

Structure and Dynamics of Br[−] Ion in Liquid Methanol

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A Car–Parrinello molecular dynamics simulation has been performed on a solution of Br[−] in liquid methanol analyzing with particular attention charge transfer and polarization effects. The first solvation shell has been characterized in terms of H-bonds, and it has been found that the high polarization of the bromide gives rise to a stable solvent cage. The differences in the coordination number with the chloride can be ascribed to the ionic radius and to the stronger perturbations brought by the solvent to the bromide ion.

1. Introduction

The solvation dynamics of ions, not only in water but also in other solvents such as methanol, acetonitrile, and ammonia, is a topic of growing interest due to the physical and chemical implications in a wide range of research and technological fields. To obtain useful insight on the structural and dynamical properties of ions in solution, a series of experimental methods¹ has been applied, such as X-ray and neutron scattering or infrared and Raman spectroscopy and, more recently, femto-second techniques.^{2–7} On the other hand, a detailed description at the atomic level has been obtained either by high level ab initio calculations,^{8–18} with the ion microsolvated by one or more solvent molecules, or by Monte Carlo^{19–24} and molecular dynamics (MD)^{25–43} simulations. As a whole, the attention has so far been focused essentially on the explanation of the water properties of the first solvation shell;⁴⁴ the analysis of the behavior of ions in the other solvents is still incomplete.^{26,45–48}

In the present work, the structural and dynamical properties of the bromide ion in methanol have been analyzed with Car–Parrinello molecular dynamics (CPMD)^{49,50} and compared with those of Cl[−].⁴⁵ Methanol is the simplest organic solvent whose molecules present both a hydrophilic head, the OH group, and a hydrophobic tail, the CH₃ group. The interaction between the halide ions and the methanol molecules occurs via the formation of H-bonds, but the number of solvent molecules involved in this interaction is still a matter of debate.^{51–56} In fact, it has been recently^{21,27,32,38,40,44,57} observed that the semiempirical potentials usually adopted in classical molecular dynamics or Monte Carlo simulations do not reproduce the coordination number accurately, since polarization and charge transfer effects are not taken properly into account and these have a high impact on the ion–solvent interactions. In particular, neutron scattering measurements⁵¹ give a coordination number for the chloride of about 3.6, while a value of ~6 has been obtained adopting a semiempirical potential.²⁷ In a recent work,⁴⁵ it has been shown that CPMD simulations reproduce the coordination number for the chloride ion in methanol correctly (3.56), since polarization effects, charge transfer, and hydrogen bond are accurately

described. In the present paper, the method is extended to the bromide ion in methanol. This is of particular interest, since the experimental data^{52,53,58} are not exhaustive as in the case of the chloride.

Particular attention has been devoted to the polarization and charge transfer effects in the formation of the H-bond between bromide and the methanol solvent, since it has been found that these effects play a key role in the stability and morphology of the first solvation shell.⁴⁵

The results of the present simulation on the bromide ion in methanol have been compared with those obtained by previous simulations⁴⁵ for the chloride ion and for the bromide in water,^{59,60} allowing for an accurate comparison of the solvent effects.

2. Computational Details

The simulations have been performed with the CPMD code⁶¹ in a cubic box of 12.05 Å side, with periodic boundary conditions and 25 methanol molecules and one ion. The Br[−] solution has been studied starting from a configuration extracted from a previous Car–Parrinello simulation on Cl[−] in fully deuterated liquid methanol,⁴⁵ substituting the chloride with the bromide ion.

Martins–Troullier⁶² pseudopotentials have been used along with the Kleinman–Bylander⁶³ decomposition for all the atomic species except the hydrogen, described with a von Barth–Car pseudopotential.⁶⁴ The plane wave expansions have been truncated at 70 Ry, following the previous studies in liquid methanol⁶⁵ and the chloride in methanol.⁴⁵ Density functional calculations in the generalized gradient approximation (GGA) have been performed using the BLYP^{66,67} exchange correlation functional.

