Dynamics of Halide Ion−Water Hydrogen Bonds in Aqueous Solutions: Dependence on Ion Size and Temperature

Snehasis Chowdhuri[†] and Amalendu Chandra*

Department of Chemistry, Indian Institute of Technology, Kanpur, India 208016

Received: December 28, 2005; In Final Form: March 28, 2006

We have carried out a series of molecular dynamics simulations to investigate the dynamics of X^-−water (X = F, Cl, Br, and I) and water−water hydrogen bonds in aqueous alkali halide solutions at room temperature and also of Cl^-−water and water−water hydrogen bonds at seven different temperatures ranging from 238 to 318 K. The hydrogen bonds are defined by using a set of configurational criteria with respect to the anion-(oxygen)−oxygen and anion(oxygen)−hydrogen distances and the anion(oxygen)−oxygen−hydrogen angle for an anion(water)−water pair. The results of the hydrogen bond dynamics are obtained for two different cutoff values for the angular criterion. In both cases, similar dynamical behavior of the hydrogen bonds is found with respect to their dependence on ion size and temperature. The fluoride ion−water hydrogen bonds are found to break at a much slower rate than water−water hydrogen bonds, while the lifetimes of chloride and bromide ion−water hydrogen bonds are found to be shorter than those of fluoride ion−water ones but still longer than water−water hydrogen bonds. The short-time dynamics of iodide ion−water hydrogen bonds is found to be slightly faster, while its long-time dynamics is found to be slightly slower than the corresponding water−water hydrogen bond dynamics. Correlations of the observed dynamics of anion(water)−water hydrogen bonds with those of rotational and translational diffusion and residence times of water molecules in ion-(water) hydration shells are also discussed. With variation of temperature, the lifetimes of both Cl^-−water and water−water hydrogen bonds are found to show Arrhenius behavior with a slightly higher activation energy for the Cl^-−water hydrogen bonds.

1. Introduction

An important issue concerning the dynamics of aqueous solutions containing hydrogen bonding solutes is the kinetics of breaking and structural relaxation of solute−water and water−water hydrogen bonds in these solutions. For ionic solutes of negative charges such as halide ions, hydrogen bonds are formed between the anions and water molecules in their first hydration shells and the dynamics of these hydrogen bonds greatly influence the mobility of both ions and water molecules in the solutions. In recent years, there have been a number of experimental studies on the dynamics of water molecules in hydration shells of halide ions which include the dynamics of anion−water hydrogen bonds[1,2] and rotational[2−4] and vibrational[4−6] relaxation of water molecules in ion hydration shells. Experimental studies have also been carried out on other related aspects of ion−water systems such as the modifications of the electronic structure of water molecules which are in direct contact with an anion,[7,8] the molecular organization of water in ion hydration shells,[9,10] and the collective dynamics of water molecules near charged macroionic surfaces.[11] In the context of hydrogen bond dynamics, we note the work of Kropman and Bakker[1,2] who employed femtosecond mid-infrared spectroscopy to investigate the dynamics of anion−water hydrogen bonds in aqueous solutions of alkali halides and reported a significant slowing down of the dynamics of anion−water hydrogen bonds as compared to that of water−water hydrogen bonds in the bulk. In particular, the length of the hydrogen bond between a water molecule and a halide ion was found to change with a

characteristic time constant of 12−25 ps which is about 20−50 times longer than the characteristic time constant of the water−water hydrogen bonds in liquid water. On the theoretical side, the dynamics of halide ion−water systems have been investigated by means of both classical and ab initio molecular dynamics methods.[12−25] In the classical molecular dynamics (MD) study of aqueous solutions of chloride and bromide ions,[12] the dynamics of anion−water hydrogen bonds were found to be slower than that of water−water hydrogen bonds by a factor of 2 at the most. Ab initio molecular dynamics studies[21,22] on halide ion−water systems have reported a slower decay of the residence correlation function and a residence time of 12−19 ps for water molecules in the hydration shells of fluoride, chloride, and bromide ions for a chosen definition of the residence time.[23] These residence times fall in similar time scales as the experimentally measured time constants of ion−water hydrogen bond dynamics for the above ions. We note, however, that since a water molecule can continue to reside in the hydration shell for sometime even after breaking its hydrogen bond with the halide ion, the ion−water hydrogen bond time constant is not necessarily the same as the residence time of a water molecule in the ion hydration shell. If the residence time is indeed comparable to the experimentally observed hydrogen bond time constant, such a comparison is also expected to be valid for water−water hydrogen bonds. The residence time of water in the solvation shell of another water has been estimated to be around 5−6 ps,[17,18] whereas the experimentally observed characteristic time constant for water−water hydrogen bond dynamics is less than a picosecond.[1] We also note that the ab initio MD study of ref 24 has found a relatively shorter residence

† Present address: Department of Chemistry, Georgetown University, Washington, DC 20057.

Halide Ion−Water Hydrogen Bonds in Aqueous Solutions

J. Phys. Chem. B, Vol. 110, No. 19, 2006 **9675**

time of 8.8 ps for water molecules in chloride ion hydration shells. For the iodide ion−water system,[25] the calculated residence time seems to differ significantly from the experimentally reported time constant of hydrogen bonds with this ion. Clearly, much more work is needed to understand the dynamical properties of halide ion−water hydrogen bonds and their relations to diffusion and residence times of water molecules in ion hydration shells. The present work is a contribution toward this end.

