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Ab initio molecular dynamics simulation of supercritical aqueous ionic solutions: Spectral diffusion of water in the vicinity of Br⁻ and I⁻ ions

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ABSTRACT

Supercritical aqueous ionic solutions containing bromide (Br⁻) and iodide (I⁻) ions have been studied using Car-Parrinello molecular dynamics simulation at two different concentrations and at two different densities. The time dependent trajectory has been used for calculating vibrational spectral diffusion, structural properties and, for other dynamical properties such as hydrogen bond dynamics, orientational relaxation and residence dynamics. The vibrational spectral diffusion of fluctuating OD stretch mode inside the solvation shell of the ions and in the bulk has been studied using frequency-frequency time correlation function. Hydrogen bond dynamics, orientational relaxation and residence dynamics of Sc-water have been investigated using population correlation function approach. The water molecules inside the solvation shell of Br⁻ and I⁻ ions are found to show complex molecular dynamics in comparison to the water-water dynamics. The concentration dependent spectral diffusion has been observed and it occurs in multiple time scales in the solvation shell of Br⁻ and I⁻ ions. At supercritical condition, the ion-water hydrogen bond shows faster dynamics with respect to the same at ambient condition and slower dynamics with respect to the water-water hydrogen bond dynamics at supercritical condition.

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1. Introduction

Supercritical fluids have been getting importance from the past several years because of their use as environmentally benign solvent medium in a wide variety of industrial applications such as food, cosmetics, pharmaceuticals, materials, chemistry, energy and waste treatment [1-6]. It can act as a substitute solvent in place of organic solvents in a range of industrial and laboratory processes because of several unusual properties like effusion through solids like gases and, dissolving materials like liquid due to non-existence of liquid and gas phases at supercritical condition [7-10]. One can easily tune the various properties of supercritical fluids by slightly changing the pressure and temperature because a small change in temperature and pressure can produce a large change in the density.

Aqueous solutions with charged species are of great interest in many physical and chemical processes. Several experimental as well as theoretical studies have been done to investigate the vibrational spectral diffusion of the aqueous ionic solutions containing F⁻, Cl⁻, Br⁻ and I⁻ ions at ambient condition [11-28]. At supercritical condition, experimental studies based on ion hydration and transport properties of solute had been done using UV-visible and NMR spectroscopic methods and also X-ray and neutron diffraction techniques [29-32]. On theoretical side, various theoretical studies have been done by Cummings and coworkers [33-35] and Rasaiah and coworkers [36,37] using molecular dynamics simulation and integral equation theory [32-39]. Most of their studies were done for hydration

structure and diffusion coefficients of alkali and halide ions over a wide range of density and temperature under supercritical conditions using empirical potential which is not appropriate to study phenomena at supercritical condition where the polarization effect will be significant enough to affect the physical and chemical properties of the aqueous ionic solutions. In 2011, Bhabani et al. [40] first performed *ab initio* MD simulation on supercritical aqueous chloride ion solutions at two different densities and at two different concentrations. Thus, they automatically included any state dependent polarization effects and many body interactions present in those complex solutions from first principle quantum chemical calculations. They mainly studied the structural and dynamical properties of supercritical water inside the solvation shell of chloride ion without using any empirical potential. They also looked at the vibrational spectral diffusion and hydrogen bond dynamics of Sc-water from non-linear spectroscopic perspective. According to their study, it has been found that the supercritical aqueous chloride ion solutions show faster hydrogen bond dynamics with respect to the ambient chloride ion solutions. However, no experimental and theoretical studies on the spectral diffusion of the aqueous ionic solution containing Br⁻ and I⁻ ions have been done yet at the supercritical condition.

In this work we have extended their studies to reveal the dynamics of water molecules inside the solvation shell of bromide and iodide ions as it is expected that the structure and dynamics of Sc-water will be different inside the solvation shell of bromide and iodide ions with respect to the dynamics of water molecules inside the solvation shell of ions at ambient condition. We have carried out our simulations for different densities and at different concentrations to see the effects of density and concentrations on the hydration shell structure and dy-

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Table 1

The details of all simulating systems at 673 K and for BLYP functional. The densities are calculated for heavy water with hydrogen mass of deuterium for convenience. The trajectory lengths at the production periods are given in ps.

Systems	Mass density (g cm ⁻³)	Name	N	Box length (Å)	Trajectory (ps)
Aq. Br ⁻	1.18 (1)	System1	64	12.418	25
"	0.41 (2)	System2	64	17.62	25
"	1.30 (3)	System3	64	12.98	33
Aq. I ⁻	1.22 (1)	System4	64	12.418	27
"	0.43 (2)	System5	64	17.62	26
"	1.33 (3)	System6	64	12.98	30

dynamics of supercritical water both inside and outside the solvation shell of the ions using Car-Parrinello molecular dynamics [41, 42] simulations without employing any empirical potentials. Wavelet analysis [43-46] has been done to the time dependent trajectories to calculate the frequency of OD stretch mode for all cases. Frequency-structure based relations have also been looked at to establish any relation between the particular OD stretching mode and ion-water and water-water hydrogen bond distances if they are found in Sc-water. Also, the rotational dynamics, hydrogen bond dynamics and residence dynamics of Sc-water have been calculated using population correlation approach for all solutions of different densities and concentrations.

Thus, we organized our paper as follows: in Section 2, the details about MD simulation has been given, equilibrium structural properties have been explained in details in Section 3 along with a brief discussion on dynamical properties such as hydrogen bond, dangling bond and, residence dynamics. The orientational relaxation in Section 4 and, spectral diffusion in Section 5 and a brief conclusion of this work has been given in Section 6, respectively.

