An extended x-ray absorption fine structure study by employing molecular dynamics simulations: Bromide ion in methanolic solution

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X-ray absorption spectroscopy is widely employed in the structural analysis of disordered systems. In the standard extended x-ray absorption fine structure (EXAFS) analysis the coordination of the photoabsorber is usually defined by means of Gaussian shells. It is known that this procedure can lead to significant errors in the determination of the coordination parameters for systems which present anharmonic thermal vibrations or interatomic asymmetric pair distribution functions. An efficient method has been recently employed in the study of the hydration shells of bromide and rubidium ions and brominated hydrocarbon molecules in diluted aqueous solutions. According to this method, pair distribution functions [g(r)] obtained from molecular dynamics simulations can be used as relevant models in the calculation of the EXAFS signals. Moreover, asymmetric shells modeled on the g(r) first peaks, have been employed in the EXAFS analysis and the parameters defining the asymmetric peaks have been optimized during the minimization procedure. In the present paper this new procedure has been used to investigate the coordination of Br⁻ in methanol. The analysis of this system is particularly interesting due to the presence of three well separated coordination shells. We show that the inclusion of the hydrogen signal is essential to perform a reliable analysis. A comparison of the analysis with asymmetric and Gaussian shells shows how the accuracy of the EXAFS data analysis is improved by using asymmetric shells. © 1996 American Institute of Physics. [S0021-9606(96)50404-4]

I. INTRODUCTION

X-ray diffraction (XRD) and neutron diffraction are very powerful techniques in the structural investigation of solid and liquid disordered systems and they are employed to determine the radial distribution functions g(r) of the system under study. The structural information contained in the structure factor for a single component system is complete and includes short-range as well as medium and long-range information. In the case of multicomponent systems the indetermination increases and the diffraction techniques, frequently, do not allow the assignment of specific pair distribution functions which contribute to the diffraction signal.

The increasing interest in characterizing disordered systems has stimulated the development of complementary structural techniques. Among these, x-ray absorption spectroscopy (XAS) has acquired a central role due to its atomic selectivity. By analyzing the oscillating behavior of the absorption cross section above the excitation threshold, the local structure around the photoabsorber atom can be determined both for crystalline¹ and disordered systems.^{2,3,4} This technique is more selective than x-ray and neutron diffraction since the partial distribution functions around a single atomic type can be determined. For an N-component system the g(r) extracted from the XAS signal contains the overlap of N independent pair distribution functions, against the N(N)(+1)/2 pair distribution functions overlapped in the XRD data. Therefore, it is easy to extract the structural information related to different coordination shells around the photoabsorber atom as compared to x-ray or neutron diffraction. A limitation of the XAS technique which has to be mentioned is its low sensitivity to the large distances. In fact, due to the broad correlation function towards the large distances and to the finite mean free path of the photoelectron, the sensitivity of the XAS technique is limited to the neighbourhood (about 5–7 Å) of the photoabsorber atom. The experimental determination of the g(r) over the full range of distances is hampered by this short range sensitivity, providing no information on the g(r) long distance tail. However the XAS signal is very sensitive to the short-distance features of the g(r) and in particular to the shape of its first rise allowing information on the short-range order. In the standard extended x-ray absorption fine structure (EXAFS) analysis the coordination of the photoabsorber is usually defined by means of Gaussian shells. Earlier studies have shown limitations in this procedure^{5,6} which can lead to significant errors in the determination of the coordination parameters for systems which present anharmonic thermal vibrations or interatomic asymmetric pair distribution functions. The cumulant method has been employed to detect and measure the effects of anharmonicity and of asymmetric distance distributions.^{4,7-12} Several EXAFS studies have been devoted to the determination of the asymmetric distribution functions in liquid metals and amorphous solids.^{3,4,6,8,13-16} A comparison of radial distribution functions obtained from Monte Carlo (MC) and molecular dynamics (MD) simulations or XRD and neutron diffraction with the asymmetric peaks used in the EXAFS analysis allows one to verify the reliability of the refined parameters. In recent years MC and MD simulations have been widely

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developed. Structural aspects of solids, liquids, and solutions^{17,18} can be predicted and the results can be compared with NMR, XRD, XAS and neutron diffraction experimental data. MC and MD simulations have been used to determine radial distribution functions of aqueous salt solutions^{19–23} which have been compared with XRD (Ref. 24) and neutron diffraction experiments.²⁵

