Structure and Dynamics of Hydrated Ion Pairs in a Hydrophobic Environment

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The structure, energetics, and dynamics of different alkali halide ion pairs hydrated in a hydrophobic medium are studied using molecular dynamics computer simulations. One or two water molecules hydrating NaCl, NaI, KCl, KI, and KF in bulk carbon tetrachloride are considered. The ion pairs remain in contact throughout the simulations, so the structure of the hydration complex is well characterized. The ions' interaction energy and hydration structure are examined and correlated with the ion sizes and charges. For the first four salts, the stronger interaction of the water molecules with the cation than with the anion of the ion pair is in agreement with recent experiments. However, when the anion is significantly smaller than the cation (as in the case of KF, which was not studied experimentally), the opposite behavior is found. The asymmetry of interaction with the cation and the anion are further elucidated by examining hypothetical ion pairs made from equal-sized cations and anions and by defining an asymmetry hydration parameter, which is found to correlate well with the structural characteristics, as well as with the water molecules' reorientation dynamics.

I. Introduction

The behavior of water confined to a hydrophobic environment and, in particular, the interaction of this water with salts have been the subject of numerous studies. Water plays an important role in determining the activity of ion channels[1,2] and the proton-pumping action in the hydrophobic core of bacteriorhodopsin.[3] Water molecules are known to be coextracted when hydrophilic inorganic ions are extracted from water to solvents such as nitrobenzene.[4] The number of coextracted water molecules per ion has been determined by several techniques.[5,6] Simulations[7−12] and experiments[13] show that hydrophilic ions are electrochemically transferred into hydrophobic organic solvents such as nitrobenzene and 1,2-dichloroethane as aqueous clusters. We have recently published a systematic study of the structure, dynamics, and energy of alkali and halide ions hydrated clusters in organic solvents.[14,15]

It was recently pointed out by Shultz and co-workers[16] that, surprisingly, ions exist even in very low polarity solvents such as CCl₄ with associated water, but the ions are transferred as ion pairs with the water/ion-pair ratio being *less than 1*. That paper provides new insight into the ion−water interactions in a highly hydrophobic medium and sheds light on the effect on water structure induced by ions and ion pairs at interfaces.[17−21]

Extensive research into the factors that determine the structure and energy of single ion and ion-pair hydration in bulk water is available,[22,23] and it would be highly beneficial to determine to what degree that insight applies to ion pairs in hydrophobic environments. However, despite their obvious importance, only a few attempts have been made to understand the behavior of ion pairs at interfaces or in mixed hydrophobic/aqueous environments. Ion pairs in immiscible electrolyte solutions have been postulated as responsible for increased liquid/liquid capacitance.[24,25] Schweighofer and Benjamin calculated the potential of mean force of NaCl at the water/1,2-dichloroethane interface and observed an increased stability relative to bulk water.[26] Recently, Wick and Dang extended this work to computing the dissociation dynamics of NaCl at the liquid/liquid interface.[27] We also note that the behavior of small amounts of neat water (no ions) dissolved in CCl₄ have been examined experimentally by Goodnough et al.[28] and theoretically by Chang and Dang.[29]

Here, we present a study of the structure, dynamics, and energy of five alkali halide contact ion pairs (NaCl, NaI, KCl, KI, and KF) hydrated by one or two water molecules in bulk CCl₄. The first four salts were studied by Shultz and co-workers in the paper cited above,[16] and the present calculations provide complementary insight into the issue of ion−water interactions in hydrophobic environments. In the case of these four salts, the cation is significantly smaller than the anion and is better hydrated in bulk water, as is clear from hydration free energy values.[15,30] To better understand the interplay of ion size and charge, we also examine KF (where the cation is much larger than the anion) and two additional hypothetical ion pairs made of equal-sized small ions (denoted by S^+S^-, or simply SS) and equal-sized large ions (denoted by LL). We also calculate, as a reference, some of the same properties for neat water in CCl₄, comparing them to available experimental and other theoretical calculations[28,29] as a validation of our choice of the potential energy functions.

The rest of this paper is organized as follows: In section II, we describe the systems studied. In section III, the structural and dynamical results are discussed. Our conclusions are presented in section IV.

II. Systems and Methods

1. Systems and Potentials. Each of the systems studied includes 214 CCl₄ molecules, one of the 7 ion pairs (NaCl, NaI, KCl, KI, KF, SS, and LL), and one or two water molecules in a truncated octahedron (TO) box whose enclosing cube has an initial size of 41.4 Å. (The volume of the TO box is half the volume of the defining cube.) The actual size slightly varies with the system and time to maintain a fixed pressure of 1 atm.[31] In addition, as a reference, two additional systems containing only one or two water molecules without ions were studied.

The CCl₄ and water models used are fully flexible. The intramolecular potential for water is a power series fitted to

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spectroscopic data.[32] For CCl$_4$, the intramolecular potential energy function includes harmonic bond stretching and angle bending.[33]

The total intermolecular potential energy is a sum of atom-based Lennard-Jones plus Coulomb terms for the CCl$_4$, the water and the ions, and all the interactions between them:

$$u_{ij}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \frac{q_i q_j}{4\pi r \varepsilon_0} \qquad (1)$$

where i and j denote atoms or ions separated by a distance r. The Lennard-Jones parameters σ_{ij} and ε_{ij} are determined from the standard (Lorentz–Berthelot) mixing rules:[34]

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2, \quad \varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \qquad (2)$$

where the Lennard-Jones parameters for the different ions σ_{ii} and ε_{ii} are given in refs 14 and 30. While many different sets of ion–water and ion–ion parameters have been used in the literature,[35-39] the parameters we use give reasonable values for the hydration free energy[15] and some structural properties.[14] The Lennard-Jones parameters of the small cation and the small anion in SS are taken to be that of Na$^+$ and of the large cation/anion in LL that of I$^-$.

