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An *ab initio* study of water molecules in the bromide ion solvation shell

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The solvation shell structure and dynamics of Br^- in an aqueous solution of HBr (1.6 M) was studied, under ambient conditions, by *ab initio* molecular dynamics using the Car–Parrinello approach. The present calculations indicate that Br^- is asymmetrically solvated by water. The calculated residence time of water in the inner Br^- anion solvation shell agrees well with the most recent experimental estimate. Analysis indicates that the large anion scarcely influences the molecular dipole moment of solvation shell molecules. © 2002 American Institute of Physics. [DOI: 10.1063/1.1421366]

I. INTRODUCTION

The solvation of ions in aqueous solution is of fundamental importance in chemical and biological processes. The unique role of water is closely related to the dynamics of ionic aqueous solvation shells. In recent years, much attention has been dedicated to the structure of ions in water both experimentally^{1–6} and theoretically.^{7–25} In order to investigate the hydration structure of ions in solution, a variety of experimental methods have been successfully applied, such as ultrafast spectroscopy^{1,26} and neutron and x-ray diffraction techniques.^{2,5} However, the determination of the detailed microscopic structure and dynamics of inner solvation shells around ions is generally difficult. In this regard, the study of ion/water molecule clusters can give an important contribution for modeling bulk solvation. Vibrational predissociation spectroscopy experiments indicate that Cl^- , Br^- , and I^- are asymmetrically solvated in clusters containing up to six water molecules.^{27–29} This contrasts with older and less direct experiments based on high-pressure mass spectroscopy^{30,31} and photoelectron spectroscopy^{32,33} from which a symmetrical solvent cage around the anion was inferred. For cations the experiments and theoretical calculations indicate the formation of fully solvated symmetrical clusters.^{16,24,34–41,43–47} On the basis of these findings, it is clear that anions exist at surface of water clusters, whereas cations are found in the interior.

The situation in bulk water is less clear. Cations are supposed to be fully solvated with a symmetric solvation cage.^{4,20,21} Moreover, the first solvation shell of cations are thought to be rigid. This is particularly true for many dications, such as Ca^{2+} , Mg^{2+} , or Cu^{2+} , for which the water exchange between the first and second solvation shells is slow.^{4,5} For anions the situation seemed to be different. The experimental residence time was generally estimated to be very short (<5 ps).⁴⁸ The residence times computed by classical molecular dynamics (MD) simulations using nonpolarizable force fields well agree with these values.⁵ In contrast, polarizable empirical force fields^{49,50} give a higher value, τ

$=12\text{--}13$ ps, for aqueous 0.3 M Cl^- . Very recently, in an elegant study, Kropman and Bakker³ used nonlinear spectroscopy to isolate the spectral response of water molecules hydrogen-bonded to the halides Cl^- , Br^- , and I^- . They found that the water molecules in the solvation shells of these anions move comparatively slowly, with mean lifetimes ranging between 12 to 20 ps for 1 to 6 M NaCl solutions and 18 to 25 ps for NaBr and NaI in the same range of concentrations, with a reported uncertainty of about 5 ps.

The new measurements³ and the lack of accurate theoretical *ab initio* studies on the dynamics of solvation shells of anions in bulk water prompted us to start a systematic investigation of anions in water.⁵¹ We report on a Car–Parrinello (CP) density functional theory (DFT) based MD simulation⁵² on an aqueous solution of HBr at 1.6 M. Conventional computer simulation techniques based on empirical potentials including or not polarization and three-body interactions have been already applied to obtain detailed and statistically reliable information about structural and dynamical properties of water molecules around both cations and anions (see, for example, Refs. 5, 7, 38). However, these studies rely on the quality of the parametrized potential energy surface. It has been demonstrated that the inclusion of three-body effects is important for a more accurate description of ion–water interaction and, hence, for a realistic description of the solvation structure.^{53,54} Moreover, it has been shown that the polarizability of the anion may be one of the most important factors in determining the structure of gas-phase clusters.^{43,38,44} Recently, several mixed QM/MM studies of the structure of the aqueous solvation shell of ions have been reported.^{8–11} However, this approach also suffers from the above mentioned parametrization problem. In contrast, the CPMD approach is able to describe the dynamics of the system in a self-consistent fashion, taking into account in a natural way polarization and many-body interactions (not only three-body terms). CPMD simulations have already been successfully employed in the study of many cations in solution and gas-phase water clusters^{12,15–22,55} and of a $\text{Cl}^- (\text{H}_2\text{O})_6$ complex,^{41,42} and are providing an increasingly important complement to experimental data.

