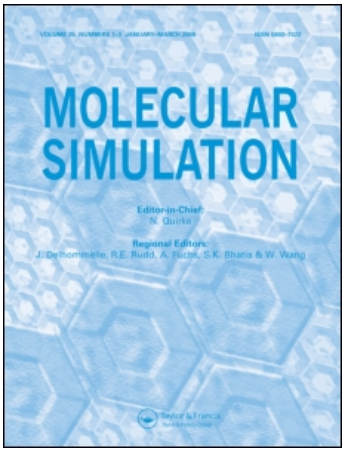

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

The solvation of bromide anion in acetonitrile: a structural study based on the combination of theoretical calculations and X-ray absorption spectroscopy

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To cite this Article Ayala, R. , Martínez, J. M. , Pappalardo, R. R. , Muñoz-Páez, A. and Marcos, E. Sánchez(2006) 'The solvation of bromide anion in acetonitrile: a structural study based on the combination of theoretical calculations and X-ray absorption spectroscopy', Molecular Simulation, 32: 12, 1035 — 1043
To link to this Article: DOI: 10.1080/08927020601089064
URL: http://dx.doi.org/10.1080/08927020601089064

Molecular Simulation, Vol. 32, Nos. 12–13, 15 October–15 November 2006, 1035–1044

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The solvation of bromide anion in acetonitrile: a structural study based on the combination of theoretical calculations and X-ray absorption spectroscopy

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(Received June 2006; in final form October 2006)

This work studies the solvation of bromide in acetonitrile by combining quantum mechanics, computer simulations and X-ray absorption near edge structure (XANES) spectroscopy. Three different sets of interaction potentials were tested, one of them derived from literature and the other two are simple modifications of the previous one to include specificities of the bromide–acetonitrile interactions. Results for microsolvation of bromide were obtained by quantum mechanical optimization and classical minimization of small clusters $[Br(ACN)_n]^-$ ($n = 9$, 20). Analysis of molecular dynamics (MD) simulations has provided structural, dynamic and energetic aspects of the solvation phenomenon. The theoretical computation of Br K-edge XANES spectrum in solution using the structural information obtained from the different simulations has allowed the comparison among the three different potentials, as well as the examination of the main structural and dynamic factors determining the shape of the experimental spectrum.

Keywords: Bromide; Solvation phenomenon; Quantum mechanics; XANES spectrum; MD simulations; Intermolecular potentials; XANES

1. Introduction

Although halide anions are the most common counter-ions in solution, the investigation of their solvation in aprotic solvents is very limited in comparison with that in water and other protic and polar solvents, such as alcohols [1]. This is in contrast to the increasing importance of these types of solutions due to their technological applications within fields such as separation chemistry, electrochemical devices or ionic recognition [1–3]. The non-aqueous solvation structures of halide anions are not completely defined so far owing to both experimental and theoretical difficulties. First of all, the central body of experimental data on halide solvation in non-aqueous solvents does not provide direct structural information. This is usually obtained by using reasonable models compatible with the available data. Spectroscopic and diffraction techniques offer more direct structural information, but the increase in the number of atom pair contributions to the global distribution function, compared to the water case, renders more difficult the structural elucidation. In addition, the high concentration of the species of interest, usually required by these techniques, does not allow us to discard ion–ion contributions from the global signal. For this reason, during the last decade an intense research activity on the study of small clusters has been developed with the aim of separating the ion–solvent from the pure solvent–solvent interactions [4,5]. On the other hand, theoretical studies of halide solvation are hampered by the fact that the halide–solvent interactions are rather weak leading to a delicate balance between the ion–solvent and solvent–solvent interactions [6]. This trend becomes particularly significant for bromide and iodide anions and for aprotic and not very polar solvents. Thus, for these two anions, solvation number within the range 1–9 are found in the literature [2,7,8] when acetonitrile is used as solvent. Furthermore, the structural arrangement adopted by the solvent molecules is far from clear. In this sense, Richardi *et al.* [3,8] propose in two theoretical studies based on molecular Ornstein–Zernike (MOZ) theory, a non-aligned orientation of the solvent molecules with respect to the ion. This is in contrast to the conventional assumption

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Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020601089064

where an ion–dipole interaction is dominant according to which the highest stabilization energy would be provided by structures where acetonitrile molecules in contact with the anion would orientate their dipole axis passing through the anion center.

Nowadays, X-ray absorption spectroscopy (XAS) is a well-established technique to study structural and electronic properties of the local environment of a given atom. A large number of investigations [9–11] have demonstrated the suitability of this technique to study ionic solutions because it requires only short-range order and can be applied to a wide range of concentrations, covering several orders of magnitude (from 10^{-4} to 10 M) [12]. The X-ray absorption spectrum has been traditionally divided into two energy regions. The low energy part of the spectrum, extending up to ~50–100 eV above the absorbing edge, called X-ray absorption near edge structure (XANES) region and the high energy part of the spectrum (over 100 eV above the threshold up to approximately 1000 eV) called extended X-ray absorption fine structure (EXAFS). The XANES region has been shown to be dependent on many parameters of the system under study: the oxidation state of the absorber atom, bond angles, coordination geometry, distances of the absorbing atom to the first and higher coordination shells, etc. [13] Contrary to the EXAFS region, there is not a simple formulation that encompasses all these parameters. This fact has led to the use of XANES information on a more qualitative level that envisages the spectrum as a "fingerprint" of the system under study. In the last years, implementation of models for the absorption phenomena have allowed the development of codes which accurately simulate the XANES region thus approaching the situation for the EXAFS region [14,15]. In this way, the theoretical simulation of XANES of ionic solutions is an emerging branch [16,17].

The aim of this work is to study the bromide solvation structure in acetonitrile by combining the experimental information derived from XANES spectroscopy with theoretical data from quantum mechanics calculations and molecular dynamics (MD) simulations. For the latter ones, simple methods to get specific interaction potentials for bromide in acetonitrile are investigated. The interplay of XAS spectroscopy with quantum mechanics and numerical simulations has shown to be as an appropriate strategy to get insight into structural information on ionic aqueous solutions [18–27] and will be explored for the case of a non-aqueous solution.

In a previous study [6] dealing with bromide solvation within the framework of a quantum-mechanical approach, we showed that the bromide anion interacts with the acetonitrile molecules through the hydrogen atoms of the methyl group. The linear minima are in all cases slightly higher in energy that the bent ones, in good agreement with the findings of Richardi *et al.* [3,8] in their statistical simulation of bromide solvation in acetonitrile.