The intermolecular potential energy functions used in this work are pairwise additive, so the polarizable nature of the solvent and the ions is only effectively included by the proper adjustment of the Lennard-Jones parameters and the point charges. Given the small number of water molecules dissolved in a polarizable solvent, it is quite likely that the use of many-body polarizable potentials[29,30,40-48] would be a more accurate approach. This will be examined in a future study.

2. Simulation Details. Each of the 18 systems is simulated for 20 ns at $T = 300$ K using a combination of the Andersen stochastic method and the Nose–Hoover thermostat.[49] The integration time step is 0.5 fs using the velocity version of the Verlet algorithm.[50] This allows for an accurate calculation of several time correlation functions, the energy distribution, and the structural properties involving the one or two water molecules in the system.

System size effects are minimized by using a molecule-centered gradual switching of the forces at the maximum possible switching distance consistent with the boundary conditions, using a switching function with continuous derivatives at the boundaries.

To further investigate a system size effect, the system NaCl(H$_2$O)$_2$ was also studied in a larger box (with a corresponding larger switching distance) containing 1712 CCl$_4$ molecules. No statistically significant variations in the quantities reported here were found between the small and the large systems.

III. Results and Discussion

1. Structural Characteristics. In bulk water, alkali halide contact ion pairs are highly unstable. The barrier to dissociation of the NaCl contact pair has been calculated to be only a few kTs.[26,27,35,51] Calculations suggest that this ion pair is only slightly more stable at the water/1,2-dichloroethane and water/CCl$_4$ interfaces, due to the strong interaction with nearby water molecules and the possibility of ion transfer to the aqueous phase.[26,27] In contrast, all the alkali halide pairs studied here in bulk CCl$_4$ with the presence of one or two water molecules are
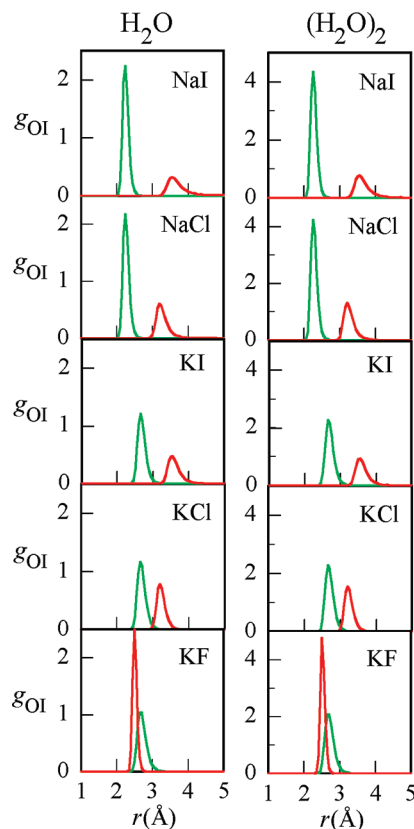

Figure 1. Ion–oxygen radial distribution functions for different alkali halide ion pairs hydrated by a single water molecule (left column) or two water molecules (right column) in bulk CCl$_4$ at 300 K. In each panel, the green line is for the cation and the red line for the anion. Note the factor of 2 scaling on the vertical axis of the right panels compared with the left panels. The salts are arranged from top to bottom in the order of decreasing $\sigma_- - \sigma_+$.

very stable diatomic species. The interionic distance remains near the equilibrium value during the 20 ns runs in all cases.

By examining the water IR spectral features, Shultz and co-workers have suggested that the water mainly interacts with the alkali cation of the ion pair in bulk CCl$_4$. While our simulations support this observation for the NaI, NaCl, KI, and KCl examined in the experiment, all of these salts are characterized by a small cation/anion size ratio. When a salt with a smaller anion than cation, like KF, is examined, the opposite behavior is found. This can be demonstrated by computing the water–ion radial distribution functions (rdf). Figure 1 shows the oxygen ion rdfs for the case of a single water molecule or two water molecules next to the five alkali halide ion pairs in bulk CCl$_4$. These functions are essentially the probability distribution for the ion–oxygen distance normalized such that $\int_0^\infty \rho_{H_2O} g(r) \, d\mathbf{r}$ (ρ_{H_2O} is water's bulk density) is the number of water molecules in the system. Figure 1 shows that the water molecule is more closely associated with the cation of the top four salts, but significantly more with the anion of KF. In general, the peak of the distribution associated with the better hydrated ion is sharper, bigger, and occurs at a shorter distance than that of the counterion. The trend exhibited in Figure 1 follows closely the size difference between the cation and anion. As one goes from the top to the bottom panels of Figure 1, $\sigma_- - \sigma_+$ gets smaller and reverses sign (in the case of KF), while the corresponding ratio of the peak height of the cation to the anion rdf gets smaller. The most symmetric hydration of the ion pair takes place in the case of KCl, where the size difference is the smallest. This correlation will be further quantified below.
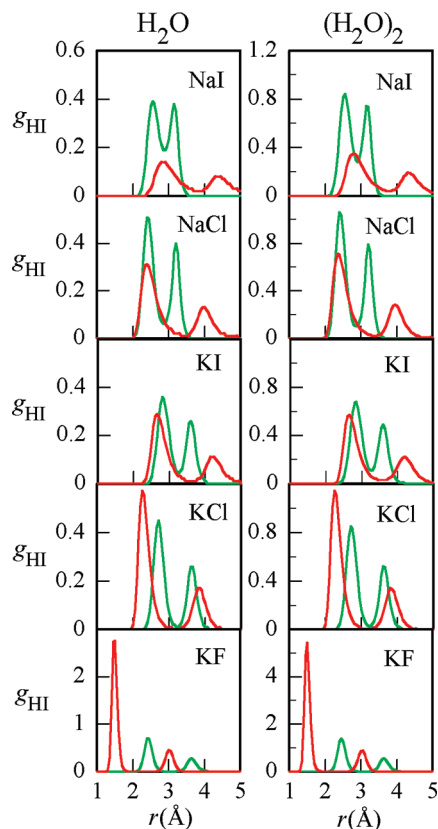
Figure 2. Ion−hydrogen radial distribution functions for different alkali halide ion pairs hydrated by a single water molecule (left column) or two water molecules (right column) in bulk CCl_4 at 300 K. In each panel, the green line is for the cation and the red line for the anion. Note the factor of 2 scaling on the vertical axis of the right compared with the left panels.

