The hydration structures of F^- and Cl^- investigated by *ab initio* QM/MM molecular dynamics simulations

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Combined *ab initio* quantum mechanical/molecular mechanical (QM/MM) molecular dynamics simulations have been performed to investigate the hydration shell properties of F^- and Cl^-. The chemically most relevant region, the hydration sphere of the anions, was treated by Born–Oppenheimer *ab initio* quantum mechanics using D95V+, 6-31+G and D95V++ basis sets for F^-, Cl^- and water, respectively, while the remaining part was described by classical pair potentials. The QM/MM simulations have predicted average coordination numbers of 4.6 ± 0.2 for F^- and 5.6 ± 0.1 for Cl^-, in contrast to the corresponding values of 5.8 ± 0.1 and 5.9 ± 0.1 resulting from classical pair potential simulations. Within the first hydration shell of F^-, the QM/MM results indicate more flexibility of the hydration complex in which the $F^- \cdots H$–O bond appears to be linear. For the case of Cl^-, a combination of linear and bridged forms, together with a competition between the solvation of the ion and hydrogen bonding among water molecules, are observed.

1. Introduction

The characteristics of ions in aqueous electrolyte solutions are of fundamental scientific interest since the structural and dynamical properties of hydrated ions can influence various physiological processes and cause specific activities in biological functions.[1–4] Computer simulations[5–11] in conjunction with X-ray and neutron diffraction experiments[12–16] have proven to be most useful tools for elucidating such properties. The results from computer simulations generally provide a much more detailed interpretation of experimental observations at molecular level. In principle, the quality and accuracy of the simulation results depend essentially on the methods used for describing all interaction types in the system. In general, *ab initio* quantum mechanics would be the most accurate method but its application to a full condensed-phase system consisting of a large number of molecules is too time-consuming. Therefore, most of the earlier simulation works was based on potential functions describing inter- and intramolecular interactions between all atoms or molecules in the system. In such an approach, the potential functions are mostly assumed to be pairwise additive. However, the contributions of many-body terms have been extensively reported to play an important role for a correct description of ion–water interactions and hence, for a realistic picture of ion solvate structures.[17,18]

Nowadays, as a result of continuous increase of computer capacity and performance, more sophisticated and accurate simulation techniques incorporating quantum mechanical algorithms have contributed a great deal to the studies of condensed-phase systems.[19–26] Recently, a "Born–Oppenheimer *ab initio* QM/MM dynamics" technique has been proposed and applied for studying structural and dynamical properties of various cations in solution.[27–37] This technique treats the active-site region, *e.g.* the solvation shell around the ions, at *ab initio* Hartree–Fock level, while the environment consisting of further solvent molecules can be described by molecular mechanical potentials. By this QM/MM method, the complicated many-body contributions which are mostly due to polarization effects within the first solvation sphere of the ions can be reliably included. The QM/MM results have already demonstrated a significant role of higher (>3) many-body terms on both structural and dynamical properties of solvated cations.[28–30,32,35]

Since the QM/MM method has been successfully applied to various cations in aqueous solution, it became of particular interest to apply this high-level method to investigating the structural properties of small anions such as F^- and Cl^- in water. Anion–water interactions are generally weaker than those of most cations and energetically comparable with the water–water interactions in bulk water. This leads to some debate as to whether the anion–water complexes, $X^-(H_2O)_n$, adopt "interior" (**I**) or "surface" (**S**) state, *i.e.*, structures with the anion on the "surface" of water clusters. In experiments, photoelectron detachment studies[38,39] of negative ion–water clusters have been interpreted in a way that, except for F^-, all halogen anions seem to reside at such "surfaces". However, these studies do not provide any definitive structural information.

In theoretical investigations,[5,8,40–43] the simulation results based on the molecular mechanical approach have been found to depend strongly on the anion–water and water–water potentials used in the simulations. On the other hand, the use of different parametrized potentials, *i.e.* with and without a treatment of molecular polarizability, always gave different structural properties.[18,43–45] In most cases, polarizable models can provide qualitative predictions in good agreement with available experimental data. However, it is very important to obtain an appropriate value of 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.[46–49] As a consequence, the contributions of the polarizability are actually not clearly

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obtainable. For example, simulations of small clusters (1–6 water molecules) have demonstrated that the inclusion of polarizability of the ion significantly affects the predicted geometrical arrangement (**I** and **S** structures),[50] while simulations of larger clusters (20–255 water molecules) have indicated that the ion's polarizability has relatively little effect on structure and energetics of these larger clusters.[42,43] It was hoped, therefore, that combined *ab initio* QM/MM molecular dynamics simulations with sufficiently good basis sets could achieve a considerable progress in obtaining realistic structures of the hydrated F^- and Cl^- ions.

