Importance of Solvents' Translational–Rotational Coupling for Translational Jump of a Small Hydrophobic Solute in Supercooled Water

Vikas Dubey, Nitesh Kumar, and Snehasis Daschakraborty*

Department of Chemistry, Indian Institute of Technology Patna, Patna 801103, Bihar, India

Supporting Information

ABSTRACT: Despite clear evidence of sudden translational jump occurrence of a solute in supercooled water, a detailed mechanism of this jump is still lacking. A previous work [Indra, S.; Daschakraborty, S. Chem. Phys. Lett. 2017, 685, 322–327] put forward a mechanism of this jump from an initial solvent cage to a final one. The proposed mechanism is astoundingly similar to that of the electron/proton transfer reaction in aqueous solution. The above study identified the spatial prearrangement (rearrangement before the jump occurrence) of cage forming water solvent molecules as the actual reaction coordinate. However, the study completely ignored the contribution of the orientational prearrangement of solvent water molecules. In this study, we have monitored both the spatial and the orientational prearrangements of water solvent molecules at subzero temperatures during the jump occurrence of the solute. We have found overwhelming contributions of both the spatial and orientational



prearrangements of water, which symmetrize the hydration structure at the initial and final cage positions to facilitate the jump event. Through a systematic temperature dependence study (from T = 240 to 270 K), we have found clear evidence that a strong synchronization between translational and rotational prearrangements of the solvent water molecules is crucial for the solute's jump from one solvent cage to another in supercooled water (below T = 252 K). The above translation-rotation synchronization is probably due to the cooperative movement of solvent water molecules forming clusters in the supercooled region. Since these cooperative dynamics are the consequence of the spatiotemporal heterogeneity in the medium, we infer that the large-amplitude translational jump of the nonpolar solute probably stems from the spatiotemporal heterogeneity of supercooled water. At temperatures above the melting point, this cooperativity is partly lost since the translational and orientational prearrangements become somewhat independent of each other.

1. INTRODUCTION

Decoupling between the self-translation and rotational diffusions of supercooled water (water below its freezing point) has been witnessed in recent experimental studies.^{1–} An increasing order of violation of the Stokes-Einstein (SE) relation-connecting the self-translation diffusion coefficient $(D_{\rm T})$ of the solvent through the radius (r) of the same molecule with the viscosity of the medium (η) by the equation $D_{\rm T} = k_{\rm B}T/6\pi\eta r$ —is witnessed with gradual cooling of the system from room temperature. On the other hand, the Stokes-Einstein-Debye (SED) relation-connecting the selfrotational diffusion coefficient (D_R) through the volume (V) of the solvent molecule with the viscosity of the medium (η) by the equation $D_{\rm R} = k_{\rm B}T/6\eta V$ —remains almost valid.

Similar decoupling is observed in other glass-forming liquids and solution of a tracer. Here, the translation diffusion of the solvent⁵⁻¹⁶ or the tracer¹⁷⁻²⁹ is decoupled from the rotational diffusion of the same entity. We note that the above violation of the SE relation is very similar for both the tracer and the solvent because the dynamics of the dissolved solute is naturally influenced by the solvent's motion. In most of the

cases, larger violation of the SE relation compared to the SED relation was found. However, the opposite picture also does exist in the literature. A molecular dynamics (MD) simulation predicted lager violation of the SED relation than the SE relation in supercooled water.^{17,23} This is exactly opposite of what has been observed in the recent experiment.¹ A more recent MD simulation,¹⁶ however, supported the experiment and showed that the violation of the SE relation is larger than that of the SED relation when the viscosity is incorporated in the calculation.

Multiple factors can cause the above decoupling between the translational and rotational diffusion in supercooled water. Microscopic spatiotemporal heterogeneity can be one of them. $^{30-49}$ It is also possible that the violation of SE relation in supercooled water can be due to the crossing of the Widom line, arising from the liquid–liquid critical point.^{3,4} Solute size is another factor for the above behaviors.^{20,24,28} It is

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worthwhile to mention that a recent MD simulation study has suggested that a strong coupling between the translation and rotational motions of a polyatomic ion in water may incite a violation of the SE relation.²¹ A hypothesis was put forward by Goldstein on the effect of temperature on the mechanism of translation of liquid molecules.⁵⁰ The theory states that at low temperature, the liquid molecules translate in the rugged freeenergy landscape and therefore hop from one free-energy minima to another through saddle points. On the other hand, the liquid molecules translate via free Brownian motion at high temperature as the thermal energy becomes comparable to the barrier heights or higher. Several theoretical and computer simulation studies confirmed characteristics of this picture.51-57 However, the detailed molecular mechanism for the solute's hopping from one free-energy minima to another is still elusive. Furthermore, the exploration of the detailed pathway of a translational jump of a hydrophobic solute in supercooled water is also important in cold denaturation of protein. A simulation analysis evidenced increase of fluctuation of some protein domains with decreasing temperature of the system, which plays an important role in cold denaturation of protein.⁵⁸ Also, the unexpectedly high fluctuating domains are generally localized within the protein core regions. It is well known that the water-soluble proteins have a hydrophobic core, in which side chains are buried from water, which stabilizes the folded state.^{59,60}

A recent study by one of us has focused on the pathway of the translational jump of a model nonpolar solute from one solvent water cage to another using classical molecular dynamics (MD) simulation.⁶¹ The solute rattles inside a clathrate-like cage of solvent water.⁶² After some waiting time, the solute escapes (partly through large-amplitude translational jump) from the cage and then gets trapped in a new cage. This rattling-jump-rattling mechanism is consistent with Goldstein's picture of molecular translation in liquid at low temperature.⁵⁰⁻⁵⁷ This study identified the solvent coordinate as the key reaction coordinate for the jump process. This solvent activated process is very similar to other solution-phase reactions like the Ando-Hynes picture (Grotthuss mechanism) of proton transfer (PT),⁶³⁻⁶⁶ the Marcus picture of electron-transfer reaction,⁶⁷ and the Laage–Hynes rotational jump mechanism of water.^{68,69} Presolvation of water molecules around the solute's future solvent cage position starts even when the solute continues rattling inside its initial cage. The solute jumps to the final cage only when the latter becomes structurally and energetically comparable to the initial cage, accommodating the solute. Therefore, the reaction coordinate for the solute's jump is the collective solvent coordinate instead of the solute's rattling motion inside the cage.⁷⁰

Notwithstanding the fact that the above study provided a great detail of the solute's jump mechanism from one water solvent cage to another and explored the role of spatial prearrangement of solvent water molecules, the role of the rotational prearrangement was completely ignored. Since there is a unique orientational structure of water solvent around a hydrophobic solute, $^{61,71-82}$ the jump of the solute to a new cage will be highly disfavored until the desired orientational hydration structure is attained via orientational prearrangement of the solvent water molecules around the new cage position. Therefore, the orientational prearrangement of solvent water is inevitable around the initial and final cage positions before a successful jump of the hydrophobic solute from the initial to the final solvent water cage.

