter ( $E_0$ ) representing the zero of the theoretical energy scale (it aligns the experimental energy scale to the theoretical one), has been refined obtaining a value of 5.2 eV above the first K-edge inflection point. As far as the other non structural parameters are concerned, the photoelectron damping and the core-hole lifetime have been included directly in the theory, while the monochromator resolution value obtained from the edge fit has been included and not moved during the fitting procedure. The agreement between theory and experiment is satisfactory: this indicates the substantial correctness of the first peak of the MD g(r) distribution function. The low-k region of the residual curve seems to contain a high-frequency oscillation which is slightly above the noise of the spectrum. This oscillation could be due to small distortions of the MD g(r) or to signal contribution which have not been taken into account in the calculation. This will be discussed in detail in the next section.

In the case of IPB and ETB a detailed description of all the structural and nonstructural parameters used in the fitting procedure has been previously made for the gaseous phase.<sup>24</sup> Provided that the structural parameters of these molecules in aqueous solution should be basically the same, we have let them refine in order to account for possible small changes in the molecular structure due to the interaction with the solvent. All the values obtained after this refinement were equal, within the statistical errors, to those reported for the gaseous molecules with the exception of the first shell bond vibrational standard deviations which have been found the 20% greater in both cases. In Figs. 4



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FIG. 4. Fit of the IPB aqueous solution experimental spectrum. From top to bottom: theoretical intramolecular signal,  $\chi(k)$  signal calculated on the basis of the MD g(r) function, sum of the previous contribution (solid line) compared with the experimental spectrum (dots), intermolecular contribution (solid line) compared with the experimental minus intramolecular signal (dots) and residual.

and 5 the fit of the IPB and ETB experimental spectra are shown. Starting from the upper part we report the intramolecular contribution, the intermolecular one, their sum compared with the experimental spectrum, the intermolecular contribution compared with the experimental minus intramolecular signal and the residuals. The intramolecular signal contains the first and the second shell Br-C contribution together with that of Br-C-C due to MS. It is evident that the intramolecular signal provides the main contribution to the total cross section; nevertheless, the intermolecular one is essential to reproduce the experimental spectra, especially in the low-k region. In the case of IPB the agreement between experiment and theory is excellent and the residual curve contains only statistical noise. This result provides a severe test supporting the correctness of the short-distance shape of the MD distribution function. On the contrary, the ETB total theoretical signal is not able to reproduce perfectly the experimental spectrum and the residuals indicate the presence of an oscillation with typical frequency of the water contribution. As for Br<sup>-</sup> the origin of such residual oscillation will be discussed in the next section.

# V. EMPIRICAL g(r) DECOMPOSITION

In the previous section an EXAFS analysis of aqueous solutions has been carried out on the basis of  $g_{Br,O}(r)$  distribution functions obtained from the MD simulations. In the present section we will address the problem of using the



FIG. 5. Fit of the ETB aqueous solution experimental spectrum. From top to bottom: theoretical intramolecular signal,  $\chi(k)$  signal calculated on the basis of the MD g(r) function, sum of the previous contribution (solid line) compared with the experimental spectrum (dots), intermolecular contribution (solid line) compared with the experimental minus intramolecular signal (dots) and residual.

high sensitivity of the EXAFS technique to improve the low-distance region of g(r) functions derived from other techniques or theoretical simulations.

In several cases dealing with ions or molecules in aqueous solution the usual procedure consisted in simulating the water signal with one or more Gaussian coordination shells. The empirical shells in some way provide a model for the short-range structure of the g(r) distribution function, its higher distance tail giving rise in any case to a negligible contribution. The results of such kind of data analysis contain some information on the distribution function that is quite difficult to be compared with g(r) functions obtained from simulations or other techniques. While it is clear that, for disordered systems, the EXAFS signal does not usually provide any information beyond approximately 4-5 Å [typically, corresponding to the first minimum of the g(r)], a data analysis method which allows one to perform a direct comparison in terms of radial distribution function would be helpful.

