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On Ion and Molecular Polarization of Halides in Water

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Abstract: The high polarizability of halide anions affects, in aqueous solutions, many phenomena ranging from hydrogen bond dynamics to water interfaces' structure. In this Letter dipolar interactions of halides in water are investigated through Car−Parrinello Molecular Dynamics simulations. Contrary to previous studies, a different polarization of first and second hydration shell water molecules is found. The analysis hints that existing classical polarizable force fields lack a description of short-range interactions which causes an overestimation of polarization effects.

I. Introduction

It is widely accepted that molecular polarization affects many properties shown by inhomogeneous systems. In particular, in ionic solutions, although dipolar interactions decay faster than coulomb interactions, they are considered to be responsible for macroscopic properties in the bulk phase and at interfaces.[1−13]

In spite of its importance, there are few simulation studies available where the features of polarizable interaction are studied in detail.[14−20] This task is currently pursued in our group. To this end, reference data to compare with are needed. In particular ab initio calculations are the only source for defining the electrostatic properties of halide−water solutions. Recently, ab initio MD simulations[21] of halide anions dissolved in water have been performed by a few authors.[2,22−27] Most of them made use of Car−Parrinello Molecular Dynamics for the whole systems, except for ref 26, where the ion was described quantum

chemically with a self-consistent field model, while the solvent molecules were described classically (including many body effects). A mixed DFT/MM Monte Carlo approach for studying the bromide ion in water has also been used by Tuñon et al.[28] The above studies focus mainly on the structure of the first solvation shell and on its dynamics. Electrostatic properties are usually not considered or they are just mentioned; to our knowledge there is not a systematic comparison of electrostatic properties of halide anions in water solution. We are aware only of the study of Krekeler et al.,[29] who performed first principle density functional calculations to look into the properties of small $[X(H_2O)_n]^-$ clusters ($n = 1,2,...,6$), X being fluoride, chloride or iodide. They found that, as the number of water molecules increases, molecular polarization is determined by water−water interactions rather than by ion−water interactions; in fact, in their calculations the dipole moments of first shell molecules tend to the same value of bulk water. This conclusion led them to support the use of nonpolarizable classical force fields, contrary to what is suggested by many authors. While, on the one hand, it is true that the dipole moment of water molecules in the solvation shells is closer to that of bulk water rather than to that of gas phase clusters with small *n*, on the other hand, it should be considered that the hydration shell is a dynamical entity, which changes in time causing the instantaneous induced dipoles to be much different than in the bulk. It would be impossible to model such dynamic response to the change in the solvation environment by using simple nonpolarizable force fields (*vide infra*). Furthermore, to study the influence of the ion on all solvation shells, larger systems should be considered. In the present work, in order to have an insight on polarizable interactions beyond the second solvation shell, we have carried out a study of electrostatic properties of halide anions dissolved in 96 water molecules by employing Car−Parrinello MD simulations. These simulations are meant to be a reference for future comparisons with polarizable classical force fields. In this contribution the contents are organized as follows: in the next section we present the details of our calculations; then, the electrostatic properties of the ion and of the water molecules belonging to different solvation shells are discussed in section III. Finally our conclusions are briefly summarized in the last section.

II. Computational Details

Ab initio MD simulations were performed using the Car−Parrinello (CP)[30] scheme for propagating the wave functions and the ionic configurations as implemented in the CPMD package.[31] In the present study we have used dispersion-corrected atom-centered pseudopotentials (DCACPs)[32,33] in
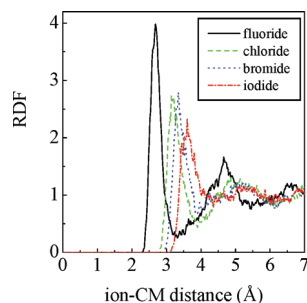
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1450 *J. Chem. Theory Comput., Vol. 5, No. 6, 2009*

Letter

Figure 1. Radial distribution function between the ion and the water center of mass.

the Troullier−Martins[35] format for oxygen and hydrogen. It has been recently shown that DCACPs are successful in accounting for London dispersion forces and that they are capable of faithfully reproducing many dynamical and structural properties of water.[33] For halides, since these kinds of pseudopotentials are still under development,[34] we have used norm-conserving Goedecker pseudopotentials.[36−38] The BLYP density functional[39,40] was used for the electronic strycture calculations. The cutoff for the wave function was set to 80 Ry, the time step was set to 4 au, and the fictitious mass for the orbital was chosen to be 400 amu The length of the cubic simulation box was computed in order to get a total density of 1 g cm^{-3}. Periodic boundary conditions were applied. Production runs of 15 ps in the microcanonical ensemble followed NVT equilibration runs of 3 ps where the temperature was set to 330 K; the initial configurations were generated with classical molecular dynamics simulations of 200 ps. The same procedure has been applied to simulate pure water (96 molecules).