In this article, we explore more detailed pathway of the jump mechanism of a very simple nonpolar solute, xenon (Xe), in water at various temperatures, ranging from T = 240 to 270 K. We study the role of both the spatial and orientational rearrangements of water solvent molecules around the Xe solute on the translation jump. Xe is indisputably a prototypical hydrophobic solute, and its hydration structure (both the spatial and orientational) resembles other popularly known hydrophobic solutes. like methane, ethane, etc., immersed in liquid water.^{82–89} Our primary objective is to monitor the translational and rotational rearrangements of nearby solvent water molecules with time during the solute's jump from one cage to another in supercooled water and water above freezing temperature. For the present study, we use MD simulation technique, which we detail below.

2. METHOD AND MODEL

2.1. Simulation Details. We perform MD simulation using GROMACS package.⁹⁰ One Xe solute molecule is dissolved in 500 water molecules in a cubic simulation box having periodic boundary conditions on all sides. TIP4P/2005 model⁹¹ of water, being one of the most successful models of water at subzero temperatures, is chosen here. The Xe solute is modeled as 12-6 Lennard-Jones (LJ) particle with force-field parameters described elsewhere.^{84,85} The solute-solvent cross parameters are deduced from the Lorentz-Berthelot mixing rules, which was proven to be correct for an aqueous solution of Xe.⁹² We have further validated this combination of the force fields of the Xe solute and water solvent in Section S1 of the Supporting Information (SI). We have compared the simulated diffusion coefficient of the solute with an experimental diffusion coefficient of the same solute at T =298 K. The unavailability of experimental results at the current temperature range (T = 240-270 K) has enforced us to check the validity of this combination of the force field at room temperature only.

We have simulated four different temperatures, 240, 250, 260, and 270 K, of which only the first two temperatures represent the supercooled state of water since TIP4P/2005 water freezes at 252 K.⁹¹ Equilibrations of all of these systems are performed for 10 ns. During the equilibration, the temperature is kept constant at the respective desired temperatures using the Nosé-Hoover thermostat,93,94 and the pressure at 1 atm using the Parrinello-Rahman barostat.95 We have set 0.5 ps for both the pressure and temperature coupling constant. We then extend the simulation for another 50 ns for obtaining the production trajectory. The Leapfrog-Verlet algorithm is used to solve the equations of motions every 1 fs time. The production trajectory is saved at a regular interval of 50 fs. A cutoff distance around half of the box length is applied for LJ interactions. The particle mesh Ewald summation technique and LINCS algorithm⁹⁶ are used to handle the long-range Coulomb interactions and to constrain the water O-H bonds, respectively. A 50 ns long production trajectory is utilized for analyses.

The validity of the above simulation protocol is ensured by the excellent agreements of the simulated density of the system with the experimental density^{97,98} (see Table S1 in the SI) and the simulated diffusion coefficients of the solvent water molecules (calculated from the mean square displacement (MSD) plot as a function of time) with the experimentally measured diffusion coefficients⁹⁹ (see Figure S2 in the SI) at all of the four temperatures. We note that while the above

experimental data are for pure water, the current simulation data are for the aqueous solutions of one hydrophobic solute. A quite good agreement between the experiment and the current simulation suggests that the small hydrophobic solute does not influence much the overall density and the diffusion coefficient of the solvent water, despite the fact that the interfacial water solvent molecules (next to the hydrophobic solute) have appreciably slower dynamics compared to the bulk water. $^{100-109}$ To elucidate further, we have carried out additional four simulations of pure water (500 TIP4P/2005 water molecules) at the same four different temperatures (T =240, 250, 260, and 270 K) using the same simulation protocol described in the previous paragraph. The final simulated densities are listed in Table S1 in the SI. These densities match well with the available experimental data. MSDs and the diffusion coefficients of the pure water at the four temperatures are reported in Figure S3 and Table S2 in the SI. The simulated diffusion coefficients of pure water are slightly closer to the experimental diffusion coefficients of pure water than that from our original simulations of the aqueous solutions of the Xe solute. This indicates that the solute reduces the overall diffusivity of water solvent only very slightly.

3. RESULTS AND DISCUSSION

3.1. Trapping of the Solute inside Solvent Water **Cage.** Trapping of the solute inside solvent water cage can be evidenced from the mean square displacement (MSD) of the solute.^{55,56,110-118} MSD is calculated using the equation $\langle |\Delta \mathbf{r}(t)|^2 \rangle = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$, where $\mathbf{r}(t)$ is the time-dependent position vector of the solute and r(0) is the solute's position at t = 0. Figure 1a exhibits MSD as a function of time for four different temperatures. The qualitative nature of the MSD plots match that of other supercooled liquids. The plateau region-in between the regular ballistic regime and the diffusive regime at the longer time-is subdiffusive with fractional time dependence $\langle |\Delta r(t)|^2 \rangle \propto t^{\alpha}$. This subdiffusive regime stems from the rattling motion of the solute inside the solvent water cage. We note that power law fitting of the MSD plots are carried out in between two stipulated time limits. While the starting time of the fitting is the moment when the ballistic regime completes, which is \sim 400 fs, the upper limit is the time when the non-Gaussian parameter $\alpha_2(t)$ is maximum (i.e., the time when the solute's dynamics deviates at the most from the Gaussian behavior). The method of calculating $\alpha_2(t)$ is detailed elsewhere.¹¹ Figure 1b presents $\alpha_2(t)$ of the solute as functions of time at four different temperatures. The maxima of $\alpha_2(t)$ plots are located at t = 7.3, 5.8, 3.3, and 2.2 ps at T =240, 250, 260, and 270 K, respectively. The power law fittings of the MSDs in the above time slices give the value of the exponents α as ~0.23, ~0.25, ~0.27, and ~0.35 for T = 240, 250, 260, and 270 K, respectively. Therefore, with decreasing temperature, the rattling part of the solute is further reinforced and therefore the solute gets trapped inside the water solvent cage for a longer time. The enhanced caging effect, with lowering the temperature, directly indicates the increased cage lifetime, ^{37,55,56,110–118} which may be due to the strengthening of water-water tangential H-bonds in the solvent cage with decreasing the temperature. The stronger H-bonding of cage water molecules at a lower temperature must increase the Hbond lifetime and thereby slows down the solvent cage opening process.^{118,119} Along with water's structural transformations (stronger H-bonds etc), one may also expect the increase of the cage lifetime and decrease of the diffusion



Figure 1. (a) Mean square displacement of the solute and (b) non-Gaussian parameter $\alpha_2(t)$ as functions of time at four different temperatures, T = 240, 250, 260, and 270 K.

coefficient to be simply related with the decrease of kinetic energy of Xe in solution at a lower temperature.