2. Details of *ab initio* MD simulation

Total six *ab initio* MD simulations have been run. For each type of ions, we generated time dependent trajectories for two different densities and for two different concentrations using Car-Parrinello molecular dynamics simulation [41,42] and CPMD code [47]. For dilute system of strength ~ 1 M, we use one ion dissolved in 63 water molecules and, 7 NaBr dissolved in 50 water molecules and 8 NaI dissolved in 48 water molecules to maintain the strength of the systems around ~ 6 M for highly concentrated solutions. We set up two more simulations of density ~ 0.39 g cm⁻³ dissolving 1 halide ion in 63 water molecules for bromide and iodide ion. All simulations were carried out using cubic box with periodic boundary condition in all directions. The simulation box lengths used in these cases are 12.418 Å for high density and 17.62 Å for lower density dilute solution and 12.98 Å for high density concentrated solution, respectively. The simulation box length has been calculated from the experimental densities [48]. The details of all systems setup have been given in Table 1. To maintain the adiabaticity of the systems, we replaced hydrogen mass with heavy deuterium mass during MD simulations. For dilute solution, the charge neutralization has been done using uniform opposite background charge. Kohn-Sham density functional theory [49] within the plane wave basis has been used to represent the electronic structure of the extended systems. Troullier Martin pseudo potential has been used for the core electron treatment [50]. The valence electron has been treated using plane wave expansion of the KS orbital truncated at a kinetic energy cut-off of 80 Ry. For electronic orbital, fictitious mass $\mu = 800$ a.u. with a time step of 3 a.u. has been used in simulation. All simulations have been performed with BLYP functional [51,52]. The initial configurations for all systems have been generated using classical molecular dynamics simulation with empiri-

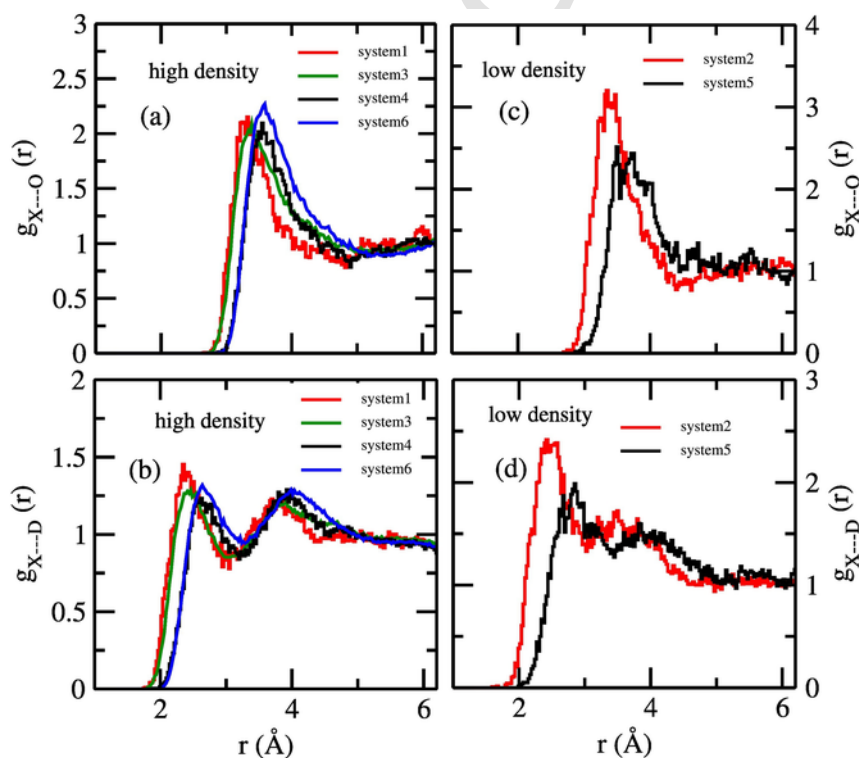


Fig. 1. Radial distribution functions for different interacting sites for both aqueous Br⁻ and I⁻ solutions at two different densities and concentrations. The density corresponds to the heavy water.

Table 2

The coordination and hydrogen bond numbers of ions and water molecules.

Quantity	Systems	Mass density (g cm ⁻³)	Inside anion	Inside cation	D ₂ O
N _{HB}	Aq. Br ⁻	1.18 (1)	6.12	-	3.34
N _{Coord}	"	1.18 (1)	15.10	-	12.12
N _{HB}	"	0.41 (2)	1.76	-	1.27
N _{Coord}	"	0.41 (2)	6.35	-	3.30
N _{HB}	"	1.30 (3)	4.84	-	3.56
N _{Coord}	"	1.30 (3)	15.66	5.02	10.59
N _{HB}	Aq. I ⁻	1.22 (1)	6.2	-	3.36
N _{Coord}	"	1.22 (1)	15.36	-	12.13
N _{HB}	"	0.43 (2)	2.23	-	1.28
N _{Coord}	"	0.43 (2)	7.37	-	3.32
N _{HB}	"	1.33 (3)	6.8	-	3.46
N _{Coord}	"	1.33 (3)	18.56	5.54	10.75

cal potential [53-55]. The final coordinates from the classical MD simulation has been taken after ~800 ps simulation in NVT ensemble followed by ~2 ns simulation in NVE ensemble. All ab initio MD trajectories have been generated after equilibration of ~10 ps in NVT ensemble and then run another ~25-33 ps in NVE ensemble for calculating the various equilibrium structural and dynamical properties. We note that the earlier study by Bhabani et al. [40] was done with comparatively shorter trajectory, with small system consisting of 32 molecules and for upto ~3 M concentrated aqueous chloride ion solution. Here, in this work we not only focus on the system size to overcome the system size effect on the equilibrium structural and dynamical properties, we also ran our simulations for highly concentrated aqueous ionic solution of strength ~6 M at supercritical condition and for two different densities for both Br⁻ and I⁻ ion solutions.

3. Structural properties, hydrogen bond, dangling bond and residence dynamics

Radial distribution functions for X...O and X...D for high and low density dilute solutions have been given in Fig. 1 (a) and (b), where X = Br⁻ and I⁻. For dilute solution, we have observed that the

