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Hydrogen bond and residence dynamics of ion–water and water–water pairs in supercritical aqueous ionic solutions: Dependence on ion size and density

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We have carried out a series of molecular dynamics simulations to investigate the hydrogen bond and residence dynamics of X^- -water ($X=F$, Cl , and I) and pairs in aqueous solutions at a temperature of 673 K. The calculations are done at six different water densities ranging from 1.0 to 0.15 g cm⁻³. 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 F^- -water hydrogen bonds are found to have a longer lifetime than all other hydrogen bonds considered in the present study. The lifetime of Cl^- -water hydrogen bonds is shorter than that of F^- -water hydrogen bonds but longer than the lifetime of water–water hydrogen bonds. The lifetimes of I^- -water and water–water hydrogen bonds are found to be very similar. Generally, the lifetimes of both anion–water and water–water hydrogen bonds are found to be significantly shorter than those found under ambient conditions. In addition to hydrogen bond lifetimes, we have also calculated the residence times and the orientational relaxation 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 as functions of the ion size and density of the supercritical solutions. © 2006 American Institute of Physics. [DOI: [10.1063/1.2403867](https://doi.org/10.1063/1.2403867)]

I. INTRODUCTION

This paper is concerned with the hydrogen bond and residence dynamics of halide ion-water and water–water pairs in supercritical aqueous solutions of varying density. For anionic solutes such as halide ions, hydrogen bonds can be formed between the ions and the water molecules in their first hydration shells and the dynamics of these hydrogen bonds can greatly influence the mobility of the ions in the solutions. In recent years, the dynamics of these anion–water hydrogen bonds under ambient conditions have been investigated both experimentally^{1,2} and theoretically^{3,4} and it is found that, depending on ion size, the dynamics of both breaking and local structural relaxation of anion–water hydrogen bonds can be rather different from those of water–water hydrogen bonds. The residence times of water molecules in ion hydration shells are also found to be quite different from that in bulk water, especially for smaller ions.³ Since the unique solvent properties of liquid water are attributed to its hydrogen bonds, it is important to investigate at molecular level what happens to these hydrogen bonds when one moves to supercritical conditions from the ambient state. Such studies of hydrogen bond properties under extreme conditions are especially important because of the very different chemical and physical properties that supercritical water exhibits when compared with those of ambient water.

In recent years, there have been a number of experimental^{5–16} and theoretical^{17–29} studies on the hydrogen

bonded structure of water and aqueous solutions under supercritical conditions of high temperature and/or high pressure. There have also been some studies^{29–39} on the dynamical properties of water and aqueous ionic solutions at supercritical states that looked primarily at the diffusion, orientational relaxation, dielectric relaxation, and solvation dynamics and also on ion mobility in supercritical water. We are aware of only two studies^{29,33} in the literature in which dynamics of hydrogen bonds in supercritical water have been looked at. However, both these studies have considered the relaxation of only water–water hydrogen bonds. Out of these two studies, we note, in particular, the work of Guardia *et al.*,²⁹ which came out very recently. In this study, the authors have investigated the dynamics of water–water hydrogen bonds in aqueous ionic solutions at infinite dilution under supercritical conditions. The dynamics of water–water hydrogen bonds are investigated for water molecules both in the vicinity of halide and alkali ions and also in the bulk for many different densities of the supercritical solutions, and the results are compared with the corresponding dynamics of water–water hydrogen bonds in ambient water. The dynamics of anion–water hydrogen bonds in supercritical aqueous solutions still remains an open problem and yet to be investigated. The present study makes a contribution toward this end. Our main objective is to study how these anion–water hydrogen bond dynamical properties are changed under extreme changes of temperature and density at supercritical conditions. Another goal of the present study is to explore how these anion–water hydrogen bonds are dynamically different from water–water hydrogen bonds and to what extent

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these hydrogen bond dynamical properties are correlated with the residence dynamics and orientational relaxation of water molecules in ion hydration shells at supercritical conditions. We note that an understanding of the dynamics of solute-water hydrogen bonds under supercritical conditions is crucial in having a molecular level understanding of various dynamical properties of supercritical aqueous solutions such as ion mobility, diffusion, orientational relaxation, and also dynamics of many chemical processes that occur in aqueous media under supercritical conditions.

In the present work, we have carried out a series of molecular dynamics simulations of aqueous solutions containing a single halide ion of F^- , Cl^- , or I^- at a supercritical temperature of 673 K and at six different densities ranging from 1.0 to 0.15 g cm⁻³ to investigate the ion size and density dependence of the dynamics of anion–water hydrogen bonds. The dynamics of both breaking and local 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 density under the same simulation conditions. We have also investigated the residence dynamics and the orientational relaxation of water molecules in the hydration shells of ions to explore the roles of translational and orientational motion of water molecules in determining the dynamics of anion–water and water–water hydrogen bonds. In addition to the above dynamical quantities, we have also calculated some of the structural quantities such as the ion–water and water–water radial distribution functions, coordination numbers and the hydrogen bond numbers which help to gain an insight into the hydrogen bonded local structure of the solutions around ions under supercritical conditions. It may be noted that the dynamics of anion–water hydrogen bonds in supercritical aqueous solutions are investigated here for the first time.

We have organized the rest of the paper as follows. In Sec. II, we describe the models and simulation details and, in Sec. III, we define the water–water and anion–water hydrogen bonds. The definitions of various hydrogen bond and residence time correlation functions are presented in Sec. IV. In this section, we also discuss the results of the dynamics of anion–water and water–water hydrogen bonds for ions of different size and for different density of the supercritical water. The residence dynamics of water molecules are also presented in this section. In Sec. V, we discuss our results of the orientational relaxation of water molecules in hydration shells and we briefly summarize our conclusions in Sec. VI.

