



Ab initio QM/MM dynamics of anion–water hydrogen bonds in aqueous solution

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Abstract

Dynamical properties of F^- –water and Cl^- –water hydrogen bonds in aqueous solution have been studied by ab initio QM/MM molecular dynamics simulations, in which the whole first hydration sphere of the anion was treated at Hartree–Fock level using D95V+, 6-31+G and D95V++ basis sets for F^- , Cl^- and water, respectively. According to a detailed analysis of the bond distortions and shifts in the corresponding bending and stretching frequencies as well as the mean residence times of water molecules surrounding the ions, F^- clearly acts as a ‘structure-maker’, while Cl^- solvation leads to a more flexible structure with frequent re-arrangements of the hydrogen bonds.

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1. Introduction

The dynamics of hydrogen bonds in aqueous electrolyte solutions of charged particles, in particular anions, has been an important subject of both experimental and computational studies [1–4]. In general, the interactions of anion with water are relatively weak and dominated by ionic hydrogen bonding. These interactions are, in several cases, even energetically comparable with the water–water interactions in pure water, implying that the dynamical properties of such weakly hydrated anions can be very sensitive to the relative strength of anion–water and water–water interactions. Recently, the dynamics of water molecules in the solvation shell of halide ions were experimentally studied by a nonlinear spectroscopic technique [1]. Following these experiments, water molecules in the solvation shells of Cl^- , Br^- and I^- were proposed to display mean lifetimes

ranging from 12 to 25 ps, which is about 20–50 times longer than in pure liquid water.

On the other hand, time-dependent simulation methods, in particular molecular dynamics (MD) technique, have been employed to provide dynamics information not accessible by experimental approaches, especially for very fast reactions as they permit to characterize specific reactions and mechanisms of the involved interactions in the femto- and picosecond scale [3,4]. Recent classical MD simulations [4], using extended simple point charge (SPC/E) model [5] for water and Lennard–Jones interactions for anions [6,7], have shown that the dynamics of anion–water hydrogen bonds for Cl^- and Br^- at room temperature should be about two times slower than that of water–water hydrogen bonds. However, the main drawback of this work, as well as the earlier MD results of Impey et al. [3], is the neglect of charge transfer and thus changing polarization of the molecules, an important factor determining many-body interactions. These effects of polarization have been shown to be very crucial for the hydrogen

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bond relaxation time [8], and it has even been concluded that simulations based on non-polarizable models are inadequate to properly describe the dynamics of water molecules in the solvation shell of ions [9].

For the treatment of polarizable systems, the use of empirical polarizable models can generally provide at least partially correct prediction of physico-chemical properties. However, it is rather difficult to obtain an appropriate value of the halogen ion polarizability since there are no direct measurements of this quantity in aqueous solution, and the available data are usually extrapolations from ionic crystals and salt solutions [10,11]. To include the effects of polarization and many-body interactions in a self-consistent fashion, Car-Parinello (CP-MD) approach [9,12] has been employed to investigate the hydrogen bond structure around Br^- , as well as the residence time of water molecules in the inner solvation shell of the ion. By the CP-MD method, the residence time of water in the bromide ion solvation shell was found to be about 19 ps, which was in good agreement with the experimentally estimated Br^- -water hydrogen bond time constant of 19 ± 5 ps for a 2 M NaBr solution [1]. However, this method has made use of a relatively small simulation box, and it has been shown that density functionals, in particular the simple BLYP potential of CP simulations can lead to an exaggerated rigidity in liquids, especially in the case of water and electrolyte solutions [13–15].

The ab initio QM/MM molecular dynamics technique has been proven to be a very reliable simulation method, providing many new insights into the structure and dynamics of various solvated ions [13–22]. For small anions, like F^- and Cl^- , QM/MM studies [20] have shown that the orientation of first shell water molecules is considerably changed by ‘quantum effects’, although, especially for the case of Cl^- , the classical simulation supplied an almost identical coordination number. Such details are of great importance as a correct geometrical description is a precondition for reliable dynamics data.

In the present work, we have extended the previous QM/MM simulations of F^- and Cl^- in water [20] in order to investigate the effects of each particular anion on the dynamical properties, such as structural distortions and shifts in the corresponding bending and stretching vibrational frequencies of the surrounding water molecules. In addition, the water exchange processes and the mean residence times of water molecules in the hydration shell of the ions were evaluated.