peak heights of Br⁻...Y rdfs are overestimating with respect to the I⁻...Y, where Y = O and D, but the rdfs obtained with iodide ions are much wider in shape for all cases. The results for low density dilute solution have been shown in Fig. 1 (c) and (d). Also the higher peak height of I⁻...O rdf for concentrated iodide solution indicates to the stronger I⁻-water hydrogen bond formation with respect to the Br⁻-water hydrogen bond at supercritical condition. The results for concentrated solutions have been given in Fig. 1 (a) and (b). A geometric criteria has been used for defining hydrogen bond and this is as follows $R_{OD} \leq R_1$ for the water-water hydrogen bond and $R_{XD} \leq R_1$ for ion-water hydrogen bond, where X = Br⁻ and I⁻ and R_1 is determined from the O(Br⁻/I⁻)...D radial distribution functions for water-water and ion-water hydrogen bonds, respectively. Similarly, the free dangling OD modes inside the solvation shell and in bulk have been defined as $R_{XD} \geq R_1$, where X = Br⁻ and I⁻ and $R_{OD} \geq R_1$, respectively. These definition of hydrogen bonds have been used to investigate the dynamics of water molecules inside and outside the solvation shell of the halide ions. We have also used the hydrogen bond number and coordination number to further investigate the structural properties inside and outside the solvation shell of the ions for all systems. A general definition for hydrogen bond number is $N_{HB} = 4\pi\rho \int_0^{R_c} g_{XD}(r) r^2 dr$ and for coordination number is $N_{coord} = 4\pi\rho \int_0^{R_c} g_{OX}(r) r^2 dr$, where X = O, Br⁻ and I⁻, where ρ is the average number density and R_c is the cut-off distance that corresponds to the location of the first minimum of the X...D and X...O correlations; where X = O, Br⁻ and I⁻. The calculated percentage of ion-water hydrogen bond is ~40% for aqueous iodide and bromide ion solutions of high density dilute solutions, respectively. We note that the % of hydrogen bond numbers is less in iodide and bromide ion solutions at supercritical solutions with respect to the ambient condition for BLYP functional [27,28]. The decrease of % of hydrogen bond numbers indicates towards the less structured water at supercritical condition at the same density. The same quantity for low

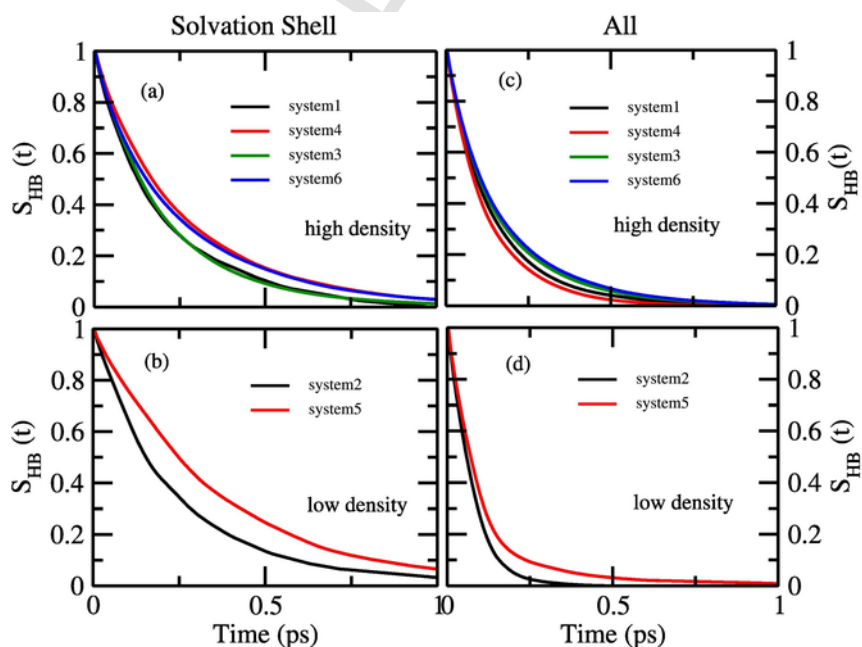


Fig. 2. Hydrogen bond dynamics inside the solvation shell and for all OD modes for both aqueous Br⁻ and I⁻ solutions at two different densities and two different concentrations. The density corresponds to the heavy water.

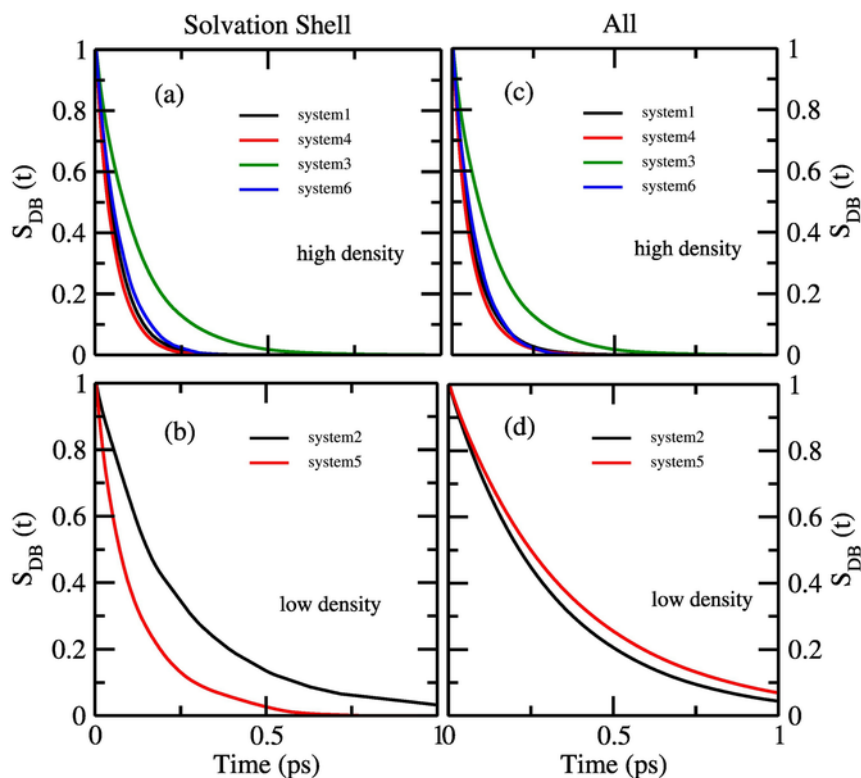


Fig. 3. Dynamics of dangling bond inside the solvation shell and for all OD modes for both aqueous Br^- and I^- solutions at two different densities and two different concentrations. The density corresponds to the heavy water.

Table 3

The average lifetimes of hydrogen bonds, residence times and dangling bond of water molecules in anion hydration shells and for all modes. All time scales are expressed in ps. Mass density has been used for heavy water (for convenience).