II. MODELS AND SIMULATION DETAILS

In the present work, the water molecules are characterized by the extended simple point charge (SPC/E) potential⁴⁰ and the ions are modeled as charged Lennard-Jones particles.^{41,42} In these models, the interaction between atomic sites or ions are expressed as

TABLE I. 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 |
| I^- | 5.167 | 0.4184 | -1.0 |

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

where q_i is the charge of the i th 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, respectively, for i th atom or ion. The values of the potential parameters q_i , σ_i , and ϵ_i for water and also for the fluoride, chloride, and iodide ions that have been considered in this study are summarized in Table I.

The molecular dynamics simulations were carried out for aqueous solutions containing a single halide ion X^- ($X = F, Cl, \text{ and } I$) in water at 673 K. The simulations are performed at six different densities: $\rho = 1.0, 0.7, 0.5, 0.35, 0.25$, and 0.15 g/cm³. For each system, a cubic box with a single ion immersed in 255 water molecules and periodic boundary conditions with minimum image condition were employed. The long-range electrostatic interactions were treated by using the Ewald method.⁴³ We employed the quaternion formulation of the equations of rotational motion and, for the integration over time, we adapted the leap-frog algorithm with a time step of 10⁻¹⁵ s (1 fs). For each of the systems, first an equilibration run of 400 ps was carried out at a constant temperature of 673 K and subsequently the run was continued for another 400 ps for calculation of the hydrogen bonding and residence properties as well as other equilibrium and dynamical properties. It may be noted that, in addition to the three halide ions mentioned above, we also carried out some preliminary calculations of the dynamics of bromide ion–water hydrogen bonds at supercritical conditions using a similar charged Lennard-Jones potential for the bromide ion.^{41,42} The dynamics of the bromide ion–water hydrogen bonds were found to be essentially identical with that of chloride ion–water hydrogen bonds⁴⁴ under supercritical conditions and so we chose to exclude the bromide ion–water systems in the present study.

III. DEFINITIONS OF THE HYDROGEN BONDS

We have used a set of geometric criteria whereby 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:^{3,45–50}

$$R^{(XO)} \leq R_c^{(XO)},$$

$$R^{(XH)} \leq R_c^{(XH)},$$

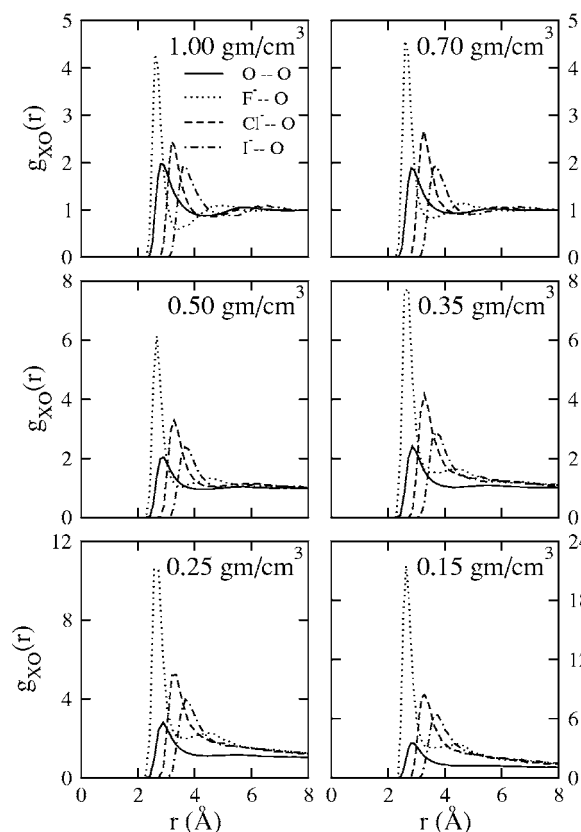


FIG. 1. The oxygen-oxygen and anion-oxygen radial distribution functions at 673 K for six different densities. The solid, dotted, dashed and dashed-dotted curves are for oxygen-oxygen, F⁻-oxygen, Cl⁻-oxygen, and I⁻-oxygen correlations, respectively.

$$\theta \leq \theta_c, \quad (2)$$

where X denotes the oxygen atom of the first water molecule in case of water-water hydrogen bonds and it denotes the halide ion in 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, the corresponding quantities with the subscript c denote the cutoff values. The angle $\theta (= \theta^{(XOH)}$, $X=O, F^-, Cl^-,$ 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 the above distances and angle is the one that participates in the hydrogen bond in the tagged water-water or anion-water pair.

The critical distances can be determined from the ion-water and water-water radial distribution functions which are shown in Figs. 1 and 2. In these figures, we have shown the $X-O$ and $X-H$ (X =ion or water oxygen) radial distribution function at the six different densities. It is seen that although the peak heights for both $X-O$ and $X-H$ radial distribution functions change rather significantly with density, the positions of the first peak and also the first minimum remain essentially at the same places for all the densities considered here. The cutoff values of $R_c^{(XO)}$ and $R_c^{(XH)}$ as determined from the locations of the first minimum of the $X-O$ and $X-H$ distribution functions for density $\rho=1.0 \text{ gm cm}^{-3}$ are included in Table II for $X=O, F^-, Cl^-,$ and I^- . Since the radial distribution functions of the low density systems either