To validate the computational strategy adopted, the structure and some of the electronic properties of the CH₃OH complex with Br[−] have been calculated with our approach and compared with density functional theory (DFT) and MP2 calculation with a localized Gaussian basis set, 6-311++G(3df,3pd), adopting the Gaussian 98 suite of programs.⁶⁸ The results, summarized in Table 1, show that the BLYP functional in conjunction with the plane wave basis set satisfactorily reproduces the structural parameters of the complex, while the binding energy (properly taking into account the BSSE correction for the calculations

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TABLE 1: Salient Structural Data of the $\text{CH}_3\text{OH}\cdots\text{Br}^-$ Complex; Distances Are in Å, Angles in Degrees (for the r_{HC} Bond Length, the Average Value Is Reported)^a

$\text{CH}_3\text{OH}\cdots\text{Br}^-$	BLYP/PW	BLYP/G	B3LYP/G	MP2/G
$r_{\text{H}\cdots\text{Br}}$	2.318	2.334	2.337	2.278
$r_{\text{O}\cdots\text{Br}}$	3.314	3.325	3.310	3.238
$r_{\text{O}-\text{H}}$	1.001	0.998	0.984	0.982
$r_{\text{O}-\text{C}}$	1.435	1.423	1.406	1.406
$\langle r_{\text{H}-\text{C}} \rangle$	1.100	1.103	1.096	1.092
$\theta_{\text{O}-\text{H}\cdots\text{Br}}$	172.5	171.9	169.9	165.7
E_{binding} (kJ mol ⁻¹)	-52.51	-55.14	-55.14	-42.01
$\Delta q(\text{e}^-)$	0.10	0.10	0.09	0.07

^a G labels the calculations with the Gaussian basis sets 6-311++G(3df,3pd). The charge transfer, $\Delta q(\text{e}^-)$, has been computed with the AIM method.⁶⁹

TABLE 2: Salient Structural Data of the $(\text{CH}_3\text{OH})_n\cdots\text{Br}^-$ Complex with $n = 2-4$; Distances Are in Å, Angles in Degrees^a

	BLYP/PW	BLYP/G	B3LYP/G	OLYP/G	HCTH407/G
$n = 2$					
$\langle \text{O}\cdots\text{Br} \rangle$	3.346	3.325	3.309	3.393	3.367
$\langle \text{H}\cdots\text{Br} \rangle$	2.362	2.339	2.345	2.411	2.394
$\langle \text{HO}\cdots\text{Br} \rangle$	7.34	7.84	9.97	4.71	6.86
$n = 3$					
$\langle \text{O}\cdots\text{Br} \rangle$	3.390	3.353	3.336	3.420	3.388
$\langle \text{H}\cdots\text{Br} \rangle$	2.405	2.362	2.364	2.436	2.411
$\langle \text{HO}\cdots\text{Br} \rangle$	5.93	4.40	6.75	1.64	4.30
$n = 4$					
$\langle \text{O}\cdots\text{Br} \rangle$	3.400	3.380	3.362	3.452	3.420
$\langle \text{H}\cdots\text{Br} \rangle$	2.422	2.392	2.392	2.472	2.446
$\langle \text{HO}\cdots\text{Br} \rangle$	6.96	4.10	6.36	1.65	3.61

^a G labels the calculations with the Gaussian basis sets 6-31++G(d,p).

with the Gaussian basis set) is close to other DFT calculations and slightly lower than that at the MP2 level of theory but within the usual uncertainty (~ 10 kJ mol⁻¹) of this kind of calculation.