Contrasting the right and left panels of Figure 1 demonstrates that the above picture is essentially unchanged when the ion pair interacts with one or two water molecules. Other than the scaling by a factor of 2, each plot on the right is very similar in the shape and location of the peak to the plot on the left.

Additional information about the structure of the hydrated ion pair is provided in Figure 2, which shows the hydrogen ion rdfs for all the cases described in Figure 1. The two peaks in each distribution function correspond to two different water protons, one generally closer to the cation and the other to the anion. Except for NaI, the closest hydrogen is closer to the anion. Consistent with the effect of the relative ionic size on the hydration discussed above, as $\sigma_- - \sigma_+$ gets smaller, the hydrogen cation distribution (green line) peak height gets smaller, and its location shifts to larger values relative to the anion distribution (red lines). The nearly identical left and right panels are again a demonstration of the equivalence of the two water molecules in the two-water molecule clusters.

Figure 3 is a snapshot depicting some of the structural motifs discussed above. In particular, note that in both $NaI(H_2O)_2$ and $KF(H_2O)_2$ the two water molecules are equivalent and are symmetrically arranged around the ion pair.

It is interesting to examine the hypothetical case of an ion pair made from an equal-sized cation and anion in order to determine the effect of charge asymmetry. Figure 4 depicts the oxygen ion rdfs for the case of a single water molecule or two water molecules next to the small and large equal-sized ion pairs in bulk CCl_4. This plot clearly demonstrates that the water is much better at hydrating the anion than the cation in the case of the small ion pair. This is consistent with the well-known fact that, in bulk water, anions are better hydrated than cations of approximately the same size due to the ability of the small water proton to get close to the negative charge.[23,52] Here, in the case of S^+S^-, the optimal arrangement of the water molecule(s) near the anion is in conflict with the nearby cation. In the case of L^+L^-, the large distance between the centers of the two ions makes it possible for water in a bridgelike configuration to interact with the two opposite charges almost equally well.
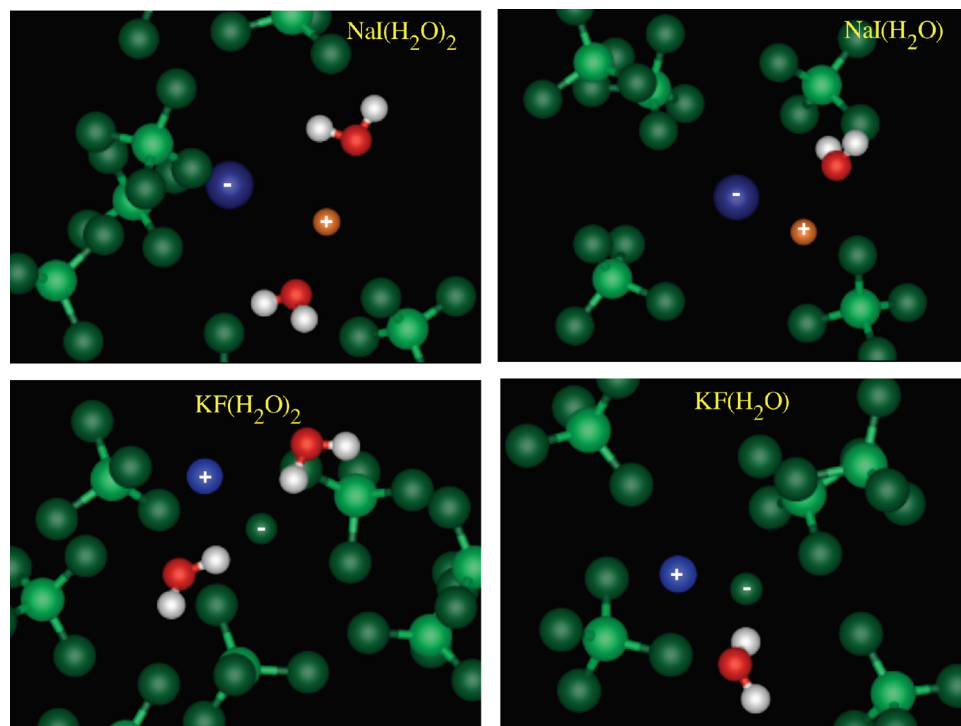

Figure 3. Simulation snapshot of several hydrated ion pairs in bulk CCl_4.