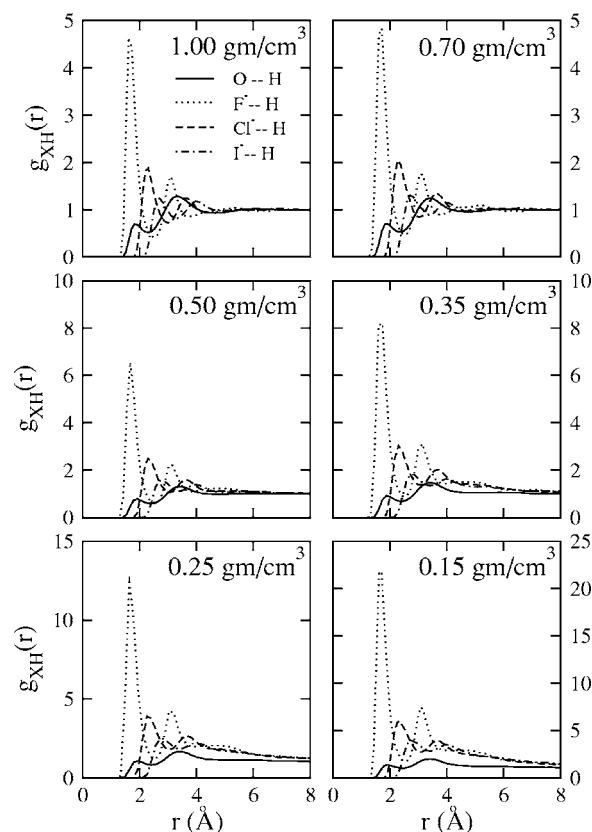


FIG. 2. The oxygen-hydrogen and anion-hydrogen radial distribution functions at 673 K for six different densities. The solid, dotted, dashed, and dashed-dotted curves are for oxygen-hydrogen, F⁻-hydrogen, Cl⁻-hydrogen, and I⁻-hydrogen correlations, respectively.

have a first minimum at essentially the same locations or do not show a prominent first minimum, we have preferred to use the same cutoff values for the $X-O$ and $X-H$ distances for all the six densities. As in ambient water,³ in supercritical solutions also both water-water and halide ion-water hydrogen bonds are found to be predominantly linear although less in number as compared to that in ambient water, and we have used an angular cutoff of 45° to give allowance for fluctuations from the linear geometry that can occur due to thermal motion. We note that this angular criterion is used in addition to the $X-H$ and $X-O$ distance cutoffs discussed above. We also note in this context that the integrated probability of hydrogen bond angle distribution essentially reaches its saturation value at $\theta=45^\circ$, so that any further increase of the cutoff angle θ_c would have practically no effect on the lifetimes or on the dynamical behavior of the hydrogen bonds. Thus, the results of hydrogen bonds that are presented here

TABLE II. The values of the ion(oxygen)-oxygen and ion(oxygen)-hydrogen cutoff distances used in the definitions of hydrogen bonds and hydration shells.

| X | $R_c^{(XO)}$ (Å) | $R_c^{(XH)}$ (Å) | $R_{c;2}^{(XO)}$ (Å) |
|-----------------|------------------|------------------|----------------------|
| O | 4.1 | 2.45 | 6.8 |
| F ⁻ | 3.4 | 2.45 | 6.1 |
| Cl ⁻ | 4.3 | 3.1 | 7.1 |
| I ⁻ | 5.0 | 3.35 | 7.8 |

TABLE III. The coordination numbers of anions and water molecules at different densities at 673 K.

| Ion/water | Density (g cm ⁻³) | | | | | |
|-----------------|-------------------------------|------|-----|------|------|------|
| | 1.0 | 0.7 | 0.5 | 0.35 | 0.25 | 0.15 |
| F ⁻ | 6.5 | 5.5 | 5.3 | 5.2 | 5.0 | 4.7 |
| Cl ⁻ | 10.5 | 8.2 | 7.8 | 7.0 | 6.4 | 6.0 |
| I ⁻ | 16.0 | 11.0 | 9.8 | 8.0 | 7.5 | 7.2 |
| Water | 9.5 | 6.5 | 5.0 | 4.0 | 3.0 | 2.5 |

would remain essentially the same when only the distance cutoffs are used without involving any angular cutoff. In Tables III and IV, we have included the average hydrogen bond numbers and also the coordination numbers of ions and water molecules at different densities. The coordination numbers are always found to be larger than the hydrogen bond numbers, implying that a number of water molecules that are not hydrogen bonded are always there in the hydration shells, especially so for the Cl⁻ and I⁻ ions. We note that the present results of the coordination numbers of the anions are in good agreement with the earlier results of Rasaiah *et al.*,²⁸ the slight differences can be attributed to the slight difference in temperature of the two studies.

IV. DYNAMICS OF HYDROGEN BONDS AND RESIDENCE TIMES

In order to calculate the dynamics of hydrogen bonds for different ion size and density, we first define two hydrogen bond population variables $h(t)$ and $H(t)$. The variable $h(t)$ 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 Sec. III 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. In order to study the breaking dynamics of hydrogen bonds, we calculate the continuous hydrogen bond time correlation function $S_{HB}(t)$, which is defined as^{3,29,48–51}

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

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

TABLE IV. The hydrogen bond numbers of anions and water molecules at different densities at 673 K.