In this work, we will use the structural information derived from quantum chemical minimizations and from statistical simulation trajectories using interactions potentials from the literature [28,29] and simple modification on them (see Section 2.2 for details) to compute the XANES spectra. Direct comparison with the available experimental XANES spectra for this system will allow the definition of new criteria to examine the validity of the results and conclusions reached, as well as to explore an additional way to define and validate intermolecular potentials.

2. Computational methods

The analysis of the structural results derived from computations is based on the examination of the main features of the simulated XANES spectra and their comparison with the experimental one. An input structure, as detailed as possible, is required since XANES is particularly sensitive to the close environment. The source of structures to be used for the simulated spectra have a double origin. First, clusters formed by one bromide anion and an increasing number of acetonitriles molecules computed at the quantum mechanical level. Second, snapshots extracted from the MD trajectories of a bromide anion immersed in a large number of acetonitrile molecules simulating the solution, at room temperature. The computer simulations have not been limited exclusively to the application of combination rules to obtain the appropriate intermolecular potentials from the literature. In addition, some easy to implement procedures have been applied to obtain new potentials. Their validity is discussed by checking the simulation results in the light of the XANES spectrum and other available experimental data.

2.1 Quantum mechanical computations

The starting structures were taken from a previous work [6] dealing with the microsolvation of the bromide anion in water, methanol and acetonitrile. The bromide–acetonitrile cluster were optimized at B3LYP level with the 6–31 + G* basis set. The energy minimized $[Br(ACN)_9]^-$ structure was characterized as minimum in the PES of the bromideacetonitrile system. Gaussian03 suite of programs were used for computations [30].

2.2 Molecular dynamics simulations

Three different sets of interaction potentials have been used to simulate the solvation of the bromide anion in acetonitrile at room temperature (298 K):

- The first set was built from the recent model of Grabuleda *et al.* [28] for acetonitrile liquid, whereas bromide anion was described by the parametrization performed by McCammon *et al.* [29] In both cases, potential parameters were developed in the framework of the Cornell *et al.* [31] force field providing flexible all-atom models for the acetonitrile molecules. Internal

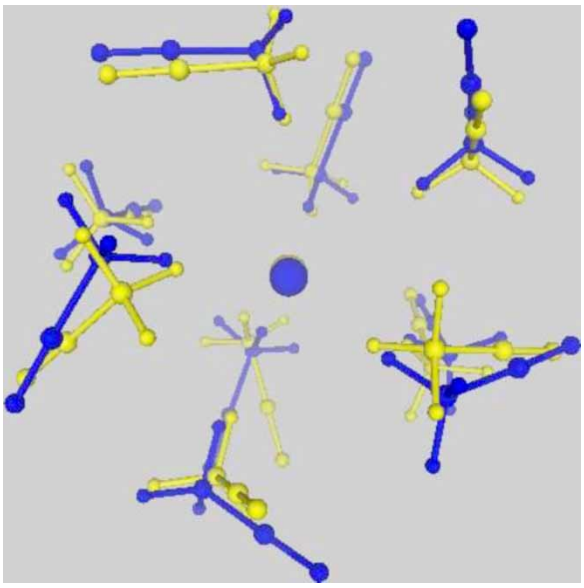


Figure 1. Quantum mechanically optimized structure (blue) for $[Br(ACN)_9]^-$ cluster together with the minimum RMSD configuration (yellow) according to the $\sigma_{Br—H}$ parameter (see text for details).

deformations were allowed by means of the usual bond, angle and torsion terms, while the non-bonded van der Waals and electrostatic terms were used to describe the intermolecular interactions. This set of potentials will be labeled Pot-A (in this set of potentials, the combination rule leads to a value for the van der Waals parameter of the Br—H pair $\sigma_{Br—H} = 3.6$ Å).

- The second set of potentials tested was a simple modification of the previous one, based on the hydrated ion concept developed by our group for the cation hydration case [32]. The solvated bromide cluster with $n = 9$, $[Br(ACN)_9]^-$, was used as a reference structure to modify the van der Waals parameter $\sigma_{Br—H}$. For this purpose, that parameter was chosen in such a way that the atomic root mean square deviation (RMSD) between the quantum mechanical and force field optimized structure was minimized. The optimum value was $\sigma_{Br—H} = 3.2$ Å(RMSD = 0.7 Å, the superposition of both structures is shown in figure 1). This set of potentials will be labeled Pot-B.
- In a similar way, a third set of potentials was used by modifying the $\sigma_{Br—H}$ parameter in order to test the sensitivity of the Br K-edge XANES spectrum of bromide in acetonitrile to changes in the closest environment of the absorber atom, as well as to other properties of the solution. Bearing in mind that the value of this parameter in the first set of interaction potentials was 3.6 and 3.2 Å for the second set, a value of 2.9 Å for $\sigma_{Br—H}$ was chosen. Thus, a range of 0.7 Å (2.9–3.6) will be used to get an insight into the relationships between spectrum and structure, on one hand and between solution properties and σ values, on the other. This set of potentials will be labeled Pot-C.

The elementary simulation cell contained 1 bromide ion and 500 acetonitrile molecules. The length of the cubic cell, $L = 30.30$ Å, was set to reproduce the experimental value for the density of liquid acetonitrile at 25°C. Periodic boundary conditions were applied. A time step of 0.25 fs was used. The cutoff distance for the non-bonding interactions was $L/2$ Å. Long-range interactions were incorporated by means of Ewald summation [33] including a charged system term [34,35]. Simulations with net charged cells can be performed using an energy correction term which is physically equivalent to adding a uniform jelly of charge that exactly neutralizes the total cell charge [36]. The system was equilibrated at the chosen temperature for 50 ps. 500 ps of simulation time was produced in the *NVT* ensemble for each set of the interaction potentials considered. The average temperature was maintained constant at 300 K by a Berendsen thermostat [37] with a time constant of 0.5 ps. Structures were saved every 2 ps for further analysis. The MD simulations were performed with DLPOLY program [38], running on a parallel multiprocessor SGI ALTIX 350 computer using 20 processors.

2.3 Computation of XANES spectra

The K-edge XANES spectrum of bromide in acetonitrile was computed for several structures. On one hand, cluster optimized structures involving nine acetonitrile molecules ($[Br(ACN)_9]^-$) were performed, the origin of the structures being quantum mechanically or potential derived, as well as for a $[Br(ACN)_{20}]^-$ cluster optimized with the set of intermolecular potentials Pot-B. On the other hand, XANES spectra obtained from MD trajectories employing 100 snapshots equally spaced (taken every 5 ps) were also produced for all the interaction potential sets. The final simulated XANES spectrum from the MD simulation corresponds to the average over the spectra of each snapshot set.