The paper is organized as follows. In Sec. II we will give

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the computational details of our simulations. In Sec. III we will report and discuss the results obtained. Then, in Sec. IV we will conclude with some final remarks.

II. COMPUTATIONAL DETAILS

The present DFT calculations utilized Troullier–Martins pseudopotentials⁵⁶ to describe the core of all atoms except for hydrogen for which a von Barth–Car analytical pseudopotential⁵⁷ has been used. The Kleinman–Bylander decomposition⁵⁸ has been used for all the atoms. We have used the new empirical exchange–correlation functional proposed by Hamprecht *et al.*,^{59,60} named HCTH. This functional has been successfully used to evaluate the geometry and the energy along the reaction pathway of simple $\text{S}_\text{N}2$ reactions^{61–63} obtaining an improvement in the energy profile with respect to the very popular Becke, Lee, Yang, and Parr (BLYP) exchange and correlation functional.^{64,65} Moreover, it has been demonstrated to be more satisfactory in describing the hydrogen bond and transport properties of liquid water⁶⁰ than the BLYP functional. The electronic wavefunctions have been expanded in a plane waves basis set up to the energy cut-off of 70 Ry. With this choice the molecular geometries converged within 0.3%. The equations of motion have been integrated with a time step of 7 a.u. (0.169 fs) using a fictitious electronic mass⁵² of 1000 a.u. We have also replaced all of the hydrogen atoms with deuterium. The simulation cell was a cubic box of 9.8988 Å containing 31 water molecules and one HBr molecule. The volume has been chosen on the basis of the experimental density of aqueous HBr solutions.⁶⁶ The size of the system is relatively small but, compared to recent CPMD studies of cations,^{16,19,20,22} we prefer to carry out a sufficiently long simulation in order to accumulate reliable statistics of the calculated properties. The simulation cell is large enough to contain the first two Br^- solvation shells. Further neighbors are partially shared by the periodic images. The simulation on HBr in water was started from a liquid water configuration consisting of 32 water molecules in which one water molecule was replaced by a HBr molecule. The starting H–Br distance was chosen to be equal to the gas-phase value. A previous study on HCl in water⁵⁵ showed that the initial configuration does not significantly influence the acid dissociation. We assumed that is also true for HBr since this acid is stronger than HCl. The system was equilibrated at 300 K for about 2 ps using a Nosé–Hoover chain of thermostats to control the temperature after an initial period of 1 ps during which the temperature was controlled by uniformly scaling the velocities. Then, the phase-space trajectories were collected for 36 ps.

In order to investigate the effects of the counter ion (the HBr proton) a second simulation was performed removing the excess proton from a randomly chosen configuration of the previous simulation and adding a uniform positive background. In this simulation, the system was re-equilibrated for 3 ps using a Nosé–Hoover chain of thermostats and the phase-space trajectory was collected for 17 ps. In the following, the two simulations will be referred to as HBr(aq) and Br^- (aq), respectively. All the calculations were done using the CPMD code.⁶⁷

A short, preliminary version of our work, restricted to the calculation of the coordination number and the residence time of the water molecules in the inner solvation shell of Br^- in HBr, has been presented elsewhere.⁶⁸

III. RESULTS AND DISCUSSION

The dissociation of HBr occurs with the same mechanism reported by Laasonen and Klein,⁵⁵ so we will not elaborate this process. Briefly, the H originally bonded to Br moves spontaneously with a barrierless, diffusion limited reaction to a neighboring water molecule, giving rise to H_3O^+ . Then, one of the hydrogens of H_3O^+ migrates to another water molecule, as already reported in the literature.^{15,55} We will return to the dynamics of the hydronium cation in Sec. III C.