| Ion/water | Density (g cm ⁻³) | | | | | |
|-----------------|-------------------------------|-----|-----|------|------|------|
| | 1.0 | 0.7 | 0.5 | 0.35 | 0.25 | 0.15 |
| F ⁻ | 6.0 | 5.0 | 4.8 | 4.6 | 4.3 | 4.2 |
| Cl ⁻ | 7.0 | 5.5 | 4.8 | 4.5 | 4.2 | 4.0 |
| I ⁻ | 6.5 | 5.0 | 4.6 | 4.4 | 4.0 | 3.8 |
| Water | 3.4 | 2.4 | 2.0 | 1.5 | 1.3 | 1.0 |

An alternative way to study the dynamics of hydrogen bonds is to calculate the so-called intermittent hydrogen bond correlation function $C_{HB}(t)$, which is defined as^{3,29,33,45–49}

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

Clearly, the correlation function $C_{HB}(t)$ does not depend on the continuous presence of a hydrogen bond. Rather, it describes the probability that an anion–water or water–water hydrogen bond is intact at time t , given that it was intact at time zero, independent of possible breaking in the interim time. Since the function $C_{HB}(t)$ allows recrossing of the dividing surface that separates the bonded and nonbonded states, its relaxation describes the local structural relaxation of hydrogen bonds.

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 re-formed 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, i.e., as nearest neighbors, but not hydrogen bonded at time t . $N_{HB}(t)$ is calculated from the simulation trajectories through the following correlation function:^{3,47}

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

where $g(t)$ is unity if the ion (oxygen)–oxygen distance of the ion–water or water–water pair is less than $R_c^{(XO)}$ at time t and it is zero otherwise. Following previous work,^{3,46–48} we can then write a simple rate equation for the “reactive flux” $-dC_{HB}/dt$ in terms of $C_{HB}(t)$ and $N_{HB}(t)$:

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

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. The inverse of the backward rate constant k'_{HB} can be interpreted as the average time over which a water molecule, after breaking its hydrogen bond with an ion or another water molecule, remains in the same hydration shell before it re-forms the hydrogen bond with the same ion or the water molecule. Thus, the backward rate constant k'_{HB} would measure how fast a hydrogen bond is re-formed after it is broken initially.

The results of the continuous correlation functions of the hydrogen bonds are shown in Fig. 3 for ion–water and water–water hydrogen bonds and the corresponding results for the intermittent correlation functions are shown in Fig. 4. The results are shown for all the six densities considered in the present study. Overall, the decay of $S_{HB}(t)$ for the F⁻-water and Cl⁻-water hydrogen bonds is found to be slower than that of water–water hydrogen bonds. The dynamics of I⁻-water and water–water hydrogen bonds are found to be very similar, especially at lower densities. For a given system, the relaxation of the intermittent correlation function $C_{HB}(t)$ is found to be slower than that of $S_{HB}(t)$ because of the presence of both hydrogen bond breaking and

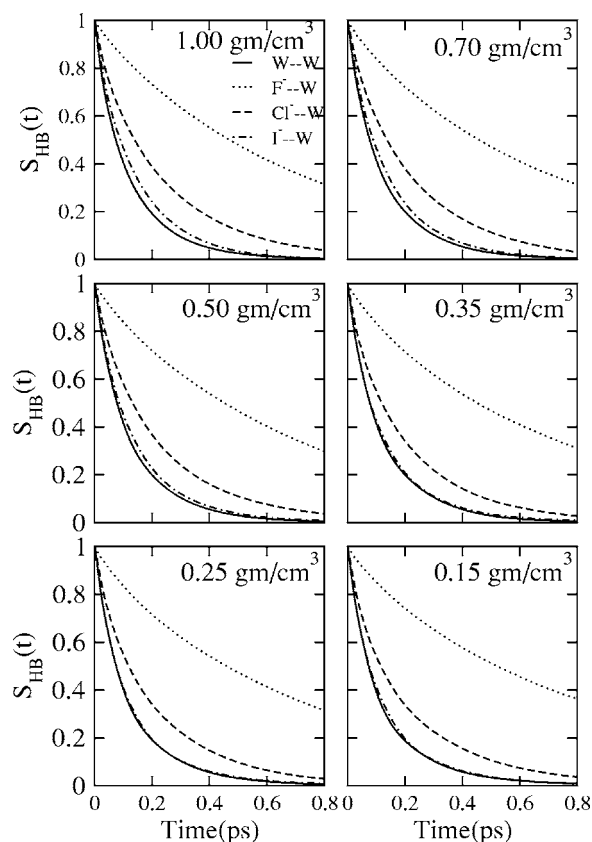


FIG. 3. The time dependence of the continuous hydrogen bond correlation functions at 673 K. The solid, dotted, dashed, and dashed-dotted curves are for water–water, F⁻–water, Cl⁻–water, and I⁻–water hydrogen bonds, respectively.

re-formation processes. In addition, the decays of both continuous and intermittent correlation functions are found to be significantly faster than those under ambient conditions found in earlier studies.³

In Fig. 5 (left panel), we have shown 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 are found to be slightly longer than that of Ref. 29, which is due to the fact that a smaller cutoff of $\theta_c=30^\circ$ was used in the latter study. Since the hydrogen bond lifetimes in supercritical solutions are not known experimentally, no direct comparison of the present results with those of experiments could be made. The longer lifetime of F⁻–water hydrogen bonds 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 relatively weaker. The Cl⁻–water hydrogen bonds are not as strong as F⁻–water hydrogen bonds but are still somewhat stronger than water–water hydrogen bonds, which explains their somewhat longer lifetimes than that of water–water hydrogen bonds. The lifetimes of I⁻–water and water–water hydrogen bonds are found to be very similar. Although the size of an oxygen atom is rather similar to the smallest ion of F⁻, the dynamics of water–water hydrogen bonds is found to be much faster