In the present work, we have carried out a series of MD simulations of aqueous solutions containing a single halide ion of varying size from F⁻ to I⁻ at room temperature or containing a single Cl⁻ ion at varying temperature from 238 to 318 K to investigate the ion size and temperature dependence of the dynamics of anion−water hydrogen bonds. The dynamics of both breaking and structural relaxation of these hydrogen bonds are studied. We have also calculated the relaxation of water−water hydrogen bonds so that the dynamics of these hydrogen bonds can be readily compared with that of anion−water hydrogen bonds for varying ion size and temperature under the same simulation conditions. We have also investigated the diffusion and orientational relaxation of water molecules in the hydration shells of ions and also in the bulk to explore the role of translational and orientational motion of water molecules in determining the dynamics of anion−water and water−water hydrogen bonds. Correlations between the residence times of water molecules in the hydration shells of ions and tagged water molecules and the observed dynamics of hydrogen bonds are also discussed. To the best of our knowledge, such an MD study on the ion size and temperature dependence of the dynamics of halide ion−water hydrogen bonds is presented here for the first time.

We have organized the rest of the paper as follows. In section 2, we describe the models and simulation details. We define the water−water and anion−water hydrogen bonds in section 3. The definitions of various hydrogen bond time correlation functions are presented in section 4. In this section, we also discuss the results of the dynamics of anion−water and water−water hydrogen bonds for ions of different size. The results of diffusion and orientational relaxation of water molecules in hydration shells are presented in section 5. In section 6, we define the residence time correlation functions and present our results of the residence times of hydration shell water molecules. The relations of the residence times to the observed hydrogen bond dynamics are also discussed in this section. The results of the temperature dependence of the dynamics of chloride ion−water and water−water hydrogen bonds are presented in section 7. Our conclusions are briefly summarized in section 8.

2. Models and Simulation Details

In the present work, the water molecules are characterized by the extended simple point charge (SPC/E) potential[26] and the ions are modeled as charged Lennard-Jones particles.[16,27] In these models, the interactions between atomic sites or ions are expressed as

$$u(r_i, r_j) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{q_i q_j}{r_{ij}} \quad (1)$$

where q_i is the charge of the ith atom (or ion). The Lennard-Jones parameters σ_{ij} and ϵ_{ij} are obtained by using the combination rules $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$, where σ_i and ϵ_i are the Lennard-Jones diameter and well-depth parameter for ith atom or ion. The values of the potential parameters q_i, σ_i, and

TABLE 1: Values of Lennard-Jones and Electrostatic Interaction Potential Parameters (*e* Represents the Magnitude of Electronic Charge)

atom/ion	σ (Å)	ϵ (kJ/mol)	charge (*e*)
O	3.166	0.6502	−0.8476
H			+0.4238
F⁻	3.117	0.7532	−1.0
Cl⁻	4.401	0.4184	−1.0
Br⁻	4.539	0.4184	−1.0
I⁻	5.167	0.4184	−1.0

ϵ_i for water and also for the fluoride, chloride, bromide, and iodide ions that have been considered in this study are summarized in Table 1.

The molecular dynamics simulations were carried out for aqueous solutions containing a single halide ion X⁻ (X = F, Cl, Br, and I) in water at 298 K and also a single Cl⁻ ion in water at seven different temperatures ranging from 238 to 318 K. For each system, a cubic box with a total of 256 molecules (water plus ion) and periodic boundary conditions with minimum image conditions were employed.[28] The long-range electrostatic interactions were treated using the Ewald method.[29] We employed the quaternion formulation of the equations of rotational motion and, for the integration over time, we adapted the leapfrog algorithm with a time step of 10^{-15} s (1 fs). The experimental density of water was used for all simulations at room temperature. For the low and high temperature simulations, we first carried out a constant pressure simulation[30] for 400−600 ps for each system to find the average density corresponding to a pressure of 1 atm and then performed constant volume simulation with box dimensions calculated from the average density found during the preceding constant pressure simulation. The average densities at a pressure of 1 atm were found to be 1.012, 1.01, 1.009, 1.005, 1.002, and 0.9835 gm cm⁻³ at temperatures of T = 238, 248, 258, 268, 278, and 318 K, respectively. In the constant volume phase of the simulations, MD runs of 400−800 ps were used to equilibrate each system at a constant temperature and then the simulations were continued in microcanonical ensemble for a period of 600−1000 ps. The average temperature of a system during the production phase of each simulation was found to be very close to the previously chosen temperature, and no systematic drift was found. The hydrogen bonding properties were calculated over this final production phase of the simulations.

3. Definitions of the Hydrogen Bonds

We have used a set of geometric criteria where a hydrogen bond between two water molecules or between a water molecule and a negative ion exists if the following distance and angular criteria are satisfied

$$R^{(XO)} < R_c^{(XO)}$$

$$R^{(XH)} < R_c^{(XH)}$$

$$\theta < \theta_c \quad (2)$$

where X denotes the oxygen atom of the first water molecule in the case of water−water hydrogen bonds and it denotes the halide ion in the case of anion−water hydrogen bonds. Thus, $R^{(XO)}$ and $R^{(XH)}$ denote the oxygen−oxygen (or anion−oxygen) and oxygen−hydrogen (or anion−hydrogen) distances and the corresponding quantities with the subscript "c" denote the cutoff values. The angle θ (=$\theta^{(XOH)}$, X = O, F⁻, Cl⁻, Br⁻, and I⁻) is the oxygen (anion)−oxygen−hydrogen angle, and θ_c is the upper limit that is allowed for a hydrogen bond to exist. The

hydrogen atom that appears in all of the above distances and angle is the one that participates in the hydrogen bond in the tagged water–water or anion–water pair.