A. Coordination number and residence time

Radial distribution functions (RDF's), $g(r)$, between the Br^- anion and O and H atoms are reported in Fig. 1. The first Br–O peak at 3.26 Å compares nicely with the experimental value of 3.21 Å determined for 1 M DBr.⁶⁹ In Br^- (aq) this distance increases to 3.37 Å approaching the value of 3.43 Å experimentally inferred from IR measurements on 0.377 M NiBr_2 .⁶ The nonzero first minimum of the RDFs indicates that the water molecules in the first solvation shells are quite mobile. Moreover, from the comparison of the first minimum of the reported RDFs, it can be inferred that the water molecules of inner solvation shell of Br^- in Br^- (aq) exchange with bulk more rapidly than in HBr(aq). The coordination number of Br^- in HBr(aq) obtained from the running integration number up to the first minimum of the Br–O pair distribution function is 6.3. More accurate information may be obtained by defining the instantaneous coordination number, $n_{\text{Br}}(t)$, as the number of hydrogens closer than 3.15 Å to the Br atom, i.e., the first minimum in the Br–H pair correlation function, with an O–H···Br angle greater than 130°, which represents the lower limit commonly used in hydrogen bond analysis.^{23,70} The distribution of the coordination number, n_{Br} , shown in Fig. 2(a), fluctuates in the range 4 to 8 with an average value of 5.8, slightly different from that obtained by integration of the $g_{\text{Br-O}}(r)$. Overall, the coordination number agrees well with the value $n_{\text{Br}}=6.0$ obtained from neutron scattering experiments on 1 M DBr⁶⁹ and $n_{\text{Br}}=6.3$ inferred from IR measurements on 0.377 M NiBr_2 .⁶ However, the experimentally proposed octahedral structure for the Br^- solvation shell in DBr (1 M)⁶⁹ is very different from the one obtained from the present study. We will discuss this point later. Interestingly, the removal of H^+ in HBr(aq) resulted in a decrease of n_{Br} to 5.1. We therefore conclude that the counter ion can influence the dynamics of the anionic solvation shell.

An important focus of the present work is the value of the residence time, τ , of water in the first coordination shell.³ The calculation of the mean residence time is quite delicate since we have to take into account that one or more water molecules can temporarily leave the first coordination shell and return to it without ever properly entering the bulk. We have estimated the mean residence time by following the prescription of Impey *et al.*,¹³ which avoids problems arising

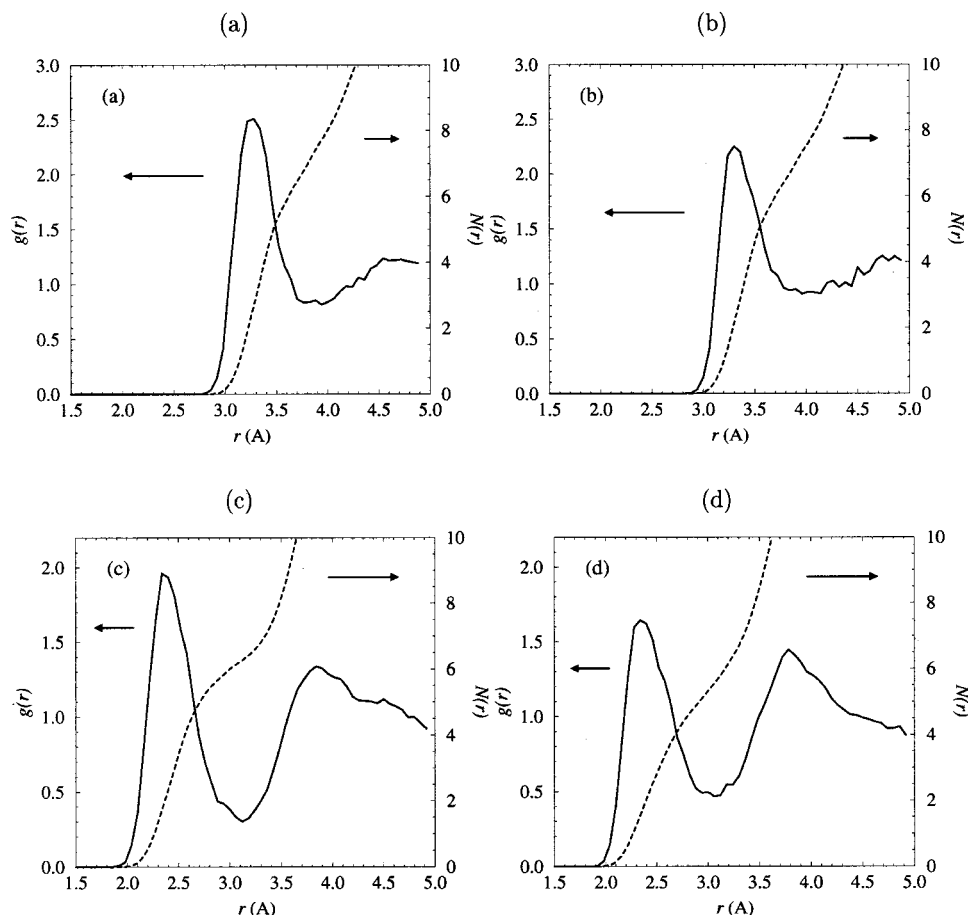


FIG. 1. Radial distribution functions, $g(r)$. (a) and (c) $g_{\text{Br-O}}(r)$ and $g_{\text{Br-H}}(r)$ for HBr(aq); (b) and (d) $g_{\text{Br-O}}(r)$ and $g_{\text{Br-H}}(r)$ for Br^- .