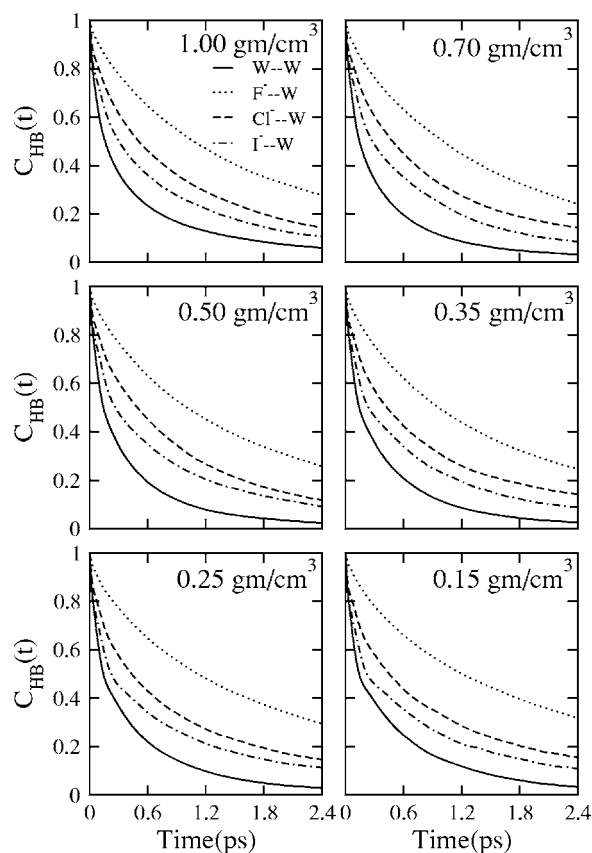


FIG. 4. The time dependence of the intermittent hydrogen bond correlation functions at 673 K. The results of both anion–water and water–water hydrogen bonds are shown. The different curves are as in Fig. 3.

than that of F⁻–water hydrogen bonds. We note that, while a F⁻ ion has a net charge of -1 , a water molecule is electrically neutral and it has a dipole moment. The net negative charge of the small F⁻ ions makes the F⁻–water hydrogen bonds very strong. For a water pair, on the other hand, the hydrogen atom of the donor not only interacts with the negatively charged oxygen atom of the acceptor, it also interacts with the positively charged hydrogen atoms of the same acceptor molecule and this combination of both attractive and repulsive interactions makes a water–water hydrogen bond not as strong as a F⁻–water hydrogen bond and this leads to a sig-

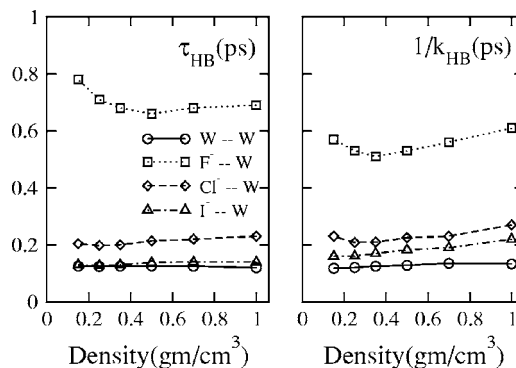


FIG. 5. The hydrogen bond lifetimes of anion–water and water–water hydrogen bonds as obtained from the routes of continuous and intermittent hydrogen bond correlation functions. The squares, diamonds, triangles, and circles are for F⁻–water, Cl⁻–water, I⁻–water, and water–water hydrogen bonds, respectively.

nificantly faster dynamics of water–water hydrogen bonds as compared to that of F^- –water hydrogen bonds.

Generally, the lifetimes of both ion–water and water–water hydrogen bonds are found to be significantly shorter than those found under ambient conditions³. For example, the lifetimes of F^- –water, Cl^- –water, I^- –water, and water–water hydrogen bonds were found to be 11.65, 2.40, 1.1, and 1.30 ps, respectively, under ambient conditions,³ which can be compared with the corresponding lifetimes of 0.69, 0.23, 0.14, and 0.12 ps found in the present study for supercritical solutions at the same density of 1.0 g cm^{-3} . The lifetimes change somewhat with changes of density but they always remain about an order of magnitude shorter for supercritical solutions than the corresponding lifetimes in ambient water. Clearly, as we move from ambient to supercritical conditions, the hydrogen bonds get weaker and they break at a faster rate due to the enhanced thermal motion of water molecules.

We used a least-squares fit of the simulation results of $C_{HB}(t)$ and $N_{HB}(t)$ to Eq. (6) to obtain the forward and backward rate constants, k_{HB} and k'_{HB} , respectively. The results of the inverse forward rate constants, which correspond to the average lifetimes of hydrogen bonds, are shown in Fig. 5 (right panel) so that these results can be readily compared with the hydrogen bond lifetimes (τ_{HB}) shown in the left panel of the same figure which are obtained from the route of continuous correlation functions. For a given density and ion, the values of τ_{HB} and $1/k_{HB}$ are found to be rather similar as expected, and the two dynamical quantities are found to vary in a similar manner with respect to their dependence on ion size and density. We note that with decrease of density, the hydrogen bond lifetimes generally decreases due to increase in the rates of rotational and translational motion of water molecules. The F^- –water system, and also to a much lesser extent the Cl^- –water system, show an increase of lifetimes with decrease of density in the very low density region. Although increased rotational and translational motion of water molecules tend to favor breaking of hydrogen bonds, the lack of cooperation with decreased density tends to keep a hydrogen bonded pair for a longer time when the hydrogen bond is sufficiently strong as it is observed for the F^- –water Cl^- –water systems. In Fig. 6, we have shown the results of the backward rate constants for all the systems. As stated earlier, the backward rate constant measures how fast a hydrogen bond is re-formed after it is broken initially, so that its inverse can be interpreted as the hydrogen bond re-formation time. It is found that re-formation times are the shortest for water molecules in the hydration shell of the F^- ion at all densities. It means that the water molecules in the hydration shell of this ion have the maximum propensity to remain hydrogen bonded. This result is consistent with the coordination and hydrogen bond numbers included in Tables III and IV, which show that, unlike other ions, nearly all water molecules in the hydration shell of the F^- ion are hydrogen bonded. The hydrogen bond re-formation times are found to be the longest for water molecules in the hydration shell of the I^- ion which again can be correlated with the fact that, on average, only less than half of the water molecules in the hydration shell of I^- ion are hydrogen bonded to this ion.