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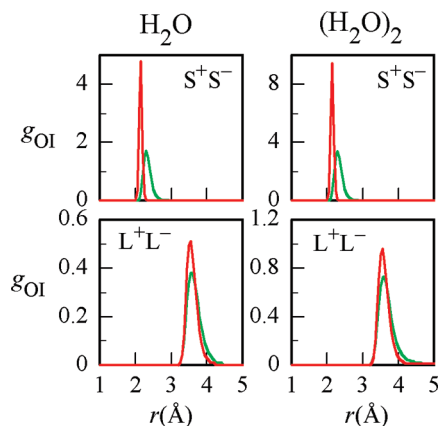*J. Phys. Chem. B, Vol. 114, No. 42, 2010* **13361**

Figure 4. Ion−oxygen radial distribution functions for equal-sized small (S) and large (L) ion pairs hydrated by a single water molecule (left column) or two water molecules (right column) in bulk CCl₄ at 300 K. In each panel, the green line is for the cation and the red line for the anion. Note the factor of 2 scaling on the vertical axis of the right compared with the left panels and for the different scales of the top and bottom panels.
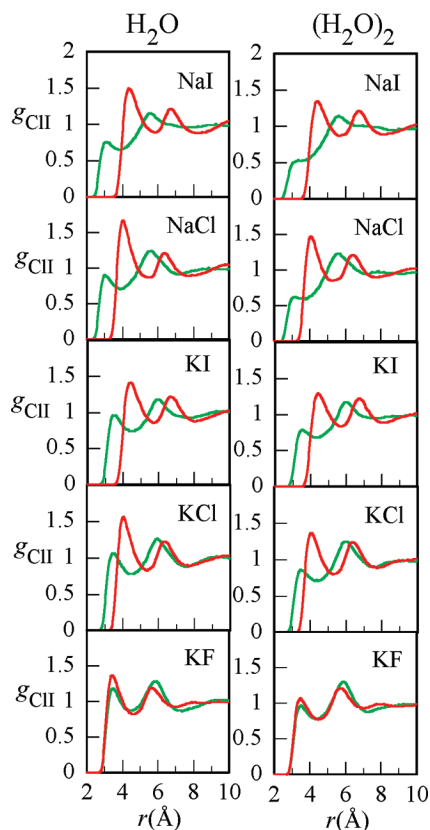

Figure 5. Ion−chlorine atoms radial distribution functions for different alkali halide ion pairs hydrated by one (left panels) or two (right panels) water molecules in bulk CCl₄ at 300 K. In each panel, the green line is for the cation and the red line for the anion.

The interaction of the ion pairs with the water has only a slight influence on the configuration of the ions with respect to the CCl₄ solvent molecules. This is demonstrated through the ion−chlorine atoms radial distribution functions in Figure 5. A similar picture is conveyed by the ion−carbon distribution functions, which are not shown.

The most noticeable feature of Figure 5 is that, for the top four panels, each corresponding to an anion larger than the cation, the peak of the anion-chloride atom distribution (red lines) is much more pronounced than the peak of the cation-

chloride atom distribution (green lines), and this is more apparent with two water molecules than with just one. This is due to the preferential interaction of the water molecules with the cation (resulting in a partial shielding of the anion from the organic solvent). The actual identity of the anion or cation makes only a very minor difference. Interestingly, in the case of KF, (and also in the cases of SS and LL which are not shown), in which it is the anion that is better hydrated, the anion/chloride and the cation/chloride distributions are nearly identical.

2. Energies. An examination of the ensemble average of the different energy terms in the total potential energy of the system provides further understanding of the behavior of the hydrated ion pair in the hydrophobic environment and adds additional insight into the roles of ion size and charge. The long trajectories used allow for a very accurate determination of these terms (error less than 2% based on 2 standard deviations of 100 segments of block averaging), with conclusions which are consistent with the structural characterization discussed above, and which also provide additional insight.

The total potential energy of the system including the CCl₄, the water, and the ion pair (abbreviated C, W, and I, respectively) can be written:

$$U = U_{CC} + U_{IP} + U_{WW} + U_{WC} + U_{IC} + U_{IW} \quad (3)$$

The total CCl₄ energy (intermolecular plus intramolecular) denoted by U_{CC} is large and negative, and nearly independent of the ions and the number of water molecules. The strong ion−ion interaction energy U_{IP}, while slightly affected by the presence of water, is the same as for the gas-phase cluster. Thus, these two terms will not be further examined here. The remaining four terms are relevant to understanding the structural aspects discussed above, and they are shown in Figure 6 for all the ion pairs considered here, arranged according to the total size of the ions, $\sigma_+ + \sigma_-$.

We first note that, in general (with minor variations), the results for the one-water and two-water systems are quite close. This is most pronounced for the ion−water interactions: $U_{IW}^{(2)} \approx 2U_{IW}^{(1)}$, where the superscript (n) refers to the number of water molecules. This is also the case to some degree for the water−CCl₄ interactions. This is consistent with the previous observation that the two water molecules are nearly equivalent. For the ion−CCl₄ interactions, the addition of one water molecule slightly increases (destabilizes) these energy terms, which is simply due to the fact that the additional water displaces a CCl₄ molecules from the ion's solvation shell. This was noted before when the ion−CCl₄ pair distributions were discussed.

Much more significant is the variation of the different energy terms with the type of the ion pair, which is made apparent by plotting the energy terms vs the sum of the Lennard-Jones ion size parameters, $\sigma_+ + \sigma_-$. As expected, the water−CCl₄ interactions (top panel) are essentially independent of the salts and are all within a kT larger than pure water (no ions) in CCl₄. (The hypothetical extreme cases of SS and LL are somewhat outside the range.)