The FEFF8.10 code program developed by Rehr's [15] group was used to calculate the spectra. The potential calculations use the Hedin–Lundqvist self-energy approximation [39]. A self-consistent field procedure (SCF) was employed. A 6.0 Å cutoff radius was chosen for the SCF treatment and for the full-multiple scattering paths. A full-multiple scattering path calculation was done taking as origin the absorber atom, i.e. the bromide anion. Then, the chosen structure included the backscatter atoms inside a sphere of 6.0 Å radius centered at the bromide. However, for the SCF procedure, for each type of atom the origin of the cutoff radius was placed in that atom, which means that the region of the solution considered for calculation is increased by the distance between the bromide anion and the corresponding atom. This SCF procedure introduces a difference between the XANES computation derived from quantum mechanical or statistical calculations, as the size of the solvent sphere surrounding the anion is, in general, not complete for all the types of atoms when clusters optimized

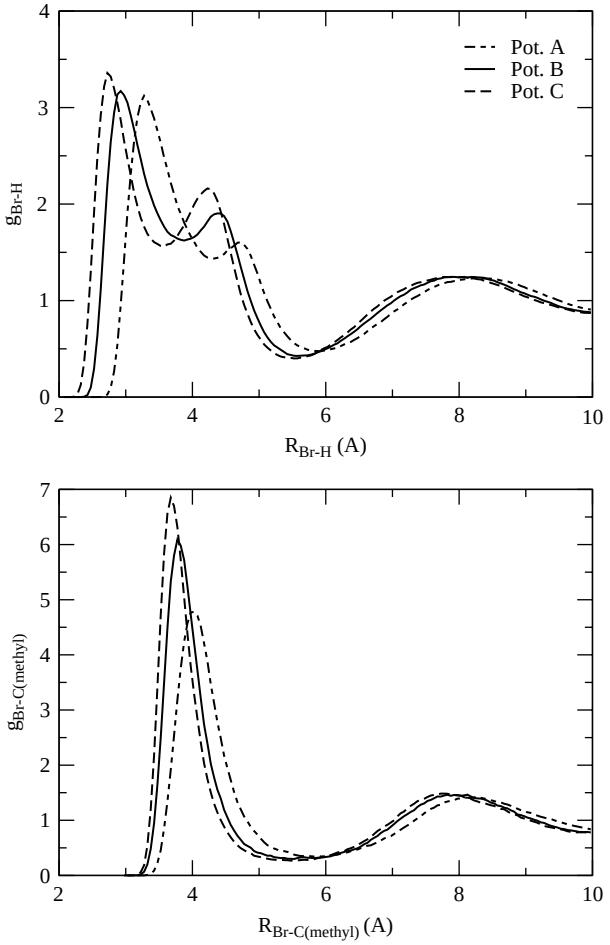


Figure 2. Radial distribution functions for (top) Br—H and (bottom) Br—C(methyl) pairs of Pot-A, Pot-B and Pot-C simulations.

quantum-mechanically are considered. A XANES spectrum calculated from 250 snapshots taken every 2 ps configurations yields very similar results to the one obtained using 100 snapshots taken every 5 ps. The consideration of a larger cutoff radius, such as 7.0 Å in the SCF computation of the wavefunction to determine potentials and/or XANES spectra calculation do not affect the results.

In a previous work [27] on bromide hydration structure, it was necessary to include the hydrogen atoms to obtain a realistic backscattering potential and a simulated XANES spectrum that resembled experimental data. This could be understood by the fact that hydrogen atoms form the closest shell around the anion. The bromide ion induces the presence of a set of hydrogen atoms of first-shell water molecules in its closest vicinity, which are found to play a significant role in both the scattering phenomenon and in the determination of electronic wavefunctions of the bromide clusters. For the same reason, hydrogen atoms were included in the calculation of both backscattering potential and XANES spectrum in this work.

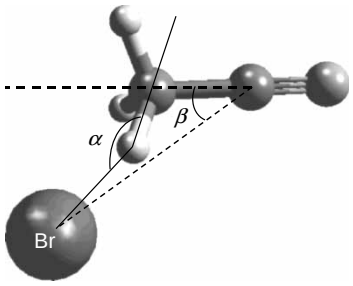
3. Results and discussion

3.1 MD analysis

Results of the MD analysis are summarized in figure 2, where the Br—H and Br—C(methyl) radial distribution functions (RDFs) are plotted and in table 1, where a set of structural parameters, solvation energy and translational self-diffusion coefficient for the bromide anion are collected. The Br—H RDF exhibits a double peak for the first solvation shell which indicates that the three hydrogen atoms of the methyl group are not symmetrically distributed around the bromide anion. The running coordination number gives a ratio 1:2 between the two peaks and the total number of atoms up to the second minimum (5.5–5.9 Å in figure 2(top)) is around 30–33 atoms, depending on the potential set employed. These RDFs reflect the different value of the $\sigma_{Br—H}$ parameter employed. The maximum of the first peak appears at 3.28 Å for Pot-A ($\sigma_{Br—H} = 3.6$ Å), at 2.93 Å for Pot-B ($\sigma_{Br—H} = 3.2$ Å) and at 2.73 Å for Pot-C ($\sigma_{Br—H} = 2.9$ Å). The mean angle BrHC (α) collected in table 1 for the closest hydrogen atom to the anion is also reflecting the increasing directionality of the hydrogen bond (a strong hydrogen bonding is roughly linear, i.e. an angle value for XHY close to 180°): 125° for Pot-A, 135° for Pot-B and 145°for Pot-C. The asymmetrical solvation of the methyl group implies that the charge (anion)–dipole (acetonitrile) interaction is not the dominant contribution in the first solvation shell. Angle β defines the angle formed by the molecular axis of the acetonitrile molecule and the vector formed by the bromide and the center of mass of the acetonitrile molecule (scheme 1). A β value equals to 0° indicates the alignment of the anion with the molecular axis. Table 1 shows that the average β value is in the range 66–80°, then the structural arrangement for the first solvation agrees with the results obtained by Richardi *et al.* [3,8] from MOZ theory and MC simulations.

Table 1. MD results.

Potentials	*Structural Results*				
	$R_{max}(g_{Br—H})$ (Å)	$R_{max}(g_{Br—C(methyl)})$ (Å)	$\sigma^2_{Br—C}$(Å^2)	$\bar{\alpha}$ (°)	$\bar{\beta}$ (°)
A	3.28	4.01	0.28	125	66
B	2.93	3.78	0.21	135	77
C	2.73	3.68	0.21	145	80
	E_{solv}(kJ mol^{-1})	D (10^{-9} m^2 s^{-1})			
A	− 259.2	1.6 ± 0.1			
B	− 275.9	1.6 ± 0.1			
C	− 284.5	1.4 ± 0.1			



Scheme 1.