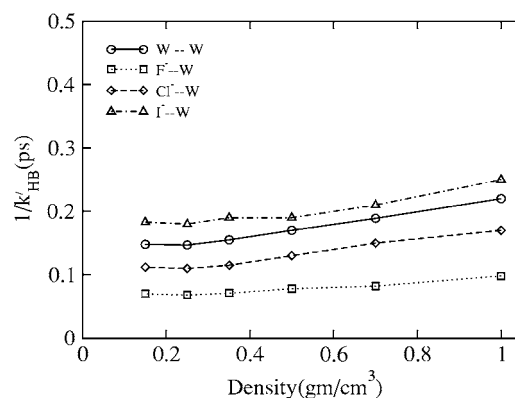


FIG. 6. The inverse backward rate constants of the dynamics of ion–water and water–water hydrogen bonds as obtained from least-squares fits of the intermittent correlation functions to Eq. (6). The different curves are as in Fig. 5.

In addition, these different re-formation times for different ion–water pairs explain why the decay of the continuous hydrogen bond correlation function for F^- –water pair is markedly different from other ion–water pairs whereas the decay of the intermittent correlation for F^- –water pair is not greatly different from other ions. The decay of the continuous correlation depends only on the lifetimes, or equivalently the forward rate constants, of a hydrogen bonded pair, whereas the decay of the intermittent correlation depends on both lifetimes and re-formation times, or equivalently the forward and backward rate constants of an ion–water pair. The presence of both breaking and re-formation processes with different rate constants for different ions makes the dynamics of intermittent correlations rather different from those of the corresponding continuous correlation functions.

The residence times of water molecules in hydrations shells can be obtained from a similar formalism involving the residence time correlation functions. We calculate the continuous residence correlation function $S_R(t)$, which 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 same hydration shell up to time t . The associated relaxation time τ_R , which we call the continuous residence time, corresponds to the time over which a water molecule resides in a hydration shell without ever leaving it. The intermittent residence correlation function $C_R(t)$, on the other hand, 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 . The second hydration shell is specified by an ion (oxygen)–oxygen distance cut-off $R_{c,2}^{XO}$ corresponding to the location of the second minimum of the X –O radial distribution function. The values of $R_{c,2}^{XO}$ as obtained from the

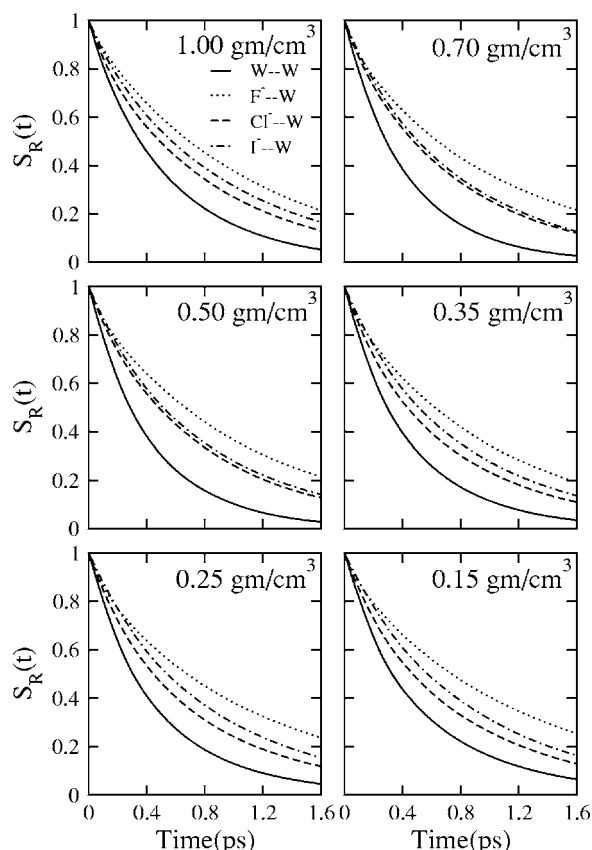


FIG. 7. The time dependence of the continuous residence correlation functions of water molecules at 673 K. The solid, dotted, dashed, and dashed-dotted curves are for water–water, F–water, Cl–water, and I–water pairs, respectively.