Computer simulations are less frequently employed in the EXAFS data analysis. A "free style EXAFS fit algorithm" has been used to search for the best agreement between the experimental and calculated signal, starting from a generic radial distribution function with free shape and variable coordination number.²⁶ A reverse Monte Carlo procedure²⁷ which allows the fit of g(r) functions by generating a three-dimensional structural model, has been applied to the EXAFS analysis.²⁸ Comparison between MD simulations and EXAFS experiments have been performed in the study of high-temperature and high-pressure solids^{9,12,14,16} and metal clusters.²⁹

Recently, it has been shown that a deeper insight into the structural organization of disordered systems can be provided by employing, in the EXAFS data analysis, some external input on the distribution functions derived from diffraction data or theoretical simulations. Radial distribution functions extracted from XRD and neutron diffraction measurements have been employed to fit realistic g(r) functions to the EXAFS spectra of monoatomic systems such as Hg,³⁰ Ga,³¹ Cu, and Pd (Ref. 32) liquid metals. Similarities and differences between the structural information obtained from EXAFS and diffraction signals are discussed in Ref. 32. An efficient method which has been employed in the study of the hydration shells of Br⁻ and brominated hydrocarbon molecules in diluted aqueous solutions, uses pair distribution functions obtained from MD simulations as relevant models in the calculation of the EXAFS signals.³³ This procedure has been successfully applied to the study of the structure of micellar aqueous solutions of rubidium salts of bile acids.³⁴

In the present paper we have used this new procedure to investigate the coordination of Br⁻ in methanol (BMOH). It is important to stress that this approach becomes extremely useful when complex systems containing several pair distribution functions are considered. In the presence of many coordination shells around the photoabsorber atom, g(r)models obtained from MD simulations can represent an essential starting point for the EXAFS analysis. By combining EXAFS and MD information it is possible to perform an accurate analysis of complex systems. Such direct information on the structural organization of disordered systems would be difficult to achieve by means of diffraction techniques. The spatial separation among the pair distribution function first peaks is a favourable condition for a successful analysis of a polyatomic system. Previous MD simulations of MgCl₂ and NaCl in methanol^{35,36} have shown that the first peaks of the pair distribution functions related to the halogen anion are well separated. Since the high absorption coefficient of the solvent hampers the acquisition of reliable data at low concentration at the chlorine K-edge, we decided to focus our attention on the bromine K-edge.

TABLE I. Charges and Lennard-Jones parameters.

	q	σ (Å)	ϵ (kJ mol ⁻¹)
Br ⁻	-1.000	4.634	0.452
Н	0.398	0.000	0.000
0	-0.548	2.955	0.849
CH ₃	0.150	3.786	0.754

The paper is organized as follows: in Sec. II the results of the MD simulations are presented, Sec. III is devoted to the description of the experimental conditions, in Sec. IV the EXAFS data analysis is presented and the results are given in Sec. V.

II. MOLECULAR DYNAMICS COMPUTATIONAL PROCEDURE

The MD simulations were performed using a rigid three site methanol model. The equilibrium distances for C-O and O-H were 1.43 Å and 0.95 Å, respectively, with a bond angle of 108.53°. An NPT ensemble was considered using an isothermal-isobaric algorithm.37 Weak coupling to an external temperature bath of 300 K with a coupling constant of 0.1 ps, and to an external pressure bath of 1.0×10^5 Pa with a coupling time constant of 0.5 ps was used to maintain constant temperature and pressure. Model potential and geometry for methanol was taken from the GROMOS software package library.³⁸ The applied empirical potential energy function contains terms representing bond angle bending, van der Waals, and electrostatic interactions.³⁹ The function used in the present study for Br⁻ was reported by Straatsma and Berendsen.²¹ The SHAKE algorithm⁴⁰ was used to constrain bond lengths. A dielectric permittivity, $\epsilon = 1$, and a time step of 2.0 fs were used. The cutoff distance for the nonbonded interactions was 10 Å. Charges and Lennard-Jones parameters are reported in Table I. Simulations were carried out using a cubic box consisting of one Br⁻ and 124 methanol molecules subjected to periodic boundary conditions. The initial length of the box edge was set so as to agree with the experimental density. Configurations were saved every 25 steps and after equilibration, 2000 configurations were used to calculate ion-solvent and solvent-solvent pair distribution functions. The $g_{BrH}(r)$, $g_{BrO}(r)$, and $g_{BrMe}(r)$ pair distribution functions are shown in Fig. 1, where the running integration numbers are also reported. These are 6.2, 6.3, and 7.5 up to the corresponding first minima (3.2 Å, 4.1 Å, and 4.8 Å) of $g_{BrH}(r)$, $g_{BrO}(r)$, and $g_{BrMe}(r)$, respectively. The Me solvation number is larger than those of H and O, indicating an interpenetration of outer molecules into the first solvation shell, as found in the case of chloride ion.^{35,36} Recently, an EXAFS study of bromide ion in various solvents provided a low value (3.7) for the Br-O coordination number in methanol, on the basis of a single Gaussian shell (Br–O) analysis.⁴¹