Br—C (methyl) RDFs for the three potentials are presented in figure 2(bottom). The maximum of the first peak is found in the range 3.7–4.0 Å, running integration numbers correspond roughly to 10 acetonitrile molecules. The height and width of the peaks for the three potentials show that the smaller σ_{Br-H} is, the more compact the first solvation shell is. Experimental estimations of coordination numbers around bromide vary in a wide range, from dielectric relaxation measurements and thermodynamic data a value of 2 is obtained [2,7], whereas from EXAFS measurements the value is close to 5 [40]. This EXAFS study also gives a Br—C distance of 3.48 Å which has associated with it a large Debye–Waller (DW) factor, $\sigma^2 = (R_{Br-C} - \overline{R_{Br-C}})^2 = 0.162\,\text{Å}^2$, implying a large static and dynamic disorder associated to the Br—C parameter. When comparing these DW factors with those computed from MD simulations (see table 1), estimations are larger than the experimental one, when using Pot-A a value of $0.28\,\text{Å}^2$ is obtained, whereas Pot-B and Pot-C give a similar and smaller value of $0.21\,\text{Å}^2$. EXAFS equation presents a strong coupling between the coordination number and the associated DW factors, whereas the first parameter contributes to increase the intensity of the signal (the larger the number of backscatter atoms, the more intense the signal becomes), the second parameter contributes to damp the intensity of the signal (the larger the static and dynamic disorder around the absorber atom are, less intense the signal is). Thus, for a given intensity, small values of DW factors are compatible with small coordination numbers, as well as larger DW factors need larger coordination numbers. The theoretical trend of the DW factors reflects that lowering the σ_{Br-H} parameter reinforces the bromide-acetonitrile interactions with respect to the MD simulation with Pot-A, giving rise to tighter structures, although they are more relaxed than the experimental one.

Regarding coordination number, Richardi *et al.* [8] from their MOZ study predicts a value close to 9.5 molecules of acetonitrile in the first solvation shell. In a later work, these authors carry out a study of halides in acetonitrile, excluding bromide, comparing MOZ and Monte Carlo simulations [3]. Maxima for the first shell of X—C (X≡Cl and I) RDFs appear at *ca.* 3.8 and 4.3 Å for chloride and iodide respectively, what may represent a reasonable range to enclose the Br—C distance.

The experimentally estimated enthalpy of solvation [2] is −337 kJ/mol, whereas the computed value for the three simulations ranged between −260 and −285 kJ/mol. The sequence of solvation energies for the three set of potentials follows the same order than the value of σ_{Br-H} and the corresponding distance of the first shell of acetonitrile around the halide. Richardi *et al.* [8] obtain similar results from their simulation when the Gibbs solvation free energy is estimated, the theoretical values underestimate (provide less negative values) the experimental data by 30–60 kJ/mol.

The translational self-diffusion coefficient for the bromide has been computed from the mean-square displacement function by following the Einstein relation, theoretical D_{Br} values are found to be in the range $1.4–1.6 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}$. There is no previous theoretical estimation for D_{Br} in acetonitrile, but Guardià and Pinzon [41] have computed D_{Cl} from MD simulations of chloride in acetonitrile, finding a value of $1.8{\cdot}10^{-9}\,\text{m}^2\,\text{s}^{-1}$. The experimental values derived from conductivity measurements are 2.66 and $2.67 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}$ for chloride and bromide, respectively [42].

3.2 *XANES spectra from* $Br(ACN)_n^-$ clusters

The usual way to relate geometrical structure around an absorber atom in a solid and features of XANES spectra is by means of the simulation of the spectrum from a reasonable geometry generally taken from crystallographic data or some related structural model. Nevertheless, when one deals with a structure in solution, the source of structural information is scarce. A strategy to get advantages of both the experimental and theoretical sources of information is to simulate spectra from the structure provided by theoretical methods and to compare them with the experimental spectra. A synergy may be established, such that theoretical procedures could be improved by approaching the computed spectrum to the experimental one and simultaneously the structural information derived from the spectrum is refined and the features of the spectra properly assigned.

First of all, we are going to compare the XANES spectra obtained for clusters formed by one bromide anion and a number of acetonitrile molecules small enough to define only the first solvation shell $[Br(ACN)_9]^-$, subsequently, the first and second solvation shells will be included, $[Br(ACN)_{20}]^-$ and both spectra compared. Figure 3 includes comparative plots of the experimental spectrum obtained by Watanabe *et al.* [40] with those computed for the optimized structures $[Br(ACN)_9]^-$ obtained by applying the three sets of potentials and the quantum mechanical level. The spectra obtained from the structures derived quantum mechanically by using Pot-B and Pot-C present the three main resonances and their relative intensities are quite similar to the experimental spectrum. On the contrary, Pot-A derived structure leads to a quite different ratio of intensities which makes the computed spectrum rather different in shape from the experimental

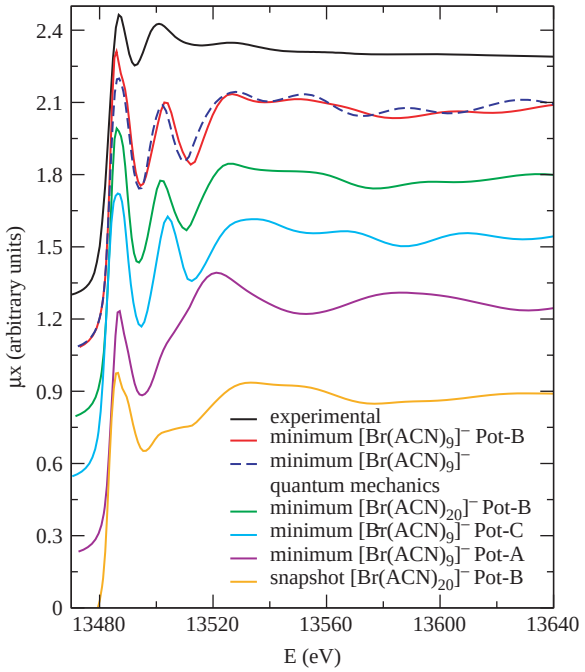


Figure 3. Experimental Br K-edge XANES spectrum (black) and theoretically simulated spectra for different bromide-acetonitrile clusters.