The second panel from the top of Figure 6 shows that with two water molecules around the ion pair, water−water non-bonded interactions are all positive, so on average no water−water hydrogen bonding exists. (There is, however, some finite small probability for the two molecules to be hydrogen-bonded in the case of the larger ion pairs: this occurs in 0.5% of the 10⁶ configurations in the NaCl system and in 3% of the configurations in KI.) This is similar to what was observed with single ions hydrated with one or two water molecules in 1,2-
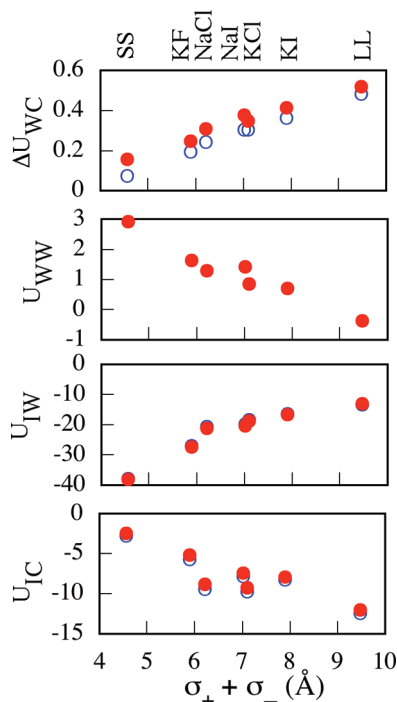
Figure 6. Several average interaction energies for five different alkali halide ion pairs and two hypothetical equal size ion pair hydrated by one (open blue circles) or two water molecules (full red circles) in bulk CCl$_4$ (kcal/mol) plotted vs the sum of the ions Lennard-Jones parameters. The panels from top to bottom depict (1) ΔU_{WC}, the water−CCl$_4$ interaction energy relative to the interaction energy of a single water molecule in bulk CCl$_4$ without ions (−2.3 kcal/mol); (2) the water−water nonbonded energy; (3) U_{IW}, the water−ion pair interaction energy; and (4) U_{IC}, the CCl$_4$ ion pair interaction energy. U_{WC} and U_{IW} for the case of two water molecules are scaled by a factor of 0.5. The error bar for each case is about half the diameter of the circles, or smaller.

dichloroethane.[14] The radial distribution functions suggest that the two water molecules are located in a bridgelike position across from the ion−ion vector, a configuration that does not allow for water−water hydrogen bonding. As the ions get larger, the water is less constrained and the U_{WW} values drop. The lack of water−water hydrogen bonding with two water molecules around the ion pair is possibly at odds with the experiment by Shultz and co-workers, who have attributed a 3440 cm^{-1} peak in the IR spectra to water hydrogen bonding. A possible resolution of this is that the ion pair−(H$_2$O)$_2$ cluster is acting as a nucleation center for additional water molecules. These water molecules can then form hydrogen bonds with the inner shell water. Indeed, a simulation of an NaCl(H$_2$O)$_3$ system, carried out to examine this, reveals that 17% of the configurations have two water molecules with an interaction energy more negative than −2.4 kcal/mol (indicating hydrogen bonding). It is worth noting that a pair of water molecules in bulk CCl$_4$ (without ions) is mostly strongly hydrogen-bonded, with a broad water−water energy distribution centered at about −5 kcal/mol (which is about twice the water pair interaction in bulk water), but also with a significant probability for the water dimer to separate (34% of 10^6 configurations). This result is consistent with the deep minima (−2.8 kcal/mol) in the water−water potential of mean force in CCl$_4$, calculated by Chang and Dang.[29] This dissociation and recombination of water in the bulk hydrophobic media, while interesting, is outside the scope of this paper.

As expected, significant variations of the ion−water and ion−CCl$_4$ interactions with the ion-pair type are observed. The
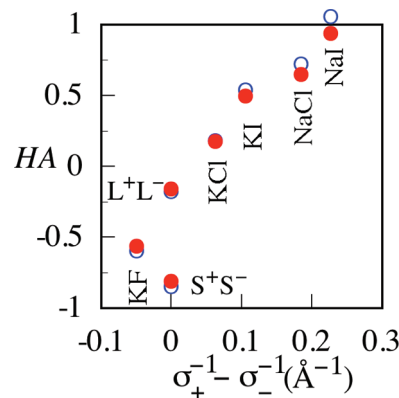

Figure 7. Hydration asymmetry parameter (defined in eq 4) of the ion pairs hydrated by one (open blue circles) or two (filled red circles) water molecules vs $\sigma_+^{-1} - \sigma_-^{-1}$.

water ion-pair interactions increase (are less stable) as the value of the anion + cation size increases. While the CCl$_4$−ion interactions are also becoming generally more favorable as σ_+ + σ_- increases, NaCl and KCl have more negative interaction energy compared with NaI and KI. This nicely correlates with the larger solubility of the chloride salts in CCl$_4$ (35.2 and 32.2 mM for NaCl and KCl, respectively) than the solubility of the iodide salts (22.2 and 19.1 mM for NaI and KI, respectively).[16]

Finally, we can use the individual interaction energies of the cations and anions with the water molecules to directly demonstrate the asymmetric hydration of the ion pairs. Specifically, denoting the cation−water *electrostatic* interaction energy by U_+ and the water−anion electrostatic interaction energy by U_-, we define the hydration asymmetry parameter HA by

$$HA = \frac{\langle U_+ \rangle - \langle U_- \rangle}{\langle U_+ \rangle + \langle U_- \rangle} \quad (4)$$

HA is near zero if the water is hydrating equally the cation and anion of a given ion pair; it is near 1 if the hydration of the cation is much more favorable ($|\langle U_+ \rangle| \gg |\langle U_- \rangle|$) and near −1 if the anion is much more favorable.