The orientation of the methanol molecules in the first solvation shell can be deduced from the distribution of $\cos \psi$, shown in Fig. 2 (the ψ angle is defined in the insertion). Most of the methanol molecules lie in an O–H–Br⁻ linear con-



FIG. 1. Br–H, Br–O, and Br–Me pair distribution functions as derived from MD simulations for Br⁻ in methanol (left scale) and corresponding running integration number (right scale).

figuration demonstrating, as in the case of Cl^- in methanol, a strong preference for a linear hydrogen bond formation of the first solvation shell molecules with Br⁻. On the other hand, the $\cos \psi$ distribution explains the sharpness of the $g_{BrH}(r)$ and $g_{BrO}(r)$ first peaks. These are indicative of a tightly structured first solvation shell.

The solvent–solvent pair distribution functions are reported in Fig. 3. The first peaks of the $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$ reflect the hydrogen bonding. The locations of the first maxima are 2.73, 1.82, and 2.48 Å, respectively, and the corresponding integrals are 2.2, 1.0, and 2.3, respectively. These values are in good agreement with earlier studies on rigid liquid methanol obtained by MC simulations.⁴² The first peaks of the $g_{MeH}(r)$, $g_{MeO}(r)$, and $g_{MeMe}(r)$ are located at



FIG. 2. Distribution of $\cos \psi$ for the methanol molecules in the first solvation shell of Br⁻.



FIG. 3. O–H, H–H, and O–O (upper panel), Me–O, Me–H, and Me–Me (lower panel) pair distribution functions for methanol–methanol interactions as derived from MD simulations for Br^- in methanol.

2.75, 3.48, and 4.1 Å, respectively. The Me–O first peak yields four oxygens within a distance of 4.2 Å. Intermolecular bonding energy distribution of methanol monomers, shown in Fig. 4, is in agreement with the MC data,⁴² where a bimodal profile was found.

III. EXPERIMENT

Tetramethylammonium bromide (Fluka purum) was used to prepare a 0.15 M methanolic solution.

The XAS spectrum above the bromine K-edge has been recorded at room temperature, in the transmission mode at the ROMO II station of the Hamburger Synchrotronstrahlungslabor HASYLAB. The ROMO II beamline (bending magnet source, Doris storage ring) was equipped with a Si



FIG. 4. Distribution of the binding energy of methanol monomers as derived from MD simulations for Br⁻ in methanol.

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(311) double crystal monochromator controlled by a special feedback system.⁴³ The ionization chambers were filled with argon at atmospheric pressure. The storage ring was running at an energy of 4.45 GeV with an electron current between 80 and 20 mA. A third ionization chamber allowed possible shifts in energy to be checked by recording a reference substance together with the investigated sample. The analysis of the edge region, performed as described in a recent paper,³³ allowed the determination of the monochromator resolution (1.1 eV).