In the case of water–water hydrogen bonds, earlier studies considered the following cutoff values (or values very close to the following values) for the oxygen–oxygen[12–14,31–36] and oxygen–hydrogen[12–14,32,33,36] distances: $R_c^{(OO)} = 3.5$ Å and $R_c^{(OH)} = 2.45$ Å and we continue to use these values in the present study. We note that these critical distances of 3.5 and 2.45 Å are essentially the positions of the first minimum of the oxygen–oxygen and oxygen–hydrogen radial distribution functions. We have used similar criteria for the anion–water critical distances. That is, the cutoff values for anion–oxygen and anion–hydrogen distances are determined from the positions of the first minimum of the corresponding radial distribution functions for a given ion. The values thus obtained are the following: $R_c^{(XO)} = 3.25, 3.90, 3.95,$ and 4.18 Å and $R_c^{(XH)} = 2.48, 3.05, 3.15,$ and 3.35 Å for X = F⁻, Cl⁻, Br⁻, and I⁻, respectively. We have used two different values for the angular cutoff: $\theta_c = 30$ and 45°. We note that both water–water and halide ion–water hydrogen bonds in aqueous solutions are predominantly linear[12] and these cutoff values give allowance for fluctuations from the linear geometry which can occur due to thermal motion. The higher cutoff of $\theta_c = 45°$ gives more flexibility to the existence of hydrogen bonds. For the more strict definition of $\theta = 30°$, orientational fluctuations would contribute significantly to the breaking of hydrogen bonds. For the less strict definition of $\theta_c = 45°$, however, diffusion would play an important role in the breaking of hydrogen bonds, although orientational motion would still contribute to the breaking process due to the presence of the anion(oxygen)–hydrogen distance criterion. Clearly, the lifetime of a hydrogen bond for the less strict definition would be longer than that for the stricter definition. We note, however, that the primary goal of the present study is to investigate the relative time scales of the dynamics of anion–water hydrogen bonds as functions of ion size and temperature, and as we will show in section 4, this functional dependence remains similar for both angular cutoffs. We also note in this context that previous studies[12] of Cl⁻–water and Br⁻–water systems have found that the integrated probability of hydrogen bond angle distribution essentially reaches its saturation value at $\theta = 45°$ and so any further increase of the cutoff angle θ_c would have practically no effect on the lifetimes or the dynamical behavior of the hydrogen bonds.

4. Dynamics of Hydrogen Bonds

In this section, we discuss the results of ion size effects on the dynamics of anion–water hydrogen bonds at room temperature and compare the results of anion–water hydrogen bonds with those of water–water hydrogen bonds. We define two hydrogen bond population variables, $h(t)$ and $H(t)$, where $h(t)$ is unity when a particular water–water or anion–water pair is hydrogen bonded at time t according to the adopted definition as discussed in section 3 and zero otherwise and $H(t) = 1$ if the water–water or anion–water pair remains continuously hydrogen bonded from $t = 0$ to time t and it is zero otherwise. To study the breaking dynamics of hydrogen bonds, we calculate the continuous hydrogen bond time correlation function $S_{HB}(t)$ which is defined as[12–14,32,33,36,37]

$$S_{HB}(t) = \langle h(0) H(t)\rangle / \langle h(0)^2\rangle \qquad (3)$$

where $\langle \cdots \rangle$ denotes an average over all anion–water or water–
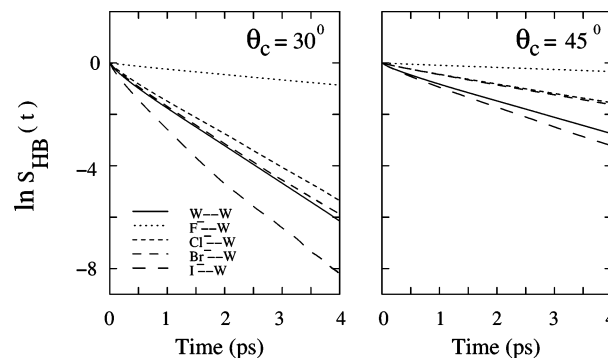

Figure 1. Time dependence of the continuous correlation functions of X⁻–water (X⁻–W for X = F, Cl, Br, and I) and water–water (W–W) hydrogen bonds at 298 K.

TABLE 2: Dynamical Properties of Anion–Water (X⁻–W) and Water–Water (W–W) Hydrogen Bonds at 298 K for X = F, Cl, Br, and I (the Values of τ_{HB}, $1/k_{HB;short}$, and $1/k_{HB;long}$ Are Expressed in ps)

quantity	θ_c (deg)	F⁻–W	Cl⁻–W	Br⁻–W	I⁻–W	W–W
τ_{HB}	30	4.50	0.64	0.58	0.36	0.54
τ_{HB}	45	11.65	2.40	2.15	1.10	1.30
$1/k_{HB;short}$	30	4.35	1.3	1.15	0.6	1.05
$1/k_{HB;short}$	45	5.0	2.4	2.0	0.9	1.2
$1/k_{HB;long}$	30	15.3	7.85	6.8	3.7	3.1
$1/k_{HB;long}$	45	20.7	8.7	7.5	5.5	3.4