Quantity	Systems	Mass density (g cm^{-3})	Solvation shell modes	All modes
τ_{HB}	Aq. Br^-	1.18 (1)	0.20	0.15
τ_R	"	1.18 (1)	0.41	-
τ_{DB}	"	1.18 (1)	0.041	0.061
τ_{HB}	"	0.41 (2)	0.25	0.073
τ_R	"	0.41 (2)	1.59	-
τ_{DB}	"	0.41 (2)	0.08	0.35
τ_{HB}	"	1.30 (3)	0.22	0.15
τ_R	"	1.30 (3)	2.02	-
τ_{DB}	"	1.30 (3)	0.12	0.067
τ_{HB}	Aq. I^-	1.22 (1)	0.30	0.15
τ_R	"	1.22 (1)	2.21	-
τ_{DB}	"	1.22 (1)	0.05	0.062
τ_{HB}	"	0.43 (2)	0.36	0.11
τ_R	"	0.43 (2)	1.23	-
τ_{DB}	"	0.43 (2)	0.11	0.37
τ_{HB}	"	1.33 (3)	0.25	0.16
τ_R	"	1.33 (3)	2.41	-
τ_{DB}	"	1.33 (3)	0.10	0.057

density dilute solutions are 30% and 27% for aqueous iodide and bromide ion solutions, respectively at 673 K. For concentrated solutions, these numbers are 37% and 31% for supercritical iodide and bromide ion solutions, respectively. The strength of hydrogen bond network is low at higher concentration contrary to the results obtained at ambient condition for those aqueous ionic solutions because the polarity of Sc-water will be different and that will effect the hydrophilic property of liquid water at supercritical condition and will make the Sc-water less hydrophilic at such a higher temperature. The ion-water hydrogen bond percentage inside the solvation shell of I^- ion is also indi-

cating towards the formation of stronger hydrogen bond in iodide ion solutions. The water-water hydrogen bond is effected more in iodide ion solutions and shows faster hydrogen bond dynamics with respect to the water molecules in aqueous bromide ion solutions. The results for calculated hydrogen bond number and coordination number are given in Table 2. In the next few paragraphs, equilibrium dynamical properties of water molecules inside the solvation shell and in bulk for all bromide and iodide ion solutions have been discussed.

The hydrogen bond dynamics is calculated using two hydrogen bond population variables, $h(t)$ and $H(t)$. $h(t)$ is unity when a particular water-water pair is hydrogen bonded at time t according to the adopted definition and zero otherwise and $H(t)=1$, if a water-water pair remains hydrogen bonded continuously from $t=0$ to time t and it is zero otherwise. The continuous hydrogen bond correlation function is defined as [56-63]

$$S_{HB}(t) = \frac{\langle h(0)H(t) \rangle}{\langle h(0)^2 \rangle}, \quad (1)$$

The integral of $S_{HB}(t)$, denoted as τ_{HB} , can be interpreted as the average lifetime of a hydrogen bond. Similarly, one can calculate the dangling bond lifetime for the dangling OD bond defined using the definition stated above. The results for hydrogen bond dynamics and dangling bond of water molecules inside the solvation shell and in bulk have been shown in Figs. 2 and 3 and in Table 3. The ion-water hydrogen bond dynamics is slow inside the solvation shell of bromide and iodide ion and, also the lifetime of $\text{I}^- \cdots \text{D}$ hydrogen bond is more than the lifetime of $\text{Br}^- \cdots \text{D}$ hydrogen bond at supercritical condition. Thus it results in faster dangling bond dynamics inside the solvation shell of the ions for high density solutions. The presence of iodide ion

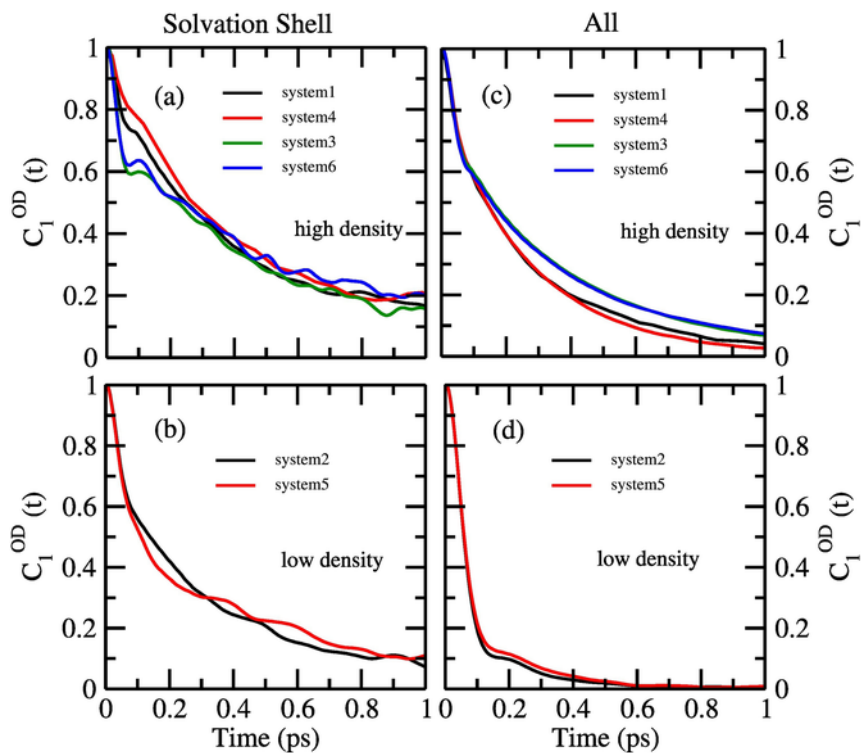


Fig. 4. Orientational relaxations of OD modes inside the solvation shell and for all OD modes for both aqueous Br^- and I^- solutions at two different densities and two different concentrations. The density corresponds to the heavy water.

Table 4

The time constants (weights) of rotational motion C_1^{OD} of D_2O molecules. The time constants are expressed in ps. Mass density has been used for heavy water (for convenience).