2. Methods

Based on the QM/MM approach, the system is partitioned into a part described by quantum mechanics (QM) and another part treated by means of molecular mechanics (MM). The interactions within the QM region were evaluated at *ab initio* Hartree–Fock level. QM regions with diameters of 7.6 Å and 9.2 Å were applied for F^- and Cl^- ions, respectively. These QM regions include all particles within the first and some parts of the second hydration shell of the anions. Within the QM region, the accurate description of inter- and intramolecular interactions at HF level principally depends only on the basis set quality. The basis sets employed in our simulations can be considered as a suitable compromise between quality and requirement of CPU time. Since the inclusion of diffuse functions is necessary for a correct treatment of such highly polarizable systems, the D95V+,[51] 6-31+G[52,53] and D95V++[51] basis sets were employed for F^-, Cl^- and water, respectively. The inclusion of electron correlation in the quantum mechanical calculations should generally improve the quality of the simulation results further, in particular in the case of anions, but it is far too time-consuming. To at least estimate the possible influence and significance of electron correlation, HF and MP2 geometry optimizations of X^-–H_2O, where X = F and Cl, have been carried out using the same basis sets as employed in the simulations. After BSSE corrections, the calculations at HF and MP2 levels of theory supply binding energies of −26.92 and −29.46 kcal mol^{-1} for the F^-–H_2O, and of −13.77 and −14.27 kcal mol^{-1} for the Cl^-–H_2O complex, respectively. The correlation contributions to binding energies amount to ~10% and can be expected, therefore, to have a significant influence on some structural properties of the hydrated anions.[54] However, the effect of electron correlation was found to be rather marginal (less than 0.1 kcal mol^{-1}) when the stabilization energies obtained by HF single point calculations of the anions plus their first hydration shells for several selected configurations of our simulations were compared to those of MP2 calculations. Therefore, and since with present computational possibilities it is not feasible to perform a QM/MM simulation even at the simple MP/2-correlated level, it was assumed that the correlation effect is small enough to be neglected and still possible to achieve a sufficient level of accuracy in the QM/MM simulation. The size of QM regions used in this work are considered to be large enough to reduce changes between forces at the transition between QM and MM region to minimal magnitudes, ensuring that the quantum mechanical forces beyond the QM region smoothly converge to pair potential forces. To ensure a completely continuous change of forces at the transition between the QM and MM regions, a smoothing function[55] was applied within an interval of 0.2 Å (*i.e.* between the F–O distances of 3.8–4.0 Å and between the Cl–O distances of 4.6–4.8 Å).

Besides the QM region, all interactions within the MM and between the QM and MM regions were described by classical pair potentials. The flexible BJH-CF2 model, which includes intermolecular[56] and intramolecular interactions,[57] was employed for water. The use of a flexible model is to be favored over any of the popular rigid water models, in order to ensure compatibility and a smooth transition, when a water molecule moves from the QM region with its full flexibility of ligand molecules to the MM region. The pair potential functions for F^-–H_2O and Cl^-–H_2O interactions were newly constructed using aug-cc-pVDZ basis sets.[58–60] The 1500 and 1400 Hartree–Fock interaction points for F^-–H_2O and Cl^-–H_2O energy surfaces obtained from Gaussian94[61] calculations were fitted to the analytical forms of

$$\Delta E_{F^-\text{–}H_2O} = \sum_{i=1}^{3} \left(\frac{A_{ia}}{r_{ia}^4} + \frac{B_{ia}}{r_{ia}^5} + C_{ia} \cdot \exp(-D_{ia} r_{ia}) + \frac{q_i q_a}{r_{ia}} \right), \quad (1)$$

and

$$\Delta E_{Cl^-\text{–}H_2O} = \sum_{i=1}^{3} \left(\frac{A_{ia}}{r_{ia}^5} + \frac{B_{ia}}{r_{ia}^6} + C_{ia} \cdot \exp(-D_{ia} r_{ia}) + \frac{q_i q_a}{r_{ia}} \right), \quad (2)$$