IV. XAS CALCULATIONS

As shown in Sec. II, the solvent molecule g(r) distribution function is made up of three pair distribution functions, as calculated by means of MD simulations. For a given g(r), the $\chi(k)$ signal can be calculated by means of a wellestablished equation in the EXAFS field,⁴ which is often applied to the study of disordered systems,

$$\chi_{\text{pair}}(k) = \int_0^\infty dr 4 \,\pi \rho r^2 g(r) A(k,r) \sin[2kr + \phi(k,r)],\tag{1}$$

where A(k,r) and $\phi(k,r)$ are the amplitude and phase functions,¹ respectively. In spite of the apparent upper integration limit of infinity in Eq. (1), the sensitivity of the $\chi(k)$ signal is limited to the neighborhood of the photoabsorber. This is due to the finite mean-free path $\lambda(k)$ of the photoelectron which generates an exponential decay of the type $\exp[-r/\lambda(k)]$. This effect, as well as the additional damping due to the monochromator resolution which mainly affects the low-k region of the spectrum, is included in the A(k,r) function. Several EXAFS investigations on disordered systems assume that the $\chi(k)$ signal is sensitive to the first coordination shell around the photoabsorber, only. The first-neighbor peak is often modeled with a Gaussian distribution although, by considering the low-distance shape of a pair distribution function, it is evident that the first peak cannot be well described by one or more Gaussian functions. A method which employs Gamma like distribution curves to describe the shape of the g(r) first peak has been previously described.³³ According to this method each model peak is defined by the mean distance R, standard deviation σ , asymmetry index β , and coordination number N_c . This function is used to calculate the EXAFS signal associated with the g(r)first peak. The asymmetric peak is subtracted from the MD g(r) obtaining a long-distance tail whose EXAFS signal is calculated by means of Eq. (1). This contribution is kept fixed during the minimization, while the four parameters describing the asymmetric peak are refined in order to achieve the best fit to the experimental spectrum. In this work three asymmetric peaks, representing the Br⁻ methanol pair distribution functions, have been employed in the EXAFS analysis.

Phase shifts have been calculated in the muffin-tin approximation starting from overlapped spherically averaged relativistic atomic charge densities. One of the molecular distributions obtained from the MD simulations of BMOH has been used to calculate the phase shifts. The values of the muffin-tin radius are 1.58 Å, 0.40 Å, 0.90 Å, and 0.70 Å for the Br⁻, hydrogen, oxygen, and carbon of the methyl group, respectively. It has been verified that different configurations give the same result. A Hedin–Lundqvist plasmon-pole approximation is used for the self-energy part of the optical potential.⁴⁴ Inelastic losses of photoelectrons in the final state are accounted for intrinsically by complex potentials.⁴⁵ The imaginary part also includes a constant factor accounting for the known core–hole width.

The total $\chi(k)$ theoretical curve is given by the sum of the $\chi(k)$ signals associated with different atoms of the solvent. These have been calculated by means of Eq. (1), starting from the pair distribution functions obtained from the MD simulations. Fits of the XAS spectra have been performed directly on the raw data using the FITHEO program.⁴⁶ For an accurate XAS analysis it is necessary to take into account the presence of discrete resonances and slope changes in the atomic background associated with the onset of multielectron excitation channels. The $KN_{2,3}$, KN_1 , $KM_{4,5}$, and $KM_{2,3}$ edges, corresponding to the simultaneous excitation of the 1s4p, 1s4s, 1s3d, and 1s3p electrons, respectively, have been detected in the absorption spectra of several brominated compounds. The background functions have been modeled accounting for the double-excitation edges by means of step shaped functions as previously described,⁴⁷ with energy onset values equal to those found for gaseous HBr within the reported errors.48

As shown previously,⁴⁷ the background parameters are practically uncorrelated with the others. Three important nonstructural parameters related to the $\chi(k)$ signal are E_0 , S_0^2 and the resolution of the monochromator. E_0 is the photon energy required for the transition to the continuum threshold and allows the theoretical and experimental energy scales to be compared. S_0^2 accounts for a uniform reduction of the signal associated with many-body effects. As previously shown⁴⁷ this parameter is equal to 1, when double-excitation effects are properly included in the atomic background. The value of the monochromator resolution has been determined from the experimental spectrum as explained in Sec. III. During the fitting procedure these three parameters were minimized. The monochromator resolution showed variations of less than 0.1 eV and S_0^2 was practically equal to one.

All the minimizations have been performed in the same k range ($3 \le k \le 16 \text{ Å}^{-1}$), including 418 experimental points. The fit index R_i is defined by Eq. (5) of Ref. 47 and a k weighting value of 2.5 was applied. The number of the structural parameters used in the fitting procedure was 3 for the analysis performed using the MD g(r) functions, 9 for the analysis in the Gaussian approximation, and 12 for the analysis with three asymmetric shells.