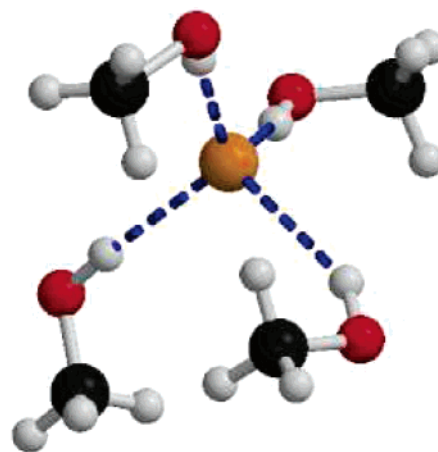
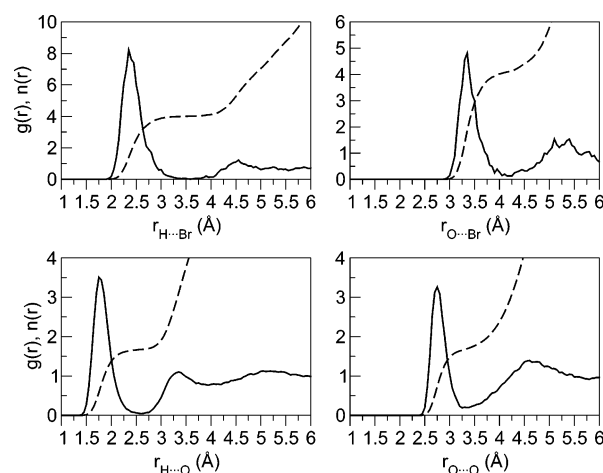
A further check of the pseudopotential and functional effects on the structural properties has been performed, see Table 2, comparing between CPMD results for a cluster with two to four methanol molecules with all electron DFT calculations with an extended Gaussian basis set. The good agreement of CPMD (BLYP/PW) and BLYP/6-31++G(d,p) results further confirms the quality of the pseudopotentials adopted. The degree of accuracy of the BLYP functional to study the solvation of the bromide ion is shown by the similar structural description obtained in the all electron calculations with different functionals^{70,71} that accurately reproduce hydrogen bonding properties.

The hydrogen has been replaced by deuterium to allow for a larger time step. A fictitious electronic mass of 800 au has been used to keep the system on the Born–Oppenheimer surface. Adopting this value, the energy has been conserved within five significant figures and no apparent drift in the fictitious electronic kinetic energy has been observed.

A charged periodic system has infinite energy due to the interaction with the images; therefore, a background uniform charge has been added to neutralize the system with the procedure implemented in the CPMD code.⁷²

After a thermalization at 300 K by velocity scaling, the equation of motions have been integrated with a time step of 5 au (~ 0.12 fs) for a total simulation time of ~ 9 ps in the NVE ensemble, storing the atomic coordinates and velocities at every step for the subsequent analysis.

Population analysis and electron localization properties have been computed averaging over 128 configurations equispaced in time (~ 60 fs) with the atoms in molecules (AIM)⁶⁹ method

**Figure 1.** Snapshot of the first solvation shell extracted from the CPMD simulation. The bromide–methanol interaction occurs through H-bonds.**Figure 2.** (upper panel) Pair radial distribution functions (full) and running integration number (dashed) for the $\text{H}\cdots\text{Br}$ (left) and $\text{O}\cdots\text{Br}$ (right) contacts. (lower panel) Pair radial distribution functions for the $\text{H}\cdots\text{O}$ (left) and $\text{O}\cdots\text{O}$ (right) contacts.

and through the position of the maximally localized Wannier function centers (WFCs).^{73–75}

3. Results and Discussion

It is well-known that the methanol molecules interact with the halide ions through H-bonds.^{11,26,27,45,51,52,55,58} A snapshot taken during the present simulation of the first solvation shell is reported in Figure 1 and shows the Br^- ion surrounded by four hydrogen bonded methanol molecules.

The solvent reorganization can be more clearly observed from the pair radial distribution functions, $g(r)$, related to the $\text{H}\cdots\text{Br}$ and $\text{O}\cdots\text{Br}$ contacts, reported in the upper panel of Figure 2. The higher dimensions of Br^- with respect to Cl^- lead to some differences in the solvent reorganization, as summarized in Table 3.