Every five time steps, the Wannier centers'[41,42] coordinates $\mathbf{r}_j(t)$ were computed; in this way, given the ionic coordinates $\mathbf{R}_i(t)$, the dipole moment of a molecule (or of the anion) I were obtained as

$$\boldsymbol{\mu}_I = \sum_{i=1}^{N_I} Q_i \mathbf{R}_i + \sum_{j=1}^{n_I} q_j \mathbf{r}_j \qquad (1)$$

with Q_i and q_j being respectively the charge of the ith ion and of the jth Wannier center.

III. Results and Discussion

Radial distribution functions between the anions and the water center of mass are shown in Figure 1. First and second hydration shells can be clearly devised for all ions. It could be appreciated that the radius of the first shell increases in the group ($R_{F^-} = 3.32$ Å, $R_{Cl^-} = 3.90$ Å, $R_{Br^-} = 3.90$ Å, $R_{I^-} = 4.36$ Å) as well as the hydration number ($N_{F^-} = 4.9$, $N_{Cl^-} = 6.5$, $N_{Br^-} = 6.5$, $N_{I^-} = 8.5$), in agreement with previous results. A deeper study of the structural properties and of water dynamics in these systems will be presented in a short coming full paper. Here we focus on the electrostatic properties within each hydration shell.

In Table I the average values of the ion and water dipole moments are shown. It can be clearly seen that, as the ion polarizability[43] increases, the average dipole moment increases as well. This is what was expected and what was found with previous ab initio calculations at condensed phase. The calcula-

Table I. Average Dipole Moments and Their Standard Deviations for the Ion and First and Second Shell Molecules^a

	ion $\langle\mu\rangle$ (σ_μ)	first shell $\langle\mu\rangle$ (σ_μ)	second shell $\langle\mu\rangle$ (σ_μ)
water-F$^-$	0.42 (0.18)	3.04 (0.31)	2.96 (0.30)
ref 25	0.39	3.07 (0.30)	3.10 (0.30)
ref 26	0.19 (0.06)	--	--
water-Cl$^-$	0.82 (0.32)	2.87 (0.27)	2.95 (0.29)
ref 23	1.00	3.14 (0.57)	3.15 (0.65)
ref 26	0.89 (0.36)	--	--
ref 27	--	3.07	3.07
water-Br$^-$	1.02 (0.40)	2.87 (0.27)	2.98 (0.29)
ref 22	0.9 (0.8)	2.9	2.9
ref 28	0.21	--	--
water-I$^-$	1.21 (0.51)	2.83 (0.27)	2.92 (0.29)
ref 24	1.3 (1.1)	3.0 (0.6)	3.0 (0.6)

^{a} Units: Debye.

tions of Öhrn and Karlström[26] give the same value of ours for chloride, while, for fluoride, the induced dipole moment is the double of what we get. For bromide, Tuñon et al.,[28] with DFT/MM Monte Carlo calculations, found a value five times lower than ours. We believe that the disagreement between our results and the above cited studies is due to the treatment of the solvent with classical models which could not faithfully describe the polarizable feedback between water molecules and the anion. This is supported by the comparison with previous Car−Parrinello MD simulations,[22−25] where also the solvent is treated at the same quantum chemical level as the anion; in Table I it can be seen that the average values for the anion are similar to previous ab initio simulations (with a maximum difference of ca. 0.1 D). In our calculations we get a smaller standard deviation (which was calculated with the proper methods for correlated data sets);[44] it is probably due to the fact that we performed longer simulations (gathering much more configurations to average over) and that the system size is larger, which causes the amplitude of fluctuations to be lower.