X–O distribution functions for density $\rho=1.0 \text{ g cm}^{-3}$, and subsequently used for all densities, are included in Table II for $X=\text{O}$, F^- , Cl^- , and I^- . The decay of the intermittent residence time correlation function is then described by a rate equation similar to Eq. (6) involving the forward and reverse rate constants k_R and k'_R , respectively. The inverse of k_R can be interpreted as the average residence time of a water molecule and can be correlated with τ_R obtained from the route of continuous correlation function $S_R(t)$, whereas the backward rate constant k'_R measures how fast a water molecule reenters a hydration shell after it left the same hydration shell at time $t=0$. The results of the continuous and intermittent residence correlation functions are shown in Figs. 7 and 8, respectively, and the results of the average residence times, τ_R and $1/k_R$ are shown in Fig. 9. It is seen that the values of $1/k_R$ are similar to the average continuous residence times τ_R obtained from the continuous hydrogen bond correlation function $S_R(t)$. The residence times are found to be consistently longer than the corresponding hydrogen bond lifetimes for all the ions. After an ion–water or water–water hydrogen bond is broken, the water molecule continues to stay in the hydration shell for some more time before diffusing away from the hydration shell. These dynamical results of the hydrogen bond and residence times are consistent with the average hydrogen bond and coordination numbers shown in Tables III and IV. The coordination numbers were found to be higher than hydrogen bond numbers because, at any point

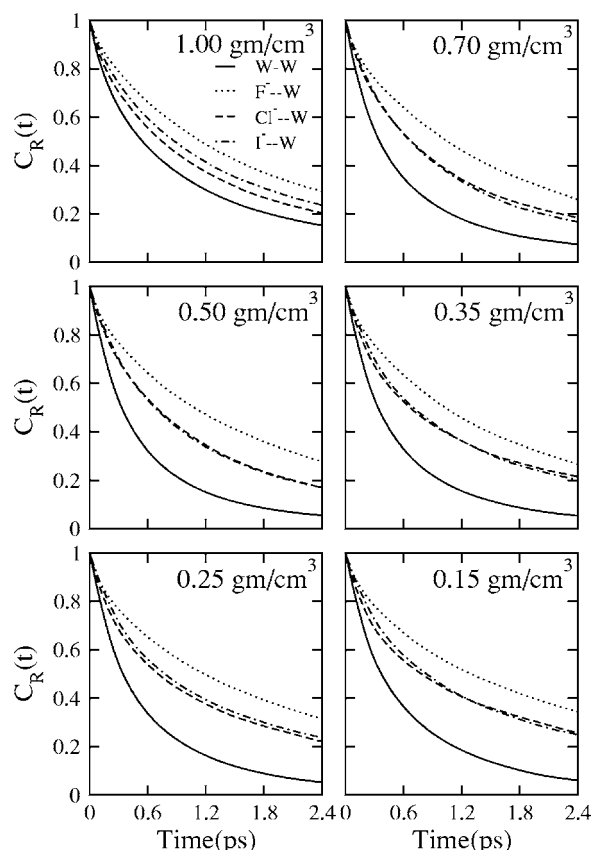


FIG. 8. The time dependence of the intermittent residence correlation functions of water molecules at 673 K. The results are shown for hydration shells of both anions and water molecules. The different curves are as in Fig. 7.

of time, some water molecules could be found in the hydration shells which were not hydrogen bonded. We note that the present results of the residence times of water in Cl^- hydration shells are found to be somewhat shorter than those reported in the recent study of Guardia *et al.*,²⁹ which can be attributed to a somewhat different way of calculations of the residence times in the latter study. In Ref. 29, the residence correlation functions were calculated by following the method of Impey *et al.*,⁵² which usually includes an arbitrarily chosen allowance time (typically 2 ps for ambient water) in the calculation of the residence correlation func-

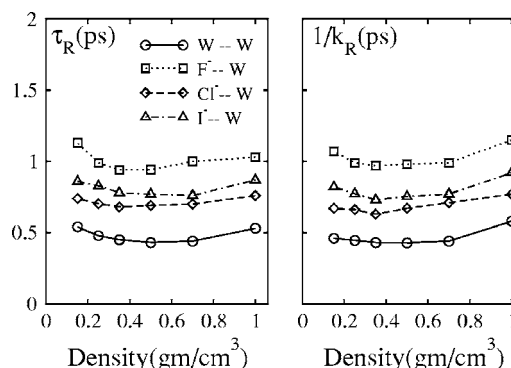


FIG. 9. The residence times of water molecules in the hydration shells of anions and water molecules at 673 K. The squares, diamonds, triangles, and circles represent residence times of water molecules in the hydration shells of fluoride, chloride, iodide ions, and water molecules, respectively.

tions, whereas in the present study no such arbitrary allowance time was incorporated in the calculation of the correlation functions.

V. ORIENTATIONAL RELAXATION OF WATER MOLECULES IN HYDRATION SHELLS

Since the residence times are found to be rather longer than the hydrogen bond lifetimes, we expect that the orientational motion of water molecules plays a more important role in the breaking of hydrogen bonds than diffusion. The orientational relaxation time τ_l^α is obtained as the time integral of the orientational correlation function:

$$\tau_l^\alpha = \int_0^\infty dt C_l^\alpha(t), \quad (7)$$

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

$$C_l^\alpha(t) = \frac{\langle P_l[e^\alpha(t) \cdot e^\alpha(0)] \rangle}{\langle P_l[e^\alpha(0) \cdot e^\alpha(0)] \rangle}, \quad (8)$$

where P_l is the Legendre polynomial of rank l and e^α is the unit vector that points along the α th axis in the water molecular frame. We have calculated τ_l^α for $l=1$ and 2 for two different e^α , the O–H vector and the H–H vector of a water molecule. These orientational relaxation times were obtained by explicit integration of $C_l^\alpha(t)$ from simulations until 0.6 ps and by calculating the integral for the tail from the fitted exponential functions. In order to obtain the orientational relaxation times of hydration shell water molecules, the above correlation function is averaged over only those water molecules that are found in the first solvation shell of the negative ion at time $t=0$. Since, under supercritical conditions, the orientational correlation functions relax very fast with times scales typically around 0.1–0.4 ps, which are shorter than the average residence times of water molecules around halide ions, 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 orientational relaxation. For the calculation of the orientational relaxation times of bulk water molecules, the orientational correlation functions were averaged over all water molecules excluding those in the solvation shells of the ions.