respectively, where A_{ia}, B_{ia}, C_{ia} and D_{ia} are the fitting parameters (see Table 1), r_{ia} denotes the distances between the anions and the i-th atom of water and q are the atomic net charges. The charges on anions were set to −1.0. The charges on O and H of water were set to −0.6598 and 0.3299, respectively, which corresponds to the experimental dipole moment of an isolated water molecule. It is known that through ion–water interactions, these values change, but this effect is partially compensated by the other terms in the potential during fitting to the *ab initio* energy surfaces.

Classical molecular dynamics simulations using these pair potentials were performed first, then, the Born–Oppenheimer *ab initio* QM/MM dynamics simulations were carried out, starting from the equilibrium configurations resulting from the pair potential simulations. All simulations were carried out in a canonical ensemble at 298 K with a time step size of 0.2 fs. This canonical ensemble was realized by coupling to an external temperature bath. The cubic box, with a box length of 18.19 Å, employed in the simulations contained one halide ion and 199 water molecules, assuming the experimental density of pure water. Long-range interactions were treated by the reaction-field procedure.[62] This method implies a compensation of the electrically non-neutral basic box. The classical pair potential molecular dynamics simulations started from random configuration and were equilibrated for 80 000 time steps. The simulations were continued for 150 000 time steps to collect configurations every 10th step. The QM/MM simulations started with the re-equilibration for 20 000 time steps, followed by another 40 000 time steps to collect configurations every 5th step. The 8 ps interval of our QM/MM simulations can be considered long enough since it has been shown that even a 2 ps simulation can deliver most of the structural and dynamical properties of similar solutions.[27,29,30,33]

Table 1 Optimized parameters of the analytical pair potentials for the interactions of water with F^- and Cl^- (interaction energies in kcal mol^{-1} and distances in Å)

Pair	A	B	C	D
	(kcal mol^{-1} Å^4)	(kcal mol^{-1} Å^5)	(kcal mol^{-1})	(Å^{-1})
F–O	−1877.5410	400.01151	23 266.077	2.6019911
F–H	−298.85572	304.52220	65.693808	0.7445921
	(kcal mol^{-1} Å^5)	(kcal mol^{-1} Å^6)	(kcal mol^{-1})	(Å^{-1})
Cl–O	580.37511	−7585.8134	54 901.103	2.8798832
Cl–H	−429.09512	690.28036	592.20862	2.2169231

3. Results and discussion

Structural properties of the hydrated F^- and Cl^- ions were characterized by means of X–O and X–H radial distribution functions (RDFs), where X = F (Fig. 1) and Cl (Fig. 2), and their corresponding integration numbers. For F^-–H_2O, the pair potential simulation gives a sharp first F–O peak at 2.53 Å. The first hydration shell is well separated from the second one, leading to an average coordination number of 5.8 ± 0.1. In the QM/MM simulation, a broader less pronounced first peak is observed at larger F–O distance of 2.68 Å and the first hydration shell is not so distinctly separated from the second one, corresponding to an average coordination number of 4.6 ± 0.2. In comparison to the results obtained by pair potential simulation, the QM/MM simulation reveals a larger first hydration shell with smaller coordination number. The QM/MM results point out a higher flexibility of the hydrated F^- complex, in which the water molecules in the first hydration shell appear to be quite mobile, allowing an easier exchange of water molecules between the first hydration shell and the outer region. In both pair potential and QM/MM simulations, a second layer of water molecules surrounding the first hydration shell of F^- is slightly recognized, as can be seen from the second F–O RDFs peaks. Some further differences can be found in the F–H RDFs. The pair potential simulation shows a sharp first F–H peak at 1.56 Å, together with a small pronounced second peak at 2.81 Å. These first two peaks correspond to the two hydrogen atoms of the first shell water molecules. The distance of about 1 Å between the first F–H and the first F–O peaks implies a preference for linear hydrogen bond formation between the F^- and the solvated waters. In the QM/MM simulation, the first two F–H peaks are observed at larger distances of 1.74 and 3.21 Å, respectively. In addition, both peaks are rather broad and less pronounced, particularly for the first one, than those obtained by the pair potential simulation. The distance between the first F–H and the first F–O peaks also indicate a preference for linear hydrogen bond formation, however the differences both on the F^-–H_2O first neighbor and the favored $F^- \cdots H$ distances being significant (about 0.15 Å and 0.18 Å, respectively).