water pairs. Clearly, $S_{HB}(t)$ describes the probability that an initially hydrogen bonded anion–water or water–water pair remains bonded at all times up to t. The associated integrated relaxation time τ_{HB} can be interpreted as the average lifetime of a hydrogen bond between an anion and a water molecule or between two water molecules. The results of the continuous correlation functions for both stricter ($\theta_c = 30°$) and less strict ($\theta_c = 45°$) definitions of the hydrogen bonds are shown in Figure 1 for halide ion–water hydrogen bonds. The results of water–water hydrogen bonds are also included for comparison in both the figures. Overall, the decay of $S_{HB}(t)$ occurs at a slower rate for the less strict definition of the hydrogen bonds, as one would expect. The dynamics of $S_{HB}(t)$ depends on the definition of the hydrogen bonds due to the frequent crossing of the dividing surface. This frequent crossing of the dividing surface leads to a faster relaxation of $S_{HB}(t)$. However, when the cutoff is short, the same hydrogen bond can be restored after the initial crossing of the dividing surface and thus the relaxation of $S_{HB}(t)$ occurs at a slower rate when a larger cutoff is used to define a hydrogen bond. For both definitions, it is found that the decay of $S_{HB}(t)$ for F⁻–water hydrogen bonds is much slower than that for other anion–water and water–water hydrogen bonds. Also, the Cl⁻–water and Br⁻–water hydrogen bonds show somewhat slower and the I⁻–water hydrogen bonds show somewhat faster dynamics than water–water hydrogen bonds for both definitions. Thus, the relative time scales of the relaxation of different hydrogen bonds remain the same for both definitions. In Table 2, we have included the average lifetimes τ_{HB}, which are defined as the time integrals of $S_{HB}(t)$, for both water–water and anion–water hydrogen bonds. We note that the calculated lifetimes of water–water hydrogen bonds agree reasonably well with the characteristic hydrogen bond time constant of 0.50 ± 0.2 ps reported by Kropman and Bakker[1] in their femtosecond mid-infrared laser studies, the relaxation time of 0.56–0.72 ps reported by Tominaga and co-workers[38,39] in their low frequency Raman studies, and an exponential relaxation time of 1.4 ps reported very recently by Tokmakoff and co-workers.[40] The longer lifetime of F⁻–water hydrogen bonds
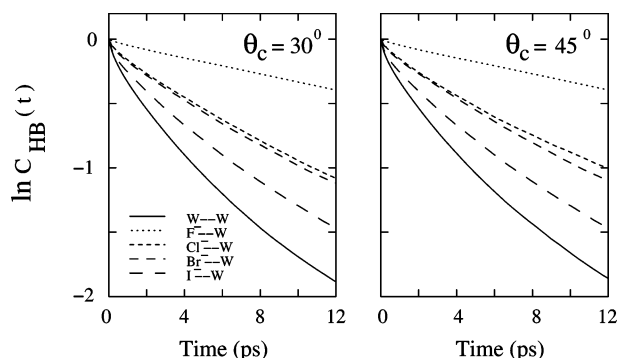
Halide Ion−Water Hydrogen Bonds in Aqueous Solutions

J. Phys. Chem. B, Vol. 110, No. 19, 2006 **9677**

Figure 2. Time dependence of the intermittent correlation functions of X⁻−water (X⁻−W for X = F, Cl, Br, and I) and water−water (W−W) hydrogen bonds at 298 K.

can be attributed to the smaller size of the fluoride ion. Because of its smaller size, the fluoride ion−water hydrogen bonds are rather strong and hence have a longer lifetime. Similarly, because of the large size of the iodide ions, the I⁻−water hydrogen bonds are weaker than water−water hydrogen bonds and hence break at a slightly faster rate. The Br⁻−water and Cl⁻−water hydrogen bonds are not as strong as F⁻−water bonds but are still somewhat stronger than water−water hydrogen bonds which explain their somewhat longer lifetimes than that of water−water hydrogen bonds. We note that, for water−water hydrogen bonds, the present result of the hydrogen bond lifetime for $\theta_c = 30°$ agrees well with the recent molecular dynamics results of ref 14. However, the dynamics of anion−water hydrogen bonds were not investigated in the latter study.[14]

Unlike the continuous correlation function $S_{HB}(t)$, the intermittent hydrogen bond correlation function $C_{HB}(t)$ does not depend on the continuous presence of a hydrogen bond. It is defined as[12−14,31−37]

$$C_{HB}(t) = \langle h(0)\, h(t) \rangle / \langle h \rangle \qquad (4)$$

It is clear that the correlation function $C_{HB}(t)$ describes the probability that an anion−water or water−water hydrogen bond is intact at time t, given it was intact at time zero, independent of possible breaking in the interim time. $C_{HB}(t)$ relaxes to zero, as the probability that a specific pair of molecules is hydrogen bonded in a macroscopic system at equilibrium is negligibly small. Since the function $C_{HB}(t)$ allows recrossing of the dividing surface that separates the bonded and nonbonded states, its relaxation describes the structural relaxation of hydrogen bonds. The results of $C_{HB}(t)$ are shown in Figure 2.

The temporal behavior of $C_{HB}(t)$ shows that the overall dynamics of hydrogen bond structural relaxation is an order of magnitude slower than that of hydrogen bond breaking. In this case, both stricter and less strict definitions lead to very similar dynamics for both anion−water and water−water hydrogen bonds, especially at long times. We note that $C_{HB}(t)$ allows reformation of a hydrogen bond after it was broken initially. For two different but physically reasonable definitions of the hydrogen bonds, the dividing surfaces in the configuration space which separate the bonded and nonbonded states are different but lie not too far from each other and trajectories cross and recross such nearby surfaces rather frequently. A change of the dividing surface will thus alter the amount of recrossings and the decay of $C_{HB}(t)$ at very short times, but its long-time dynamics will not change significantly, as has been observed in the present study and was also noted earlier in ref 31 in the context of water−water hydrogen bonds. The relaxation of $C_{HB}(t)$ is found to be nonexponential because of the presence

of both hydrogen bond breaking and reformation processes and their coupling with diffusion motion of water molecules. After a hydrogen bond is broken, the ion−water or the water−water pair can remain as nearest neighbors for some time before either the bond is reformed or the molecules diffuse away from each other. We define $N_{HB}(t)$ as the time dependent probability that a hydrogen bond is broken at time zero but the two molecules remain in the vicinity of each other, that is, as nearest neighbors, but not hydrogen bonded at time t. $N_{HB}(t)$ is calculated from the simulation trajectories through the following correlation function[34,41]

$$N_{HB}(t) = \langle h(0)[1 - h(t)]g(t) \rangle / \langle h(0)^2 \rangle \qquad (5)$$

where $g(t)$ is unity if the ion(oxygen)−oxygen distance of the ion−water or water−water pair is less than $R_c^{(OO)}$ at time t and it is zero otherwise. Following previous work,[31,32,34,41] we can then write a simple rate equation for the "reactive flux" $-dC_{HB}/dt$ in terms of $C_{HB}(t)$ and $N_{HB}(t)$