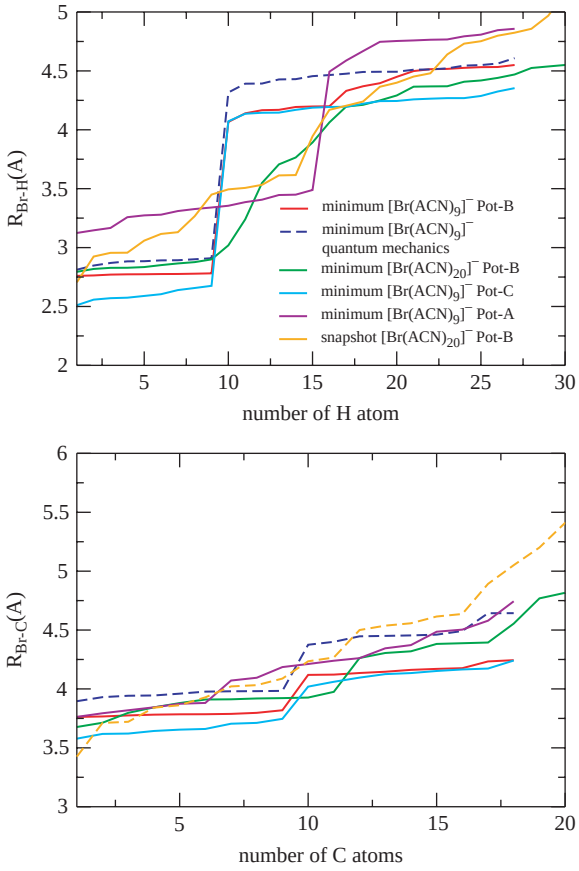


Figure 4. Br—H and Br—C distances for the clusters used in figure 3.

one, even though resonances appears at the same energy values. The spectrum derived from the structure optimized quantum-mechanically has been over-imposed to that derived of Pot-B to show the sensitivity of XANES features to small changes, since the fitted $\sigma_{Br—H}$ value was chosen just to bring the potential-derived structure containing nine acetonitrile molecules as close as possible to quantum-mechanical one. (The RMS for the structure was 0.7 Å and figure 1 shows the similarity between both structures). The changes that a second solvation shell induces on the spectrum features can be observed in the XANES generated for the $[Br(ACN)_{20}]^-$ cluster (obtained through the use of Pot-B). The comparison with the nona-acetonitrilated cluster for Pot-B suggests that second-shell effects are marginal: a small change in the relative intensities of the three resonances and a slight smoothing, both at the white line and at the high-energy part of the spectrum. It is worth noting that the computed spectra show more intense features at the high energy region than the experimental one. This is a consequence of the rigidity and symmetry of the structures used, since their origin is an energy minimization. In contrast, the spectrum obtained for a cluster of 20 acetonitrile molecules but whose structure is a snapshot of the MD trajectory with Pot-B is smeared out and the intensity of the second resonance is reduced.

To show the relationships between XANES features and structure around bromide, figure 4 plots the distribution of the distances for the two first types of backscatter atoms surrounding the halide, that is hydrogen and carbon atoms of acetonitrile molecules. Ordinate contains the corresponding distance of the backscatter atoms to the bromide whereas abscissa gives the order number established on the basis of the H (or C)—Br distance. Thus, the curve $R_{Br—H}$ vs. n_H for the minimum $[Br(ACN)_9]^-$ structure obtained quantum-mechanically shows nine H atoms placed at 2.79–2.90 Å. The additional 18 hydrogen atoms of the cluster are placed at larger distances within the range 4.30–4.60 Å. The structure obtained by Pot-A exhibits the most distant first shell of H atoms, located in between the two previous ranges of distances (3.2–3.5 Å) and with almost a double number of backscatters [15]. Its XANES spectrum is that differing most from the experimental one. An intermediate distribution is shown by the snapshot with 20 molecules, where $R_{Br—H}$ values increases monotonically, although the closest distances are more similar to the two minimum geometries obtained with Pot-B. In the case of the optimized cluster with 20 solvent molecules using the set of potentials B, the shape of the spectrum is more similar to the corresponding structure with 9, indicating that the second set of H atoms play a minor role on the XANES features. It is worth pointing out that the sequence of Br—H distance for Pot-C, Pot-B and quantum mechanics compared with the energy gap between the two first resonances illustrates pretty well the Natoli's rule [13], i.e. the difference in energy between the white line and the energy of a given feature is inversely proportional to the coordination distance of the shell of atoms related with this feature. The Br—C distributions show a sequence of distances for the

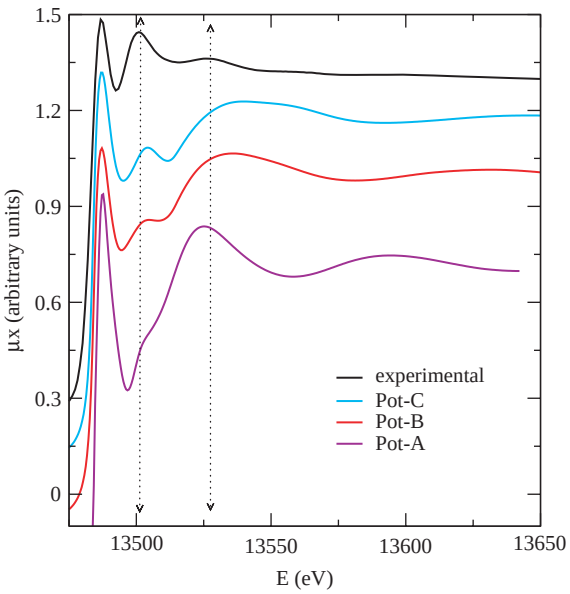


Figure 5. Comparison of the experimental Br K-edge XANES spectrum with the ones obtained from MD simulations for bromide in acetonitrile.

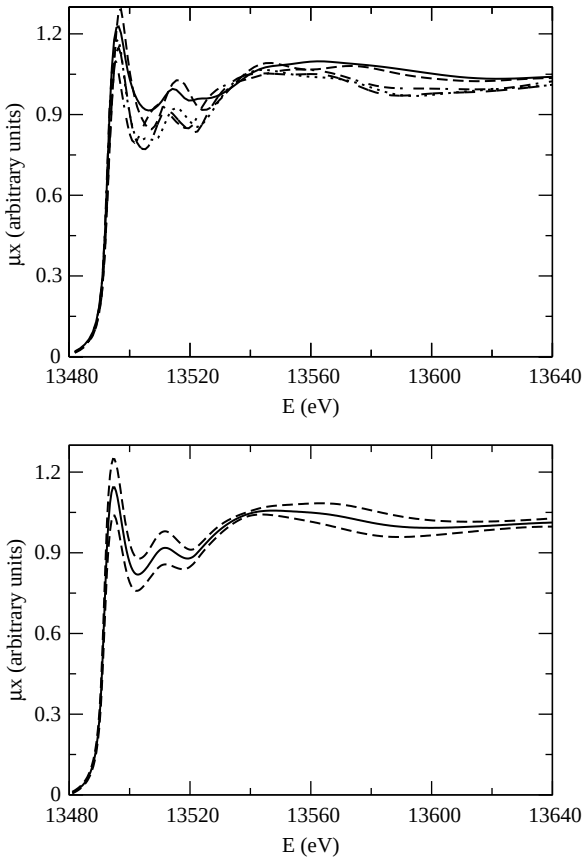


Figure 6. Several individual XANES spectra computed from snapshots of Pot-C simulation (top). Averaged XANES spectrum from the same simulation including the standard deviation for the whole energy range.