2. Methods

By the QM/MM technique, the chemically most relevant region, the anion and its first hydration sphere, is treated by Born–Oppenheimer ab initio quantum mechanics, while the rest of the system is described by

ab initio generated pair potentials. In this work, the QM/MM molecular dynamics simulations of F^- and Cl^- in water were carried out with a similar protocol as reported in the previous paper [20]. The QM regions with diameters of 8.0 and 9.2 Å were applied for the solutions of F^- and Cl^- , respectively. For the description of all particles within the QM regions, the D95V+ [23], 6-31+G [24,25] and D95V++ [23] basis sets were employed for F^- , Cl^- and water, respectively. The sizes of the respective QM regions and the basis sets employed in the simulations are considered as a suitable compromise between the quality of the simulation results and the requirement of CPU time. In principle, the inclusion of electron correlation in the quantum mechanical calculations should improve the quality of the simulation results, but it is far too time-consuming, even at the simple MP2-correlated level. The effect of electron correlation has been checked and was found to be rather minor [20]. On the other hand, to achieve a sufficient level of accuracy at HF-level of theory, the use of basis sets containing diffuse functions in the QM calculations was recognized as essential. To ensure a continuous change of forces during transitions of water molecules between the QM and MM regions, a smoothing function [26] was applied for an interval of 0.2 Å (i.e., between the F–O distances of 4.0–4.2 Å and between the Cl–O distances of 4.6–4.8 Å).

A flexible model, which describes intermolecular [27] and intramolecular [28] interactions, was employed for water, ensuring the compatibility and a smooth transition, when water molecules move from the QM region with full flexibility to the MM region. The pair potential functions for F^- - H_2O and Cl^- - H_2O interactions were obtained from the previous work [20]. Both simulations were performed in a canonical ensemble at 298 K with a time step of 0.2 fs. The cubic box, with a box length of 18.19 Å, employed in the simulations contained one anion and 199 water molecules, assuming the experimental density of pure water. Long-range interactions were treated using the reaction-field procedure [29]. The QM/MM simulations were performed for 75000 time steps, to collect configuration data every 10th step.

Since the characteristics of pure water represent the most important reference to correctly describe the influence of anions on the dynamical properties of their surrounding water molecules, a QM/MM molecular dynamics simulation of pure water was performed using the same simulation protocol, describing all water molecules within a QM diameter of 4.0 Å by the ab initio HF formalism using the same D95V++ basis set [23]. The system was initially equilibrated for 20000 time steps, using a configuration of pure water obtained from the previous QM/MM study [17], followed by another 75000 time steps to collect configurations every 10th step. To ensure a continuous

change of forces at the transition between QM and MM region, the smoothing function [26] was again applied within an interval of 0.2 Å (i.e., between the O–O distances of 4.0–4.2 Å). Thus the bulk water properties used as reference in this work refer to the properties obtained for pure water treated at the same QM/MM level of accuracy.

3. Results and discussion

3.1. Arrangement of water molecules in the hydration shells of F^- and Cl^-

The distributions of $F\cdots O-H$, $Cl\cdots O-H$ and $O\cdots O-H$ angles are plotted in Fig. 1, calculated up to first minimum of the $F-O$, $Cl-O$ and $O-O$ RDFs, respectively. The arrangement of water molecules around F^- and Cl^- reveals clear differences between the two anions. Within the hydration sphere of F^- , most neighboring water molecules donate one of their hydrogen atoms in a linear hydrogen bond to the ion, while water molecules in the hydration shell of Cl^- show a combination between water orientations pointing with only one or both hydrogen atoms towards the ion. These observed water orientations are in accordance with the previously observed hydration structures of F^- and Cl^- in water [20]. In comparison to the distributions of $O\cdots O-H$ angle of water in the bulk, F^- clearly forms its own framework of H-bonds, whereas Cl^- perturbs the solvent's hydrogen bond network in its neighborhood without creating a specific new order.