A rough estimate of the free parameters that can be fitted in the EXAFS data analysis⁴⁹ is given by the $2\Delta k\Delta r/\pi + 2$ relation,⁵⁰ which supports the present least-square fitting procedure. Δk is the *k*-space range over which the $\chi(k)$ signal is fitted and Δr is the width of the *r* space Fourier filter window. In our case Δk is approximately 13 Å⁻¹ and Δr is limited by the mean-free path only, since we are not Fourier filtering the data.

Parameter correlations and standard deviations can be determined, for the *p* free parameters used in the minimization, by tracing constant chi-square boundaries, also known as correlation maps.⁵¹ R_i is calculated around the minimum as a function of two parameters, keeping fixed the others $\nu = p-2$ parameters. Three contours are drawn for ΔR constant shifts from the minimum $R_i \times (N-p)/N$ and correspond to the 68.3% $(\pm \sigma)$, 95.4% $(\pm 2\sigma)$, and 99.73% $(\pm 3\sigma)$ confidence regions. ΔR is defined by the equation $\Delta R = \chi_{\nu}^2 \times R_N/(N-p)$. χ_{ν}^2 represents the value of the reduced chi-square corresponding to a defined confidence level, and R_N is an estimate of the experimental noise calculated in the FITHEO program, as described elsewhere.⁴⁶

The confidence region ellipses that contain 68.3% of normally distributed data were used to determine the standard deviations, which were obtained by projecting the higher dimensional region onto the lower-dimension space.⁵¹ From the correlation maps, drawn for different couples of parameters, standard deviation values can be obtained. The largest ones have been chosen to define the standard deviation magnitudes associated with the parameters obtained from the XAS analysis.

V. XAS ANALYSIS OF Br- IN METHANOL

The XAS analysis of the Br^- methanolic solution has been carried out starting from the results described in Sec. II. The outstanding observation of this analysis concerns the strong amplitude of the Br^--H signal. Due to the well ordered structure of the solvent molecules, it was possible to identify, for the first time, the contribution of the hydrogen atoms of the solvent to the x-ray absorption cross section. Generally, the low scattering amplitude prevents the hydrogen signal to be identified, especially in the case of disordered systems. It is clear from the MD pair distribution functions that the presence of the negative charge of the $Br^$ enforces the methanol molecules to take up a well ordered structure with the hydrogen atoms directed towards the ion. This occurrence explains the unusually strong amplitude of the hydroxyl hydrogen signal.

The first step of the analysis involved the calculation of the theoretical signal by means of Eq. (1), starting from the g(r) pair distribution function obtained from the MD simulations. A fitting procedure was applied in order to improve, as far as possible, the agreement with the experimental spectrum. The upper panel of Fig. 5 shows the Br-H, Br-O, and Br-Me theoretical signals, the comparison between the sum of these contributions and the experimental spectrum, and the residuals (from top to bottom, respectively). The agreement between the experimental and the theoretical signal is satisfactory and a $R_i = 0.495 \times 10^{-6}$ has been obtained. From the minimization no significant shifts of the g(r) functions have been observed. From the upper panel of Fig. 5 it is evident that the total signal is dominated by the Br-O and Br-Me contributions, while the Br-H signal is weaker and mainly affects the low-k region of the spectrum. Neverthe-

FIG. 5. Fit of the BMOH experimental spectrum. Upper panel: from top to bottom the $\chi_{BrH}(k)$, $\chi_{BrO}(k)$, and $\chi_{BrMe}(k)$ theoretical signals corresponding to the MD pair distribution functions, their sum compared with the experimental spectrum, and the residual are shown. Bottom 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.

less, the inclusion of this low-frequency contribution has been found to be essential to properly reproduce the experimental spectrum.

Proof of the importance of the Br–H signal was also obtained by excluding this contribution from the fitting procedure. The lower panel of Fig. 5 shows the comparison between the total theoretical signal, including the Br–O and Br–Me contributions only, and the experimental spectrum, together with the residuals. In this case, the agreement between experiment and theory is unsatisfactory $(R_i=1.030\times10^{-6})$ and the residual curve contains a frequency and amplitude component which is similar to the $\chi_{BrH}(k)$ signal shown in the upper panel of Fig. 5.