first shell of atoms which differs from that obtained for the Br—H one. Thus, the quantum mechanical cluster bears the longest $R_{Br—C}$ for the seven closest C atoms to Br. The $[Br(ACN)_9]^-$ clusters for Pot-B, Pot-C and quantum mechanics level, as well as the $[Br(ACN)_{20}]^-$ for Pot-B retains similar shape of $R_{Br—C}$ distributions than the R_{BrH} ones. There is a plateau of $R_{Br—C}$ for the first shell of C atoms which denotes the consistency of the shell in these simulations. In fact this pattern, which is defined by a regular coordination sphere of C atoms placed at quite similar distance of bromide, seems to be the most direct contribution to the XANES features. In particular, the intensity of the second resonance and the relative height of the white line with respect to the second resonance are affected by the $R_{Br—C}$ value and the symmetry of its distribution. This is observed when the XANES spectrum is computed for two modified structures of the quantum mechanic $[Br(ACN)_9]^-$ minimum, where selectively the Br—C distance is changed by $+0.1$ and -0.1 Å.

As previously remarked in the literature [16,25,26,43], these findings show that for the XANES definition the geometrical arrangement of atoms around the photo-absorber is essential, such that slightly different structures could lead to clearly different spectra.

3.3 XANES spectra from MD simulations

The computed Br K-edge XANES spectrum of bromide in acetonitrile solution at 298 K obtained from MD simulations which used the three different set of potentials are shown in figure 5. In contrast with the structure of clusters, these spectra are the average for a large number of structures (100 snapshots), which result from the fluctuations of the solvent structure around the bromide. The relevance of the changes induced by the fluctuation might be seen either by individual inspection of spectra corresponding to several snapshots or by drawing the standard deviation of the absorption line along the whole energy range. These two plots have been included in figure 6. The individual XANES spectra coming from different snapshots show significant differences among them, specially at low energy. The interesting fact derived from this figure is that the majority of the individual spectra are quite different to the average. This stresses the importance of carrying out a thorough sampling of the configurational space to properly compute the XANES spectra in solution. This is not surprising if one bears in mind the differences found in the XANES features when using the different clusters studied in the previous section. Similar results were found in an earlier theoretical–experimental study on the hydration of bromide [27]. Geometrical fluctuations generate quite different local hydration environments around bromide, then leading to quite different shape of spectra derived by each individual snapshot (for instance see figure 2 in Ref. [27]).

As shown in figure 5, the spectrum computed from the MD snapshots of Pot-A gives a rather poor reproduction of the experimental spectrum, something that was already observed for the minimized structure using this potential (figure 3). The other two spectra are more similar to the

experimental one, although in both cases the relative intensity of the second resonance decreases with respect to the simulated XANES obtained with their corresponding optimized clusters (figure 3). On the contrary, the global shape of these spectra are smoother compared to the non-statistically averaged spectra obtained for the clusters. Thus, the tail of the XANES is smeared out in contrast to the XANES computed for clusters and the global spectrum is damped by the statistical average. Considering the magnitude of the deviations of the individual spectra with respect to the averaged one, the similarity among the experimental spectra and those obtained from the cluster structures (quantum mechanics or classical potentials, Pot-B and Pot-C) could be surprising because the clusters ones are based on an unique structure which correspond with the minimum for each cluster size. Nevertheless, there is a fundamental difference between the snapshots and the structures derived from an energy minimization. The latter ones are the direct consequence of the balanced interaction potentials operating in the system (represented by a cluster of a given size) and on this basis, they could be considered as single representative configurations. When solvation of a monoatomic ion is considered, a relatively small region of the solvent around the ion is perturbed by it, so that the microscopic picture could be envisaged as that of an ionic cluster immersed in a pure solvent. The short-range sensitivity of the XANES spectroscopy implies that a cluster of a few angströms around the ion is responsible for the spectrum shape. When the ion–solvent interactions are stronger than the solvent–solvent ones, the fluctuations of the solvent molecules in the closer environment of the ion (and simultaneously the absorber atom) are small and an averaged structure may be representative of the ion solvation shells. Even more, strong attractive interactions around the ion promotes a quite harmonic behavior of the ion–solvent interactions in this region which generates averaged structures quite consistent with those corresponding to the potential energy minimizations. The comparison of experimental and computed XANES indicates that the main features of the spectrum are pretty well reproduced by some of the energy optimized clusters, that is, these structures are representative ones, although the fluctuations included by the averaging of snapshots is needed to smear out the whole spectrum.

When comparing the distribution of distances for the first backscatterers of bromide in the clusters (figure 3) and the peak of the corresponding RDF in figure 2, a shift appears in the Br—H distance of about 0.18 Å from the optimized clusters Pot-B and Pot-C to their first maxima in Br—H RDF (2.75–2.93 Å for Pot-B and 2.55–2.73 Å for Pot-C), in addition to wide peaks that allows a significant range of asymmetric arrangements compatible with the dynamic of the system. This shifting indicates that solvent effects and/or temperature effects induces a significant relaxation of the first solvation shell for the set of potentials Pot-B and Pot-C, where the bromide–acetonitrile interactions may become stronger in the first shell. The main geometrical feature changing with $\sigma_{Br—H}$ when going from structures of minimum for clusters in gas phase to solution is just the Br—H distance. The interactions between the solvated ion and bulk solvent and those between the solvent–solvent molecules play a role equivalent to an increase of this parameter, $\sigma_{Br—H}$. This is one of the reasons that make the computed XANES derived from MD simulation with Pot-C more similar to the experimental one. The solvent effects on the Br—C distances are much smaller in these two simulations compared with the cluster minima (from 3.75 to 3.78 Å for Pot-B and from 3.62 to 3.68 Å for Pot-C), which indicates a decrease of the orientational angles α and β (see scheme 1).

