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Dynamics of Water Molecules in the Br^- Solvation Shell: An ab Initio Molecular Dynamics Study

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The solvation of ions in water is of fundamental importance in chemical and biological processes. The unique role of water is closely related to the dynamics of ionic solvation shells. In recent years, much attention has been dedicated to the structure of ions in water both experimentally[1] and theoretically.[1a,2] To investigate the hydration structures, a variety of experimental methods have been successfully applied, such as ultrafast spectroscopy[1b,c] neutron and X-ray diffraction techniques.[1d−f] However, determination of the detailed microscopic structure and dynamics of inner solvation shells is generally difficult. To date, theoretical studies have mostly focused on solvation of cations,[2a−l] and less attention has been focused on anions[2k−r] and the lifetimes of solvation shells.

Very recently, in an elegant study, Kropman and Bakker[3] used nonlinear spectroscopy to isolate the spectral response of water molecules hydrogen-bonded to the halides Cl^-, Br^-, and I^-. They found that water molecules in the solvation shells of these anions move comparatively slowly, with mean lifetimes ranging from 12 to 20 ps for 1−6 M NaCl solutions and 18−25 ps for NaBr and NaI in the same range of concentrations.

The new measurements[3] and the lack of accurate theoretical ab initio studies on the dynamics of solvation shells of anions in bulk water prompted us to start a systematic investigation of anions in water.[4] In this communication we report on a Car−Parrinello (CPMD) density functional theory (DFT)-based molecular dynamics simulation[5] on an aqueous solution of HBr 1.6 M. Conventional computer simulation techniques based on semiempirical potentials have already been applied to obtain detailed and statistically reliable information about structural and dynamical properties of water molecules around both cations and anions (see for example ref 2a and references therein). However, these studies rely on the quality of the parametrized potential energy surface. It has been demonstrated that the inclusion of three body effects is important for a more accurate description of ion−water interaction and, hence, for a realistic description of the solvation structure.[2p,6a] Moreover, it has been shown that the polarizability of the anion may be one of most important factors in determining the structure of gas-phase clusters.[6b,c] Recently, several mixed QM/MM studies of the structure of the aqueous solvation shell of cations have been reported.[2c,d] However, this approach also suffers from the above-mentioned parametrization problem. In contrast, the CPMD approach is able to describe the dynamics of the system in a self-consistent fashion, taking into account in a natural way polarization and many-body interactions. CPMD simulations have already been successfully employed in the study of many cations in solution[2b,e−j,m,r] and are providing an increasingly important complement to experimental data.

The present DFT calculation utilized Troullier−Martins pseudopotentials[7] to describe the core of all atoms except hydrogen, for which a von Barth−Car analytical pseudopential[8] has been used. The Kleinman−Bylander decomposition[9] has been used for all the atoms. The electronic wave functions have been expanded in a plane waves basis set up to the energy cutoff of 70 Ry. With this choice the molecular geometries converged to within 0.3%. We have used the new empirical exchange-correlation functional proposed by Hamprecht et al.,[10] named HCTH. This functional has been demonstrated to be more satisfactory in describing the hydrogen-bond and transport properties of liquid water[10b] than the very popular Becke, Lee, Yang, and Parr (BLYP) exchange and correlation functional.[11] The equations of motion have been integrated with a time step of 0.169 fs, using a fictitious electronic mass[5] of 1000 au. We have also replaced all of the hydrogen atoms with deuterium. The simulation cell was a cubic box of 9.8998 Å containing 31 water molecules and one HBr.[12] The size of the system is relatively small, but compared to recent CPMD studies of cations,[2f−j] we prefer to carry out a sufficiently long simulation to accumulate reliable statistics of the calculated properties.

The simulation was started from a liquid water configuration consisting of 32 water molecules in which one water was replaced by an HBr. The starting H−Br distance was chosen to be equal to the gas-phase value. A previous study on HCl in water[2r] showed that the initial configuration does not significantly influence the acid dissociation. We assumed that is also true for HBr, since this acid is stronger than HCl. The system was equilibrated at 300 K for ∼2 ps using a Nosé−Hoover chain of thermostats to control the temperature after an initial period of 1 ps during which the temperature was controlled by uniformly scaling the velocities. Then, the trajectory in phase space was sampled for ∼36 ps.

The dissociation of HBr occurs with the same mechanism reported by Laasonen and Klein.[2r] The H originally bonded to Br moves spontaneously with a barrierless, diffusion-limited reaction, to a neighboring water molecule, giving rise to H_3O^+. Then, one of the hydrogens of H_3O^+ migrates to another water molecule, as already reported in the literature.[2m,r]

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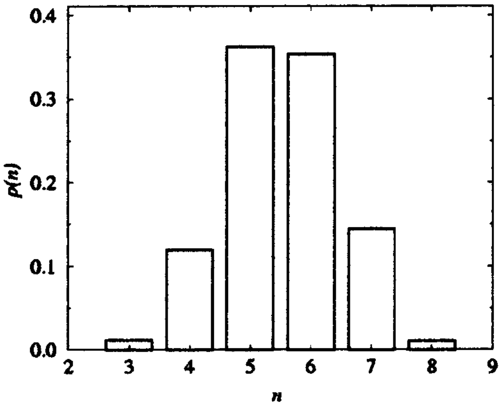

Figure 1. Distribution of the coordination number of Br^- in HBr at 1.6 M.