The second step of the analysis was the substitution of the pair distribution functions with three asymmetric shells representing the g(r) first peaks. Each peak is narrow enough to be described by one asymmetric peak, only. The difference between the MD g(r) and the asymmetric peak defines a long-distance tail³³ whose contribution is calculated by means of Eq. (1). The three tail signals have been found to be negligible in the whole k-range and therefore they have not been included in the calculated curve. This result confirms the low sensitivity of the XAS technique to the large distances. The $\chi(k)$ signals associated with the asymmetric peaks were calculated by using the previously described procedure.³³ During the minimization, the shape of the asymmetric peaks has been optimized by varying the peak parameters. The upper panel of Fig. 6 shows the Br-H, Br-O, and Br-Me theoretical signals, the comparison between the total $\chi(k)$ signal and the experimental spectrum, and the residuals.



FIG. 6. Fit of the BMOH experimental spectrum performed with asymmetric shells. Upper panel: from top to bottom the $\chi_{BrH}(k)$, $\chi_{BrO}(k)$, and $\chi_{BrMe}(k)$ asymmetric peak contributions, their sum compared with the experimental spectrum, and the residual are shown. Bottom 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.

The agreement between the calculated and the experimental signal is satisfactory and this result is confirmed by the fit index value ($R_i = 0.490 \times 10^{-6}$), 1.6 times greater than R_N . Notice that the residual curve shows a high frequency oscillation which is above the noise of the spectrum. The high frequency of this signal could be associated with a long-path contribution and in particular with multiple scattering (MS) effects due to well-defined three body arrangements. This oscillating behavior is less evident, but still detectable in the residual curve shown in the upper panel of Fig. 5. The presence of triplet correlations in the hydration shell of aquaions has been already evidenced in other systems.⁵² This finding suggests the necessity of a deeper investigation on the triplet correlation contributions to the XAS spectra of liquid systems.

The parameters describing the three asymmetric shells together with the standard deviations are shown in Table II. The standard deviations of the refined parameters are obtained from the correlation maps, as explained in Sec. IV.

The importance of the hydrogen contribution has been pointed out also by performing a minimization without the Br–H signal. The results of this analysis are shown in the lower panel of Fig. 6. The agreement between theory and experiment is not satisfactory (R_i =1.093×10⁻⁶) and the residual curve contains a low-frequency oscillation which is due to neither the oxygen nor the methyl coordination shell. The Br–O and Br–Me asymmetric shell parameters, shown in Table II, are similar to those obtained from the previous analysis with the exception of the coordination numbers. In the absence of the hydrogen shell, an increase of about 18%

TABLE II. First solvation shell parameters of Br⁻ in methanol, for the minimizations with asymmetric (AS) and Gaussian (GS) shells. The standard deviations are given in parentheses for the minimizations including the hydrogen shell. *R* represents the average distance in Å, σ^2 is the vibrational variation in Å², β is the asymmetry parameter, and *N* is the coordination number.

	AS	AS (without H)	GS	GS (without H)
R _H	2.46 (0.03)		2.34 (0.04)	
$\sigma_{\rm H}^2$	0.072 (0.013)		0.031 (0.009)	
$\beta_{\rm H}$	1.58 (0.15)			
N _H	6.8 (0.9)		5.9 (1.7)	
R _O	3.40 (0.01)	3.41	3.28 (0.01)	3.30
σ_0^2	0.058 (0.005)	0.059	0.023 (0.002)	0.027
β_0	1.18 (0.04)	1.11		
No	6.1 (0.2)	7.2	4.8 (0.3)	6.3
R _{Me}	4.23 (0.03)	4.21	3.92 (0.02)	3.93
σ_{Me}^2	0.124 (0.016)	0.125	0.067 (0.013)	0.047
$\beta_{\rm Me}$	1.32 (0.09)	1.15		
N _{Me}	7.0 (0.7)	7.4	9.0 (2.8)	7.6

and 6% can be observed for the oxygen and methyl coordination numbers, respectively. The standard deviations are not reported, as the low agreement with the experimental spectrum does not allow a measure of reliable errors from the correlation maps.