To this purpose we developed a procedure suitable to treat disordered solids and liquid systems. The method, previously applied to the case of liquid Hg,<sup>29</sup> is based on the following steps:

(1) A model g(r) is decomposed into one or more peaks plus a long-distance tail. The EXAFS can improve only the short-range region of the g(r) model, for this reason the final g(r) derived from EXAFS is modified with respect to the MD one only for what concerns the shortrange features. For the tail our analysis method relies entirely on the original MD model.

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(2) The signals corresponding to the average value of each peak are calculated and damping corrections accounting for its width and shape are applied. The peaks have to be narrow enough so that the damping corrections can be calculated with high accuracy.

(3) The signal associated with the tail is calculated by means of Eq. (2), and it is advisable to choose the near end of the tail at sufficiently large distance so that the tail signal contribution becomes negligible or, at least, lower than the residuals.

(4) The previous steps (2) and (3) allow the structural features to which the EXAFS signal is sensitive to be identified. A fitting procedure is applied to the parameters of these peaks in order to improve as much as possible the agreement with the experimental spectrum. The tail shape is left fixed and its signal is included in the model spectrum if not negligible.

(5) Finally a g(r) model is recalculated using the peaks with the refined parameters plus the fixed tail, thus combining the short-range EXAFS information with the long-range tail shape of the original model.

Clearly 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) 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.

In order to apply this procedure some guidelines to produce a reliable initial model g(r) possibly from MD models, theoretical results or diffraction experiments is in general extremely useful. It is known that the diffraction techniques are more sensitive to the medium real space range of distances. For this reason, the EXAFS and diffraction techniques can be combined in order to obtain better defined radial distribution functions.

Peak shapes can be in principle considered Gaussian. We found, however, quite helpful to model them with a family of Gamma like distribution curves with mean R, standard deviation  $\sigma$  and asymmetry index (third cumulant divided by  $\sigma^3$ )  $\beta = 2p^{-1/2}$  that can be gradually varied in a wide range. The general expression is

$$f(r) = N_c \frac{p^{1/2}}{\sigma \Gamma(p)} \left[ p + \left(\frac{r-R}{\sigma}\right) p^{1/2} \right]^{p-1} \\ \times \exp\left[ -p - \left(\frac{r-R}{\sigma}\right) p^{1/2} \right],$$
(3)

where  $\Gamma(p)$  is the Euler's Gamma function for the parameter p, and  $N_c$  is the coordination number providing the correct normalization. Just as for the Gaussian case, the damping of the  $\chi(k)$  signal averaged over distribution expressed as in Eq. (3), can be calculated exactly. The average can be expressed in terms of amplitude, phase and their derivatives calculated for r=R, namely  $A_0=A(k,R)$ ,  $\psi_0=\psi(k,R)$ ,  $A_1=\partial A(k,r)/\partial r|_{r=R}$ , and  $\psi_1=\partial \psi(k,r)/\partial r|_{r=R}$ . We find

$$\chi(k) = \mathscr{I} \bigg[ A_0 e^{i\psi_0} \\ \times \bigg( 1 + i \frac{A_1}{A_0} \frac{\psi_1 \sigma^2}{(1 - i\psi_1 \sigma p^{-1/2})} \bigg) \frac{e^{-i\psi_1 \sigma p^{1/2}}}{(1 - i\psi_1 \sigma p^{-1/2})^p} \bigg],$$
(4)

where  $\mathscr{I}$  indicates the imaginary part. Equation (4) is based on the linear expansion for amplitudes and phases around the average distance value R that are strictly valid only in a narrow range around R.<sup>30</sup> For this reason the peak must be necessarily rather sharp. In the present investigation in the case of IPB and ETB, peaks as wide as 1 Å have been used due to the strong disorder in the bromine coordination. We verified the validity of the linearized damping equation comparing its result with exact integrations on the g(r) peak and found that the approximation was still sufficiently accurate. The width of 1 Å should be really considered an upper limit for its validity.

It should be stressed that no physical meaning should be necessarily attributed to the peak structures. They will in general overlap and a generic atom at a distance in the overlap region between two peaks by no reason can be classified to belong to any of them. The only meaning of the peaks is that their sum generates a model g(r) reproducing experimental data with a certain accuracy.