We now study the structure of the solvent water cage. The spatial and orientational structures of the water molecules around the solute are shown in Figure 2. Figure 2a presents two-dimensional probability density distribution $(P(r,\theta))$ of the angles θ —between water O_W ···Xe vector and the water O_W -H_w bond vector—and the distances *r* between water O_W atom and the Xe solute at T = 250 K. Similar figures at the other three temperatures (T = 240, 260, and 270 K) are presented in Figure S4 in the SI. Figure 2a shows that the firsthydration-shell water molecules (interfacial water molecules) $(r \sim 5.5 \text{ Å})$ are arranged in such a way that the majority water OH bonds are oriented either nearly tangential with the solute (tangential OH with $\theta \sim 65^{\circ}$) or toward the bulk water (bulk OH with $\theta \sim 180^{\circ}$). No water OH bonds are found aiming toward the solute (dangling OH with $\theta \sim 0^{\circ}$), persuading no H-bonds between the solute and the solvent water molecules. The above hydration structure of Xe solute guarantees that this solute acts perfectly like a small hydrophobic solute in TIP4P/ 2005 water solvent.^{71–81} We note that the peak situated at $r \sim$ 6.5 Å and $\theta \sim 0^{\circ}$ indicates that the majority of the second-shell solvent water OH bonds are aligned toward the solute such that these water molecules form H-bonds with the interfacial water solvent molecules.

Figure 2b presents radial distribution function (g(r)) between the solute and water O_W at four different temperatures. The first peak (intensity ~ 2.3) is located at ~4 Å and ranges up to ~5.5 Å distance. The slight increase in the first



Figure 2. Spatial and orientational structure of water molecules around the hydrophobic solute. (a) Radial distribution function between solute and water O atom (red solid line: values given by the right-hand-side ordinate axis) and two-dimensional probability density distribution of the angle θ between water O–H bond and the water O atom…Xe vectors in the *y* axis (values given by the lefthand-side ordinate axis) and the distance (between the Xe solute and solvent water O atom) in the *x* axis. (b) Radial distribution functions between Xe and water O atoms at the four different temperatures. (c) Angular distribution of θ for the first-hydration-shell (r < 5.5 Å) water molecules at four different temperatures.

peak height indicates slightly more ordering of interfacial hydration structure around the solute by decreasing the temperature. This is consistent with earlier studies.^{61,82} The normalized probability distribution $(p(\theta))$ of the angles θ —between the Xe…water O_W vector and the water OH bond vectors—is presented in Figure 2c for the interfacial solvent water molecules. Visibly, the majority of the interfacial water OH orientations are either tangential or bulk. The probability of the bulk OH orientation. However, the integration of $P(\theta)$ in the region $0^{\circ} < \theta < 65^{\circ}$ is almost equal to that in the region $65^{\circ} < \theta < 180^{\circ}$. So, nearly half of the cage water OH bonds are

oriented at $0^{\circ} < \theta < 65^{\circ}$, while the other half is aligned at $65^{\circ} < \theta < 180^{\circ}$. With decreasing the temperature, we find a slight increase of the orientational order of water since both the tangential and bulk peak heights increases to some extent by decreasing the temperature. Figure 2c also indicates that the probability of finding the dangling OHs is nil.

3.2. Translational Jump of the Solute: Time-Dependent Solute Coordinate. We now turn our focus on the translational jump of the solute from one solvent water cage to another. We first calculate the displacement of the solute along the trajectory with respect to its position at the starting point of the simulation trajectory. Then, we search for the translational jumps of the solute. Here, we define a jump by the large displacement of the solute at a short time interval. This method of identifying jumps suffices the purpose of understanding the jump mechanism of the solute.

Figure 3a presents an example of a such jump occurrence when the solute moves by \sim 4 Å in \sim 1 ps. This motion is much



Figure 3. (a) Small portion of the solute's displacement from 50 ns long trajectory at T = 250 K to show a representative jump. The large-amplitude jump of the solute from one cage to another is highlighted by the arrow; t = 0 ps is set at the time when the solute particle jumps from the initial to final cage. (b) Comparison of the probability distributions between the 41 jump distances, presented by a dashed line, and the total displacement of the solute (solid line), calculated at 1 ps interval. Note that the time required for completion of the jump is ~1 ps. Similar plots at other three temperatures are presented in Figures S5 and S6 in the SI.

faster than the normal diffusion of the solute with a diffusion coefficient value of 1.75×10^{-5} cm²/s, which suggests the movement of ~0.4 Å in ~1 ps. We have considered a set of such 41 large-amplitude jumps of the solute throughout the full 50 ns trajectory at T = 250 K. The number of translational jumps of 23, 49, and 71 are considered at T = 240, 260, and 270 K, respectively. In this section, we show the result only for

T = 250 K as the representative temperature. (The results for other three temperatures are shown in the SI.) The jump occurrence times and their amplitudes for all of the four temperatures are listed in Table S3 in the SI. Figure 3b presents the normalized distribution of displacements of the solute in 1 ps time duration (1 ps time is required for completion of a jump occurrence) for the full trajectory at T =250 K. The above distribution is obtained from samples of the start-to-end vector distances of 1 ps segments of the full 50 ns trajectory by progressively shifting the origin by 100 fs. The distribution of the 41 translational jump amplitudes of the solute is also plotted in the same figure. (The distributions at all of the four temperatures are presented in Figure S5 in the SI.) Since the displacement distribution—having a peak at 0.65 Å-has a long distance tail, it provides a clear signature of large-amplitude displacement of the solute. The peak of the 41 jump amplitude distribution is located around the tail of the displacement distribution. This confirms the validity of our choices of the translational jump occurrences of the solute.

Before calculating the solute jump coordinate, we investigate the contribution of these 41 translational jumps in the overall diffusion of the solute at T = 250 K. The detailed method for calculating jump-only diffusion coefficient D_{iumps}—diffusion coefficient solely due to the translational jumps of the solute— is described elsewhere.^{120,121} D_{jumps} is estimated as $D_{\text{jumps}} = (1/$ 6) $\nu \lambda^2$, where ν is the jump frequency and λ is the average jump length; ν is calculated by dividing the total number of jumps, considered in the calculation, by the total simulation trajectory length and λ is actually the linear distance between the initial and final cage positions of the solute. In the present case at T =250 K, $\nu = 0.82$ ns⁻¹, and $\lambda = 3.5$ Å. With both the numbers, we obtain $D_{\text{jumps}} = 1.92 \times 10^{-7}$ cm²/s, which is ~10% of the overall diffusion coefficient of the solute at T = 250 K (1.93 × 10^{-6} cm²/s), obtained from the MSD plot (see Figure 1a). We note that the present method of identifying a translational jump is completely based on the displacement of the solute with respect to the position at the starting time of the production trajectory. Despite the fact that this method suffices the objective of the present work, which is to comprehend the translational jump mechanism of the solute in supercooled water, the translational jump frequency is undermined in this method. A better way of jump characterization, such as a method based on the radius of gyration of solutes trajectory,^{120,121} can increase the contribution of the jumps in the overall diffusion of the solute. However, the applicability of the latter method in understanding the explicit mechanism of the jump from one solvent cage to another, especially the identification of reaction coordinate (as we have done here), is a matter of concern.