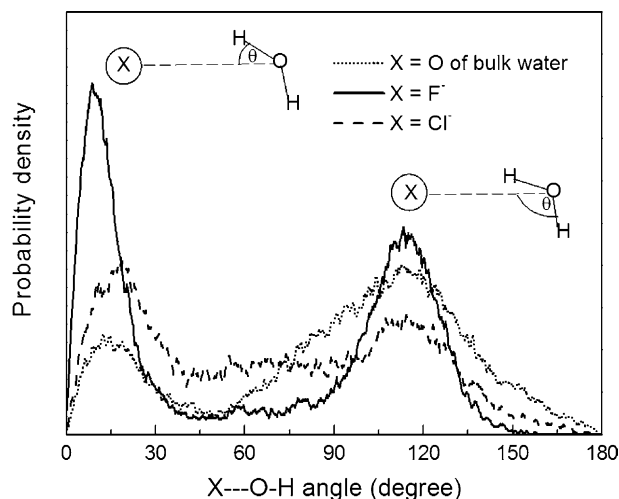


Fig. 1. Distributions of $X\cdots O-H$ angle ($X = O, F^-$ and Cl^-), calculated up to first minimum of the $O-O$, $F-O$ and $Cl-O$ RDFs, respectively.

3.2. Intramolecular geometry of water molecules in the hydration shells of F^- and Cl^-

Fig. 2 shows the distributions of O–H distances and H–O–H angles of water molecules within the first hydration shells of anions, compared to the corresponding geometry of water in the bulk obtained from the QM/MM simulation and being used for the description of ligand distortions due to the influence of the anions. For the hydration of F^- , the predominantly linear character of the F^- –water hydrogen bonds in the shell results in an asymmetric elongation of the two O–H bond lengths of waters, i.e., the ones that are hydrogen bonded to the ion are longer than the others. The distortion is also reflected in a decrease of the H–O–H angle, compared to the bulk. In contrast to F^- , Cl^- has only a minor influence on the O–H bond length of its surrounding water molecules, reflecting the relatively weak

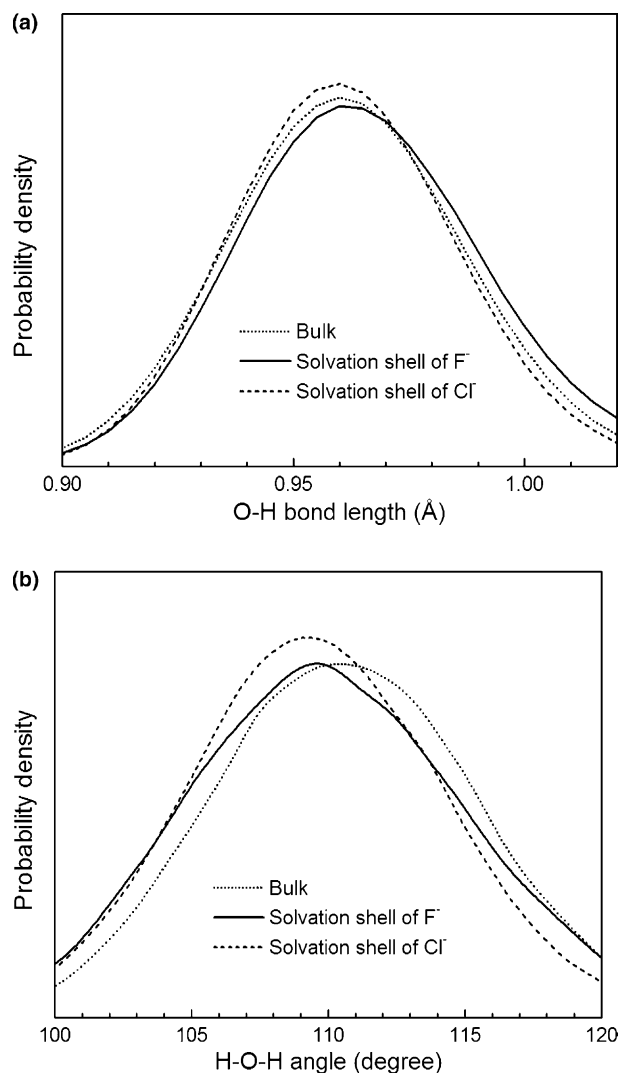


Fig. 2. Distributions of (a) bond length and (b) angle of water molecules in the bulk and in the hydration shells of F^- and Cl^- .

ion–water interactions. However, the anion still decreases the average H–O–H angle, partly due to configurations, where one water ligand forms two H-bonds simultaneously.