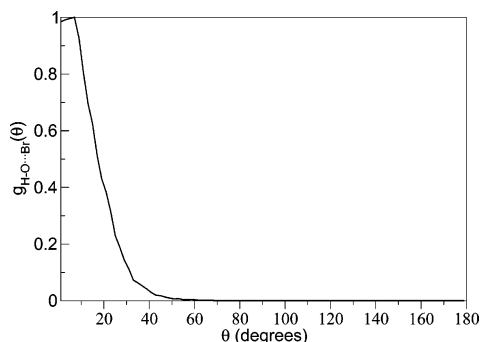
The coordination number for the bromide ion obtained from $g(r)_{\text{H}\cdots\text{Br}}$ is 4.01. This value compares very well with experiments^{52,58} (3.7), whereas it is much lower than values obtained by classical simulations, that showed a hexa-coordination,⁵³ and were used as a guideline in the experimental data analysis.⁵³ As pointed out by many authors,²⁷ the absence of polarization effects leads to an incorrect picture of the first solvation shell and to larger coordination numbers²⁷ than expected. In the determination of the coordination number, it has been shown⁵³ that the choice of the fitting procedure is important and can

TABLE 3: First Peak Position in the Pair Radial Distribution Functions and Coordination Number, n_c ^a

Br ⁻	this work	D'Angelo et al. ⁵³	Watanabe ⁵²	
$r_{\text{H}\cdots\text{Br}}$	2.35	2.46	2.34	
$r_{\text{O}\cdots\text{Br}}$	3.35	3.40	3.28	3.15
n_c	4.01	6.8	5.9	3.7

Cl ⁻	Pagliai et al. ⁴⁵	Megyes et al. ⁵⁴	Ozutsumi et al. ⁷⁶	Yamagami et al. ⁵¹
$r_{\text{H}\cdots\text{Cl}}$	2.20			2.21
$r_{\text{O}\cdots\text{Cl}}$	3.20	3.16	3.16	3.26
n_c	3.56	6.2	3.4	3.6

^a The two values of D'Angelo et al.⁵³ refer to different fitting procedures.

**Figure 3.** Angular distribution functions for H⁺Br and O⁺Br distances lower than the position of the first minimum in the respective $g(r)$.

lead to values differing by approximately one unit. This problem has been shown to be important, for example, in the case of the chloride ion. In fact, it has been reported that the coordination number for the chloride in methanol derived from neutron diffraction⁵¹ and EXAFS⁷⁶ studies is considerably lower than that from X-ray measurements.⁵⁴

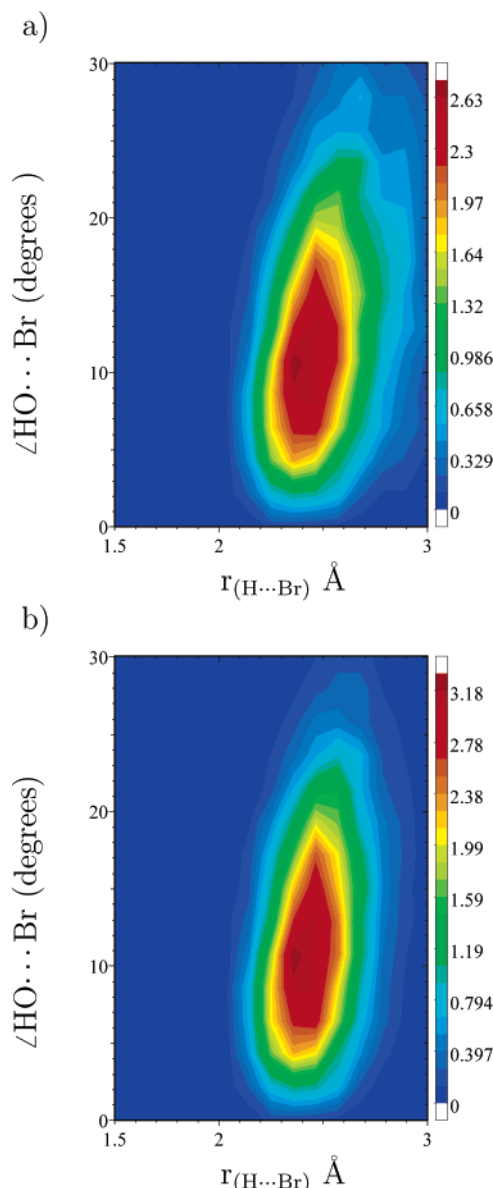
On the other hand, values of the coordination number in methanol lower than those in water^{59,60} are expected due to the larger dimensions of the methanol molecule. In fact, in previous CPMD simulations in water, coordination numbers of ~ 5 for Cl⁻^{77–79} and ~ 6 for Br⁻^{59,60} have been found.