It is interesting to notice that previous studies on cation hydration [24–26] following the same methodology have shown that the mismatch between individual spectra and the averaged one is less important than that observed in the anion solvation [27]. The reason is that anion–solvent interactions are weaker than the cation–solvent ones. Additional factors derived from simulation contribute to modify the shape of the spectrum whose detailed analysis cannot be easily split. A general conclusion is that for the set of potentials employed, the acetonitrile–acetonitrile interactions are too much dominant with respect to the bromide–acetonitrile ones. Provided that acetonitrile simulations of the pure solvent gives consistent results [28], a strategy to improve the description of the bromide solution could be to define a more attractive bromide–acetonitrile interaction potential by including in the fitting *ab initio* interaction energies of clusters, in addition to geometrical criteria. Likewise, as pointed out by Richardi *et al.* [3] for the case of aprotic solvents, or by Ayala *et al.* [44] for the case of water, the consideration of a polarizable model certainly must introduce some improvements in the detailed balance among the ion–solvent and solvent–solvent interactions. The results derived from simulations are consistent with previous simulations of related systems, using other intermolecular potentials and/or computational modeling, such as integral equations or Monte Carlo [1].

4. Concluding remarks

Simulations of bromide in acetonitrile have been carried out by means of the use of interaction potentials available in the literature and simple modifications of them based on structural criteria associated to the hydrated ion concept.

The structural description of the local environment of bromide anion in acetonitrile is a rather relaxed first solvation shell formed by *ca.* 10 acetonitrile molecules where one of the hydrogen atoms of the methyl group is placed closer to the anion, 2.7–2.9 Å, than the other two hydrogen atoms of the methyl group (*ca.* 4.2–4.4 Å) due to the bent orientation of the acetonitrile molecules (approximately 130°) with respect to the bromide anion. This allows the carbon atom of the methyl group to be

closer to the bromide, *ca.* 3.7–3.8 Å. A small second peak at 8 Å shows a quite diffuse shell that is more dominated by the acetonitrile solvent structure than by the anion.

Taken into account that different theoretical approaches have been employed as source of structural information, several solvation environment around the bromide have been described, allowing us a detailed analysis of the relationship between structures, XANES features and static and dynamic disorder of the solution. Given the difficulty of establishing a direct relation with other observables in solution, XANES (and EXAFS) has revealed as an interesting guide to validate or improve computer simulations. In this particular case, it has been shown that the coordination shells beyond the first one do not make an important contribution to the spectrum.

The resemblance between the theoretical spectra obtained from quantum mechanically optimized clusters ($n \geq 9$) and the average spectra derived from MD simulations with some of the set of potentials allows us to conclude that those clusters are a good model picture of the structure of bromide in acetonitrile. Nonetheless, the discrepancies among the individual spectra derived from MD simulations indicate that this representation should be taken as an average model picture with important standard deviations. The set of potential called Pot-B seems the most appropriate to deal with small clusters of $[Br(ACN)_n]^-$ (for $n \geq 20$), whereas the set Pot-C seems the more convenient to describe acetonitrile solutions containing bromide.

Acknowledgements

This work was supported by Spanish DGICYT (CTQ2005-03657 and BQU2002-04364-CO2-01). We thank Prof. I. Watanabe (Osaka University) for supplying the EXAFS experimental data of the bromide anion in acetonitrile. His interesting comments and suggestions are also acknowledged.

References

[1] J.M.G. Barthel, H. Krienke, W. Kunz. *Physical Chemistry of Electrolyte Solutions*, Steinkopff, Darmstadt (1998).
[2] Y. Marcus. *Ion Solvation*, Wiley, Chichester (1985).
[3] R. Fischer, J. Richardi, P.H. Fries, H. Krienke. The solvation of ions in acetonitrile and acetone. II. Monte Carlo simulations using polarizable solvent models. *J. Chem. Phys.*, **117**, 8467 (2002).
[4] G. Markovich, O. Cheshnovsky, L. Perera, M.L. Berkowitz. The solvation of Cl^-, Br^-, and I^- in acetonitrile clusters: Photoelectron spectroscopy and molecular dynamics simulations. *J. Chem. Phys.*, **105**, 2675 (1996).
[5] T. Megyes, T. Radnai, A. Wakisaka. A mass spectrometric study of solvated clusters of ions and ion pairs generated from lithium halide solutions in polar solvents: Acetonitrile compared to methanol. *J. Mol. Liq.*, **103–104**, 319 (2003).
[6] R. Ayala, J.M. Martínez, R.R. Pappalardo, E. Sánchez Marcos. Theoretical study of the microsolvation of the bromide anion in water, methanol, and acetonitrile: Ion-solvent vs solvent-solvent interactions. *J. Phys. Chem. A*, **104**, 2799 (2000).
[7] J. Barthel, M. Kleebauer, R. Buchner. Dielectric-relaxation of electrolyte-solutions in acetonitrile. *J. Solution Chem.*, **24**, 1 (1995).
[8] J. Richardi, P.H. Fries, H. Krienke. The solvation of ions in acetonitrile and acetone: A molecular Ornstein-Zernike study. *J. Chem. Phys.*, **108**, 4079 (1998).
[9] D.C. Koningsberger, R. Prins (Eds.). *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, Wiley, New York (1988).
[10] H. Ohtaki, T. Radnai. Structure and dynamics of hydrated ions. *Chem. Rev.*, **93**, 1157 (1993).
[11] D.T. Richens. *The Chemistry of Aqua Ions*, John Wiley, Chichester (1997).
[12] A. Muñoz-Páez, R. Pappalardo, E. Sánchez Marcos. Determination of the second hydration shell of Cr^{3+} and Zn^{2+} in aqueous solutions by extended X-ray absorption fine structure. *J. Am. Chem. Soc.*, **117**, 11710 (1995).
[13] A. Bianconi. X-ray absorption: principles, applications, techniques of EXAFS, SEXAFS and XANES.. D.C. Koningsberger, R. Prins (Eds.), John Wiley, New York (1988).
[14] C.R. Natoli, M. Benfatto, C. Brouder, M.F. Ruiz López, D.L. Foulis. Multichannel multiple-scattering theory with general potentials. *Phys. Rev. B*, **42**, 1944 (1990).
[15] A. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson. Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure. *Phys. Rev. B*, **58**, 7565 (1998).
[16] M. Benfatto, J.A. Solera, J. Chaboy, M.G. Proietti, J. García. Theoretical analysis of X-ray absorption near-edge structure of transition-metal aqueous complexes in solution at the metal K edge. *Phys. Rev. B*, **56**, 2447 (1997).
[17] S. Díaz-Moreno, A. Muñoz-Páez, J. Chaboy. X-ray Absorption Spectroscopy (XAS) study of the hydration structure of Yttrium(III) cations in liquid and glassy states: eight or nine-fold coordination?. *J. Phys. Chem. A*, **104**, 1278 (2000).
[18] B.J. Palmer, D.M. Pfund, J.L. Fulton. Direct Modeling of EXAFS spectra from molecular dynamics simulations. *J. Phys. Chem.*, **100**, 13393 (1996).
[19] D. Roccatano, H.J.C. Berendsen, P. D'Angelo. Assessment of the validity of intermolecular potential models used in molecular dynamics simulations by extended X-ray absorption fine structure spectroscopy: A case study of Sr^{2+} in methanol solution. *J. Chem. Phys.*, **108**, 9487 and references therein (1998).
[20] A. Filipponi, P. D'Angelo, N.V. Pavel, A. Di Cicco. Triplet correlations in the hydration shell of aquaions. *Chem. Phys. Lett.*, **225**, 150 (1994).
[21] D. Spångberg, K. Hermansson, P. Lindqvist-Reis, F. Jalilehvand, M. Sandström, I. Persson. Model Extended X-ray Absorption Fine Structure (EXAFS) Spectra from molecular dynamics data for Ca^{2+} and Al^{3+} aqueous solutions. *J. Phys. Chem. B*, **104**, 10467 (2000).
[22] F. Jalilehvand, D. Spångberg, P. Lindqvist-Reis, K. Hermansson, I. Persson, M. Sandström. Hydration of the calcium ion. An EXAFS, large-angle X-ray scattering, and molecular dynamics simulation study. *J. Am. Chem. Soc.*, **123**, 431 (2001).
[23] L. Campbell, J.J. Rehr, G.K. Schenter, M.I. McCarthy, D. Dixon. XAFS Debye-Waller factors in aqueous Cr^{+3} from molecular dynamics. *J. Synchrotron Radiat.*, **6**, 310 (1999).
[24] P.J. Merkling, A. Muñoz-Páez, J.M. Martínez, R.R. Pappalardo, E. Sánchez Marcos. Molecular-dynamics-based investigation of scattering path contributions to the EXAFS spectrum: The Cr^{3+} aqueous solution case. *Phys. Rev. B*, **64**, 012201 (2001).
[25] P.J. Merkling, A. Muñoz-Páez, R.R. Pappalardo, E. Sánchez Marcos. Combination of XANES spectroscopy and molecular dynamics to probe the local structure in disordered systems. *Phys. Rev. B*, **64**, 092201 (2001).
[26] P.J. Merkling, A. Muñoz-Páez, E. Sánchez Marcos. Exploring the capabilities of X-ray absorption spectroscopy for determining the structure of electrolyte solutions: computed spectra for Cr^{3+} or Rh^{3+} in water based on molecular dynamics. *J. Am. Chem. Soc.*, **124**, 10911 (2002).
[27] P.J. Merkling, R. Ayala, J. Martínez, R. Pappalardo, E. Sanchez Marcos. Interplay of computer simulations and X-ray absorption spectra in the study of the bromide hydration structure. *J. Chem. Phys.*, **119**, 6647 (2003).
[28] X. Grabuleda, C. Jaime, P.A. Kollman. Molecular dynamics simulation studies of liquid acetonitrile: New six-site model. *J. Comput. Chem.*, **21**, 901 (2000).