For Cl^-–H_2O, the pair potential simulation produces a small unsymmetric first Cl–O peak at 3.15 Å, with an average coordination number of 5.9 ± 0.1. In the QM/MM simulation, an even less pronounced first peak is observed at larger Cl–O distance of 3.24 Å, corresponding to an average coordination number of 5.6 ± 0.1. As can be seen from Fig. 2a, the Cl–O RDFs are quite similar for both pair potential and QM/MM simulations. A significant difference is found in the Cl–H RDFs (Fig. 2b) in which a broader first Cl–H peak with maximum at 2.42 Å and considerable tailing up to 3.2 Å is observed in the QM/MM simulation, compared to the corresponding peak with maximum at 2.29 Å resulting from pair potential simulation. The QM/MM simulation indicates that the hydrogen atoms of water molecules in the first hydration shell of Cl^- are not bound by classical H-bonds to the anion. A second hydration shell is not found, as can be seen from further curves of Cl–O RDFs in both pair potential and QM/MM simulations.

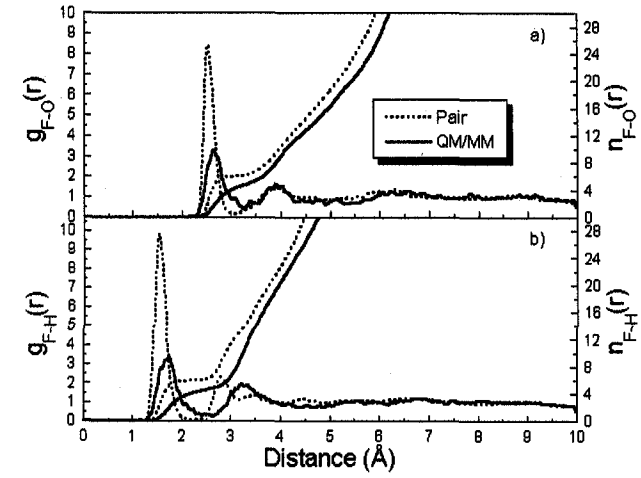

Fig. 1 (a) F–O and (b) F–H radial distribution functions and their corresponding integration numbers.

Fig. 3 shows the probability distributions of the coordination numbers, calculated within the first hydration shells of F^- and Cl^-, respectively. For F^-–H_2O (Fig. 3a), the QM/MM simulation reveals a preferred coordination number of 5 (in addition to 4 and 6 in comparable amounts), while the pair potential simulation gives a favored coordination number of 6 (followed by 5 in smaller amount). For Cl^-–H_2O (Fig. 3b), a coordination number of 6 (in addition to 5 and 4 in decreasing amount) is preferred in both pair potential and QM/MM simulations. Fig. 4 displays the O–X–O angular distributions, calculated up to the first minima of the X–O RDFs for X = F and Cl, respectively. For F^-–H_2O (Fig. 4a), the octahedral arrangement is clearly recognized in the pair potential simulation, by the two pronounced peaks between 70–110° and between 160–180°. In the QM/MM simulation, a broader

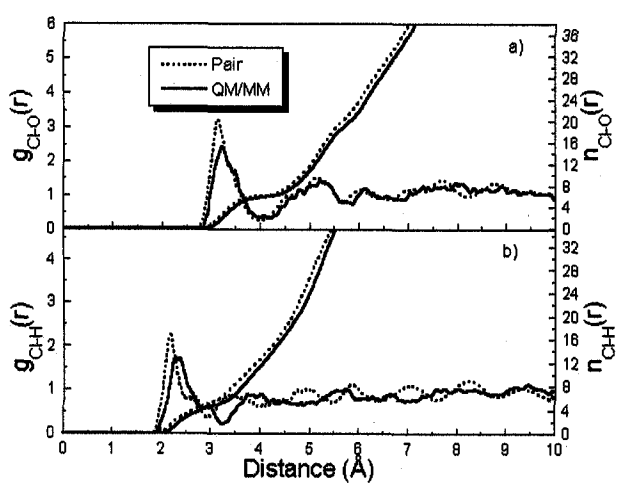

Fig. 2 (a) Cl–O and (b) Cl–H radial distribution functions and their corresponding integration numbers.