Now, we calculate the solute jump coordinate, Q_J , which is actually the position of the solute as a function of time during the jump from one water solvent cage to another. We obtain the Q_J parameter using the following equation⁶¹

$$Q_{\rm J} = \frac{[\mathbf{r}(t) - \mathbf{R}_{\rm i}] + [\mathbf{r}(t) - \mathbf{R}_{\rm f}]}{[\mathbf{r}(t) - \mathbf{R}_{\rm i}] - [\mathbf{r}(t) - \mathbf{R}_{\rm f}]}$$
(1)

We note that the above equation is motivated from the normalized proton transfer (PT) coordinate, a parameter to monitor the position of a transferring proton from a proton donor acid to a proton acceptor base during PT reaction.^{122,123} Here, r(t) is the time-dependent position of the solute and R_i and R_f are the average positions of the solute inside its initial

and final cages, respectively. This is essentially based on the assumption that the solute moves stochastically inside a solvent cage and covers the entire spherical space such that its average position is identical to the COM positions of the cage. We note that R_i and R_f mimic the positions of the acid and base, respectively, in an acid-base PT complex.^{122,123} Equation 1 is normalized in the sense that $Q_J = -1$ when the solute is inside the initial cage and $Q_J = 1$ when the solute is inside the final solvent cage. Figure 4a presents trajectory-averaged $\langle Q_J \rangle$ as a



Figure 4. (a) Solute jump coordinate as a function of time. Time evolution of the 41 trajectory-averaged jump coordinate $\langle Q_j \rangle$ (black solid line) with t = 0 fixed at the jump occurrence time for T = 250 K. While the vertical dashed line represents the jump occurrence time (t = 0 ps), $\langle Q_j \rangle = 0$ is indicated by horizontal dashed line. The inset displays $\langle Q_j \rangle$ during the jump occurrence from the initial cage to the final cage. (b) Speed of the Xe solute as a function of time. The speed shows quick increase at the jump occurrence time (t = 0 ps).

function of time for T = 250 K. ($\langle Q_I \rangle$ for all of the temperatures are shown in Figure S6 in the SI.) The trajectory averaging has been performed by first setting the jump occurrence time at t = 0 ps and then averaging Q_{I} for all of the 41 jumps (for T = 250 K). Figure 4a shows that $\langle Q_I \rangle$ remains almost constant at $\langle Q_I \rangle = -1$ before the jump occurrence time and quickly shifts to $\langle Q_I \rangle = +1$ after the jump occurrence via $\langle Q_{\rm I} \rangle = 0$, when the solute is in the middle of the two water solvent cages. It is evident, from the inset of Figure 4a, that the jump occurrence completes within ~ 1 ps time interval. The near constancy of the solute jump coordinate at $\langle Q_I \rangle = -1$ (before the jump occurrence) and $\langle Q_I \rangle = 1$ (after the jump occurrence) indicates that while the solute rattles inside the solvent cage, the overall motion of the solvent cage is almost negligible. However, the solvent water molecules forming the initial and final cages around the solute diffuse individually. We will see in the next section the time-dependent solvent reorganization to facilitate the solute's jump occurrence.

To elucidate further, we have plotted in Figure 4b, the trajectory-averaged speed of the solute, S_{Xe} , against time. Notably, S_{Xe} shows a quick rise at t = 0 ps. Therefore, the solute moves faster at the jump occurrence time than before and after the jump occurrence.

3.3. Role of Solvent Coordinate. 3.3.1. Equilibrium Structure. We now turn our focus to the role of solvent water for the jump occurrence of the solute. First, we examine how the spatial structure of the water solvent—forming the initial and the final cages—changes with time during the jump occurrence of the solute. The objective of this calculation is to understand how the final cage builds up during the jump occurrence at the cost of the dissolution of the initial cage.

We have plotted, in Figure 5, the spatial distribution of water molecules around the initial solvent cage position R_i and the final solvent cage position R_f at seven different instants of time



Figure 5. Spatial distribution of the water solvent molecules around the R_i (blue line) and R_f (red line) positions at seven different time intervals during the solute's jump at T = 250 K.

along the solute's jump trajectory at T = 250 K. (The results for other three temperatures are presented in Figures S7–S9 in the SI). These seven different instants connote seven different time intervals between t = -10 and 10 ps, where t = 0 ps refers to the jump occurrence time. These seven time intervals are: (i) t = -10 to -7 ps, (ii) t = -7 to -4 ps, (iii) t = -4 to -1 ps, (iv) t = -1 to 1 ps, (v) t = 1-4 ps, (vi) t = 4-7 ps, and (vii) t = 7-10 ps.

Figure 5a, g shows that the distribution near the R_i position is distinctly different from the one near the $R_{\rm f}$ position. Figure 5a shows that before the jump occurrence time, the distribution around R_i position is due to the hydrophobic hydration. This is consistent with the fact that the solute is situated inside the initial cage before the jump occurrence time. On the other hand, the distribution around the $R_{\rm f}$ position is merely parabolic with the distance from the $R_{\rm f}$ position. This parabolic nature signifies the increasing volume effect of the spherical shells with distance. Figure 5g shows that after the jump occurrence—when the solute reaches the final solvent cage—a complete reversal of the above hydration structure occurs near the two cage positions. While the distribution around the $R_{\rm f}$ position resembles the hydrophobic hydration structure, the distribution around the R_i position is parabolic with the distance. The similar nature of Figure 5a,g-including a complete switch of the hydration structures around the two cage positions-guarantees the successful jump of the solute from the initial to the final water solvent cage.

Comparative analyses of Figure 5a-c show that the distributions around the R_i position tend toward an equivalence with the distribution around the $R_{\rm f}$ positions as the time elapses toward the jump occurrence time t = 0 ps. Finally, at the jump occurrence time, the spatial distributions around the R_i and R_f positions become almost identical (see Figure 5d). This indicates complete symmetry of the hydration structures around the initial and final cage positions. The above symmetrization of the spatial hydration structure, by means of solvent water prearrangement around the two cages, is the key for the successful jump of the solute from one cage to another. The above spatial prearrangement was already observed in the preceding paper.⁶¹ The similar picture emerges while proton or electron hops from one site to another in aqueous solution.⁶³⁻⁶⁷ Comparative analyses of Figure 5e-g show that after the jump occurrence time, the distributions gradually differ from each other with time and the solute gets stabilized inside the final solvent cage position. The timedependent behavior of the solvents' spatial rearrangement will be discussed in Section 3.3.2.