We have calculated the radial distribution functions, $g(r)$, for the Br−O and Br−H pairs. The nearest neighbor Br−O and Br−H peaks are at 3.26 and 2.34 Å, respectively. The coordination number inferred from the first minimum in the Br−O pair distribution function is 6.3. More accurate information may be obtained by defining the instantaneous coordination number, $n_{Br}(t)$, as the number of hydrogens closer than 3.15 Å to the Br atom, that is the first minimum in the Br−H pair correlation function, with a OH−Br angle higher than 130°, which represents the lower limit commonly used in hydrogen bond analysis.[2n,13] The distribution of the coordination number, n_{Br}, shown in Figure 1, fluctuates in the range 4−8 with an average value of 5.8, slightly different from that obtained by integration of the $g_{Br-O}(r)$. For comparison, the distribution of the coordination number, n_{Cl}, obtained in the previous study of HCl in H_2O,[2r] shows smaller fluctuations with an average value of 4.5, which reflects the smaller radius of Cl^-.

The presence of the H_3O^+ counterion influences the dynamics of the solvation shell. From the simulation, a strong correlation between the motion of the hydronium and the center of mass of the bromine water cage, $\mathbf{R}_{cage}$, is evident. The distribution of the angle between H_3O^+−Br^- and $\mathbf{R}_{cage}$-Br^- is quite broad and peaked at 130°. On the time scale of our simulation, the water molecules occupy well-defined positions around the anion. We have observed that, on average, when a water molecule leaves the first solvation shell, another one enters in a different position, giving rise to a pseudorotation of the cage around the Br^-.[14] The average distribution of O atoms around Br^- is a square antiprism with C_{4v} symmetry. This kind of coordination has been already proposed for Ca^{2+}.[2c]

An important focus of the present work is the value of the residence time, τ, of water in the first coordination shell.[2m] The calculation of the mean residence time is quite delicate since we have to take into account that one or more water molecules can temporarily leave the first coordination shell and return to it without ever properly entering the bulk. We have estimated the mean residence time by following the prescription of Impey et al.,[2k] which avoids problems arising from the rattling motion of water molecules of the first hydration shell. In accordance with these authors, any molecule that leaves the solvation shell for a time less than t^*, is treated as not having left the solvation shell at all. Following former studies,[2a,k,q] we have chosen a tolerance time $t^* = 2$ ps. On the basis of this criterion, one water molecule stayed in the first coordination shell as long as 33 ps. Two other molecules stayed longer than 18 ps. We also noticed that hexacoordinated configurations last longer than penta- and heptacoordinated ones. The longest hexa-coordinated configuration persisted for ~7 ps, which has to be compared with ~2 ps for each of the others. Figure 2 shows two configurations separated by 30 ps.

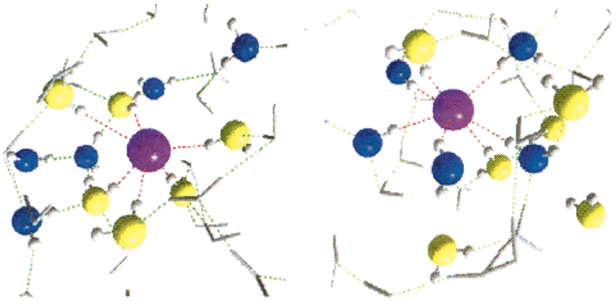

Figure 2. Dynamics of water molecules in the solvation shell of a dissolved Br^- ion in HBr at 1.6~M. Two configurations separated by a time interval of 30 ps are shown. Hydrogen bonds of the solvation shell are drawn in red. During the depicted interval, five solvent molecules, whose oxygen atoms are drawn in blue, replace four hydrogen-bonded water molecules, whose oxygen are drawn in yellow, thereby causing Br^- to increase its coordination number from 6 to 7. The seventh water molecule is more weakly bonded (see text). For visual clarity, most of the solvent molecules are drawn as gray sticks.

The limited statistics does not allow a precise evaluation of the residence time, τ, of water molecules. However, the observed decay of the population of the hydration shell suggests a value $\tau \approx 19$ ps. Considering the very different nature of the counterion, our theoretical estimate is in fairly good agreement with the experimental value for Br^- of $\tau = 19 \pm 5$ ps in 2M NaBr.[2k] This contrasts with the very short residence time (~5 ps) calculated using classical MD with nonpolarizable force fields.[1a] It has already been proposed that polarization effects could be very important in determining τ.[2o,q] It is also important to note that the reported uncertainty of experimentally measured residence time is about 5 ps,[3] which is comparable to our calculated uncertainty. Also, Kropman and Bakker[3] observed that changing the nature of the cation does not affect the experimental residence time as long as the concentration is the same.

To conclude, the present study shows that the evaluation of the residence time and the reorganization of the solvent around anions using ab initio molecular dynamics is feasible. We have also identified an important role played by the counterion on the dynamics of the hydration shell of its partner. Clearly, it is very important to study larger samples at high solute concentration to gain a deeper understanding of the latest generation of experimental results. In this regard, we are currently studying aqueous solutions of KBr and KCl.

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