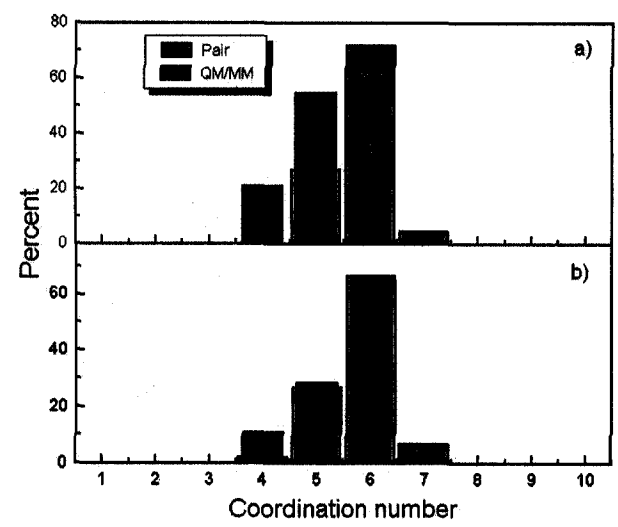

Fig. 3 Coordination number distributions, calculated up to the first minimum of the anions–O RDFs: (a) F^-–H_2O and (b) Cl^-–H_2O.

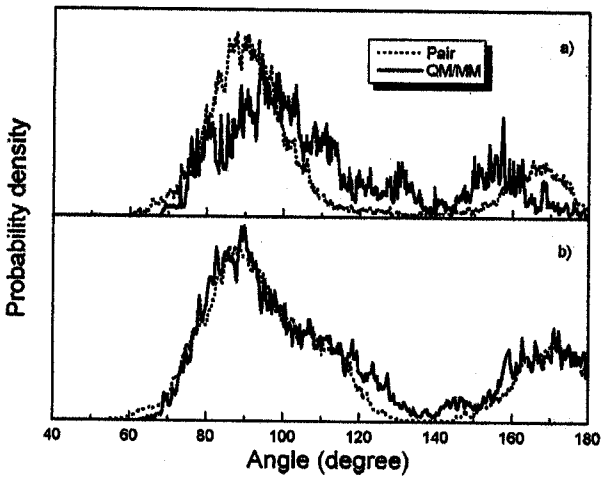

Fig. 4 (a) O–F–O and (b) O–Cl–O angular distributions, calculated up to first minima of the anions–O RDFs.

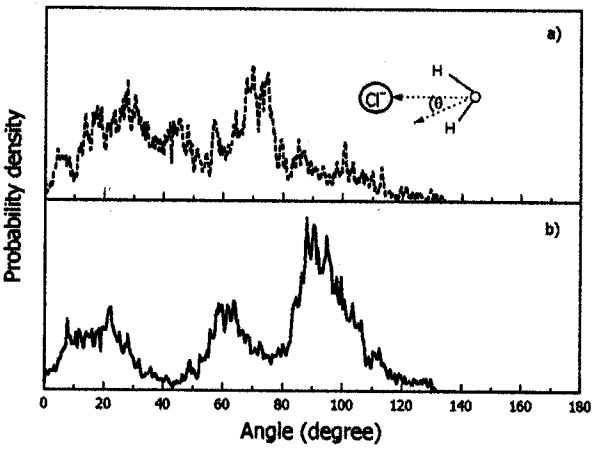

Fig. 6 Distributions of θ in the first hydration shell of Cl^- obtained by (a) pair potential and (b) QM/MM simulations.

O–F–O peak between 75–140° and a narrower one around 145–170° are related to the smaller number of water molecules in the first hydration shell of F^-. For Cl^-–H_2O (Fig. 4b), an octahedral arrangement is observed in both pair potential and QM/MM simulations, as can be seen from the O–Cl–O peaks around 70–130° and around 150–180°.