The EXAFS analysis of disordered systems is often carried out by using Gaussian peaks to model the photoabsorber coordination shells. The reliability of this approach can be checked by comparing the results of this method with those obtained from the asymmetric peak analysis. The minimization performed in the Gaussian approximation gives rise to more dumped calculated signals and to a poorer agreement between the total calculated and the experimental signal $(R_i=0.608\times10^{-6})$, compared to the previous analysis. Significant differences have been observed in the structural parameters obtained from the two methods. The parameters describing the Gaussian shells and standard deviations are listed in Table II. The iteration procedure has been carried out starting from fitting parameters similar to those obtained from the asymmetric shell analysis.

As in the above-mentioned cases the fit index of the analysis omitting the hydrogen contribution was $R_i = 0.998 \times 10^{-6}$ and the structural parameters are given in Table II. A comparison of the structural parameters obtained from the analysis with the inclusion and the exclusion of the hydrogen shell, shows significant variation of the oxygen and methyl coordination numbers. These values are similar to those obtained from the asymmetric shell analysis. This co-incidence is due, merely, to the low sensitivity of the minimization procedure to the variation of the coordination numbers. Minimizations carried out using different starting coordination numbers failed to show any significant shift from the initial values.

A more direct description of the differences between the coordination shell parameters obtained from the two EXAFS analysis can be obtained by comparing the refined asymmetric and Gaussian peaks. In Fig. 7 these peaks are shown together with the MD g(r)'s. Strong differences between the



FIG. 7. From top to bottom: asymmetric (dashed) and Gaussian (full) peaks obtained from the EXAFS analysis compared with the $g_{BrH}(r)$, $g_{BrO}(r)$, and $g_{BrMe}(r)$, respectively, obtained from the MD simulations.

Gaussian and the asymmetric shells are evident from this figure. In particular, the Gaussian shells do not reproduce the shape and the integration numbers of the MD g(r) first peaks. The Gaussian methyl peak is shifted towards lower distances, giving rise to a partial overlap with the oxygen shell, while the integration number and the full-width at half-maximum (FWHM) values are both increased for the methyl shell, as opposed to the decreased values observed for the oxygen one. From these results it is evident that the analysis performed with Gaussian shells does not allow a good description of the distribution of methanol molecules around the bromine anion.

Notice that the constraint rule $\Delta N=0$ (ΔN represents the variation of the sum of the coordination numbers during the minimization) suggested for the refinement of monatomic systems with more coordination shells,³² cannot be applied in the case of a polyatomic system, in particular in the case of the Gaussian approximation. In the present case, the total coordination number varies of 0.2 only (going from 19.9, for the asymmetric shell analysis, to 19.7 for the Gaussian shell analysis) in spite of the difference between the agreement indexes. It is evident that for systems with coordination shells constituted by atoms with similar phases and scattering amplitudes, the constraint rule $\Delta N=0$ cannot be applied in the minimization procedure. As in the case of oxygen and

carbon atoms, such shells give rise to non distinguishable EXAFS signals.

The statistical significance of the inclusion of the hydrogen signal can be checked by performing the F-test⁵³ for the three cases under study.⁵⁴ In all these cases, the F-test applied for the 95% confidence level, assesses that the decrease of the fitting index after the addition of the hydrogen shell, is statistically significant.

At this point, the problem of the accuracy of the structural parameters shown in Table II, needs to be addressed. By neglecting systematic errors in the experimental data and in the theory, the errors affecting the fitted values can be estimated on the basis of standard statistical concepts. Nevertheless, correlation effects can increase the standard deviation of the parameters and a deeper insight into this problem can be provided by using contour maps for each couple of parameters.⁵¹ In Figs. 8–11 some of the most meaningful correlation maps calculated for the asymmetric and Gaussian shells can be compared.

The correlation between E_0 and the shell distances is shown in Fig. 8. E_0 appears to be strongly correlated with the shell distances. The errors on E_0 and on the hydrogen and oxygen distances, shown in Table II, have been obtained from the R E_0 correlation maps. This result is consistent with the well-known indetermination on distances produced by E_0 (see for example, Refs. 1–3).

The $R\sigma^2$ correlation maps are shown in Fig. 9. The distance and the Debye–Waller factors are strongly correlated in the case of the asymmetric shells. However, it has to be stressed that the FWHM of a Gaussian shell is determined by the σ value, only, while the width of an asymmetric shell is determined by two parameters (σ and β). The narrow confidence regions of the oxygen shells point out that the accuracy of the minimization depends mainly on the oxygen contribution.