If the dipole moments of the first and second hydration shells are considered, our data are still in fair agreement with previous ab initio simulations, the bigger differences being due to the different treatment of the electronic structure calculations in our simulations (see discussion on DCACPs in section II). In passing we should mention that the dipole moment obtained for pure water is 2.96 ± 0.30 D, in agreement with previous ab initio simulations of Silvestrelli and Parrinello[42] (who obtained $\mu = 2.95$ D).[45] Even if all the values for the solvation shell water molecules are within the error, it should be pointed out that, in our calculations, there are always differences of ca. 0.1 D between the average dipole moments of the first and of the second solvation shell (the latter being very close to the bulk water dipole moment). Such a trend was not observed in previous simulations, probably because of the lower accuracy in the statistics (see above). In this aspect our work is the first where a different polarization of first and second hydration shell molecules in water−halide solutions has been found. Although such a difference in the water polarization is not that big if related to the total dipole moment (only a 3%), it should be noted that it constitutes approximately 10% of the induced dipole moment, which is due to the balance of the electrostatic interactions with the ion and with other water molecules. The difference in the induced dipole moment might be due to the fact that the negative charge on the ion is somewhat screened
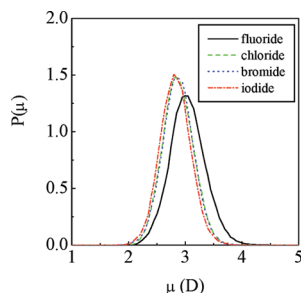
Letter

J. Chem. Theory Comput., Vol. 5, No. 6, 2009 **1451**

Figure 2. Probability distribution function for the dipole moment of water molecules in the first hydration shell.
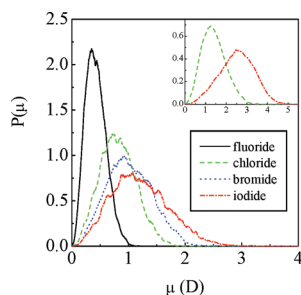

Figure 3. Probability distribution function for the dipole moment of halide anions. In the inset the PDFs of classical simulations of chloride (dots) and iodide (dash−dots) in water are shown; the latter, kindly provided by Wick and Xantheas, appears in Figure 6 of ref 49.

by the first shell molecules, causing second shell molecules to be less polarized. Similar results were recently obtained with Car−Parrinello MD simulations of water−cation solutions (the cations being K^+ and Ca^{2+}).[48]

A feature which particularly strikes one's attention is the different polarization of first shell molecules in the fluoride−water system. While in the case of chloride, bromide, and iodide the average dipole moment of first shell water molecules is ca. 2.85 D, i.e. 0.1 D lower than bulk water, in the case of fluoride, the dipole moment is ca. 0.2 D higher. The difference could be better appreciated from an inspection of the probability distribution functions (PDFs) for the first shell molecules in each system considered (Figure 2). The different response of water molecules in the first solvation shell of fluoride was previously observed in small water−halide clusters with Car−Parrinello MD simulations (see Figure 3(c) of ref 29); in fact for a small number of water molecules, the induced dipole moment is higher than for other halides. Since the values converge for 4 and 5 water molecules the authors concluded that, adding more molecules, would only cause the dipole moment to be the same as in the bulk. It should be considered that the first hydration shell of halide anions contains more than five water molecules; moreover, for each cluster, only one configuration was studied. Since the solvation shell is a dynamical entity, where both the structure and the hydration number fluctuate, we believe that the above clusters cannot be considered as representative samples of the first solvation shell. The difference in the behavior of the fluoride solution with respect to the solution of the other anions could be ascribed to the low polarizability of F^-. To better understand this point it is useful to compare the PDFs of the ionic dipole moments as shown in Figure 3. First of all it can be noticed that the PDFs extend for more than 3 D for the most