The Br⁺O distance obtained by Watanabe from the EXAFS experiments^{52,58} is lower than that reported by D'Angelo et al.⁵³ and lower than the Cl⁺O distance.^{51,55,76} Since the ionic radius of the chloride is lower than that of the bromide, a longer O⁺Br distance is actually expected as well as a slightly higher coordination number.

The O⁺O and O⁺H pair correlation functions are also reported in the lower panel of Figure 2 to show the overlap of the solute–solvent and solvent–solvent contacts in the experimental data. This explains the difficulties of obtaining accurate experimental data on such a system without an accurate theoretical model to help in the deconvolution procedure.

To characterize the interactions between the bromide ion and methanol in terms of H-bonds, not only the H⁺Br distance but also the HO⁺Br angular distribution must be taken into account. The angular distribution functions for the simulated system are reported in Figure 3. The function presents a maximum at values of the HO⁺Br angle near 10° in agreement with previous estimates.⁵¹

A clear representation of the H-bond configurational space can be achieved through the pair radial and angular distribution functions, $g(r, \theta)$. Recently, a more appropriate function for the characterization of the H-bond has been introduced and applied with success in the description of the interactions in liquid

**Figure 4.** $g(r, \theta)$ weighted functions for the HO⁺Br interactions obtained with the classical (a) and with the new (b) definition of the H-bond.^{65,80}

methanol⁶⁵ and for the chloride ion in methanol.⁴⁵

$$F_j^{\text{HB}} = A(r(t)) \cdot B(\theta(t)) \quad (1)$$

with $A(r(t))$ and $B(\theta(t))$ given by

$$\begin{cases} A(r(t)) = e^{-(r_e - r_f(t))^2 / (2\sigma_r^2)} & \text{if } (r_e - r_f(t)) < 0 \\ A(r(t)) = 1 & \text{if } (r_e - r_f(t)) \geq 0 \\ B(\theta(t)) = e^{-(\theta_e - \theta_f(t))^2 / (2\sigma_\theta^2)} & \text{if } (\theta_e - \theta_f(t)) < 0 \\ B(\theta(t)) = 1 & \text{if } (\theta_e - \theta_f(t)) \geq 0 \end{cases}$$

The values of the parameters r_e , θ_e , σ_r , and σ_θ are directly extracted from the unnormalized pair radial, $h(r)$, and angular, $h(\theta)$, distribution function.

In the above definitions, r_e is the position of the first peak in $h(r)_{\text{H}\cdots\text{Br}}$ and θ_e is the position of the first peak in $h(\theta)$, whereas σ_r and σ_θ are the half widths at half-maximum in $h(r)$ and $h(\theta)$, respectively.

The $g(r, \theta)$ functions computed with both the classical geometrical criteria and weighted by the function (1) are reported in Figure 4.