3.3. Vibrational motions of water molecules in the hydration shells of F^- and Cl^-

In general, the power spectra obtained by the Fourier transformations of VACFs are discussed in terms of shifts of peak maxima resulting from the ion's influence. Based on the normal-coordinate analyses [30], the three quantities Q_1 , Q_2 and Q_3 , calculated from the VACFs of hydrogens for describing symmetric stretching and bending and asymmetric stretching motions, respectively, are shown in Fig. 3. Due to rather constant systematic errors of HF frequencies, a scaling factor of 0.89 [31] was employed to scale all frequencies obtained by the QM/MM simulations. For water molecules in the bulk, a peak maximum at $1650 \pm 2 \text{ cm}^{-1}$ is found for the

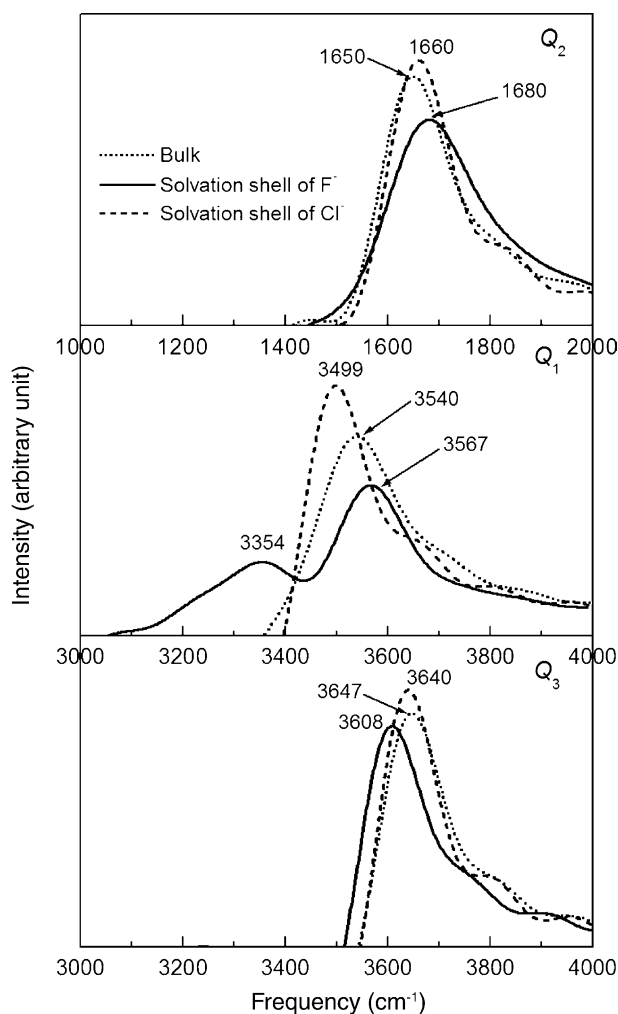


Fig. 3. Power spectra of the intramolecular vibrational motions of water molecules in the bulk and in the hydration shells of F^- and Cl^- .

symmetric bending, and peak maxima at 3540 ± 2 and $3647 \pm 2 \text{ cm}^{-1}$ are observed for the symmetric and asymmetric stretching frequencies, respectively. In the hydration shells of F^- and Cl^- , the bending frequencies of water molecules are blue-shifted by 30 and 10 cm^{-1} , respectively. These effects correlate with the observed decrease in the bending angle of water molecules in the hydration shells of the ions, compared to that of water molecules in the bulk. For the stretching frequencies, water molecules in the hydration shell of F^- reveal two broad symmetric stretching peaks, one being red-shifted by 186 cm^{-1} and another one blue-shifted by 27 cm^{-1} , and an asymmetric stretching peak shifted by 39 cm^{-1} to the red. The observed symmetric and asymmetric stretching peaks correspond to the presence of different O–H bond lengths of water molecules in the shell as a consequence of the stronger F^- –water hydrogen bonds and the concomitant weakening of the hydrogen bonds between the second hydrogen and water molecules in the bulk. The stronger $F^- \cdots H-O$ hydrogen bonds lead to a more linear $F^- \cdots H-O$ arrangement, which, in turn, destabilize the directional $O \cdots H-O$ interactions, resulting in a less favorable $O \cdots H-O$ angle. For water molecules in the hydration shell of Cl^- , the symmetric and asymmetric stretching frequencies are red-shifted by 41 and 7 cm^{-1} , respectively, indicating a relatively small influence of this ion, compared to the case of F^- , on the vibrational motions of its surrounding water molecules. On the other hand, the increase of anion radius implies a loss in linearity, and thus, a weakening of the anion–water hydrogen bonds, resulting in O–H stretching vibrations close to the unperturbed values.