The investigation of water orientations within the first hydration spheres of the anions provides more details for the structure of the hydrated anions. Fig. 5 and Fig. 6 display the orientations of water molecules within the first hydration shells of F^- and Cl^-, respectively. The orientation of water molecules is described in terms of the distribution of angle θ, as defined by the dipole vector of the water molecule and the X···O vector for X = F and Cl, respectively. For F^-–H_2O (Fig. 5), the pair potential simulation indicates that first shell water molecules strongly prefer to form linear hydrogen bonds to F^-. In contrast to this, in the QM/MM simulation a more flexible dipole-oriented arrangement of the first shell waters is observed, as can be seen from a broad peak between 30–90°. For Cl^-–H_2O (Fig. 6), the pair potential simulation depicts an orientation changing between the linear and bridged (the orientation where the two hydrogen atoms are pointing towards the ion) forms for the hydrated Cl^- complex, as can be seen from a broad θ distribution ranging from 0° to 120°. In the QM/MM simulation, more specific orientations of the first shell waters are observed, in which the first two peaks between 0–40° and 50–80° correspond to the arrangements of bridged and linear forms, respectively. Furthermore, a strong peak between 80–120° indicates that water molecules in the first shell of the ion are oriented not only under the influence of Cl^- but also by the forces exerted by the neighbouring water molecules in the same shell and/or the bulk. This reflects a competition between the solvation of the ion and hydrogen bonding among the water molecules.

A comparison of some essential structural parameters from this work and the data from earlier theoretical and experimental studies is summarized in Table 2. In experiments, only few investigations have been performed for F^-, and an average coordination number of 4.5 is frequently cited for this anion.[66] For Cl^-, almost all experimental investigations yielded hydration numbers between 6 and 8 with a strong preference for 6.[15,16] The observed variation in the experimental hydration numbers is obviously a consequence of concentration dependence.[12–16] In the theoretical investigations, various potential functions have so far been applied to describe anion–water and water–water interactions and, surprisingly, most simulation works reported data in good agreement with the experimental observations.[5,6,8,41,63,65] However, a discrepancy in the structural properties, in particular in coordination numbers, is visible. Apparently, the application of simplified potentials such as pairwise additivity, can lead to error compensations where overestimation and underestimation of molecular interactions are mutually balanced and hence provide reasonable predictions.[5,6,65] At higher classical MM level, simulations with polarizable models could provide more accurate results,[8,11,42–44] but the complicated attractive and repulsive contributions, especially within the hydration sphere of the anions, pose serious difficulties for obtaining a suitable value for the anion's polarizability.[46–49]

In the QM/MM approach, the charge distributions on ions and first hydration shell waters are allowed to vary dynamically during the simulation process. This is of considerable importance, as the polarizability of water molecules that affects the real structure of the hydrated anions, is directly included. These effects of polarization are a most essential difference to the molecular mechanical potentials using fixed/scaled partial charges for each atom in the system. In particular, for the linearly hydrogen bonded F^-–H_2O complex, the charge distributions on the two hydrogen atoms of first shell water molecules, with one hydrogen atom pointing towards and another one away from the ion, are significantly different. Based on QM/MM simulation technique, the average Mulliken charges on those two hydrogen species are +0.526 and +0.412, respectively. The QM/MM results indicate that those hydrogen atoms nearby the F^- are strongly polarized, and that the bridging hydrogen bond orientation is unfavorable. For the Cl^-–H_2O complex, the QM/MM simulation reveals comparable

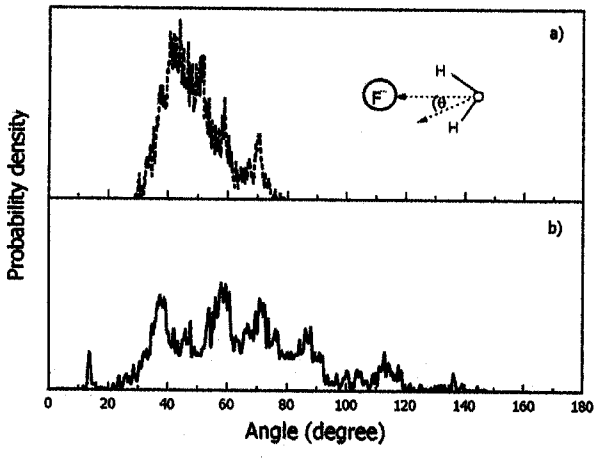

Fig. 5 Distributions of θ in the first hydration shell of F^- obtained by (a) pair potential and (b) QM/MM simulations.