polarizable ions; on the other hand, the fluoride's PDF tail is slightly higher than 1 D. If one considers that fluoride is not as polarized (the induced dipole moment is small) as the rest of the halides in the series, it seems reasonable to expect the dipole−dipole interaction between the ion and water to be small; in this case the coulomb repulsion between the negatively charged ion and the water electron cloud dominates, causing the induced dipole moment on water to be higher than in the bulk. Following the same reasoning, when we consider bigger anions, as the dipole−dipole interaction becomes stronger, the coulomb repulsion does not longer dominate; overall, it all brings to a decrease of the induced dipole moment on water; such an effect is slightly more evident in iodide−water than in chloride−or bromide−water. On top of that, it should be noticed that the damping effect is stronger for bigger anions;[15] it means that the strength of charge−charge, charge−dipole, and dipole−dipole interactions does not increase monotonically as the ion approaches the water molecule but rather shows a turnover at short distances (within the range of the first shell radius).[15] The damping effect is more evident if our results for chloride− and iodide−water solutions are compared with the recent results of the same systems studied with classical molecular dynamics.[49] Until recently, there has been high uncertainty on the values of halide dipole polarizability. This was basically due to the inaccuracy of experimental data on one side and to the low level of ab initio calculations on the other side. According to accurate high level quantum chemical calculation,[50] the dipole polarizability values are 2.47, 5.48, 7.27, and 10.27 $Å^3$ for F^-, Cl^-, Br^-, and I^-, respectively. These values are higher than the ones[51] taken for granted until then (respectively 1.38, 3.94, 5.22, and 7.81 $Å^3$); however, nowadays it is still common to find classical MD or Monte Carlo studies of anions where the old values are considered. It is known, in fact, that using high anion polarizabilities, the dipole moment increases up to values which do not have physical sense. The common approach, then, is to use low polarizabilities rather than to damp the polarizable interactions. Nevertheless, as already stated in refs 15 and 16 such practice only serves to hinder hyperpolarization but not to reproduce the response of the ion at short anion−water distances. In the inset of Figure 3 we show the PDFs as obtained in classical MD simulations[49] using $\alpha_{Cl^-} = 4.5$ $Å^3$ and $\alpha_{I^-} = 6.9$ $Å^3$; the ionic dipole moments are peaked at ca. 1.3 and 2.5 D, i.e. where the respective ab initio PDFs are already decreasing to zero. This big difference among classical and ab initio results should be taken into account when the properties of simulated systems depend on the ionic and molecular polarization. For example, the high propensity for surface states of halide anions in water is explained through the anion induced dipole moments as obtained with classical simulations.[8] Doubts about the physical sense of using gas phase polarizabilities in condensed phase simulations could arise if one takes into account the common view according to which, in the liquid, there is a reducing effect due to electron clouds interactions. Nonetheless, in contrast to this view, it has been recently demonstrated by means of Car−Parrinello MD simulations that both the polarizability tensor of water molecules and of fluoride in CsF at liquid state are distributed around the gas phase values with a narrow distribution.[52] This result encourages the use of gas phase polarizabilities in classical MD simulations,

1452 *J. Chem. Theory Comput., Vol. 5, No. 6, 2009*

Letter

which, additionally, allows for a higher transferability of the force field from gas to condensed phase simulations.

IV. Concluding Remarks

Although accurate polarizable force fields for modeling (halide) ion−water interactions are needed, up to now few studies have pointed out the need for benchmark data on the electrostatic properties of such systems. We have performed Car−Parrinello MD simulations of one halide ion with 96 water molecules. Such a big system is needed to account for the long-range nature of electrostatic interactions which spread up to the bulk. In previous simulations, the systems were barely formed by the first and second hydration shell of the ion, which would not allow the studying of the differences in the polarizable interaction between those shells and the bulk. To our knowledge this is the first study where the (expected) differences in the polarization of first and second solvation shells could be devised. In previous studies those differences could not be found given the small size of the systems and the short simulated times. Chloride, bromide, and iodide, as an average trend, do polarize first shell water molecules such that their molecular dipole moment is lower than the one of second shell (and bulk) molecules, the difference being ca. 0.1 D (which represents approximately a 10% of the induced dipole moment). Fluoride, on the contrary, tends to overpolarize first shell water molecules so that their molecular dipole moment is higher by ca. 0.1 D than the one of second shell molecules.

The broadness of molecular and ionic dipole moment PDFs justifies the implementation of polarizable models in classical simulations which could account for dynamical effects due to dipolar interactions. The implementation of new ion−water polarizable models cannot be made without considering *Pauli effects* which extend beyond the first solvation shell. Existing classical force fields tend to include those effects by simply reducing the ionic polarizability. We have shown that this is not enough as the induced dipole moment in our ab initio simulations is more than 1 D smaller than what was found in classical simulations.

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Letter

J. Chem. Theory Comput., Vol. 5, No. 6, 2009 **1453**

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