$$-\frac{dC_{HB}(t)}{dt} = k_{HB}C_{HB}(t) - k'_{HB}N_{HB}(t) \qquad (6)$$

where k_{HB} and k'_{HB} are the forward and backward rate constants for hydrogen bond breaking. The inverse of k_{HB} can be interpreted as the average lifetime of a hydrogen bond and can be correlated with τ_{HB} obtained from the route of continuous hydrogen bond time correlation function. We used a least-squares fit of the simulation results of the reactive flux, $C_{HB}(t)$ and $N_{HB}(t)$ to eq 6 to produce the forward and backward rate constants. We performed the fitting in the short-time region 0 ps < t < 2.0 ps to obtain the rate constants for the short-time part of the relaxation, and we also carried out the fitting on the longer time region 2.0 ps < t < 12 ps to calculate these quantities for the slower, long-time part of the relaxation. The inverses of the corresponding forward rate constants, which correspond to the average hydrogen bond lifetimes and which we denote as $1/k_{HB;short}$ and $1/k_{HB;long}$, are included in Table 2. We note that the values of $1/k_{HB;short}$ are similar to the average hydrogen bond lifetimes τ_{HB} obtained from the continuous hydrogen bond correlation function $S_{HB}(t)$ which is not unexpected because both $S_{HB}(t)$ and the short-time part of the reactive flux capture the hydrogen bond "breaking" dynamics due to fast librational and short-time rotational and translational motion. The hydrogen bond lifetime as given by $1/k_{HB;long}$ is significantly longer because it excludes the fast librational and short-time rotational and translational relaxation and it includes primarily the long-time diffusive motion. We expect it to be correlated with the residence times and also with the diffusion coefficients of water molecules in ion (water) hydration shells. These issues are discussed in the next two sections.

5. Diffusion and Orientational Relaxation of Water Molecules in Hydration Shells

The dynamics of anion−water hydrogen bonds is likely to be correlated with the diffusion and orientational relaxation of water molecules in the vicinity of anions. The diffusion coefficient D is calculated from the time integral of the velocity−velocity autocorrelation function (VAF) by

$$D = \frac{k_B T}{m} \int_0^\infty C_v(t)\, dt \qquad (7)$$

where k_B is the Boltzmann constant, m is the mass of the solute,

TABLE 3: Diffusion Coefficients and Orientational Relaxation Times of Water Molecules in the Vicinity of Halide Ions and in the Bulk at 298 K (the Diffusion Coefficients and the Relaxation Times Are Expressed in Units of 10^{-5} cm^2 s^{-1} and ps, Respectively)

region	D	τ_2^μ	τ_2^{HH}	τ_2^{OH}
vicinity of F$^-$	1.5	3.2	4.2	4.6
vicinity of Cl$^-$	2.1	2.1	2.7	2.5
vicinity of Br$^-$	2.2	2.0	2.6	2.45
vicinity of I$^-$	2.7	1.7	2.2	1.9
bulk	2.65	1.55	1.9	1.75

and $C_v(t)$ is the velocity—velocity time correlation function

$$C_v(t) = \frac{\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle}{\langle \mathbf{v}(0)\cdot\mathbf{v}(0)\rangle} \tag{8}$$

where $\mathbf{v}(t)$ is the velocity of the solute at time t and the average is carried out over the initial time. For calculation of the diffusion coefficient of water molecules in the vicinity of a negative ion, the correlation function $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$ is averaged over only those water molecules which are found in the first solvation shell of the negative ion at time $t = 0$. Since the velocity correlation function relaxes very fast and it decays to zero in about 1 ps which is much shorter than the average residence time of a water molecule around a halide ion,[17,18] a water molecule, which was in the first solvation shell of an anion at $t = 0$, is likely to remain in the vicinity of the negative ion over the time scale of its velocity relaxation. For the calculation of the diffusion coefficient of bulk water molecules, the velocity correlation function was averaged over all water molecules excluding those in the solvation shells of ions.

The orientational relaxation time τ_l^α is obtained as the time integral of the orientational correlation function:

$$\tau_l^\alpha = \int_0^\infty dt\, C_l^\alpha(t) \tag{9}$$

where the orientational correlation function $C_l^\alpha(t)$ is given by

$$C_l^\alpha(t) = \frac{\langle P_l[e^\alpha(t)\cdot e^\alpha(0)]\rangle}{\langle P_l[e^\alpha(0)\cdot e^\alpha(0)]\rangle} \tag{10}$$

where P_l is the Legendre polynomial of rank l and e^α is the unit vector which points along the α-th axis in the water molecular frame. We have calculated τ_l^α for $l = 2$ and for two different e^α, the molecular dipole vector μ, and the O—H vector. These orientational relaxation times were obtained by explicit integration of $C_l^\alpha(t)$ from simulations until 7 ps and by calculating the integral for the tail from the fitted exponential functions. As discussed before, the averages were carried out separately for bulk and solvation shell water molecules in order to obtain the orientational relaxation times of water molecules in the bulk phase and in the vicinity of an anion.

In Table 3, we have shown the results of the diffusion coefficients and orientational relaxation times for $l = 2$ for all the systems at 298 K. It is seen from Table 3 that both diffusion and orientational relaxation of water molecules become slower in the vicinity of the halide ions. The extent of slowing down is, however, not as great as it was observed for the hydrogen bond dynamics, especially so for the fluoride ion, which could be attributed to more than one reason. First, in the present calculations, the correlation functions of hydration shell water molecules correspond to those which are found in the hydration shell at the initial time $t = 0$. Some of these water molecules

might have left the solvation shell at a later time within the time scale of calculations of the correlation functions, particularly so for orientational correlations which decay at slower rates than velocity correlations. Second, the whole solvation shell might translate or rotate, keeping the relative distance and orientation of ion—water pairs unchanged. Such a motion of the whole solvation shell would contribute to diffusion and orientational relaxation of hydration shell water molecules but would not break the ion—water hydrogen bonds. This could be particularly significant for fluoride ion where the hydration shell is much more rigid than other ions, and we observed a greater slowing down of the relaxation of anion—water hydrogen bonds for this ion than the ones between other halide ions and water molecules or between two water molecules.