Quantity	Systems	Mass density (g cm^{-3})	Solvation shell modes	All modes
$\tau_1(a1)$	Aq. Br^-	1.18 (1)	0.07 (0.19)	0.15 (0.34)
$\tau_2(a2)$	"	1.18 (1)	0.60 (0.81)	0.31 (0.66)
$\tau_1(a1)$	"	0.41 (2)	0.05 (0.33)	0.06 (0.85)
$\tau_2(a2)$	"	0.41 (2)	0.44 (0.67)	0.29 (0.15)
$\tau_1(a1)$	"	1.30 (3)	0.03 (0.30)	0.05 (0.29)
$\tau_2(a2)$	"	1.30 (3)	0.58 (0.70)	0.46 (0.71)
$\tau_1(a1)$	Aq. I^-	1.22 (1)	0.19 (0.56)	0.06 (0.22)
$\tau_2(a2)$	"	1.22 (1)	0.62 (0.44)	0.29 (0.78)
$\tau_1(a1)$	"	0.43 (2)	0.07 (0.52)	0.07 (0.85)
$\tau_2(a2)$	"	0.43 (2)	0.37 (0.48)	0.25 (0.15)
$\tau_1(a1)$	"	1.33 (3)	0.04 (0.33)	0.05 (0.40)
$\tau_2(a2)$	"	1.33 (3)	0.70 (0.67)	0.54 (0.60)

affects the water-water hydrogen bond inside the solvation shell more than the bromide ion at 673 K. We looked at the hydrogen bond dynamics for all OD modes in high density dilute solution and the hydrogen bond dynamics are found to follow the dynamics of pure supercritical water indicating towards the local effects of ions on the dynamics of water molecules inside the first solvation shell of the

ions. The hydrogen bond lifetime for low density dilute solution inside the solvation shell increases from 0.25 to 0.36 ps from bromide (Br^-) to iodide (I^-) ions, respectively. The same for high density dilute solutions are 0.30 ps and 0.20 ps and the corresponding dangling bond lifetimes are 0.05 ps and 0.06 ps inside the solvation shell of iodide and bromide ions, respectively. The ion-water hydrogen bond shows faster dynamics at high concentration with respect to the dilute solution and this is also confirmed by the increase in the values of lifetime of dangling OD bonds from 0.06 ps for the dilute solution to 0.12 ps for the concentrated solution for bromide ion and from 0.05 ps for the dilute solution to 0.10 ps for the concentrated solution for iodide ion solutions at supercritical condition. The hydrogen bond lifetimes are 0.22 ps and 0.25 ps inside the solvation shell of concentrated bromide and iodide ion solutions, respectively. The ion-water hydrogen bond lifetime decreases in concentrated solutions at the supercritical condition with respect to the same at ambient condition [28,27]. The strength of ion-water hydrogen bond is found to increase in concentrated aqueous iodide ion solutions with respect to the aqueous bromide ion solutions and which is contrary to the results we already observed in case of aqueous ionic solutions at ambient condition [28,27]. Our results have been correlated with the dangling bond lifetime for all cases at the supercritical condition.

The residence bond dynamics has been calculated by using the continuous residence correlation function ($S_R(t)$) by following the method in Ref [27,28,64,65]

$$S_R(t) = \frac{\langle g(0)g'(t) \rangle}{\langle g(0)^2 \rangle}, \quad (2)$$

where $S_R(t)$ describes the probability that a water molecule, which was in the hydration shell of the ion at time $t = 0$, remains continu-

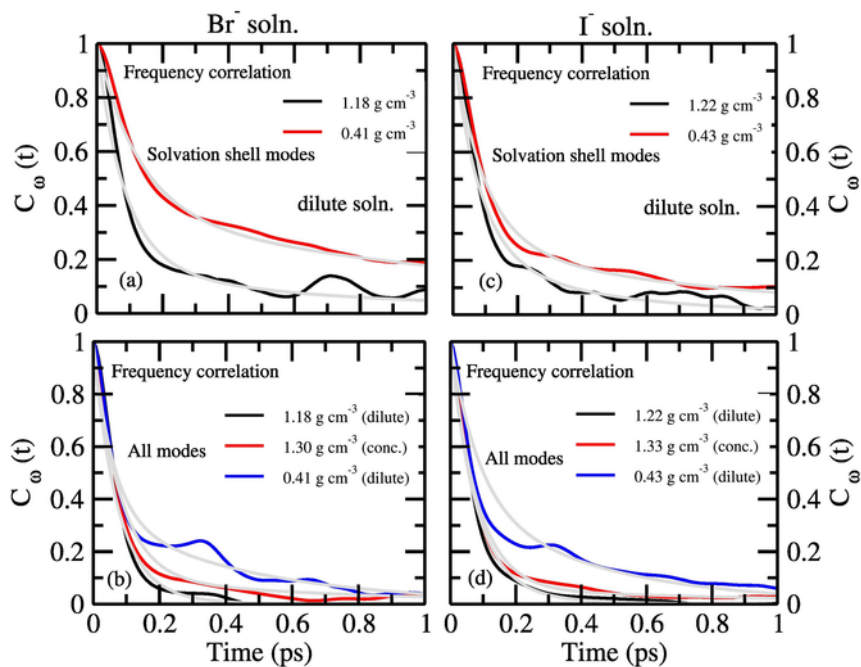


Fig. 5. Frequency correlation functions of OD modes inside the solvation shell and for all OD modes for both aqueous Br^- and I^- solutions at two different densities and two different concentrations. The density corresponds to the heavy water.

Table 5

The time constants (weights) of frequency time correlation function of heavy water. The time constants are expressed in ps. Mass density has been used for heavy water (for convenience).

Quantity	Systems	Mass density (g cm^{-3})	Solvation shell modes	All modes
$\tau_1(b1)$	Aq. Br^-	1.18 (1)	0.08 (0.67)	0.07 (0.89)
$\tau_2(b2)$	"	1.18 (1)	0.18 (0.12)	0.14 (0.11)
$\tau_3(b3)$	"	1.18 (1)	0.41 (0.21)	–
$\tau_1(b1)$	"	0.41 (2)	0.12 (0.54)	0.06 (0.66)
$\tau_2(b2)$	"	0.41 (2)	0.25 (0.10)	0.45 (0.34)
$\tau_3(b3)$	"	0.41 (2)	1.46 (0.36)	–
$\tau_1(b1)$	"	1.30 (3)	–	0.08 (0.90)
$\tau_2(b2)$	"	1.30 (3)	–	0.77 (0.10)
$\tau_3(b3)$	"	1.30 (3)	–	–
$\tau_1(b1)$	Aq. I^-	1.22 (1)	0.07 (0.63)	0.07 (0.90)
$\tau_2(b2)$	"	1.22 (1)	0.15 (0.20)	0.17 (0.10)
$\tau_3(b3)$	"	1.22 (1)	0.48 (0.17)	–
$\tau_1(b1)$	"	0.43 (2)	0.09 (0.70)	0.09 (0.60)
$\tau_2(b2)$	"	0.43 (2)	0.36 (0.12)	0.43 (0.40)
$\tau_3(b3)$	"	0.43 (2)	1.14 (0.18)	–
$\tau_1(b1)$	"	1.33 (3)	–	0.08 (0.94)
$\tau_2(b2)$	"	1.33 (3)	–	1.04 (0.06)
$\tau_3(b3)$	"	1.33 (3)	–	–