Figure 7 shows the hydration asymmetry parameters for all the ion pairs hydrated by one or two water molecules plotted vs the difference in size between the cation and anion. We found a good linear correlation between the alkali halide HA and the *inverse* Lennard-Jones parameter $\sigma_+^{-1} - \sigma_-^{-1}$.

The results for one or two water molecules are almost identical, consistent with the nearly independent interaction of the two water molecules with the ion pair. (When NaI is hydrated by one water molecule, the strong orienting force of the small cation is at odds with the preferred orientation of the water around the anion, so U_- is slightly positive, which makes HA slightly larger than 1.) Figure 7 is consistent with the observations described earlier. In particular, in KF the water interacts much more favorably with the anion, and so too is the case of the equal-sized ions. It is noteworthy that the asymmetry parameter is near −1 for S$^+$S$^-$, showing the dramatically favorable interaction with the anion in this case.

3. Water Dynamics. Valuable information about the interaction of water molecules with the ion pair in a hydrophobic medium can be obtained by examining the reorientation dynamics of water. Experimentally, information about dilute water in CCl$_4$ is available through NMR measurements[28] and also qualitatively through the rotational structure of the IR spectrum. Information about ion effects on water dynamics in

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bulk electrolyte solutions has been obtained in recent years via a variety of techniques.[53−56]

Computationally, we examine several equilibrium orientational correlation functions defined generally as:

$$C_l(t) = \langle P_l[\mathbf{d}(t) \cdot \mathbf{d}(0)] \rangle \qquad (5)$$

where $\mathbf{d}(t)$ is a unit vector fixed in the water molecular frame and P_l is the lth-order Legendre polynomial. $C_l(t)$ is, in general, nonexponential, and the corresponding average orientational relaxation time is taken as the integral

$$\tau_l = \int_0^\infty C_l(t) \, dt \qquad (6)$$

We will examine the $l = 2$ correlations for the water OH and HH vectors, which in principle could be accessible through NMR measurements,[57] as well as the water $l = 1$ dipole correlation function, which gives additional useful information, as discussed below. Our results for one or two water molecules in bulk CCl$_4$ with no ions are in reasonable agreement with the experiment by Goodnough et al.[28] and the calculations by Chang and Dang,[29] giving HH rotational correlation time on the order of 80 fs for the water monomer and 113 fs for the water dimer.

The correlation functions defined in eq 5 and calculated in the fixed frame of the simulation box give information about the water dynamics as the hydrated ion pair tumbles in bulk CCl$_4$. We find that the OH vector reorientation relaxation times of the hydrated ion-pair tumbling dynamics in bulk CCl$_4$ are around 1 ps and are nearly independent of the ion pair or the number of water molecules. τ_1 values for the water dipole vector are in the range of 1−3 ps for one water molecule and 4−6 ps for two water molecules, with no clear correlation with the type of the ion pair. These correlation times, while experimentally accessible, mainly represent the overall reorientation of the ion pair and thus are not a useful probe of the water−ion pair interactions.

To gain information about the water reorientation relative to the ion pair, we have also calculated the correlation function in the *local frame of the ion-pair interionic vector*. These time-correlation functions will be denoted by C_l^{IP} and some of them are shown in Figure 8.

The reorientation correlation functions C_l^{IP} exhibit a very fast component on the tens of femtoseconds time scale, corresponding to inertial motion of the water hydrogens. This is followed by a slower and highly oscillatory decay on the subpicosecond time scale, corresponding to the libration of the water molecules relative to the ion-pair vector (see as an example the inset in the middle panel). This is then followed by a much slower (tens of picoseconds), nearly exponential, tail. Clearly, the strong binding of the water molecules to the ion pair markedly slows down the reorientation of the water with respect to the ion pair.

The dependence of the reorientation dynamics on the nature of the ion pair correlates nicely with the asymmetry parameter HA. The constraint on the water dipole is weakest in the case of small cation/large anion (NaI). As HA decreases and the water molecule begins to favor the anion, the relaxation time increases. For KF (large cation/small anion) with HA = −0.6, the water dipole is essentially locked in place, except for a small libration within a cone whose angular width can be estimated from the long-time value of the correlation function.[58] Since one of the OH bonds and the H−H vector are relatively more free to rotate, the corresponding correlation functions shown in the middle
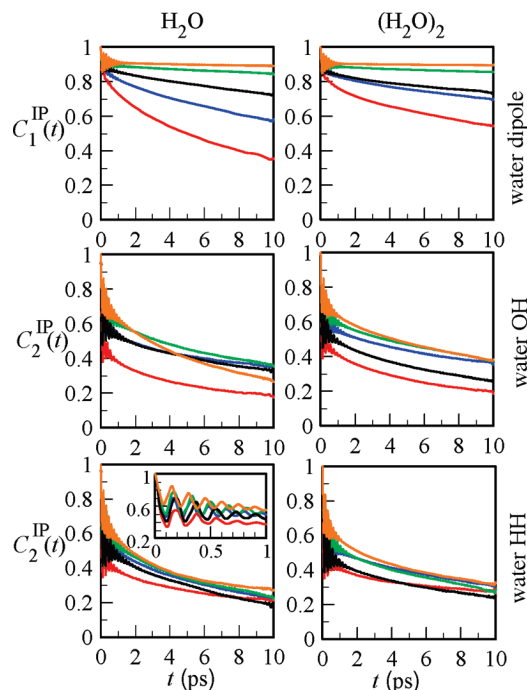