6. Residence Times of Water Molecules in Hydration Shells

We have calculated the residence times of water molecules in hydration shells in two different ways. As defined in section 4, we consider the population variable $g(t)$ which is equal to 1 when two given water molecules (or a water molecule and an ion) are nearest neighbors at time t and it is zero otherwise. We also define another population variable $g'(t;t^*)$ which is 1 when a water molecule, which was in the hydration shell of an ion or another water molecule at time $t = 0$, remains continuously in the same hydration shell up to time t subject to an allowance time t^*. That is, in this case, if the water molecule leaves the hydration shell for a period less than t^* between the time 0 and t, it is assumed to have not left the hydration shell at all. We construct the correlation functions

$$S_R(t;t^*) = \langle g(0)\, g'(t;t^*)\rangle/\langle g(0)^2\rangle \tag{11}$$

and

$$C_R(t) = \langle g(0)\, g(t)\rangle/\langle g(0)^2\rangle \tag{12}$$

where $S_R(t;t^*)$ describes the probability that a water molecule, which was in the hydration shell of an ion or a water molecule at time $t = 0$, remains continuously in the hydration shell up to time t subject to the allowance time t^* and the associated relaxation time, which we call the residence time, is denoted as $\tau_{R;t^*}$. In the limit of $t^* = 0$, it becomes the continuous residence time which corresponds to the time over which a water molecule resides in a hydration shell without ever leaving it. The correlation function $C_R(t)$ gives the probability that a water molecule, which was in the hydration shell of an ion or a water molecule at the initial time, is also found to be in the same hydration shell at time t irrespective of what has happened in the interim period. After a water molecule has left the hydration shell of an ion or another water molecule, it can stay in the second hydration shell for some time before either returning to the hydration shell or diffusing into the bulk. We define $N_R(t)$ as the time dependent probability that a water molecule, which was in the hydration shell of an ion or a water molecule at time $t = 0$, resides in the second hydration shell at time t. $N_R(t)$ can be expressed as the following time correlation function

$$N_R(t) = \langle g(0)[1 - g(t)]f(t)\rangle/\langle g(0)^2\rangle \tag{13}$$

where $f(t)$ is unity if the ion(oxygen)—oxygen distance of the ion—water or water—water pair is less than $R_{c;2}^{(XO)}$ at time t and is zero otherwise. The cutoff distance $R_{c;2}^{XO}$ corresponds to the location of the second minimum of the corresponding XO radial

Halide Ion−Water Hydrogen Bonds in Aqueous Solutions

J. Phys. Chem. B, Vol. 110, No. 19, 2006 **9679**

TABLE 4: Residence Times of Water Molecules in Hydration Shells of an Anion X⁻ (X = F, Cl, Br, and I) and of a Tagged Water Molecule (the Values of $\tau_{R;t*}$, $t*$, $1/k_{R;short}$, and $1/k_{R;long}$ Are Expressed in ps)

| quantity	$t*$	hydration shell →	F⁻	Cl⁻	Br⁻	I⁻	H₂O
$\tau_{R;t*}$	0		10.7	3.2	2.9	1.75	2.3
$\tau_{R;t*}$	2.0		17.2	7.5	7.0	5.6	5.1
$1/k_{R;short}$			13.5	3.4	3.1	1.65	1.0
$1/k_{R;long}$			29.75	12.65	9.85	7.4	5.0

distribution function. We express the decay of the intermittent residence time correlation function by a rate equation of the following form

$$-\frac{dC_R(t)}{dt} = k_R C_R(t) - k'_R N_R(t) \qquad (14)$$

where k_R and k'_R are the forward and backward rate constants for leaving the hydration shell. The inverse of k_R can be interpreted as the average residence time of a water molecule and can be correlated with $\tau_{R;t*}$ obtained from the route of $S_R(t;t*)$. We used a least-squares fit of the simulation results of $C_R(t)$ and $N_R(t)$ to eq 14 to produce the forward and backward rate constants. As before, we performed the fitting in the short-time region 0 ps < t < 2.0 ps to obtain the rate constants and the corresponding average residence times for the fast diffusional motion and we also carried out the fitting on the longer time region 2.0 ps < t < 12 ps to calculate these quantities for slower diffusional relaxation. The inverses of the corresponding forward rate constants, which correspond to the average residence times and which we denote as $1/k_{R;short}$ and $1/k_{R;long}$, are included in Table 4. We note that the values of $1/k_{R;short}$ are similar to the average continuous residence times $\tau_{R;t*=0}$ obtained from the continuous hydrogen bond correlation function $S_R(t;t* = 0)$ which is not unexpected because both $S_R(t;t* = 0)$ and the early part of the intermittent residence time correlation function describe the residence dynamics of hydration shells due to fast diffusional motion at short times. The values of these quantities are also found to correlate with $1/k_{HB;short}$ for $\theta_c = 45°$ because, in the latter case, short-time breaking of hydrogen bonds is primarily determined by the fast rotational and translational motion of water molecules. The values of $\tau_{R;t*=2ps}$ correlate with those of $1/k_{HB;long}$ for both $\theta_c = 30$ and 45° which shows that the long-time component of hydrogen bond dynamics corresponds to the departure of water molecules from hydration shells due to slower diffusive motion. The values of $1/k_{R;long}$ are found to be even larger than $\tau_{R;t*=2\ ps}$ which shows that a water molecule can return to a hydration shell even after staying outside of it for more than 2 ps.