Now, we turn our focus on how the orientational structures of the solvent water molecules near the R_i and R_f positions change with time during the jump of the solute. The orientation of solvent water molecules, which is actually the angular orientation of water OH bond vector, is characterized by an angle θ between the following two vectors: (i) the vector between the solvent water O_W atom and R_i (or R_f) position and (ii) water O_W···H_W bond vector. Figure 6 plots the distribution of the angle θ (corrected over solid angle) at seven different time intervals for the water near the R_i and R_f positions (r < 5.5 Å) at T = 250 K.^{71–81} (The distributions for the other three temperatures are exhibited in Figures S10– S12 in the SI.) Figure 6a,g, the orientational structure of solvent water molecules before and after the jump occurrence, shows that the angular distribution near the R_i position is distinctly different from the one near the R_f position both



Figure 6. Probability distribution of angles θ between water O–H bond vector and the vector between solvent water O··· R_i (R_f) position for the cage solvent water molecules at T = 250 K. The blue and red lines indicate the distributions around the R_i and R_f positions, respectively.

before and after the jump occurrence times. Before the jump occurrence time (see Figure 6a), the angular distribution around R_i is similar to that around Xe solute (see Figure 2c). On the contrary, the distribution around R_f position is almost uniform, indicating an approximately random orientation of water molecules around the final cage. After the solute jumps to the final cage (see Figure 6g), the above picture simply flips. Now, the angular distribution around the R_f position resembles

the angular distribution around the Xe solute (see Figure 2c). On the other hand, the angular distribution around the R_i position becomes almost uniform. The above role reversal around the two cage positions implies the successful completion of the complete process of the solute's jump from one cage to another.

A closer inspection of Figure 6a-c reveals that the orientational distributions around the R_i and R_f positions gradually symmetrize as the time approaches the jump occurrence time t = 0 ps. This is evident in Figure 6d, where these two distributions become almost identical. This symmetrization of orientational and spatial structures⁶¹ is crucial for the successful jump of the solute from one cage to another. Figure 6e-g shows that the two orientational distributions again start differing from each other with time after the jump occurrence time as the solute gets trapped inside the final solvent cage position.

Figures 5 and 6 indicate that the transformations of the spatial and orientational structures of the cage-forming solvent water molecules are not one-step processes. Instead, they require continuous rearrangement of water solvent molecules near the two cages such that the hydration structures near the initial cage are akin to that near the final cage position. These time-dependent spatial and orientational rearrangements of cage solvent water molecules will be discussed in the following.

3.3.2. Time-Dependent Rearrangement. In the preceding section, we have shown the spatial and orientational distributions of solvent water around the two reference positions, R_i and R_b at seven different times along the jump trajectory. We now follow the solvent water rearrangement process with time.

Spatial rearrangements of water solvent molecules are monitored separately in two key regions $(R_1 \text{ and } R_2)$. The regions R_1 and R_2 are identified from Figure 5 by the following distances criteria. The region R_1 is identified by the space inside the distance r = 3.5 Å from either of the two reference positions. On the other hand, the R2 region is limited by the distance criteria 3.5 Å < r < 5.0 Å. The following is the rationale of the separate analysis at the two different regions. Comparative analyses of Figure 5a-g show that while the spatial distribution of the water molecules inside the R₁ region continuously increases (decreases), the spatial distribution inside the R_2 region decreases (increases) gradually around the R_i (R_f) position with time. Therefore, the nature of changes of the spatial distribution depends on the location of the water solvent molecules around the reference positions (whether R₁ or R_2).

Figure 7a plots the number of solvent water molecules (N_W) inside the R₁ region around the R_i and R_f positions against time for T = 250 K. These are 41 jump trajectory-averaged plots. Figure 7a shows that while the number of water molecules N_W around the R_f position decreases from ~4 to ~2, N_W near the R_i position increases from ~2 to ~4. At the jump occurrence time (t = 0 ps), $N_W \sim 3$ near both the reference positions, R_i and R_f . Therefore, the symmetrization of spatial hydration structures near the R_i and R_f positions inside the R₁ region occurs due to the above prearrangement of ~1 water molecule before the jump occurrence time. This is important for solute's jump occurrence from the initial to the final solvent cage.

Figure 7b presents the time-dependent number of water solvent molecules, N_{W} , located in the R_2 region around the R_i and R_f positions. N_W increases with time near R_f position from a value of ~9 to ~13. Therefore, the inclusion of ~4 water



Figure 7. Number of solvent water molecules in two regions: (a) R_1 and (b) R_2 around the R_i (blue line) and the R_f (red line) positions as a function of time for T = 250 K. (Similar figures for T = 240, 260, and 270 K are presented in Figures S13, S14, and S15 in the SI, respectively.) The two regions R_1 and R_2 are specified from Figure 5. The region R_1 denotes the space inside the sphere of r < 3.5 Å from the initial or the final reference position of the solute, while the region R_2 denotes the spherical shell of width 3.5 Å < r < 5.0 Å.

molecules occurs in the R_2 region of the R_f position. On the other hand, near the R_i position, N_W decreases from a value of ~13 to ~9 after the jump occurrence of the solute. Therefore, the inclusion (exclusion) of ~4 water molecules in (from) the R_2 (R_1) region is the key rearrangement of solvent water around the final (initial) cage positions.

Presumably, about two of the total four newly added water molecules in the R_2 region of the R_f position come from the R_1 region of the same position. On the other hand, about two of the total four departed water molecules in the R_2 region of the R_i position go to the R_1 region at the same position. The remaining (two) water molecules may diffuse from the R_2 region of the R_i position to the same region of the R_f position. This spatial rearrangement of solvent water near the initial and final cages of the solute is crucial. Importantly, half of the total rearrangement occurs before the jump occurrence time t = 0ps. This prearrangement is the key solvent activation for this jump. (The time-dependent spatial rearrangement of solvent water at the three other temperatures, T = 240, 260, and 270 K, are shown in Figures S13, S14, and S15 in the SI, respectively.)