from the rattling motion of water molecules of the first hydration shell. In accordance with these authors, any molecule that does not leave the solvation shell for a time longer than t^* , without returning into it in the interim, is treated as not having left the solvation shell at all. Following former studies,^{7,13,49,50} we have chosen a tolerance time of $t^* = 2$ ps. On the basis of this criterion, in HBr(aq) one water molecule left the first coordination shell after 33 ps and some molecules stayed longer than 18 ps. We have also noticed that hexa-coordinated configurations last longer than penta- and hepta-coordinated ones in agreement with the distribution of Fig. 2(a). The longest hexa-coordinated configuration

persisted for about 7 ps, which has to be compared with about 2 ps for each of the others.

The computed decay of the population of the hydration shell, $n(t)$, reported in Fig. 3, suggests a value of $\tau \approx 19$ ps for HBr(aq). Unfortunately, there is large uncertainty on the computed τ . However, considering the very different nature of the counter ion, our theoretical estimate is in fairly good agreement with the experimental value for Br^- of $\tau = 19 \pm 5$ ps in 2 M NaBr.³ The residence time calculated for $\text{Br}^-(\text{aq})$ is slightly lower as the RDF's of Fig. 1 also suggested.

It has been demonstrated that the polarization effects are

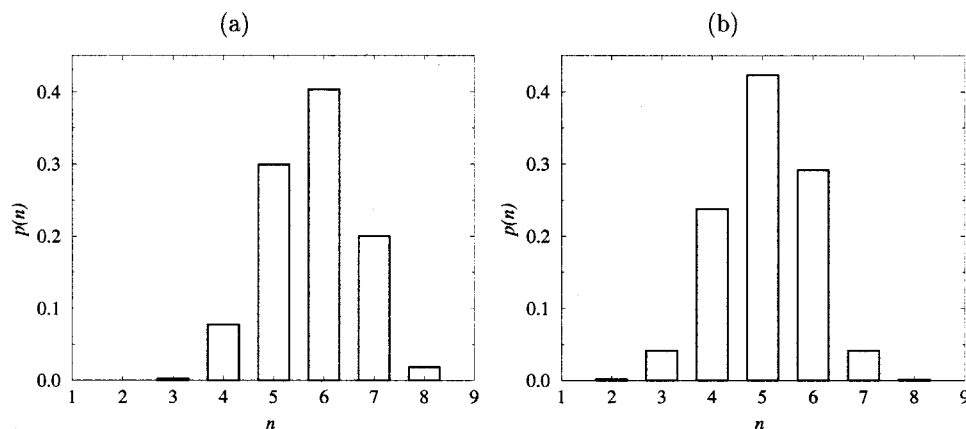


FIG. 2. The distribution of the coordination number, n , of Br^- in (a) HBr(aq) and (b) $\text{Br}^-(\text{aq})$ at 1.6 M.

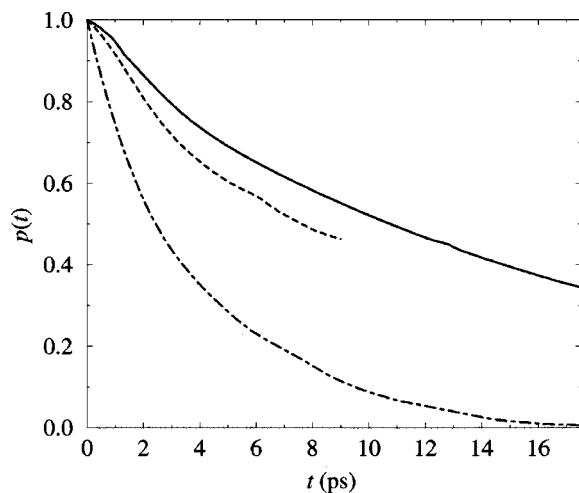


FIG. 3. Inner solvation shell population decay. Solid line: HBr(aq) ; dashed line: $\text{Br}^-(\text{aq})$; dotted-dashed line: classical MD simulation of $\text{Br}^-(\text{aq})$ using a nonpolarizable force field.