7. Dependence on Temperature

In Figures 3 and 4, we have shown the time dependence of the continuous hydrogen bond correlation functions for Cl⁻−water and water−water hydrogen bonds, respectively, at varying temperature from $T = 318$ to 238 K. In Figure 5, we have plotted the logarithm of the corresponding average lifetimes versus $1/T$. An Arrhenius behavior is found for both water−water and chloride ion−water hydrogen bonds. The values of the activation energies are included in Table 5. It is found that, for a given definition, the breaking of chloride ion−water hydrogen bonds has somewhat higher activation energy than that of water−water hydrogen bonds. We note that the activation energy for water−water hydrogen bonds as obtained in the present study is in good agreement with the value reported by Starr et al.[42] for θ_c
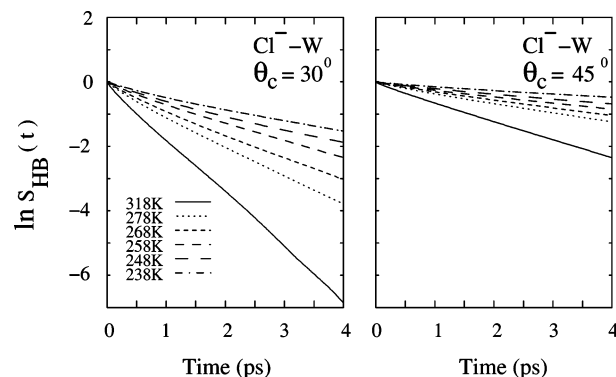
Figure 3. Time dependence of the continuous correlation functions of Cl⁻−water hydrogen bonds at varying temperatures from 238 to 318 K.
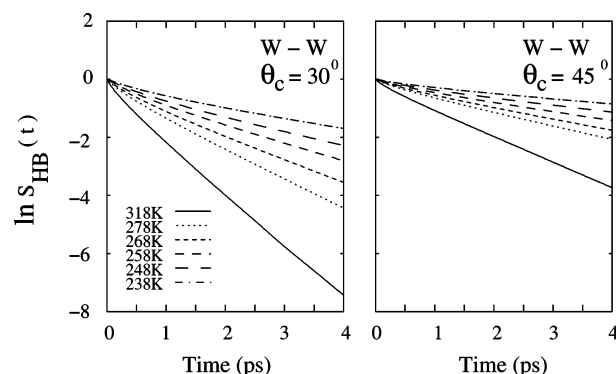
Figure 4. Time dependence of the continuous correlation functions of water−water hydrogen bonds at varying temperatures from 238 to 318 K.
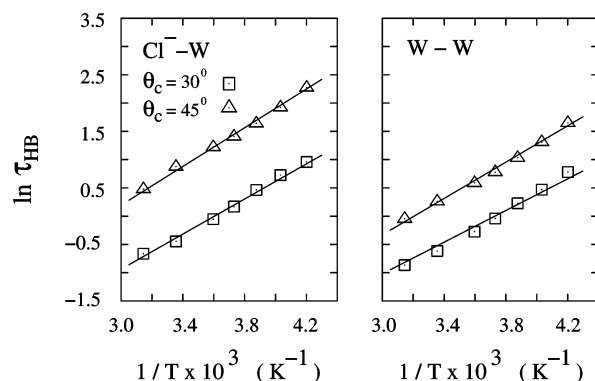
Figure 5. Temperature dependence of the logarithm of average lifetimes of Cl⁻−water and water−water hydrogen bonds.

TABLE 5: Values of the Activation Energies for Breaking Dynamics of Water−Water and Cl⁻−Water Hydrogen Bonds (the Values of E_{HB} Are Expressed in kJ/mol)

quantity	θ_c (deg)	water−water	Cl⁻−water
E_{HB} (kJ/mol)	30	11.64	12.90
E_{HB} (kJ/mol)	45	13.36	14.23

= 30°. The corresponding results for chloride ion−water hydrogen bonds are presented here for the first time.

8. Conclusions

We have investigated the dynamics of anion−water hydrogen bonds for halide ions of different sizes and compared the results with those of water−water hydrogen bonds. It is found that the relaxation of anion−water hydrogen bonds occurs with a longer time scale than that of water−water hydrogen bonds. The

9680 *J. Phys. Chem. B, Vol. 110, No. 19, 2006*

Chowdhuri and Chandra

slowest dynamics is found for the fluoride ion−water hydrogen bonds which is attributed to the rather small size of the fluoride ion. The lifetimes of chloride and bromide ion−water hydrogen bonds are found to be shorter than those of fluoride ion−water hydrogen bonds but longer than those of water−water hydrogen bonds. Despite its larger size, the iodide ion forms hydrogen bonds with water whose long-time dynamics is still slower than that of water−water hydrogen bonds. The short-time relaxation of iodide ion−water hydrogen bonds is, however, found to be slightly faster when compared with the corresponding water−water hydrogen bond dynamics. We have also calculated the rotational and translational diffusion and residence times of water molecules in ion(water) hydration shells and have discussed the correlations of these dynamical quantities with the observed dynamics of anion(water)−water hydrogen bonds in the solutions. We have also calculated the temperature dependence of the lifetimes of the chloride ion−water and water−water hydrogen bonds over a wide range of temperature from hot solution at 318 K to deeply supercooled solution at 238 K. An Arrhenius behavior is found for the breaking dynamics of both chloride ion−water and water−water hydrogen bonds with a slightly higher activation energy for the chloride ion−water hydrogen bonds.