We now focus on the time-dependent orientational rearrangement of solvent water molecules near the initial and final cage positions, \mathbf{R}_i and \mathbf{R}_f . Here, we follow with time the rearrangement of water solvent molecules separately for four different orientations, characterized by the angle between solvent water O_W . We solute vector and solvent water $O_W - H_W$ bond vector (θ). The four different orientations are: (i) D (0° < $r < 45^\circ$), (ii) T₁ ($45^\circ < r < 85^\circ$), (iii) T₀ ($85^\circ < r < 145^\circ$), and (iv) B ($145^\circ < r < 180^\circ$). We note that the D-type

orientation is liable for H-bond formation with the solute. Therefore, D type is also called as dangling. The second type of water OH bond (T_I) is almost tangential to the solute surface (slightly inward). We call this group of OH bonds inner tangential ones. The third group (T_O) is in between the tangential and the bulk orientation. We term this group as outer tangential. The last group of water OHs (B) are oriented toward the bulk environment, and therefore, we call this group as bulk OH.

Figure 8a-d exhibits time-dependent arrangement of the above four differently oriented water solvent molecules near



Figure 8. Number of solvent water OH bonds as a function of time near the R_i (blue line) and R_f (red line) positions of the solute. The four panels present results separately for four differently orientated solvent water molecules. They are: (a) D (0° < $r < 45^{\circ}$), (b) T₁ (45° < $r < 85^{\circ}$), (c) T₀ (85° < $r < 145^{\circ}$), and (d) B (145° < $r < 180^{\circ}$). These four regions are identified from Figure 6. These results are for T = 250 K. (Similar figures for T = 240, 260, and 270 K are presented in Figures S16, S17, and S18 in the SI, respectively.)

the R_i and R_f positions. Figure 8a shows that the number of dangling water OH decreases from ~6 to ~3 near the $R_{\rm f}$ position. Increment by the same number occurs near the R_i position. The angular prearrangement of water OH bonds starts near the R_i and R_f positions at least 5 ps before the jump occurrence time and continues to happen until a final solvent cage is formed around the solute after the jump occurrence time. We note that the symmetrical hydration structures are formed around the two solvent water cage positions at the jump occurrence time (t = 0 ps). Figure 8b shows that the number of T_I water OHs near the R_f position increases from a value of ~ 13 to ~ 19 , while the same number of water OH (~ 6) decreases near the R_i position due to the jump of the solute. Similar to the prearrangement of the dangling OHs, the prearrangement of the T_I water OHs occur by ~50%. It is clear in Figure 8c that the number of T_O OHs near the R_f position decreases from ~ 19 to ~ 16 , while the same number of water OH (~3) increases near the R_i position due to the jump. Also, half of the total solvent orientational rearrangement occurs by the jump occurrence time (t = 0 ps). This is crucial for the

jump occurrence of the solute from the initial to the final cage. Finally, Figure 8d shows that the number of B-type water OH bonds increases from ~4 to ~6 near the R_f position, while the same number of water OH (~2) decreases near the R_i position due to the jump. Similar to the prearrangement of D OHs, the prearrangement of the T_I OHs occurs by ~50% at the jump occurrence time. (The time-dependent orientational rearrangements of solvent water at the three other temperatures, T = 240, 260, and 270 K, are shown in Figures S16, S17, and S18 in the SI respectively.)

The above prearrangement symmetrizes the hydration structures around the two solvent cage positions, as seen in Figures 5 and 6. This symmetrization facilitates the solute's jump from one cage to another. The similar prearrangement is also essential in proton-transfer reaction⁶³⁻⁶⁶ in water and rotational jump motion^{68,69} of liquid water molecules.

3.4. Synchronization of Spatial and Orientational Coordinates of Solvent Water. In this section, we compare the solvent spatial and orientational coordinates during the jump along with the solute jump coordinate. We note that the solute coordinate is actually the jump coordinate Q_J presented in Section 3.2. The solvent spatial and orientational coordinates are extracted from Figures 7 and 8, respectively. The methodology is discussed below.

First, we identify four different segments of each of the four rearrangement lines in Figure 7. This segmentation is based on the rate of change of $N_{\rm W}$. For instance, we have shown in Figure 9a the four different steps of the spatial rearrangement of the solvent water molecules in the R₁ region near the R_i and R_f positions at T = 250 K. To quantify the above, we have fit each segment with linear equations. The slopes of the straight lines, signifying the rate of the rearrangement processes, are listed in Table 1. These four steps are described below. First,



Figure 9. (a) Four different steps of the spatial rearrangement of the solvent water molecules in the R_1 region near the R_1 and positions at T = 250 K and their fittings with linear equations. (b) Five steps of the orientational rearrangement of the T_1 solvent water OH bonds near the two cages at T = 250 K and the linear fits.

Table 1. Rate of the Four Different Steps of the Spatial Rearrangement of Solvent Water in Two Regions (R_1 and R_2) of the Initial (R_i) and the Final Solvent Water Cage Position (R_f)

		rate of rearrangement (ps^{-1})						
regions	initial/final cage	Ι	II	III	IV			
R_1	$oldsymbol{R}_{ m i}$	0.077	0.748	0.206	0.017			
	$m{R}_{ m f}$	-0.052	-1.159	-0.164	0.042			
R_2	$oldsymbol{R}_{ m i}$	-0.205	-0.883	-0.162	-0.096			
	$m{R}_{ m f}$	0.096	3.313	0.397	0.022			

the rearrangement process starts slowly with a rate less than 0.2 ps⁻¹. Next, the process speeds up right before the jump occurrence time with a rate of ~0.8–3 ps⁻¹. The process then slows down to a rate of ~0.2–0.4 ps⁻¹ immediately after the jump occurrence time and then almost levels off ~5 ps after the jump occurrence time. Interestingly, the above rearrangement rates are comparable near the R_i and R_f positions at the same time interval. Therefore, the spatial rearrangement of the solvent water molecules near the R_i position occurs almost parallel to the solvent rearrangement near the R_f position. This motivates one to obtain an average picture of the spatial rearrangement of water solvent molecules. We will come back to the above averaged picture later in this section.