ously in the hydration shell up to time t and the associated relaxation time, which we call the residence time, is denoted as S_R . We calculated the residence time τ_R by explicit integration of $S_R(t)$ from simulations ~ 10 ps and by calculating the integral for the tail part from fit-

ted exponential functions. For our calculation of the residence dynamics, we have taken an allowance time 2 ps [27,28,64,65] for the continuous residence function. The results are given in Table 3. The associated integrated relaxation time τ_R gives the average residence time of water molecule in the hydration shell of an ion. The continuous residence dynamics is found to increase from high to low density for the dilute bromide ion solution, from low to high density for the dilute iodide ion solution and, from low to high concentration for high density solutions. The trend found in the residence dynamics has been correlated by the dynamics of hydrogen bond and dangling bond of water inside and outside the solvation shell of Br^- and I^- ions. In general, we observed slower water dynamics, in the vicinity of I^- ion with respect to the Br^- ion.

4. Orientational relaxation

It is already known from the previous study [24-28] that the breaking of hydrogen bond is effected by the rotational motion of water molecules. Thus, it will be interesting to look at the effect of rotational motion on hydrogen bond dynamics of water molecules at supercritical condition. The rotational dynamics of water molecules has been captured using orientational correlation function which is defined as follows

$$C_l^{OD} = \frac{\langle P_l[e^{OD}(t), e^{OD}(0)] \rangle}{\langle P_l[e^{OD}(0), e^{OD}(0)] \rangle}, \quad (3)$$

where P_l is Legendre polynomial of rank l and e^{OD} is the unit vector along the OD bond in the water molecular frame. The rotational dynamics inside the solvation shell is found to be faster from high to low density dilute solution and from high to low concentration for the Br^- and I^- ion solutions. The rotational motion of water molecules is hindered more inside the solvation shell of iodide ion. A biphasic decay has been observed in all cases consisting a fast decay due to iner-

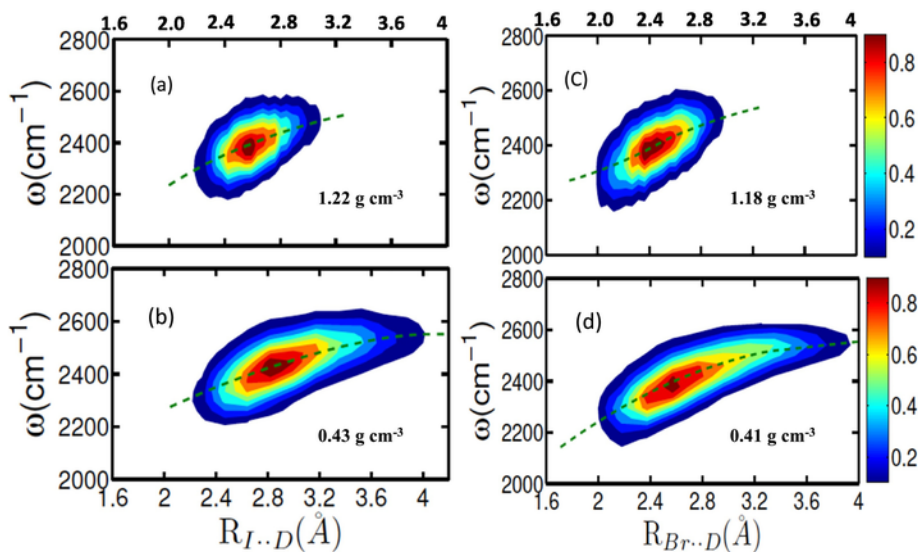


Fig. 6. Contour plots for solvation shell OD modes for both aqueous Br^- and I^- solutions at two different densities and for dilute solutions. The density is corresponding to the heavy water.

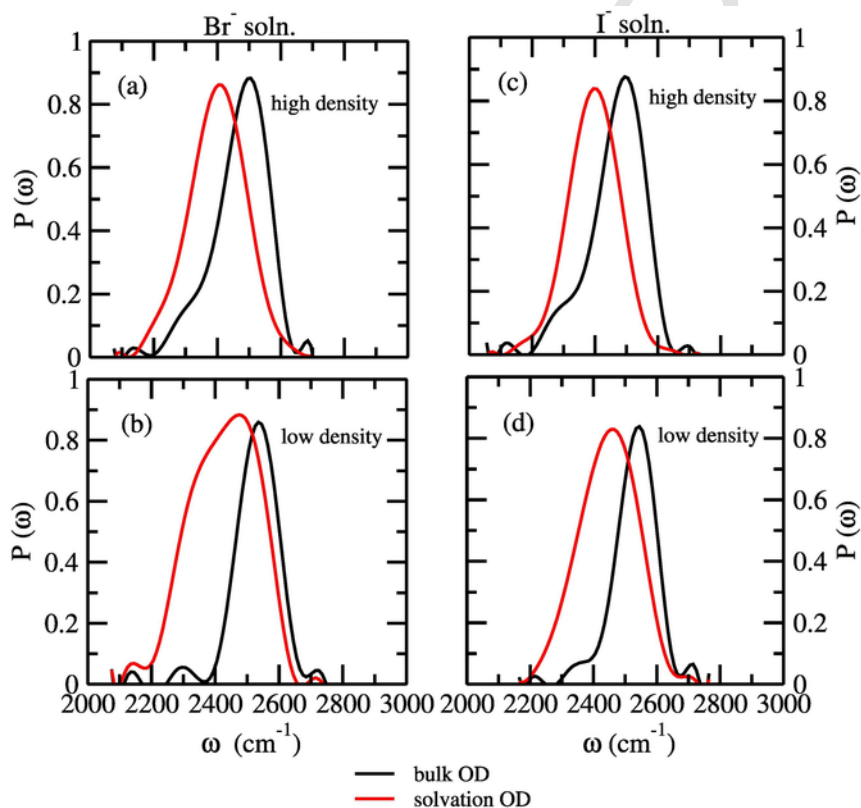


Fig. 7. Distribution of OD stretching frequency inside and outside the solvation shell of ions for two different densities and for dilute solutions. The density is corresponding to the heavy water.

tial rotation of the water molecules which is followed by a relatively slower decay. The results for rotational dynamics have been fitted using bi-exponential function with a short and long time scales of the type $C_l^{OD} = a_1 + a_2$ with associated weight $a_1 + a_2 = 1.0$. The results for rotational motion have been shown in Fig. 4 and Table 4. The results for all OD modes are found to follow the dynamics of pure supercriti-

cal water. Therefore, the effect of ions is local in nature and confined to the first solvation shell of ion for dilute solution. The slower dynamics at high ion concentration indicates towards the hindered motion of water molecules due to the increasing ion concentration which effects the rotational motion of water molecules more than the dilute solution where the ion concentration of the medium is less.