3.4. Water exchange in the hydration spheres of F^- and Cl^-

According to the F–O and Cl–O RDFs [20], the non-zero first minimum of the RDFs in both systems indicates the lability of water molecules in the first hydration shells of the ions. Numerous water exchange processes, following either associative (A) or dissociative (D) as well as associative (I_A) and dissociative (I_D) interchange mechanisms, were observed when the F–O and Cl–O distances were plotted against time during the QM/MM simulations. The rate of water exchange processes at the anions and in the bulk were evaluated by means of mean residence times (MRT) of the water molecules. In this work, the MRT values were calculated using a ‘direct’ method [32] as a function of t^* , and are summarized in Table 1. The time parameter t^* is defined as the minimum duration for a ligand to remain inside/outside the hydration shell upon a migration process to be accounted. The accuracy limit of this direct method has been estimated as $\pm 10\%$ [32].

Table 1

Mean residence times of water molecules in bulk and in the hydration shells of F^- and Cl^- , calculated using the direct method [32] in ps as a function of t^*

Solute/ion	CN	t_{sim}	$t^* = 0$ ps		$t^* = 0.5$ ps	
			N_{ex}^0	$\tau_{H_2O}^0$	$N_{ex}^{0.5}$	$\tau_{H_2O}^{0.5}$
H ₂ O	4.7	15.0	357	0.20	52	1.36
F^-	4.6	15.0	173	0.40	28	2.46
Cl^-	5.6	15.0	386	0.22	41	2.05

N_{ex} is the number of accounted exchange events, t_{sim} the simulation time in ps and CN the average coordination number of the first hydration shell of water and ions.

Although, the MRT data reported here are calculated from rather short simulation trajectories with a limited number of exchange processes, simulation results obtained under the same simulation conditions and at the same level of accuracy provide a good basis for comparison. $t^* = 0$ ps allows to determine the life time of a H-bond, while $t^* = 0.5$ ps gives a good measure for the migration processes of water molecules. The absolute values for the H-bond life times resulting from our simulations are too short by a factor of ~ 2 , as can be seen from the value of 0.2 ps for pure water (expt.: 0.5 ps [33]). This can be considerably improved by inclusion of a second hydration shell into the QM region [14], although with an enormous increase of computational effort. The relative order, however, can be seen as a reliable measure for the H-bond properties. It delivers a twice as long life time for $F^- \cdots H$ bonds than for $O \cdots H$ bonds in water, while $Cl^- \cdots H$ bonds appear only about 10% more stable than H-bonds in the pure solvent.

Setting t^* to 0.5 ps it is clearly recognized that water ligand mobility is considerably restricted by the presence of both anions, the effect of F^- being considerably stronger. This trend is confirmed by the self-diffusion coefficients, calculated from the center-of-mass VACFs of waters using the Green–Kubo relation [34], as 3.12, 3.75 and 4.08 ($\times 10^{-5}$) $cm^2 s^{-1}$ for water molecules in the hydration shells of F^- and Cl^- , and in the pure water, respectively. With respect to the question whether the anion–water complexes, $X^-(H_2O)_n$, adopt ‘interior’ (I) or ‘surface’ (S) states [35], it can be concluded that both F^- –water and Cl^- –water hydrogen bonds are strong enough to compensate for the structure-breaking effects they have on the neighboring water molecules, i.e., both F^- –water and Cl^- –water hydrogen bonds overtake the water–water interactions and the ions will try to form as many hydrogen bonds as they can, preferring the ‘internally’ solvated species in aqueous solution. However, the Cl^- –water hydrogen bond is relatively weak, leading to a delicate balance between the directional hydrogen bond(s) of each water to the ion and the hydrogen bonding among water molecules, thus producing an asymmetrically solvated Cl^- [20]. In this

context, the ‘structure-making’ behavior of F^- is well reflected, while Cl^- shows much less of this ‘structure-making’ ability, but at the same time not yet a ‘structure-breaking’ effect.

4. Conclusion

The ab initio QM/MM MD simulations presented here provide a fairly accurate picture of the hydration of F^- and Cl^- anions. The data suggest that the absolute values of the dynamics could still be improved by the inclusion of a second hydration shell in the QM region of the simulations, which would boost the necessary CPU time, however, by a factor of ~ 10 . The details of solvate structure and dynamical changes between solvate configurations revealed by the simulations may prove helpful in developing refined models for the interpretation of spectroscopic data.

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