very important in determining τ . Smith and Dang⁴⁴ evaluated the water residence time in the Cl^- solvation shell in a solution of 0.26 M NaCl in the region between the $\text{Na}^+:\text{Cl}^-$ contact ion pair and the solvent-separated ion pair. They performed a MD simulation with the simple SPCE/POL fixed charge plus point polarizability (plus Lennard-Jones interactions) empirical force field⁴⁹ obtaining the value $\tau=12$ ps. Sprik *et al.*⁵⁰ using a fluctuating charges potential model obtained for a solution Cl^- in water of similar concentration a residence time $\tau=13$ ps. These values are in very good agreement with the experimental $\tau=12$ ps for a solution of 1.0 M NaCl.³ The value of the residence time estimated in the present study and by Smith and Dang⁴⁹ and Sprik *et al.*⁵⁰ should be compared with 4.5 ps calculated for Cl^- by Impey *et al.*¹³ using the nonpolarizable MCY water. In order to confirm the underestimation of the residence time by nonpolarizable force fields, we have also performed a MD simulation on a system composed by 1 bromide and 31 water molecules ion using the rigid SPC (nonpolarizable) potential function for water.⁷¹ The decay of solvation shell population, reported in Fig. 3, has a time constant $\tau=5$ ps, a value much shorter than that inferred from the *ab initio* simulation and comparable to that obtained for Cl^- by Impey *et al.*¹³ The value

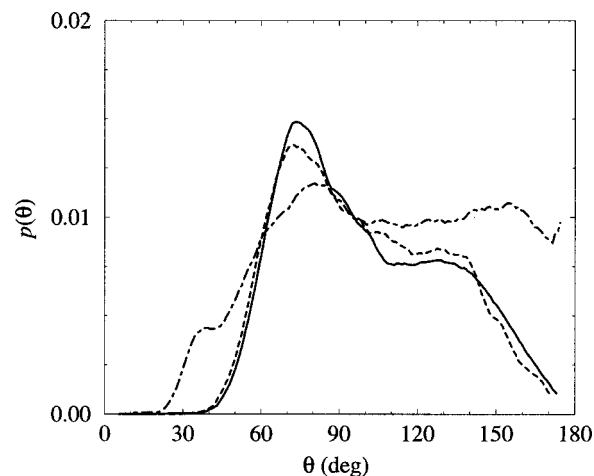


FIG. 5. O-Br-O angular distribution for water molecules in the first solvation shell of Br^- . Solid line: HBr(aq) ; dashed line: $\text{Br}^-(\text{aq})$; dotted-dashed line: classical MD simulation of $\text{Br}^-(\text{aq})$ using a nonpolarizable force field.

$\tau=11$ ps found for Cl^- in 1 M NaCl by Lyubartsev and Laaksonen⁴⁵ can be related to the adopted flexible SPC water model, in which polarization is indirectly taken into account to some extent.

B. Structure of the first solvation shell

A first important information on the structure of the solvation cage is given by the analysis of the distance, R_{cage} , between the center of mass of the cage and the anion. If the anion is spherically solvated, this distance should approach zero. This is not the case of Br^- in water solution as can be easily seen from Fig. 4(a) where the distribution of R_{cage} for both HBr(aq) and $\text{Br}^-(\text{aq})$ is reported. The distribution of $\text{Br}^-(\text{aq})$ is broader than that of HBr(aq) . However, when the solvation shell is defined according to the criterion of Impey *et al.*,¹³ the $\text{Br}^-(\text{aq})$ distribution narrows considerably, as shown in Fig. 4(b). From Fig. 4(a) strong asymmetry of the solvation shell can be inferred.

Although the first solvation shell is asymmetric, on the time scale of our simulation, the water molecules occupy well defined positions around the anion. This is evident from Fig. 5 where the distribution of the O-Br-O angles for the water molecules in the solvation cage is shown. Once again,