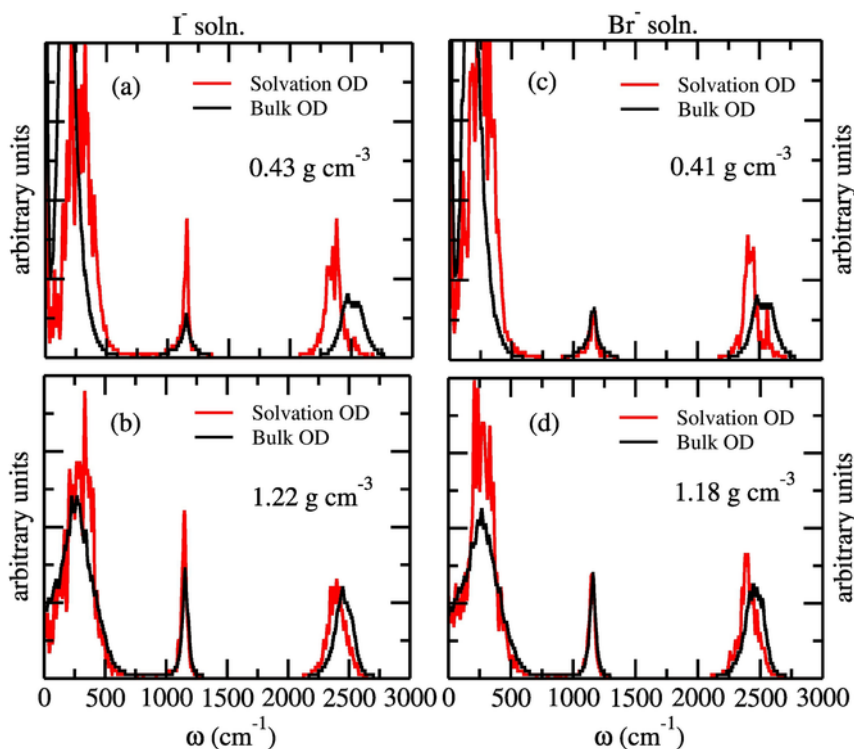


Fig. 8. The power spectrum of the velocity time correlation of deuterium atoms of heavy water in the I hydration shell (red) and in the bulk region (black) for (a) System 4 and (b) for System 5. The same has been shown for Br hydration shell (red) and in the bulk region (black) for (c) System 1 and for (d) System 2.

5. Spectral diffusion

The spectral diffusion inside the solvation shell of ions and for all OD modes are calculated using frequency-frequency time correlation function

$$C_{\omega}(t) = \frac{\langle \delta\omega(t)\delta\omega(0) \rangle}{\langle \delta\omega(0)^2 \rangle} \quad (4)$$

where $\delta\omega(t)$ is the fluctuation from the average frequency at time t . The dynamics of all water molecules are calculated over all OD modes and the above equation is averaged over the initial time.

The time dependent vibrational frequencies of the OD bonds have been calculated from the time dependent trajectory using wavelet method using time series analysis. In the wavelet method [43-46], a time dependent function $f(t)$ has been defined in the following way

$$\psi_{a,b}(t) = a^{-\frac{1}{2}} \psi\left(\frac{t-b}{a}\right) \quad (5)$$

The coefficients of this expansion are the wavelet transform of $f(t)$ which is defined as

$$L_{\psi}f(a,b) = a^{-\frac{1}{2}} \int_{-\infty}^{+\infty} f(t) \psi\left(\frac{t-b}{a}\right) dt \quad (6)$$

for $a > 0$ and b real. For the mother wavelet, we have used the Morlet-Grossman wavelet

$$\psi(t) = \frac{1}{\sigma\sqrt{2\pi}} e^{2\pi i \lambda t} e^{-\frac{t^2}{2\sigma^2}} \quad (7)$$

with $\lambda=1$, $\sigma=2$, and i represent the imaginary number. The wavelet transform of Eq. (7) produces a complex surface as a function of the variables a and b . The inverse of the scale factor a is proportional to the frequency and thus the wavelet transform at each b gives the frequency content of $f(t)$ over a time window about b . Following previous work [66,67], the time dependent function $f(t)$ for a given OD bond is constructed to be a complex function with its real and imaginary parts corresponding to the instantaneous fluctuations in OD distance and the corresponding momentum along the OD bond at time t . The stretch frequency of this bond at a given time $t=b$ is then determined from the scale a that maximizes the modulus of the corresponding wavelet transform at b . The process is then repeated for all the OD bonds that are there in a given system.

The calculated frequency-frequency time correlation has been fitted with a tri-exponential function $f(t) = b_1 e^{-\frac{t}{\tau_1}} + b_2 e^{-\frac{t}{\tau_2}} + b_3 e^{-\frac{t}{\tau_3}}$, where $b_1 + b_2 + b_3 = 1.0$ for the solvation shell OD modes while a bi-exponential function, $f(t) = b_1 e^{-\frac{t}{\tau_1}} + b_2 e^{-\frac{t}{\tau_2}}$, where $b_1 + b_2 = 1.0$, has been taken to fit the results for all OD modes. For the solvation shell OD modes of high and low density dilute solutions, the first short time scale corresponds to the time scale for dangling bond and fast inertial rotation of water molecules, the second small time scale corresponds to the ion-water hydrogen bond life time inside the solvation shell and the third long time scale corresponds to the residence dynamics of water molecules inside the solvation shell of the ions. For all OD modes and for high density solutions: first short time scale corresponds to the inertial rotation of OD bond and dangling OD