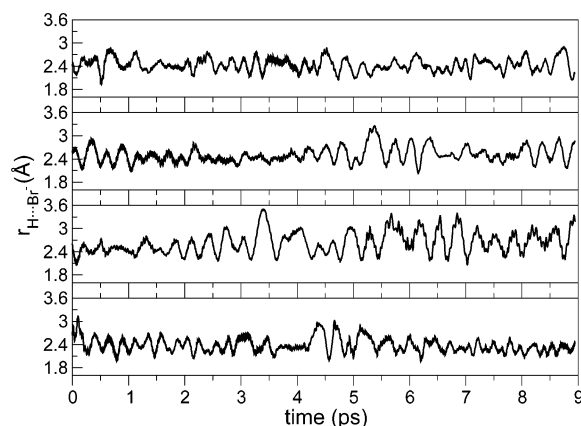


Figure 5. H...Br distances along the simulation run. Distances refer to solvent molecules in the first coordination shell, that always satisfied the geometrical criteria as described in the text.

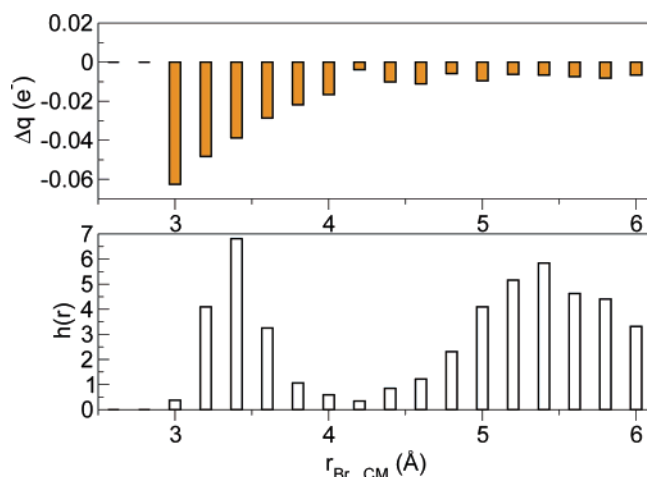


Figure 6. Charge transfer, $\Delta q(e^-)$, and $h(r)$ as a function of the $r_{Br...CM}$ distance.

The surfaces spanned by the H-bond of the bromide ion are very close to those of the chloride ion,⁴⁵ and the main differences arise from the respective ionic radii (1.81 for Cl^- and 1.96 for Br^-). Although the overall picture of the H-bond is quite similar for the two ions, apart from the $X...H$ distance (with $X = Cl$ or Br) which is lower for the chloride, the behavior of the methanol molecules in the first solvation shell is quite different. In fact, for the bromide ion, a rather stable cage of four methanol molecules is present during the simulation, as shown in Figure 5, whereas the chloride ion interacts with a number of solvent molecules that ranges from two to five.⁴⁵

Since the differences between the bromide and chloride ions are related to the ionic radii and to the coordination number, a slightly different behavior can be expected also for the electronic structure related properties such as the charge transfer and the polarization effects. The former have been computed through a population analysis with the method proposed by Bader⁶⁹ (AIM), whereas the latter have been studied with the Wannier function centers (WFCs).^{73,75}

The AIM population analysis has been shown to be a useful tool in the description of the charge transfer in systems consisting of ions in solution like lithium and chloride in methanol⁴⁵ or sodium, potassium, chloride, and bromide in water.⁸¹ The charge transferred from the bromide ion as a function of the distance of the center of mass of the solvent molecules is reported in Figure 6. The charge transferred by Cl^- and Br^- ions is very close ($\Delta q(e^-) = 0.24 \pm 0.02$ for Cl^- and 0.28 ± 0.02 for Br^-) and is essentially localized on the