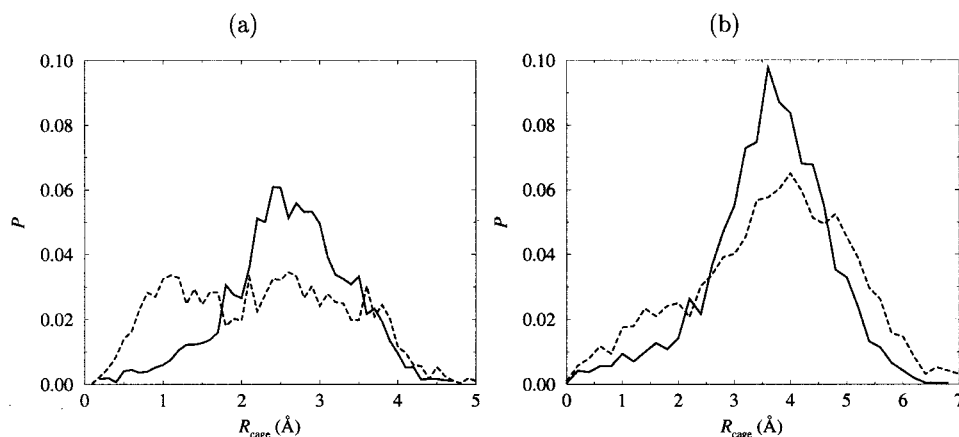


FIG. 4. The distribution of R_{cage} , the distance between the center of mass of the first solvation shell and the Br^- anion, (a) without and (b) with the correction for the rattling motion of the water molecules. Solid line: HBr(aq) ; dashed line: $\text{Br}^-(\text{aq})$.

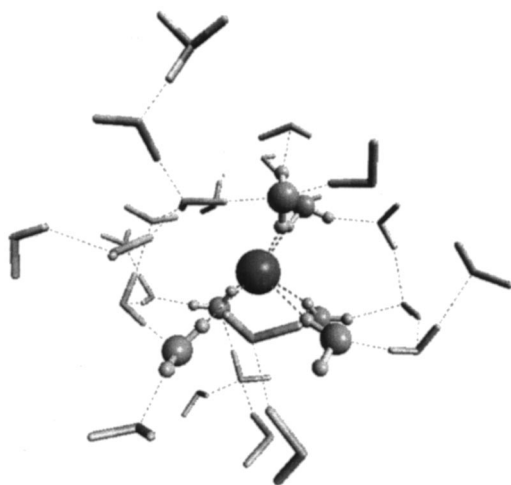


FIG. 6. Snapshot of a configuration of the $\text{HBr}(\text{aq})$ system: the water molecules in the first solvation shell are drawn as balls and sticks.

$\text{HBr}^-(\text{aq})$ and $\text{Br}^-(\text{aq})$ show a similar behavior. We have observed that, on average, when a water molecule leaves the first solvation shell another one enters in a different position, giving rise to a pseudorotation of the cage around the Br^- . In Fig. 6 a configuration with $n_{\text{Br}}=6$ is shown. A typical configuration of the inner solvation shell contains four water molecules coordinated Br^- according to a hypothetical square pyramidal geometry. Then, depending on the coordination number, other water molecules are coordinated to Br^- on the other side, resulting in a $4+1$, $4+2$, or $4+3$ structure. We also observed other types of structures with any apparently well-defined symmetry. From a careful investigation of the trajectories it is evident that on average the O atoms occupy the vertices of a square antiprism of C_{4v} symmetry centered on Br^- for both $\text{HBr}(\text{aq})$ and $\text{Br}^-(\text{aq})$. The interaction with the periodic images seems to have little effect in determining the structure of the cage. As a matter of fact, in our MD simulation with SPC water the first solvation shell is rather unstructured (see Fig. 5) and more symmetric than that inferred from the CPMD simulation. Moreover, also the asymmetry of the solvation cage is much less pronounced.

As already mentioned, in the present simulations the instantaneous water cage around the ion is similar to that of a surface-like state reported for $\text{X}^-(\text{H}_2\text{O})_n$ clusters (see Refs. 24, 38, 40, 41 and references therein). We have observed that a water molecule in the inner solvation shell is rarely involved in a hydrogen-bond with another molecule in the solvation shell, but spends almost all the time coordinated to second solvation shell molecules. It is well known that the arrangement of water around halide ions in gas phase clusters (even of large size) is determined by the competition between the solvation of the anion and the hydrogen bonding among the solvent molecules. As already discussed by Stuart and Berne³⁸ for the $\text{Cl}^-/\text{H}_2\text{O}$ system, whether or not the surface solvation occurs depends on a delicate balance among stabilization of the first solvation shell, the destabilization of the second one, and longer distance interactions. The strongly favorable anion–water bonds come with an associ-

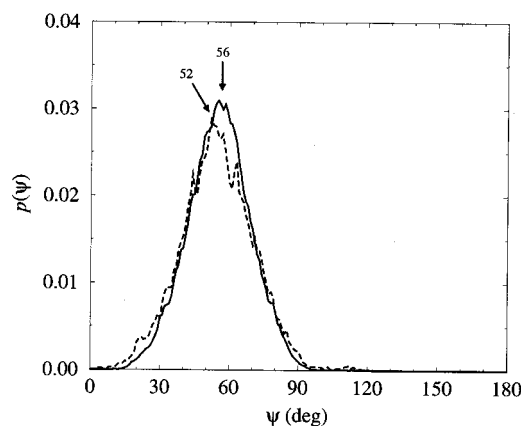


FIG. 7. The distribution of ψ , the angle between the dipole moment of solvating water molecules and the O–Br vector. Solid line: $\text{HBr}(\text{aq})$; dashed line: $\text{Br}^-(\text{aq})$.