Let us show how the present analysis scheme works for the Br<sup>-</sup> case. The Br<sup>-</sup>  $g_{Br,O}(r)$  distribution function obtained from the MD calculations shown in Fig. 1 has been decomposed into a main asymmetric peak, accounting for the first hydration shell, modeled according to Eq. (3), plus the remaining long-distance tail defined as the difference between the MD g(r) and the asymmetric peak. The  $\chi(k)$  signals associated with the asymmetric peak and the long-distance tail were calculated by using the previously described procedures. A comparison between experimental and calculated spectra has been performed with the help of a fitting routine and is shown in Fig. 6. The first signal from the top refers to the tail contribution as given from the decomposition. As previously commented its weak intensity is due to the short-distance range sensitivity of the EXAFS that cannot provide any reliable information on this range. It has been kept fixed in the minimization. On the other hand, the second curve in Fig. 6 is the signal associated with the first hydration shell peak plus the tail contribution, the former clearly dominating the structural  $\chi(k)$  signal. The shape of the asymmetric peak signal has been optimized varying the four peak parameters that represent the average distance R, the coordination number  $N_c$ , the vibrational standard deviation  $\sigma$ , and the asymmetry try  $\beta$ . The optimized values are reported in Table I. The shape of the first hydration shell peak basically remained unaltered. Only the standard deviation increased by about 8% from the MD value. The improved g(r) model is reproduced in Fig. 7 that reports the MD g(r) function, and with a continuous line the one obtained from the EXAFS refinement, with a slightly lower and larger first peak. The tail, derived from the MD g(r) function, is clearly not





FIG. 6. Fit of the Br<sup>-</sup> aqueous solution experimental spectrum. The theoretical signal has been calculated by means of an asymmetric peak plus a fixed tail. From top to bottom: the tail signal contribution,  $\chi(k)$  theoretical signal, sum of the tail and the asymmetric peak signals (solid line) compared with the experimental spectrum, and residual.

modified. The peak contribution calculated as in Eq. (3) is reported as a dashed line.

By comparing the residuals shown in Figs. 3 and 6 we can see that their trend is basically the same, their frequency being higher than that of the Br–O  $\chi(k)$  structural signal. For this reason the disagreement between the theory and the experiment can be associated with a long-path structural contribution rather than with the inaccuracy of the model g(r) at short distances. In particular the existence of ion-ion contacts or Br-O-O MS effects has to be taken into account. In concentrated aqueous solutions of brominated salts (more than 2M) a  $Br^--Br^-$  coordination at about 3.9-4.0 Å has been individuated.<sup>14</sup> Br<sup>-</sup>-Rb<sup>+</sup> interactions are expected to occur at even shorter distances. Nevertheless, it has been verified that the  $\chi(k)$ signals corresponding to these two-body contributions give rise to a higher frequency with respect to that found in the residuals. In addition, such ionic interactions are expected to disappear by increasing the dilution of the sample. An

TABLE I. First hydration shell fitting parameters:  $N_c$  is the coordination number, R represents the average distance,  $\sigma$  represents the vibrational standard deviation, and  $\beta$  is the asymmetry parameter.

Sample	N <sub>c</sub>	R(Å)	$\sigma(\text{\AA})$	β
Br <sup>-</sup>	6.9	3.34	0.20	0.81
IPB	5.2	3.55	0.32	0.76
	4.5	4.15	0.30	0.12
ETB	4.6	3.60	0.31	1.10
	4.5	4.10	0.29	0.40

FIG. 7. Model  $g_{Br,O}(r)$  function of the Br<sup>-</sup> aqueous solution obtained from the EXAFS refinement (solid line) compared with the MD  $g_{Br,O}(r)$ function (dots). The asymmetric peak obtained from the fitting procedure is reported with a dashed line.

analysis of all the Br–O–O triangles has been performed by considering all the configurations of the snapshots generated from 100 ps MD simulation. The existence of threebody signals of similar frequency as that of the residuals cannot be discarded, but a detailed analysis of the multibody contributions requires an extremely low-noise experimental spectrum since the magnitude of these effects is known to be only a few percent of the total signal.<sup>31</sup>