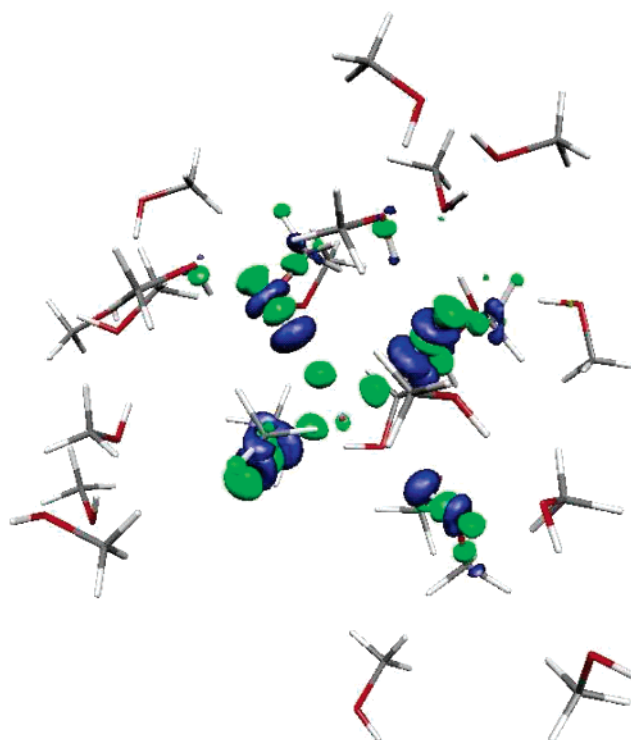


Figure 7. Density difference isosurfaces, $\Delta\rho$, at ± 0.003 (au) for the bromide solution. Volumes with negative values are shown in green, and volumes with positive values are shown in blue.

first shell molecules, as is evident from the distributions. This behavior can be easily justified on the basis of the H-bond interactions between the ion and the first solvation shell molecules.

A description of the charge flow from the ion to first shell molecules can be obtained from the differences between the electron densities, $\Delta\rho$, of the two systems:

$$\Delta\rho = \rho_{ion+solvent} - (\rho_{ion} + \rho_{solvent}) \quad (2)$$

as shown in Figure 7.

This description must be taken only as qualitative, and in addition, it should be considered that also H-bonds and polarization effects concur to the perturbation of the charge density. However, it is clear that the ion–solvent interaction is mainly localized in the first solvation shell.

The polarization effects and in particular the dipole moment of the methanol molecules and the induced dipole moment on the ion have been computed from the WFCs. The wave function of the system for a high number (128) of equispaced geometrical configurations (every 512 steps, ~ 60 fs) has been described in terms of maximally localized Wannier functions with the method proposed by Marzari and Vanderbilt⁷³ and implemented in the CPMD code, as explained by Berghold et al.⁷⁵ The position of the maximally localized Wannier centers is directly related to the position of the electrons in the systems, and as a consequence, it is possible to compute the molecular dipole moment assuming that these electrons belong to the nearest neighbor atom. In this sense, the WFCs give an average description of the polarization and charge transfer effects that characterize the system.

Since the charges transferred from the Br^- and Cl^- ions to the solvent molecules are very close, a similar perturbation of the first solvation shell molecules must be expected, whereas due to the higher stability of the bromide cage a higher induced dipole moment should be observed. In fact, the induced dipole

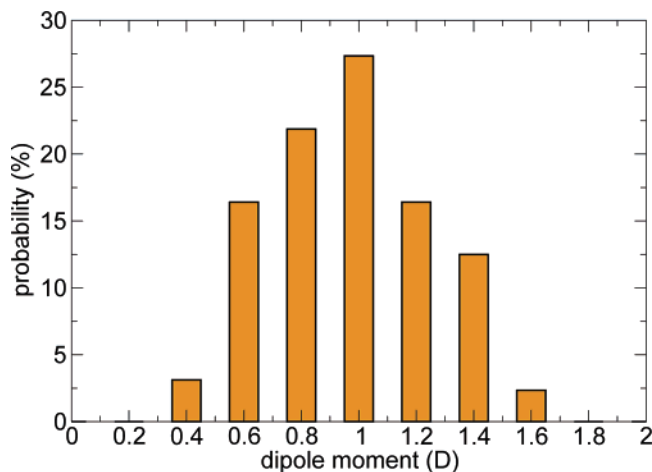


Figure 8. Induced dipole moment distribution of the bromide anion.