[29] T.P. Lybrand, I. Ghosh, J.A. McCammon. Hydration of chloride and bromide anions: determination of relative free energy by computer simulation. *J. Am. Chem. Soc.*, **107**, 7793 (1985).
[30] M.J. Frisch, G.W. Trucks, H.B. Schlegel, E. G, M.A.R. Scuseria, *et al. Gaussian 03*, Gaussian, Inc., Wallingford CT (2004).
[31] W.D. Cornell, P. Cieplak, C.I. Bayly, I.R. Gould, K.M. Merz, D.M. Fergusson, D.C. Spellmeyer, T. Fox, J.W. Caldwell, P.A. Kollman. A second generation force field for the simulation of proteins, nucleic acids, and organic molecules. *J. Am. Chem. Soc.*, **117**, 5179 (1995).
[32] J. Martínez, R.R. Pappalardo, E. Sánchez Marcos. First-principles ion-water interaction potentials for highly charged monatomic cations. Computer simulations of Al^{3+}, Mg^{2+}, and Be^{2+} in water. *J. Am. Chem. Soc.*, **121**, 3175 (1999).
[33] M.P. Allen, D.J. Tildesley. *Computer Simulation of Liquids*, Oxford University Press, Oxford (1987).
[34] M. Leslie, M.J. Gillan. The energy and elastic dipole tensor of defects in ionic-crystals calculated by the Supercell method. *J. Phys.C-Solid State Phys.*, **18**, 973 (1985).
[35] J.E. Roberts, Schnitker. Boundary conditions in simulations of aqueous ionic solutions: A systematic study. *J. Phys. Chem.*, **99**, 1322 (1995).
[36] F. Figueirido, G.S. Del Buono, R.M. Levy. On finite-size effects in computer simulations using the Ewald potential. *J. Chem. Phys.*, **103**, 6133 (1995).
[37] H. Berendsen, J. Postma, W. van Gusteren, A. DiNola, J. Haak. Molecular dynamics with coupling to an external bath. *J. Chem. Phys.*, **81**, 3684 (1984).
[38] W. Smith, T.R. Forester. "DL_POLY 2.13" (1996).
[39] L. Hedin, B.I. Lundqvis, S. Lundqvis. Local exchange-correlation potentials. *Solid State Comm.*, **9**, 573 (1971).
[40] Y. Sawa, T. Miyanaga, H. Tanida, I. Watanabe. Temperature dependence of EXAFS for bromide ion in solution. *J. Chem. Faraday Trans.*, **91**, 4389 (1995).
[41] E. Guardià, R. Pinzón. On the solvation shell of Na^+ and Cl^- ions in acetonitrile: A computer simulation study. *J. Mol. Liquids*, **85**, 33 (2000).
[42] B.S. Krumgalz. Separation of limiting equivalent conductances into ionic contributions in non-aqueous solutions by indirect methods. *J. Chem. Soc. Faraday Trans. 1*, **79**, 571 (1983).
[43] P. D'Angelo, M. Benfatto, S. Della Longa, N.V. Pavel. Combined XANES and EXAFS analysis of Co^{2+}, Ni^{2+}, and Zn^{2+} aqueous solutions. *Phys. Rev. B*, **66**, 0642091 (2002).
[44] R. Ayala, J. Martínez, R. Pappalardo, H. Saint-Martin, I. Ortega-Blake, E. Sánchez Marcos. Development of first-principles interaction model potentials. An application to the study of the bromide hydration. *J. Chem. Phys.*, **117**, 10512 (2002).