The IPB  $g_{Br,O}(r)$  obtained from the MD simulation shows a broader first peak as compared with Br<sup>-</sup>. For this reason two asymmetric peaks have been used to reproduce the g(r) model function up to 4.2 Å. As previously described for Br<sup>-</sup> the  $\chi(k)$  signals associated with the two peaks and with the long-distance tails have been calculated and the parameters defining the peaks have been optimized, while the tail signal has not been changed. In Fig. 8 the results of such a procedure are reported. The first signal from the top is the intramolecular contribution as previously calculated and it has been kept fixed during the minimization, the second and the third ones refer to the two asymmetric peaks while the fourth represents the tail contribution. The last three curves are the total theoretical contribution compared with the experimental spectrum, the intermolecular contribution compared with the experimental minus intramolecular signal and the residuals. The peak parameters obtained from the fitting procedure are reported in Table I. All of them did not change from the original values with the exception of the vibrational standard deviation of the second peak which increased by about 20%. The g(r) model obtained from the EXAFS refinement is reported in Fig. 9 and it is compared with



FIG. 8. Fit of the IPB aqueous solution experimental spectrum. From top to bottom are reported the intramolecular  $\chi(k)$  theoretical contribution, the two asymmetric peak  $\chi(k)$  signals, the tail signal, the sum of all the above-mentioned curves (solid line), compared with the experimental spectrum, the intermolecular contribution (solid line) compared with the experimental minus intramolecular signal (dots) and the residual.

the MD g(r) function. The two refined asymmetric peaks are reported with a dashed line. From Fig. 9 it is evident that in the case of IPB the behavior of the MD and EX-AFS g(r) functions in the short-distance region is basically the same.

It is important to stress that with respect to the usual fitting procedure within the Gaussian approximation, the fitting with asymmetric peaks implies only one additional parameter to be fitted for each peak. This slight increment is largely compensated by the shape correctness of the first g(r) rise which could not be modeled with a Gaussian peak. The starting asymmetric peaks are not casually generated. In fact, the MD g(r) provides a realistic starting model on which trial g(r) functions can be refined. When the MD simulations are not wide of the mark, we are under favorable circumstances to apply a fitting process similar to a minimization with constrained parameters. These conditions shrink meaningfully the indetermination on the parameters which in last instance contribute to define the g(r) first peak. A rough estimate of the free parameters that can be fitted is given by the  $2\Delta k\Delta r/\pi$  rule,<sup>32</sup> which supports the present least square (LS) fitting procedure.  $\Delta k$  is the k-space range over which the  $\chi(k)$  signal is fitted



FIG. 9. Model  $g_{Br,O}(r)$  function of the IPB aqueous solution obtained from the EXAFS refinement (solid line) compared with the MD  $g_{Br,O}(r)$ function (dots). The two asymmetric peaks obtained from the fitting procedure are reported with a dashed line.

and  $\Delta r$  is the width of the *r*-space Fourier filter window. In our case  $\Delta k$  is about 8 Å<sup>-1</sup> (the fact that the intermolecular signal dies out is anyway an information) and the  $\Delta r$ interval is limited by the mean-free path only, since we are not Fourier filtering the data.

The same procedure described for IPB has been applied to ETB. Also in this case two asymmetric peaks have been used to reproduce the first peak region of the MD g(r) and the associated  $\chi(k)$  signals have been minimized, while the tail signal has been kept fixed. The intramolecular contribution has not been varied during the fitting procedure. In Fig. 10 the intramolecular contribution together with the two refined asymmetric shells and the tail signals are reported. The last three curves are the total theoretical signal compared with the experimental spectrum, the intermolecular contribution compared with the experimental minus intramolecular signal and the residuals. By comparing Figs. 5 and 10 it can be seen that the agreement between the experimental and the theoretical signals was considerably improved by the refinement of the g(r) model. After the minimization, we have found a variation of 0.12 and 0.08 Å, respectively for the average distances of the two peaks while the coordination numbers did not appreciably change. All the refined parameters are listed in Table I. It is important to notice that the residuals obtained after the peak refinement contain only statistical noise. Thus, the oscillation present in the residual curve of Fig. 5 can reasonably be associated with an erroneous position of the first rise of the g(r) obtained from the MD calculation. As previously noticed the frequency of the signal contained in the residual is comparable to that of the Br-O contribution.