bond life time, second long time scale correspond to the hydrogen bond lifetime, while for low density dilute solution: first short time scale corresponds to the hydrogen bond lifetime and the second long time scale corresponds to the dangling OD bond lifetime. Overall, the calculated spectral diffusion inside the solvation shell of iodide ion is found to show a faster dynamics with respect to the same for aqueous bromide ion solutions for dilute solutions. This also indicates towards the strong interaction between the iodide ion and water at supercritical condition. All aqueous ionic solutions show faster spectral diffusion with respect to the ambient solutions. The calculated spectral diffusion for all OD modes is slow at high concentration for both the ions and the results are fitted using a bi-exponential function. At the concentrated solutions, it is very difficult to distinguish the solvation shell and bulk OD modes because water molecules will rapidly change their solvation shells due to the rapid molecular motion and thus will soon enter in another solvation shell of an ion without any noticeable change in OD stretching frequency. The spectral diffusion results have been shown in Fig. 5 and Table 5. We also observed that the spectral diffusion inside the solvation shell of ions occurs in multiple time scales and it gets slower from bromide to iodide ions for the concentrated solution. We also calculated the frequency structure correlations for water molecules inside the solvation shell of the ions. A one to one correlation has been observed between a particular OD stretching frequency and the corresponding ion-water hydrogen bond distance inside the solvation shell of Br^- and I^- ions in Fig. 6 and, that also indicates towards the correlation between these two quantities even at supercritical condition. The elongated feature of the contour plots along the X-axis indicates towards the presence of weaker ion-water hydrogen bond interactions at supercritical condition with respect to the ambient condition. A red shift has been observed in the solvation shell OD modes stretching frequencies with respect to the bulk OD modes indicating towards the formation of stronger ion-water hydrogen bond in the solvation shell of an ion at supercritical condition for both aqueous bromide and iodide ion solutions. The results have been shown in Fig. 7. We also calculated the power spectra for both the hydrogen bonded solvation shell OD modes and bulk OD modes for the low and high density solutions for aqueous ionic solutions containing Br^- and I^- anions. Unlike the blue shift observed in the case of aqueous halide ion solutions at ambient conditions, we observed a red shift in the OD stretching frequency of the hydration shell water molecules with respect to the all OD modes and the red shift is found to increase with the decreasing density of the solution and from the aqueous Bromide ion solutions to the aqueous Iodide ion solutions. This observation in the OD stretch frequency indicates towards the formation of stronger hydrogen bond between the Iodide ion and water molecule with respect to the hydrogen bond between Bromide ion and water molecule at the supercritical condition. The results have been shown in Fig. 8 (a) and (b) for the aqueous Iodide ion solutions and in Fig. 8 (c) and (d) for the the aqueous Bromide ion solutions.

6. Conclusions

A series of first principle calculations has been done to investigate the effects of hydrogen bond dynamics on spectral diffusion of aqueous ionic solutions containing bromide and iodide ions at supercritical conditions for two different densities and for two different concentrations. The main focus of the study has been given to the solvation shell structure of the bromide, iodide ions and the dynamics of water molecules inside and outside the solvation shell. The equilibrium structural properties have been investigated through the ion-wa-

ter pair correlations, hydrogen bond numbers, coordination numbers of the ions and water molecules and, frequency-structure correlations of water molecules in the bromide and iodide ion hydration shells and in bulk. For all cases, we observed a red shift in OD stretch mode in solvation shell with respect to the bulk OD mode. This indicates stronger ion-water hydrogen bond formation with respect to the water-water hydrogen bond formation in bulk contrary to the results obtained at ambient condition. Also, we observed a significant increase in average OD stretching frequency from higher to lower density which also indicates weaker hydrogen bond formation with decreasing density at supercritical conditions.

The dynamical properties have been gauged by the dynamics of hydrogen bond, dangling OD groups, residence dynamics and orientational relaxation of water molecules in ion hydration shells and in bulk for a particular density and concentrations. The ion-water hydrogen bond lifetime is stronger with respect to the water-water hydrogen bond lifetime at supercritical condition. We found these results qualitatively in good agreement with the classical results earlier obtained for the supercritical aqueous chloride ion solutions and the *ab initio* results obtained from Bhabani et al. The rotational dynamics of water molecules have been calculated both inside the solvation shell and in bulk solution. A biphasic decay has been observed for all cases consisting of a fast inertial and a slow diffusive components. The frequency-frequency time correlation has been calculated to investigate the dynamics of vibrational spectral diffusion. A connection between the spectral diffusion and underlying molecular motion has been created. The spectral diffusion of OD stretch mode is faster at supercritical conditions with respect to the ambient condition. The spectral diffusion of water molecules happens through the multiple time scales inside the solvation shells of ions: a faster time scale corresponds to the inertial rotations of water molecules and OD dangling bond lifetime, a much slower time scale corresponds to the ion-water hydrogen bond lifetime and a long time scale corresponds to the residence dynamics of Sc-water in the vicinity of halide ions. At low density, we observed slow dynamics and spectral diffusion of water molecules inside the solvation shell of ions because the distance between the molecules will increase at low density resulting in a decrease in the effective interactions between molecules at supercritical condition. The lifetime of hydrogen bond will be more inside the solvation shell of ion on average due to the lack of forming of instantaneous hydrogen bond in the absence of neighbor molecule at low density and hence will reduce the stochastic interactions between the hydrogen bond forming molecules and thus will result in slower spectral diffusion. At high concentration, it will become impossible to separate the solvation shell and bulk OD modes in terms of OD stretching frequencies because when a water molecule will leave the solvation shell of an ion it will soon enter the solvation shell of another ion and thus will create a very indistinguishable environment in terms of OD stretching frequency at such high concentration. The spectral diffusion for all OD modes is found to show slower dynamics with increasing ion concentrations for all cases as the spectral diffusion will appear as a collective phenomena of total number of ions present in the solutions and hence will be slower for the highly concentrated aqueous ionic solutions. For all OD modes, spectral diffusion has two time scales: a fast time scale corresponds to the dangling OD bond lifetime and fast inertial motion and the second long time scale appears due to the hydrogen bond lifetime for high density solutions, however we observed a different phenomena at low density solution: the fast time scale corresponds to the hydrogen bond lifetime and the long time scale corresponds to the dangling OD modes.

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