A similar picture emerges for time-dependent reorientational rearrangement of solvent water molecules for differently orientated water solvent molecules (D, T_{I} , T_{O} , B) at four different temperatures. Unlike translation, we identify five steps of the orientational rearrangement of the solvent water molecules near the two cage positions in Figure 8. Figure 9b represents these five steps of the orientational rearrangement of the T_I solvent water OH bonds near the two cages at T = 250 K. To get a more quantitative picture, we have fit the five steps of the rearrangement process with linear equations, the slopes of which are listed in Table 2. We note that the slopes

Table 2. Rate of Five Different Steps of the Orientational Rearrangement of Four Differently Orientated Solvent Water (D, T_{I} , T_{O} , and B) around the Initial (R_{i}) and Final Solvent Water Cage Positions (R_{f})

		rate of rearrangement (ps ⁻¹)						
regions	initial/final cage	Ι	Ш	III	IV	V		
D	R_{i}	0.031	0.103	0.817	0.192	0.028		
	$m{R}_{ m f}$	-0.021	-0.089	-1.276	-0.101	0.028		
T_{I}	$m{R}_{ m i}$	0.017	-0.269	-1.862	-0.262	-0.074		
	$m{R}_{ m f}$	0.027	0.435	1.603	0.442	0.029		
To	$oldsymbol{R}_{ m i}$	-0.018	0.330	0.655	0.132	0.166		
	$m{R}_{ m f}$	-0.008	-0.327	-1.574	-0.383	0.065		
В	$oldsymbol{R}_{ m i}$	-0.016	-0.122	-0.859	-0.070	-0.037		
	$R_{ m f}$	-0.003	0.150	0.548	0.144	0.027		

determine the rates of the rotational rearrangements. The above five different steps of the orientational rearrangement are: (i) insignificant rearrangement with negligible rate, (ii) slow rearrangement with a rate of $0.1-0.4 \text{ ps}^{-1}$, (iii) faster rearrangement with a rate of $0.6-2.0 \text{ ps}^{-1}$, (iv) slower rearrangement with a rate of $0.1-0.4 \text{ ps}^{-1}$, and (v) almost no rearrangement. Similar to the spatial arrangement, the rates of the rotational rearrangement processes near the R_i and R_f positions are very close to each other at the same time interval.



Figure 10. Solvent water translational coordinate $\langle Q_{ST} \rangle$ (blue lines), orientational coordinate $\langle Q_{SO} \rangle$ (red lines), and the solute jump coordinate $\langle Q_{J} \rangle$ (black lines) as functions of time at four different temperatures: (a) T = 240 K, (b) T = 250 K, (c) T = 260 K, and (d) T = 270 K.

Therefore, the orientational rearrangement of the solvent water molecules near R_i occurs almost parallel to that near the R_f position. This is the basis for calculating the average water solvent orientational coordinate.

Now, we calculate the normalized translational and rotational solvent coordinates using the following equations

$$Q_{\rm ST} = \frac{[N_{\rm W}(t) - N_{\rm W}(0)] + [N_{\rm W}(t) - N_{\rm W}(\infty)]}{[N_{\rm W}(t) - N_{\rm W}(0)] - [N_{\rm W}(t) - N_{\rm W}(\infty)]}$$
(2)

$$Q_{\rm SO} = \frac{[N_{\rm OH}(t) - N_{\rm OH}(0)] + [N_{\rm OH}(t) - N_{\rm OH}(\infty)]}{[N_{\rm OH}(t) - N_{\rm OH}(0)] - [N_{\rm OH}(t) - N_{\rm OH}(\infty)]}$$
(3)

In eq 2, $N_W(t)$ is the number of water molecules in either the R_1 or the R_2 region around the R_i and R_f positions of the solute at time *t*. We note that $N_W(t)$ is plotted as a function of time in Figure 7. $N_W(0)$ and $N_W(\infty)$ are the numbers of water molecules in either the R_1 or the R_2 region around the R_i or R_f position at t = -10 and 10 ps, respectively. In eq 3, $N_{OH}(t)$ is the time-dependent number of water OH aligned in either of the four possible orientations (D, $T_{1\nu} T_{O}$, and B) near the R_i or R_f position. $N_{OH}(0)$ and $N_{OH}(\infty)$ are the values of $N_{OH}(t)$ at t = -10 and 10 ps, respectively. Equations 2 and 3 are the normalized versions of the water solvent spatial and orientational coordinates in the sense that both the values of Q_{ST} and Q_{SO} are ca. -1, while the solute resides in the initial solvent cage before the jump occurrence and ~ 1 when the solute stays inside the final solvent cage after the jump occurrence.

Next, we obtain the average spatial and orientational solvent coordinates $\langle Q_{ST} \rangle$ and $\langle Q_{SO} \rangle$ using the following equations

$$\langle Q_{ST} \rangle = \frac{1}{4} [(Q_{ST}^{R_1} + Q_{ST}^{R_2})_{\mathbf{R}_i} + (Q_{ST}^{R_1} + Q_{ST}^{R_2})_{\mathbf{R}_f}]$$
(4)

$$\langle Q_{SO} \rangle = \frac{1}{8} [(Q_{SO}^{D} + Q_{SO}^{T_i} + Q_{SO}^{T_o} + Q_{SO}^{B})_{\mathbf{R}_i} + (Q_{SO}^{D} + Q_{SO}^{T_i} + Q_{SO}^{T_o} + Q_{SO}^{B})_{\mathbf{R}_i}]$$
(5)

In eq 4, the component Q_{ST}^{X} is the solvent spatial coordinate in the X region. The quantity Q_{SO}^{Y} , in eq 5, is the solvent orientational coordinate for Y-type-oriented solvent water molecules.

 $\langle Q_{\rm ST} \rangle$ and $\langle Q_{\rm SO} \rangle$ are plotted in Figure 10 against time at four different temperatures. The solute jump coordinate $\langle Q_J \rangle$ is also plotted in the same figure. Apparently, both $\langle Q_{ST} \rangle$ and $\langle Q_{SO} \rangle$ start increasing well before the solute actually jumps from the initial to the final water solvent cage at the jump occurrence time (t = 0). This indicates decoupling of the solute jump coordinate from the solvent coordinate. We note that this decoupling, actually originated from jump translation of the solute, may give rise to serious violation of SE relation, which connects the solute's translation with the viscosity of the solvent medium. The jump rotation (instead of small angle rotation) of water,^{68,69} ionic liquid,¹²⁴ deep eutectic mixture, ^{125,126} and some polyatomic ion⁸ also induce serious breakdown of SED relation. Both the $\langle Q_{ST} \rangle$ and $\langle Q_{SO} \rangle$ reach the value 0, indicating half prearrangement of the solvent water molecules to symmetrize the spatial and orientational structures of the initial and final cages, when the solute jumps to the new cage. Therefore, half of the full solvent rearrangement is the key for the jump process. The rest of the rearrangement of the solvent water occurs after the jump occurrence time. Closer inspections of Figure 10a,b further reveal that at the supercooled condition (T = 240 and 250 K), $\langle Q_{\rm ST} \rangle$ and $\langle Q_{\rm SO} \rangle$ almost overlap at almost all of the times from t = -10 to 10 ps. This indicates that the spatial and orientational rearrangement of solvent water molecules around the R_i and R_f positions occur almost at the same time. This synchronization of translational and rotational motion can also be termed as translation-rotation coupling. We note that the



Figure 11. Plot of the solvent water translational coordinate $\langle Q_{ST} \rangle$ against the solvent water orientational coordinate $\langle Q_{SO} \rangle$ at four different temperatures: (a) T = 240 K, (b) T = 250 K, (c) T = 260 K, and (d) T = 270 K. The blue straight lines are drawn through the data for visual guide.