ated penalty: every water molecule in the first solvation shell of the bromide ion must sacrifice one or more water–water hydrogen bond interactions in order to interact favorably with the anion. The interaction anion–water is stronger than that between two water molecules and this gives a negative solvation energy of the ion. For instance, at the HCTH level, the bromide–water and the water–water interaction energies are 53.0 and 18.2 kJ mol^{-1} , respectively. However, the water molecules in the second solvation shell will be involved in fewer hydrogen bonds than if they were in the bulk.⁷² The interaction of the second shell water molecules with the anion will not necessarily be favorable enough to compensate for the disruption of the local hydrogen bond network. The overall unfavorable balance of these effects give rise to a surface-like solvation.

Additional insight into the structure of water molecules around the ion is given by the analysis of the distribution of the angle ψ between the first solvation water molecules dipole moment and the O–Br axis. This angle measures the deviation from linearity of the $\text{O–H}\cdots\text{Br}^-$ hydrogen bond. The calculated distribution is reported in Fig. 7 for both $\text{HBr}(\text{aq})$ and $\text{Br}^-(\text{aq})$. These distributions and the nearest neighbor Br–O and Br–H distances (Fig. 1) are consistent with a nearly linear hydrogen bond ($\psi_{\text{linear}} \approx 50^\circ$) in agreement with previous calculations on anions in water.^{5,8} No evidence of a bifurcated hydrogen bonds, where the two hydrogens of a water molecule are bridged by the anion, was found.

To analyze the polarization effects a set of doubly occupied localized orbitals has been obtained using the maximally localized Wannier functions technique.^{73,74} In this way, the delocalized electronic density was partitioned between the ion and the molecules. As described in Refs. 74–76, from the center of charge of Wannier functions the dipole moment, μ , of the species present in solution can be calculated. We have computed μ for H_2O and Br^- averaging over configurations equally spaced in time by 0.5 ps . The anion dipole moment has been calculated with respect to the nucleus position. The calculated dipole distribution is shown in Fig. 8. The average value of the dipole moment of the water molecules in the first solvation shell is equal to that of bulk

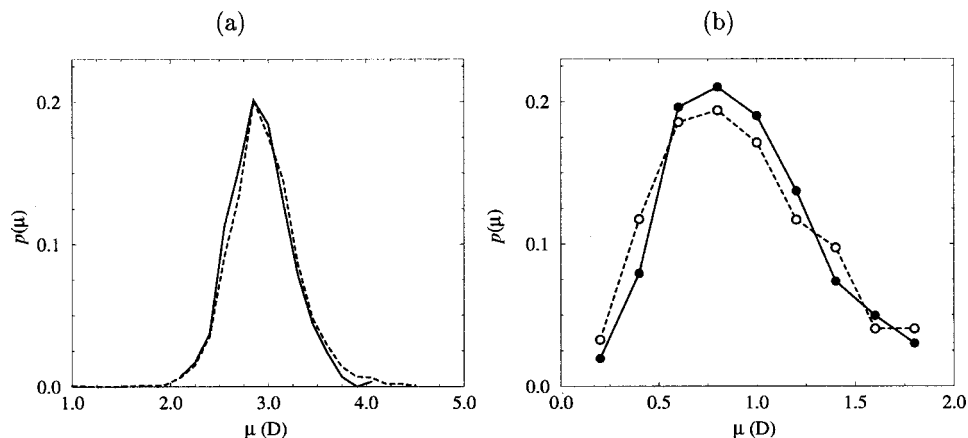


FIG. 8. The distribution of the modulus of the water (a) molecules and (b) anion dipole moments (μ). In (a) the solid and dashed lines represent the distribution of μ for water molecules in the first solvation shell of the anion and the bulk molecules, respectively, calculated for HBr(aq) . In (b) the solid and dashed lines represent the distribution of μ for Br^- in HBr(aq) and Br^- (aq), respectively.