The correlations between the coordination numbers, as shown in Fig. 10, are more pronounced in the case of the hydrogen and methyl shells, both in the Gaussian and in the asymmetric shell analysis. The narrow confidence region of the correlation maps associated with the oxygen shell is due to both the large difference of the scattering amplitude of the hydrogen and oxygen atoms, and the long Br–Me distance.

The existence of a strong correlation between the coordination numbers and the Debye–Waller factors is a well established phenomenon in the EXAFS data analysis. This effect is responsible for the large uncertainty on the coordination numbers which is a characteristic of EXAFS performed in the Gaussian approximation, and in general of diffraction techniques. A strong correlation between N_c and σ^2 is evident from the maps associated with the Gaussian shells shown in Fig. 11. On the other hand from the correlation maps associated with the asymmetric shells a smaller correlation between these parameters can be observed. In addition, the confidence regions are narrower, showing a better reliability of the refined parameters. The most interesting conclusion which can be drawn from a comparison of the correlation maps is that the correlations between the Gauss-



FIG. 8. Correlation maps of the R E_0 couples for asymmetric and Gaussian shells minimizations (left and right column, respectively). The contours correspond to the 68.3% ($\pm \sigma$), 95.4% ($\pm 2\sigma$), and 99.73% ($\pm 3\sigma$) confidence regions. For the asymmetric shells, R represents the average value shell distance.

ian parameters are not equivalent to those of the asymmetric shells. Moreover, these maps allow the identification of the most correlated parameters and of the couples which give rise to the maximum standard deviation for each parameter. These results provide new insight into the limits of the EX-AFS data analysis of polyatomic systems. importance of refining EXAFS data using realistic g(r) models. In the case of polyatomic disordered systems, a proper description of the photoabsorber coordination shells is difficult to achieve by means of the standard EXAFS analysis. In particular, the strong correlation between the parameters hampers an unerring set of coordination shells to be identified. Minimizations carried out using peak parameters far

The last remark we would like to make concerns the



FIG. 9. Correlation maps of the $R\sigma^2$ couples for asymmetric and Gaussian shells minimizations (left and right column, respectively). The contours correspond to the 68.3% ($\pm\sigma$), 95.4% ($\pm2\sigma$), and 99.73% ($\pm3\sigma$) confidence regions. For the asymmetric shells, R represents the average value shell distance.

from the MD ones failed to provide a definite description of the studied system.

VI. CONCLUSIONS

The results presented in this paper represent a step forward in the EXAFS analysis of disordered systems. Some outstanding results can be deduced.

- (1) The importance of using realistic g(r) models as a starting point for the EXAFS analysis of disordered systems, has been shown. This approach becomes essential when complex disordered systems are considered.
- (2) It has been shown that the inclusion of the hydrogen signal is essential to perform a reliable analysis of the studied system.



FIG. 10. Correlation maps of the $N_c N_c$ couples for asymmetric and Gaussian shells minimizations (left and right column, respectively). The contours correspond to the 68.3% ($\pm \sigma$), 95.4% ($\pm 2\sigma$), and 99.73% ($\pm 3\sigma$) confidence regions.

(3) A proper method, based on well-established statistical concepts,⁵¹ has been used to calculate statistical errors of the fitting parameters. Due to the strong correlations between some parameters the necessity to use correlation maps in the EXAFS error evaluation has been pointed out. and asymmetric peak analysis has been accomplished. In particular, for the first time the most significant correlation maps obtained from the asymmetric peak and the Gaussian analysis have been compared. This analysis allowed the limit of the Gaussian approximation to be assessed; in the case of disordered multicomponent systems, the accuracy of the EXAFS data analysis is

(4) A comparison of the results obtained from the Gaussian



FIG. 11. Correlation maps of the $N_c \sigma^2$ couples for asymmetric and Gaussian shells minimizations (left and right column, respectively). The contours correspond to the 68.3% ($\pm \sigma$), 95.4% ($\pm 2\sigma$), and 99.73% ($\pm 3\sigma$) confidence regions.

improved by using asymmetric shells, especially in the medium-distance range.

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