above coupling of the two motions is very different from the conventional coupling between translational and rotational diffusion of solvent. While the rotational coupled translational motion purely refers to the concerted movement of translational and rotation (in the analogy of proton-coupled electrontransfer reaction), the coupling between translational and rotational diffusions refers to the validity of the two hydrodynamic relations, SE and SED relations. The synchronization of translational and rotational motions of supercooled water is the consequence of water solvent molecules forming cluster and moving cooperatively.^{1-49,57,127-137} This cooperative dynamics in supercooled liquid is usually related to the presence of spatiotemporal heterogeneities. This is the most important result, which infers that the spatially heterogeneous dynamics can result in jump translation of a nonpolar solute in supercooled water. With increasing the temperature of the medium above the freezing temperature, 252 K, the above overlap between the translation and rotational solvent coordinate decreases, indicating weak water solvent translation-rotation coupling for solute's jump motion from one solvent cage to another. This is evident from Figure 10c,d for T= 260 and 270 K, respectively.

To elucidate further, we have plotted $\langle Q_{ST} \rangle$ against $\langle Q_{SO} \rangle$ in Figure 11 at four temperatures. Figure 11d shows that at the highest temperature, T = 270 K, $\langle Q_{ST} \rangle$ increases from ca. -1to ~0 without much change of $\langle Q_{SO} \rangle$. This indicates the occurrence of translational prearrangement almost solely without significant rotational prearrangement of solvent water. Next, the translation takes the lead and the rotation is almost switched off. Therefore, the two processes occur almost independently from each other and give rise to the suitable structure of the cages for enabling the jump of the solute. Finally, after the jump occurrence, both the $\langle Q_{ST} \rangle$ and $\langle Q_{SO} \rangle$ increase together at the same rate, indicating rotation driventranslational rearrangement of the solvent after the solute's jump occurrence time. As we decrease the temperature to T =260 K, we see, in Figure 11, that $\langle Q_{ST} \rangle$ increases almost to 0 while $\langle Q_{\rm SO} \rangle$ increases to -0.5. Then, $\langle Q_{\rm SO} \rangle$ increases to 0, while $\langle Q_{\rm ST} \rangle$ increases only slightly to reach the value of exactly 0. After the jump occurrence of the solute, both the $\langle Q_{\rm ST} \rangle$ and $\langle Q_{\rm SO} \rangle$ increase together at the same rate, indicating rotationdriven translation of the solvent water during postjump rearrangement. This is similar to that at T = 270 K. As we further decrease the temperature to T = 250 K (2 K below the freezing temperature, T = 252 K), we see much stronger coupling between $\langle Q_{\rm ST} \rangle$ and $\langle Q_{\rm SO} \rangle$ at all times during the jump event. Both translation and rotation occur almost at the same rate. The similar coupling is also seen at T = 240 K. This further strengthens our proposition that there is an absolute necessity of synchronized translational and rotational movement of solvent water for successful translation jump of a nonpolar solute from one cage to another in supercooled water. However, the jump event does not require similar synchronization above the melting temperature of water. The above observation derives an important conclusion. The rotation-driven translational motion of solvent water in the supercooled state can be a crucial factor for the breakdown of the SE relation, which is observed in supercooled water. This picture is consistent with a recent simulation study,⁸ suggesting the role of rotation-assisted translation of a polyatomic ion in violation of the SE relation.

4. CONCLUSIONS

In this paper, we have put forward a mechanism of the translational jump of a nonpolar solute in TIP4P/2005 water both below and above its freezing temperature, T = 252 K. We have identified the water solvent's translational and rotational rearrangement as the reaction coordinates for the translational jump of the solute from one solvent cage to another. The solute jumps from the initial to the final cage only when the

spatial and orientational prearrangement of the solvent water molecules symmetrize the hydration structure around the solvent cage positions. Half of the total solvent rearrangement completes by the solute's jump occurrence time. Interestingly, a similar symmetrization of hydration structure around electron/proton donor and acceptor drives the electron/ proton transfer reaction (which are the solvent activated reactions) in the forward direction.⁶³⁻⁶⁷

The systematic temperature dependence study has shown that the above picture remains valid at all of the temperatures, we have studied here. However, the comparative analysis between the spatial and orientational prearrangements of solvent water at different temperatures dictates a very different story. In the supercooled region, both the translational and rotational prearrangements occur at the same time to facilitate the jump process. The above synchronization between the translational and the rotational motion of solvent water stems from the strong translation-rotation coupling in the supercooled medium. At this point, we must emphasize that the above translational-rotational coupling refers to the translational and rotational movements of water in a concerted way. This is different from the conventional definition of coupling of translational and rotational diffusion, which is purely hydrodynamic in nature because the latter coupling is characterized by the validity of the SE and SED relations. The above concerted translational and rotational movements are the result of cooperativity of the solvent water molecules in supercooled condition. The cooperativity actually originated from the spatiotemporal heterogeneity of the medium.1-49,57,127-137 Therefore, this study infers that the spatially heterogeneous dynamics in supercooled water can cause a solute molecule to diffuse via large-amplitude jumps from one solvent cage to another. As the temperature is increased above the freezing point, the above coupling decreases and the solvent's spatial prearrangement becomes somewhat independent of their rotational prearrangement near the solvent cage positions.

Finally, the present work explores the detailed pathway of jump translation of a very simple hydrophobic solute Xe in supercooled water. Due to that fact that the Xe solute closely resembles another relatively simple hydrophobic solute, like methane, ethane, etc., the current mechanism should be equally applicable to the translational jump of other small, purely hydrophobic solutes. However, the translational jump mechanism of slightly more complex solutes, like hydrophilic and amphiphilic solutes, where iceberg formation is not seen to occur,^{107–109} can be very different. More studies need to be conducted in this context.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.8b03177.

(i) Checking the validity of the combination of the solute's and water solvent molecule's force field, (ii) checking the validity of the simulation methodology and parameters by calculating the simulated densities of the system and the diffusion coefficients of water at the four temperatures, (iii) spatial and orientational hydration structure of the Xe solute at three different temperatures, (iv) table listing the jump occurrence times and their amplitudes at four different temperatures, (v) displacement distribution and the normalized jump coordinates

at the four different temperatures, (vi) spatial and angular distribution functions around the R_i and R_f positions at seven different time intervals during the solute's jump occurrence, and (vii) time-dependent spatial and angular rearrangement of solvent water molecules near the R_i and R_f positions during the jump occurrence of the solute (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: snehasis@iitp.ac.in.

ORCID 🔍

Snehasis Daschakraborty: 0000-0002-2694-7142

Notes

The authors declare no competing financial interest.

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