molecules [the differences are within the statistical uncertainty; see Fig. 8(a)]. Moreover, for both HBr(aq) and Br^- (aq) the average dipole moment is essentially the same. Our estimate, $\mu_{\text{H}_2\text{O}} = 2.9$ D, is very close to that calculated for pure water by Silvestrelli and Parrinello^{75,76} using the BLYP functional ($\mu_{\text{H}_2\text{O}}^{\text{BLYP}} = 2.95\text{--}3.00$ D, depending on the size of the simulation cell). The present calculations indicate that the ion scarcely influences the polarization of the water molecules. However, the water molecules near the H_3O^+ or H_5O_2^+ cations are more polarized and show a relatively high dipole moment, giving rise to the tail beyond 3.8 D in the distribution of Fig. 8(a). On the other hand, the large Br^- anion is strongly influenced by the presence of surrounding water. The computed average value of the anion dipole moment is $\mu_{\text{Br}} \approx 0.95$ for HBr(aq) and slightly lower in Br^- (aq) [Fig. 8(b)], with a standard deviation in both cases of about 0.8 D. The presence of an induced net dipole moment must be related to the asymmetry of the first solvation shell.

In a previous Monte Carlo QM/MM study of Br^- in water by Tuñón *et al.*,⁸ one “*ab initio*” anion, treated at DFT/VWN level of theory with no gradient corrections, was embedded in 216 TIP3P (nonpolarizable) water molecules. They found for Br^- an average dipole moment of 0.21 D, much lower than the one obtained in the present study. We think that the discrepancy between their result and ours arises from the use of a nonpolarizable potential for water in the simulation by Tuñón *et al.*, which could give rise to a more symmetric solvation cage, like that observed in our MD simulation with SPC water. This is also suggested by the high value of the coordination number ($n_{\text{Br}} = 7.7$) obtained by these authors. We are also aware that our estimate could be influenced to some extent by size effects.

C. Hydronium motion

After dissociation, the proton was found either bonded to a single water molecule as H_3O^+ or located between two molecules as H_5O_2^+ . This parallels what was found in $\text{HCl/H}_2\text{O}$.⁵⁵ Following the separation of Br^- and H_3O^+ , we found that the proton is rarely bound to a water molecule in the first solvation shell, but was located, most of the time, at the next nearest neighbor distance of about 4.8 Å. Sometimes the hydronium was found in the third solvation shell at 6.5 Å, namely the maximum separation allowed by the simula-

tion cell. We recall that the third solvation shell is partially shared with the periodic images. As in the case of HCl , this observation suggests an effective repulsive potential of mean force between the Br^- and H_3O^+ ions at the nearest neighbor distance, which, at a larger distance, becomes attractive. The solvent separated $\text{Br}^-:\text{H}_3\text{O}^+$ (or $\text{Cl}^-:\text{H}_3\text{O}^+$) ion pairs is similar to those that were found for NaCl in water.^{49,77}

IV. CONCLUSIONS

We have reported the results of *ab initio* CPMD simulations on the solvation dynamics of Br^- in aqueous solution HBr at 1.6 M. We have found that the anion is asymmetrically solvated by water. The most stable inner solvation shell has a 4+2 structure where four water molecules are coordinated to Br^- according to a hypothetical square pyramidal geometry and the other two molecules are coordinated to the other side. The asymmetry of the solvation cage resembles what is observed in MD simulations of halide $\text{X}^-(\text{H}_2\text{O})_n$ clusters for which a surface-like behavior has been proposed. In the present we study give a residence time of water in the first solvation shell of about 19 ps in agreement with the most recent experimental measures. Empirical nonpolarizable force fields generally give a shorter residence time. The *ab-initio* simulations fully take into account polarization and many-body effects and, when compared to previous classical MD simulations with^{49,50} and without⁵ polarizable potential models, confirm the importance of polarization in determining the water exchange rate. Also the structure of the solvation shell seems to be largely influenced by polarization effects. In fact, a test calculation with a nonpolarizable potential⁷¹ gave a quite unstructured solvation cage. The importance of the anion polarizability in determining an inner or surface state for $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters has been pointed out by Dang and Smith⁴⁴ and Stuart and Berne,⁴³ who showed as the inclusion of the Cl^- polarizability favors the formation of surface-like clusters. The present calculations indicate that the ion scarcely influences the average dipole moment of the inner solvation shell water molecules, the dipole mean value being identical, within our statistical uncertainty, to that of bulk water. On the other hand, the large Br^- anion is strongly influenced by the presence of surrounding water, and, as a consequence of the asymmetry of the inner solvation shell, it has a net dipole moment close to 1 D. The removal of the

excess proton does not substantially alter our findings. It remains to explore the effect of the limited size of the simulation cell, which could perhaps alter to some extent the conclusions.

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