References and Notes

(1) Kropman, M. F.; Bakker, H. J. *Science* **2001**, *291*, 2118. *J. Chem. Phys.* **2001**, *115*, 8942.
(2) Bakker, H. J.; Kropman, M. F.; Omta, A. W.; Woutersen, S. *Phys. Scr.* **2004**, *69*, C14.
(3) Kropman, M. F.; Nienhuys, H.-K.; Bakker, H. J. *Phys. Rev. Lett.* **2002**, *88*, 77601.
(4) Laenen, R.; Thaller, A. *J. Mol. Liq.* **2003**, *103*, 291.
(5) Laenen, R.; Thaller, A. *Chem. Phys. Lett.* **2001**, *349*, 442. Kropman, M. F.; Bakker, H. J. *Chem. Phys. Lett.* **2002**, *362*, 349.
(6) Kropman, M. F.; Bakker, H. J. *Chem. Phys. Lett.* **2003**, *370*, 741.
(7) Robertson, W. H.; Johnson, M. A. *Annu. Rev. Phys. Chem.* **2003**, *54*, 173.
(8) Cappa, C. D.; Smith, J. D.; Wilson, K. R.; Messer, B. M.; Gilles, M. K.; Cohen, R. C.; Saykally, R. J. *J. Phys. Chem. B* **2005**, *109*, 7046.
(9) Leberman, R.; Soper, A. K. *Nature* **1995**, *378*, 364.
(10) de Jong, P. H. K.; Neilson, G. W.; Bellisent-Funel, M.-C. *J. Chem. Phys.* **1996**, *105*, 5155.
(11) Bhattacharyya, K. *Acc. Chem. Res.* **2003**, *36*, 95 and references therein.
(12) Chandra, A. *Phys. Rev. Lett.* **2000**, *85*, 768; *J. Phys. Chem.* **2003**, *107*, 3899.
(13) Guardia, E.; Marti, J.; Garcia-Tarres, L.; Laria, D. *J. Mol. Liq.* **2005**, *117*, 63.
(14) Guardia, E.; Laria, D.; Marti, J. *J. Phys. Chem. B* **2006**, *110*, 6332.
(15) Balbuena, P. B.; Johnston, K. P.; Rossky, P. J. *J. Phys. Chem.* **1996**, *100*, 2706.
(16) Koneshan, S.; Rasaiah, J. C.; Lynden-Bell, R. M.; Lee, S. H. *J. Phys. Chem. B* **1998**, *102*, 4193.
(17) Chowdhuri, S.; Chandra, A. *J. Chem. Phys.* **2001**, *115*, 3732.
(18) Lyubartsev, A. P.; Laaksonen, A. *J. Phys. Chem.* **1996**, *100*, 16410.
(19) Zasetsky, A. Y.; Svishchev, I. M. *J. Chem. Phys.* **2001**, *115*, 1448.
(20) Ghorai, P. K.; Yashonath, S.; Lynden-Bell, R. M. *J. Phys. Chem. B* **2005**, *109*, 8120.
(21) Raugei, S.; Klein, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 9484; *J. Chem. Phys.* **2002**, *116*, 196.
(22) Heuft, J. M.; Meijer, E. J. *J. Chem. Phys.* **2003**, *119*, 11788; **2005**, *122*, 94501.
(23) Impey, R. W.; Madden, P. A.; McDonald, I. R. *J. Phys. Chem.* **1983**, *87*, 5071.
(24) Ikeda, T,; Hirata, M.; Kimura, T. *J. Chem. Phys.* **2003**, *119*, 12386.
(25) Heuft, J. M.; Meijer, E. J. *J. Chem. Phys.* **2005**, *123*, 94506.
(26) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269.
(27) Dang, L. X. *Chem. Phys. Lett.* **1992**, *200*, 21. Dang, L. X.; Garrett, B. C. *J. Chem. Phys.* **1993**, *99*, 2972.
(28) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford: New York, 1987.
(29) The implementation of the Ewald method for a single ion in an infinite periodically replicated solvent system is discussed in, for example, Day, T. J. F.; Patey, G. N. *J. Chem. Phys.* **1997**, *106*, 2782.
(30) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684.
(31) Luzar, A.; Chandler, D. *Phys. Rev. Lett.* **1996**, *76* 928; *Nature (London)* **1996**, *379*, 53.
(32) Luzar, A. *J. Chem. Phys.* **2000**, *113*, 10663.
(33) Balasubramanian, S.; Pal S.; Bagchi, B. *Phys. Rev. Lett.* **2002**, *89*, 115505.
(34) Xu, H.; Berne, B. J. *J. Phys. Chem. B* **2001**, *105*, 11929. Xu, H.; Stern, H. A.; Berne, B. J. *J. Phys. Chem. B* **2002**, *106*, 2054.
(35) Sutmann, G.; Vallauri, R. *J. Phys: Condens. Matter* **1998**, *10*, 9231.
(36) Chandra, A.; Chowdhuri, S. *Proc. Ind. Acad. Sci: Chem. Sci.* **2001**, *113*, 591.
(37) Rapaport, D. C. *Mol. Phys.* **1983**, *50*, 1151.
(38) Mizoguchi, K.; Ujike, T.; Tominaga, Y. *J. Chem. Phys.* **1998**, *109*, 1867. Ujike, T.; Tominaga, Y.; Mizoguchi, K. *J. Chem. Phys.* **1999**, *110*, 1558.
(39) Amo, Y.; Tominaga, Y. *Physica (Amsterdam)* **2000**, *275A*, 33.
(40) Fecko, C. J.; Loparo, J. J.; Roberts, S. T.; Tokmakoff, A. *J. Chem. Phys.* **2005**, *122*, 54506.
(41) Boese, D.; Chandra, A.; Martin, J. M.; Marx, D. *J. Chem. Phys.* **2003**, *119*, 5965.
(42) Starr, F. W.; Nielsen, J. K.; Stanley, H. E. *Phys. Rev. Lett.* **1999**, *82*, 2294.