Figure 8. Several water reorientation correlation functions in the ion-pair vector local frame for KF (orange), KCl (green), KI (black), NaCl (blue), and NaI (red) hydrated by one (left panels) or two (right panels) water molecules in bulk CCl$_4$. Top panels, the water dipole C_1^{IP}; middle panels, the water OH vector C_2^{IP}; bottom panels, the water HH vector C_2^{IP}. The inset in the bottom left panel shows the early time behavior.
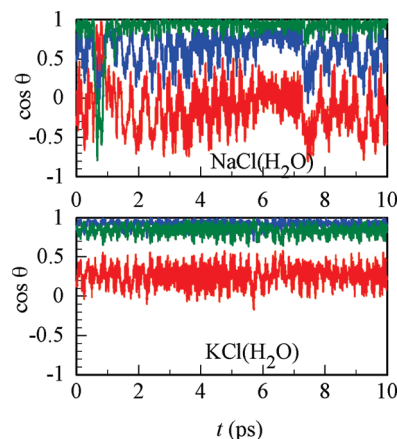

Figure 9. Sample rotational trajectories depicting the angle θ between the NaCl (top panel) and KCl (bottom panel) interionic vectors and the water OH bonds (green and red lines) and the water dipole (blue lines).

and bottom panels of Figure 9 experience a wider cone of angular distribution and a faster long-time decay than the dipole correlation function, but the general trend of a slower relaxation with a smaller HA is observed.

The sample trajectories for NaCl(H$_2$O) and KCl(H$_2$O) shown in Figure 9 illustrate this behavior.

Each panel shows as a function of time (for 10 ps) the angle between the ion-pair vector and the water dipole, as well as the angle between the ion-pair vector and each of the two OH bonds. For NaCl, both OH bonds experience large-amplitude oscillations about their average orientation. One OH bond (green line) is parallel to the ion-pair vector and the other (red line) nearly perpendicular, so the water dipole is pointing about 50° from the ion pair and undergoes relatively large-amplitude oscilla-

tions. The two OH bonds can switch roles by a 180° rotation of the HH vector around the water dipole. (In this trajectory, this happened twice near $t = 1$ ps.) For KCl, one OH bond points toward the Cl^- anion (green line), and the water dipole is nearly parallel to the ion pair and experiences very little displacement from this average orientation. Rotation of the HH vector around the water dipole occurs very rarely (not in this trajectory). It is interesting to note that water dynamics locked in two directions due to cooperative interactions with the cation and anion was proposed as an interpretation of recent time-resolved femtosecond infrared and tetrahertz dielectric relaxation spectroscopies of electrolyte solutions by Bakker and co-workers.[55]

IV. Conclusions

Despite the significantly different bulk environments, the structure and dynamics of hydrated ion pairs in bulk CCl_4 resemble several aspects of the hydration in bulk water. The hydration of five alkali halide ion pairs and two hypothetical ion pairs made from equal-size ions by one or two water molecules in bulk CCl_4 is characterized by strong water−ion interactions, strongly favoring the water binding to the smallest ion. Thus, water favors binding to the cation in the case of NaI, NaCl, KI, and KCl (in agreement with experimental data), but with the anion in the case of KF. Water favors bindings to the anion when the two ions have the same size, especially when the two ions are small. There is no significant water−water hydrogen bonding in the two water molecules systems. Water−water hydrogen bonding in these systems requires the hydration of the ion pair by at least three water molecules. A significant restriction of water reorientation dynamics that varies with the degree of the asymmetric hydration is found, with the dynamics becoming more restricted as the water interacts more strongly with the anion.

While there are certain similarities with the water reorientation dynamics around ions in bulk water, the lack of neighboring water molecules excludes water exchange and puts a significant constraint on the reorientation dynamics. And, unlike the situation in bulk water, the ion pair is a stable diatomic species, with both ions simultaneously affecting water structure and dynamics.