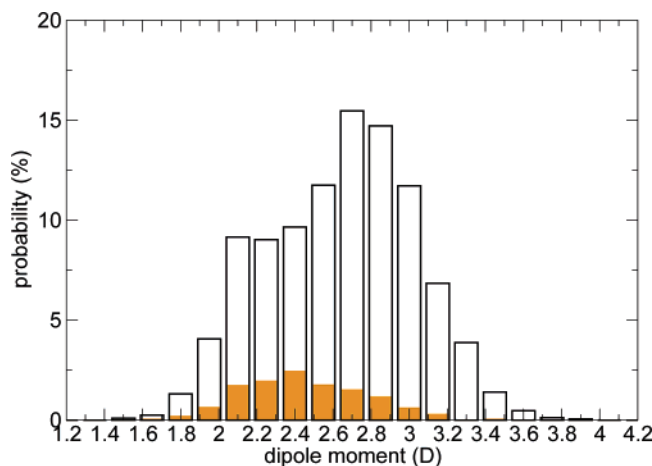


Figure 9. Dipole moment distribution for the methanol molecules: the colored bar refers to the dipole moment distribution of the first solvation shell molecules.

moment on the ion arises from the perturbation of the charge density due to the formation of the H-bonds with the methanol molecules. The induced dipole moment for the bromide ion is reported in Figure 8.

The distribution of the induced dipole moment for Br⁻ and Cl⁻ is strongly related to the H-bond interactions with the methanol molecules. The larger coordination number of the bromide leads to a wider distribution, centered at 1 D, instead of 0.6 D,⁴⁵ with the average induced dipole moment that goes from 0.75 D for the Cl⁻ to 0.97 D for the Br⁻. However, as observed for the charge transfer, the dipole moment distributions of the first solvation shell molecules are very close (2.44 D for Cl⁻ and 2.41 D for Br⁻), with an average dipole moment lower by ~0.2 D with respect to the average value found for the pure solvent (2.64 D). The dipole moment of the second shell molecules is quite similar to that of the pure solvent, confirming once again that the ion–solvent interaction is essentially localized in the first solvation shell, as reported in Figure 9.

To further support that the influence of the bromide ion on the electronic properties is restricted to the first solvation shell molecules, a cluster analysis with increasing number of methanol molecules from 1 to 4 has been performed. In a cluster with one molecule, a value of 2.47 D has been obtained. This value is lower than the average value in pure liquid methanol (2.64 D) but, as expected, much higher than the isolated molecule (1.75 D). Increasing the number of methanol molecules in the cluster from two to four, the value of the average dipole moment

is of 2.40, 2.31, and 2.25 D, respectively. This clearly shows that the H-bond interactions between methanol molecules in the solvent are more effective in changing the average value of the dipole moment than the interaction with the bromide.

4. Conclusions

The structural properties of the Br⁻ ion in methanol have been studied with CPMD simulations. Particular attention has been devoted to the study of the H-bond interactions between the ion and the solvent molecules of the first solvation shell. The bromide ion is surrounded by four methanol molecules, that give rise to a stable cage. It has been observed from the AIM population analysis and density of charge redistribution that the mutual ion–solvent interactions are essentially localized in the first shell region. The charge flows from the ion to the solvent molecules through the H-bonds so that the ion is strongly perturbed by the presence of the solvent, as shown by the WFC analysis, whereas a lower perturbation occurs for the solvent molecules of the first solvation shell.

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