FIG. 10. Fit of the ETB aqueous solution experimental spectrum. From top to bottom are reported the intramolecular  $\chi(k)$  theoretical contribution, the two asymmetric peak  $\chi(k)$  signals, the tail signal, the sum of all the above-mentioned signals (solid line), compared with the experimental spectrum, the intermolecular contribution (solid line) compared with the experimental minus intramolecular signal (dots) and the residual.

In Fig. 11 the g(r) model obtained from the EXAFS refinement is compared with the MD one. The two asymmetric peaks obtained from the minimization are reported with a dashed line. The difference in the position of the first rise of the  $g_{Br,O}(r)$ , amounting to about 0.1 Å can be clearly observed in Fig. 11. The steric hindrance around the bromine atom is lower in ETB than in IPB. Therefore, in the MD simulations, the water molecules could fictitiously approach the bromine atom a little more in the ETB case. These findings based on the XAS investigation stimulate further investigations on the set of Lennard-Jones potentials and partial charges to be used for such systems. By means of the EXAFS analysis it has been possible to improve the short-distance shape of the starting MD g(r). It is important to stress that from the EXAFS analysis no information on the tail behavior can be obtained.

# **VI. CONCLUSIONS**

Br-O radial distribution functions for RbBr, IPB, and ETB diluted aqueous solutions have been calculated by means of MD simulations. As expected for a hydrated ion,



FIG. 11. Model  $g_{Br,O}(r)$  function of the ETB aqueous solution obtained from the EXAFS refinement (solid line) compared with the MD  $g_{Br,O}(r)$ function (dots). The two asymmetric peaks obtained from the fitting procedure are reported with a dashed line.

the height, and sharpness of the first and second Br-O peaks are pronounced for the bromine anion. For IPB and ETB, the molecular steric hindrance hampers the formation of a tightly, well-ordered water first coordination shell. The MD g(r) functions have been used to calculate the EXAFS spectra, obtaining a good agreement with the experiment for Br<sup>-</sup> and IPB. It has been shown that the first g(r) peak can be decomposed into asymmetric peaks. whose parameters can be refined by means of a fitting procedure on the basis of the EXAFS experimental spectrum. Finally, the g(r) first peak can be remodeled and shortrange order structural information on disordered systems can be obtained. In the case of IPB and ETB, we have shown that in spite of a strong intramolecular signal, the contribution due to the local disorder can be determined. The analysis procedure presented here may be applied to several cases where an overlapping of ordered and disordered coordination contributions occurs, as in the case of amorphous systems containing covalently bonded atoms. From the MD simulations of the IPB and ETB water solutions we have obtained g(r) functions with equal first rise distances, whereas the EXAFS analysis has shown that in the case of ETB the first g(r) peak has to be shifted. These results demonstrate that the EXAFS technique can be used to check and to improve the first shell of radial distribution functions obtained from MD simulations. Moreover, it can be used to verify if a set of potential energy functions and partial charges employed in the MD simulations give rise to realistic structural information on disordered systems, or not. The comparison between MD simulations and EX-AFS experiments may have promising applications. For

example, it has been shown that in the rubidium deoxycholate micellar aggregates in aqueous solutions, the rubidium cation has the same (or very similar) peculiar coordination as that inside the helices of the crystal and macromolecular fiber of rubidium deoxycholate. This coordination is remarkably different from that observed in the aqueous solutions of rubidium oxalate.<sup>33</sup> By describing the  $g_{\rm Rb,O}(r)$  first hydration shell as it has been done in the present paper for the Br-O pair correlation function, in the lack of structural models it could be possible to discriminate a preferred coordination from a completely disordered one in micellar systems. A study of rubidium bile salts and rubidium dodecyl sulfate aqueous micellar solutions is in progress. The comparison between MD and EXAFS may be also useful to individuate three-body correlation functions in ionic aqueous solutions which present a regular symmetry in the average positions of the first neighbor water molecules, as evidenced in the  $[Mn(H_2O)_6]^{2+}$  aqueous solution.<sup>31</sup>

#### ACKNOWLEDGMENTS

This work was sponsored by the Italian Consiglio Nazionale delle Ricerche and by the Italian Ministero per l'Università e per la Ricerca Scientifica e Tecnologica.

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