References and Notes

(1) Eisenman, G.; Dani, J. A. *Annu. Rev. Biophys. Biophys. Chem.* **1987**, *16*, 205.
(2) Gouaux, E.; MacKinnon, R. *Science* **2005**, *310*, 1461.
(3) Grigorieff, N.; Ceska, T. A.; Downing, K. H.; Baldwin, J. M.; Henderson, R. *J. Mol. Biol.* **1996**, *259*, 393.
(4) *Solvent Extraction for the 21st Century*; Cox, M., Hidalgo, M., Valiente, M., Eds.; SCI: London, 2001.
(5) Osakai, T.; Ogata, A.; Ebina, K. *J. Phys. Chem. B* **1997**, *101*, 8341.
(6) Osakai, T. The role of water molecules in ion transfer at the oil/water interface. In *Interfacial Catalysis*; Volkov, A. G., Ed.; Marcel Dekker: New York, 2003; p 53.
(7) Benjamin, I. *Science* **1993**, *261*, 1558.
(8) Schweighofer, K. J.; Benjamin, I. *J. Phys. Chem.* **1995**, *99*, 9974.
(9) Schweighofer, K. J.; Benjamin, I. *J. Phys. Chem. A* **1999**, *103*, 10274.
(10) Chorny, I.; Benjamin, I. *J. Phys. Chem. B* **2005**, *109*, 16455.
(11) Dang, L. X. *J. Phys. Chem. B* **1999**, *103*, 8195.
(12) Wick, C. D.; Dang, L. X. *J. Phys. Chem. C* **2008**, *112*, 647.
(13) Sun, P.; Laforge, F. O.; Mirkin, M. V. *J. Am. Chem. Soc.* **2007**, *129*, 12410.
(14) Benjamin, I. *J. Phys. Chem. B* **2008**, *112*, 15801.
(15) Rose, D.; Benjamin, I. *J. Phys. Chem. B* **2009**, *113*, 9296.
(16) Bisson, P.; Xiao, H.; Kuo, M.; Kamelamela, N.; Shultz, M. J. *J. Phys. Chem. A* **2010**, *114*, 4051.
(17) Ghosal, S.; Hemminger, J. C.; Bluhm, H.; Mun, B. S.; Hebenstreit, E. L. D.; Ketteler, G.; Ogletree, D. F.; Requejo, F. G.; Salmeron, M. *Science* **2005**, *307*, 563.
(18) Jungwirth, P.; Tobias, D. J. *Chem. Rev.* **2006**, *106*, 1259.
(19) Ghosal, S.; Brown, M. A.; Bluhm, H.; Krisch, M. J.; Salmeron, M.; Jungwirth, P.; Hemminger, J. C. *J. Phys. Chem. A* **2008**, *112*, 12378.
(20) Xu, M.; Tang, C. Y.; Jubb, A. M.; Chen, X. K.; Allen, H. C. *J. Phys. Chem. C* **2009**, *113*, 2082.
(21) Allen, H. C.; Casillas-Ituarte, N. N.; Sierra-Hernandez, M. R.; Chen, X. K.; Tang, C. Y. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5538.
(22) *The Chemical Physics of Solvation; Part A*; Dogonadze, R. R., Kalman, E., Kornyshev, A. A., Ulstrup, J., Eds.; Elsevier: Amsterdam, 1985.
(23) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.
(24) Yufei, C.; Cunnane, V. J.; Schiffrin, D. J.; Mutomäki, L.; Kontturi, K. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 107.
(25) Daikhin, L. I.; Urbakh, M. *J. Electroanal. Chem.* **2003**, *560*, 59.
(26) Schweighofer, K. J.; Benjamin, I. *J. Chem. Phys.* **2000**, *112*, 1474.
(27) Wick, C. D.; Dang, L. X. *J. Chem. Phys.* **2010**, *132*.
(28) Goodnough, J. A.; Goodrich, L.; Farrar, T. C. *J. Phys. Chem. A* **2007**, *111*, 6146.
(29) Chang, T. M.; Dang, L. X. *J. Phys. Chem. A* **2008**, *112*, 1694.
(30) Lamoureux, G.; Roux, B. *J. Phys. Chem. B* **2006**, *110*, 3308.
(31) Andersen, H. C. *J. Chem. Phys.* **1980**, *72*, 2384.
(32) Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 814.
(33) Benjamin, I. *J. Chem. Phys.* **2004**, *121*, 10223.
(34) Hansen, J.-P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed.; Academic: London, 1986.
(35) Pettitt, B. M.; Rossky, P. J. *J. Chem. Phys.* **1986**, *84*, 5836.
(36) Lee, S. H.; Rasaiah, J. C. *J. Chem. Phys.* **1994**, *101*, 6964.
(37) Obst, S.; Bradaczek, H. *J. Phys. Chem.* **1996**, *100*, 15677.
(38) Koneshan, S.; Rasaiah, J. C.; Lynden-Bell, R. M.; Lee, S. H. *J. Phys. Chem. B* **1998**, *102*, 4193.
(39) Jensen, K. P.; Jorgensen, W. L. *J. Chem. Theory Comput.* **2006**, 1499.
(40) Sprik, M.; Klein, M. L. *J. Chem. Phys.* **1988**, *89*, 7556.
(41) Ahlstrom, P.; Wallqvist, A.; Engstrom, S.; Jonsson, B. *Mol. Phys.* **1989**, *68*, 563.
(42) Sprik, M.; Klein, M. L.; Watanabe, K. *J. Phys. Chem.* **1990**, *94*, 6483.
(43) Wallqvist, A. *Chem. Phys.* **1990**, *148*, 439.
(44) Dang, L. X.; Rice, J. E.; Caldwell, J.; Kollman, P. A. *J. Am. Chem. Soc.* **1991**, *113*, 2481.
(45) Bader, J. S.; Berne, B. J. *J. Chem. Phys.* **1996**, *104*, 1293.
(46) Small, D. W.; Matyushov, D. V.; Voth, G. A. *J. Am. Chem. Soc.* **2003**, *125*, 7470.
(47) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. A* **2002**, *106*, 379.
(48) Vrbka, L.; Mucha, M.; Minofar, B.; Jungwirth, P.; Brown, E. C.; Tobias, D. J. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 67.
(49) Nosé, S. *J. Phys.: Condens. Matter* **1991**, *2*, SA115.
(50) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon: Oxford, UK, 1987.
(51) Pratt, L. R.; Hummer, G.; Garcia, A. E. *Biophys. Chem.* **1994**, *51*, 147.
(52) Latimer, W. M.; Pitzer, K. S.; Slansky, C. M. *J. Chem. Phys.* **1939**, *7*, 108.
(53) Wachter, W.; Fernandez, S.; Buchner, R.; Hefter, G. *J. Phys. Chem. B* **2007**, *111*, 9010.
(54) Park, S.; Fayer, M. D. *Proc. Natl. Acad. Sci.* **2007**, *104*, 16731.
(55) Tielrooij, K. J.; Garcia-Araez, N.; Bonn, M.; Bakker, H. J. *Science* **2010**, *328*, 1006.
(56) Bakker, H. J.; Skinner, J. L. *Chem. Rev.* **2010**, *110*, 1498.
(57) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: London, 1961.
(58) Lipari, G.; Szabo, A. *Biophys. J.* **1980**, *30*, 489.