In Fig. 10, we have shown the results of the orientational relaxation times for the rotation of O–H vectors for $l=1$ and 2 for all the systems at 673 K. The orientational relaxation times of the H–H vector show very similar behavior and hence are not included in the figure. It is seen that the orientational relaxation of water molecules becomes faster with decrease of density and in addition, the dynamics slows down in the vicinity of the halide ions. Generally, the orientational relaxation times of hydration shell water molecules are not too different from the corresponding hydrogen bond lifetimes, which confirms the fact that the rotational motion of water molecules plays the primary role in the hydrogen bond kinetics in supercritical solutions. When it comes to the more detailed analysis of the rotational time scales, it is found that the extent of slowing down of rotational motion in the vicinity of an ion is, however, not as great as it was observed for the hydrogen bond dynamics, especially so for

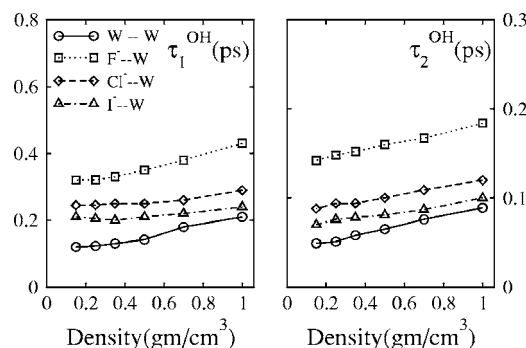


FIG. 10. The first- and second-rank orientational relaxation times of water molecules in the hydration shells of anions and water molecules at 673 K. The squares, diamonds and triangles represent the orientational relaxation times of O–H vectors of water molecules in the hydration shells of fluoride, chloride, and iodide ions, respectively, and the circles represent the corresponding orientational relaxation times in bulk water.

the fluoride ion. We note that the whole solvation shell might rotate keeping the relative distance of ion–water pairs unchanged. Such a motion of the whole solvation shell would contribute to the orientational relaxation of hydration shell water molecules but would not break the ion–water hydrogen bonds. This is likely to be significant for fluoride ion where the water molecules are held in the hydration shell relatively more strongly than those in the hydration shells of other ions. However, we stress that this argument of the rotation of the whole solvation shell is yet to be explicitly verified through numerical calculations. For water molecules in the hydration shells of other ions, the first-rank orientational relaxation times are found to be somewhat longer than the corresponding hydrogen bond lifetimes. It may be noted that the orientational relaxation time τ_1^α corresponds to the average time taken for the molecular vector e^α to rotate by an angle of about 68° , while a rotation by a smaller amount can break a hydrogen bond leading to a somewhat shorter hydrogen bond lifetimes as compared to the orientational relaxation times of water molecules in ion hydration shells.

VI. CONCLUSIONS

We have investigated the dynamics of anion–water hydrogen bonds in supercritical water for halide ions of different sizes and compared the results with those of water–water hydrogen bonds. The calculations are done at 673 K for six different water densities ranging from 1.0 to 0.15 g cm^{−3}. 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 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 ion–water hydrogen bonds are found to be shorter than fluoride ion–water but longer than water–water hydrogen bonds while the times scales of iodide ion–water and water–water hydrogen bonds are found to be rather similar. Generally, the lifetimes of both ion–water and water–water hydrogen bonds are found to be significantly shorter than those found under ambient conditions.^{1–3} Apart from hydrogen bond lifetimes, we have also calculated some of the structural quantities such as the ion–water and water–water radial distribution

functions, coordination, and the hydrogen bond numbers, which help to gain an insight into the hydrogen bonded structure of the solutions under supercritical conditions. In addition, we have also calculated the residence times and the orientational relaxation 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. The residence times are found to be significantly longer than the hydrogen bond lifetimes while the orientational motion of water molecules are found to play the primary role in the breaking of ion(water)–water hydrogen bonds.

In the present work, the SPC/E model⁴⁰ is used for water and the ions are modeled as charged Lennard-Jones particles with potential parameters developed by Dang *et al.*⁴¹ Although these fixed-charged models were originally developed for ambient water and aqueous solutions, we have employed them to model supercritical aqueous solutions in the present study as was also done in many of the earlier studies of supercritical water and aqueous solutions.^{28,29,34–37} Although an SPC/E water molecule has a dipole moment somewhat larger than that of a gas phase water molecule, the SPC/E water has been shown to have critical constants rather close to those of real water. In addition, the dielectric constant of SPC/E water in the supercritical region is much smaller than that of ambient water and agrees well with experimental values. The ion potentials have been shown to give good solvation and dynamical properties under ambient conditions and we assume that the fixed potential parameters would not cause significant errors in the calculated properties of the supercritical solutions. Nevertheless, it would be interesting to go beyond the fixed-charged models so that the effects of variations of the interaction potentials with thermodynamic conditions can be incorporated in the simulations. Such a study can be made by employing the method of *ab initio* molecular dynamics in which many-body interaction potentials are calculated quantum mechanically as the simulation progresses and thus no predefined empirical interaction potentials are used. Work in this direction is in progress.

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