Table 2 Positions of the maxima of the first X–O, X–H_1 and X–H_2 RDFs for X = F and Cl, and the numbers of water molecules within the first hydration shell of the anions

Ion	$g_{X-O}(r)$	$g_{X-H_1}(r)$	$g_{X-H_2}(r)$	CN	Method	Ref.
F^-	2.67	1.73	3.07	5.8	MCY–water MD	5
	2.60–2.67	1.65–1.73	—	4.1–6.8	CF–water MD	6
	2.60	—	—	4.1	QCDF–water MC	8
	2.57	1.62	3.02	6.7	TIP4P–water MC	11
	2.61	1.67	—	6.0	TIP4P–water MD	41
	2.60	1.65	—	6.2	TIP4P–water MC	63
	2.60	—	—	6.3	SPC/E–water MD	64
	3.0	—	—	4.5	PCM–water MC	65
	2.53	1.56	2.81	5.8	CF2–water MD	This work
	2.68	**1.74**	**3.21**	**4.6**	**QM/MM**	**This work**
	2.6–2.9[a]	—	—	4–6[a] (4.5)		16,66
Cl^-	3.29	2.35	3.73	7.2	MCY–water MD	5
	3.22–3.29	2.24–2.35	—	7.2–8.4	CF–water MD	6
	3.25	—	—	8.36	QCDF–water MC	8
	3.22	2.32	3.72	7.5	TIP4P–water MC	11
	3.19	2.25	—	7.0	TIP4P–water MD	41
	3.21	2.25	—	7.4	TIP4P–water MC	63
	3.20	—	—	7.2	SPC/E–water MD	64
	3.9	—	—	5.1	PCM–water MC	65
	3.15	2.29	—	5.9	CF2–water MD	This work
	3.24	**2.42**	–	**5.6**	**QM/MM**	**This work**
	3.1–3.3[a]	—	—	4–9[a] (6)	15,16	

[a] Experimental observations, with average value given in parenthesis. See references inside ref. 15 and 16.

amounts of average Mulliken charges on the corresponding two hydrogen types, namely +0.516 and +0.498. This observation implies a higher possibility of forming a bridged structure of the hydration complex of Cl^-. Besides the inclusion of polarization effects, the *ab initio* calculations include all other effects of charge-transfer in the anion–water complexes. The QM/MM simulations indicate that there is a transfer of charges from the anions to water molecules and, thus, the actual charges on both anions are usually less negative than −1 (*i.e.*, about -0.94 ± 0.01 and -0.89 ± 0.01 for F^- and Cl^-, respectively). As a consequence, if one employs a constant value of −1 for the charges of both anions in the pair potential simulations, an over-stabilization for the short-range anion–water interactions can be expected.

An interesting property that is somewhat comparable to the experimental observations is the hydration enthalpy. The experimental values for F^- and Cl^- are estimated to be in the ranges from −123.8 to −113.1 kcal mol^{-1} and from −89.9 to −81.5 kcal mol^{-1}, respectively.[67–69] In general, the experimental determination of this property of halide ions in aqueous solution depends strongly on the models assumed. Consequently, the uncertainty in experimental data, based on different measurements, is rather large. In terms of simulations, these quantities can be obtained by calculating the energy difference between ion–water and water–water interactions of the solution and the water–water interaction energy of the pure water under the identical conditions. By this scheme, the QM/MM results show good agreement with the experimental values, giving computed hydration energies of −121.2 and −87.3 kcal mol^{-1} for F^- and Cl^-, respectively. In the pair potential simulations, an overestimation is found, with the corresponding values of −127.1 and −91.7 kcal mol^{-1}. These energetic differences could still have a significant influence on important processes, as the specific adsorption of ions from the solution onto a metal surface.[70] In this process, the structure of the first hydration shells of the ions is significantly modified before ion adsorption to the surface takes place, and hence, an accurate energetic description, in association with the specific structure and reorientation of the first shell water is of particular importance.

4. Conclusion

Classical simulations, even with polarizable models, can supply only limited insight into the structures of weak anion–water complexes. This calls for a more accurate simulation technique, like the QM/MM method, in which the *ab initio* calculations can fully take into account the complex many-body polarization and charge-transfer effects, at least within the first hydration shell of the anions. Therefore, the QM/MM approach chosen in this work, including all of this shell and some further area seems to provide sufficient accuracy for most of the chemically relevant data of the hydrates.

Acknowledgements

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