The opposite effects of sodium and potassium cations on water dynamics

(Supporting Materials)

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A: Further discussion on the observations of NMR, neutron scattering as well as fsIR experiments:

The results of NMR (Table.4 in ref.1) [1] suggest that Na^+ makes the water rotation slower (than that in pure water) while K^+ accelerates the water rotation. A similar phenomenon is also observed herein using the fsIR measurement. On the other hand, neutron scattering experiment [2] shows that "....hydration of both ions must involve significant disruption to the water network, with highly bent or broken hydrogen bonds...this bond bending is achieved not by disrupting the immediate tetrahedral-like coordination shell of a water molecule, but by modifying the second shell, which is pulled inward...under the influence of dissolved ions...". These observations imply an accelerating effect from both cations on jump component of rotation (consistent with the theoretical modeling result herein) due to their abilities to disrupt the hydrogen bond network, and therefore (if the ion effect on the diffusive rotation component was negligible as in the anion case) on the overall water rotation.

We note that neutron scattering measurement [2] also found that "...*if we look at the cation hydration shell, the orientational distribution of water molecules is broader around a K ion compared with a Na one*...". This observation, although indicating a stronger structure breaking effect of *K* ion on water structure, provides no insight on why potassium cation accelerate the water rotation while sodium retard it *comparing to that in pure water*, since it gives no information about whether the Na^+ -O(water) and K^+ -O(water) interactions are stronger or weaker *than the water-water hydrogen bonding*. In fact, the theoretical modeling results on the jump rotation components suggests that Na^+ -O(water) and K^+ -O(water) interactions are the influence on the jump component is much less significant than the influence from the aforementioned disrupting effect on the second water shell.

A further concern may be raised about the different concentration dependences between the results of NMR and fsIR experiments. In the NMR relaxation measurement, the combination of the B factors for the Na^+ (or K^+) cation and for the *SCN*⁻ anion (see e.g. table 4 in ref. 1) [1] leads to aoverall slope of respectively -0.01 M⁻¹ for *NaSCN* and of -0.08 M⁻¹ for *KSCN*, which suggests a net increment in both cases with increasing salt concentration. This is different from what was found in the ultrafast infrared anisotropy measurement (Fig.2 in main context).NMR T_1 relaxation measurement used for this matter [3] has the time resolution of millisecond to second, which is a time scale several orders longer than the residence time of water molecules in a certain local environment (typically several picoseconds). The NMR results therefore contain the highly averaged information of water rotations in various local environments as well as the information about fast exchanges between different states.Further, to connect the relaxation time constant and the molecular rotational time constants, complicated models containing both the intramolecular and intermolecular relaxations are adopted. In particular, the intermolecular component contains the information of both rotational and translational relative motions between the water molecules. On the other hand, what we measured using fsIR technique is specifically the rotation of water O-H bonds within picosecond time scale. How to directly compare the results of these measurements is still a question open to the future discussion.

B: Details of the Classical MD simulations:

Molecular dynamics simulations were carried out for the NaSCN and KSCN aqueous solution systems at a series of concentrations up to 2M. The SPC/E model [4]was used for the water molecules. Modified Dang models [5] were used for the ions, which were designed to be consistent with the SPC/E water model.

A series of research works have been reported on using *ab initio* calculation or polarizable force fields to obtain the more accurate description about the ion-water interaction and structure [6-8]. For the theoretical modeling in current work, however, the *ab initio* method is obviously too expensive for constructing the converged free energy profiles as well as inspecting the concentration dependences of the rotational times constants. We therefore only carried out the *ab initio* simulation at one concentration to validate the classical model (see section C). As for the polarizable models, to the best of our knowledge, no suitable model of SCN⁻ has been reported. On the other hand, a series of our previous works suggested that at least for the systems under study, the non-polarizable models we pick can reasonably reproduce the rotational dynamics of water. We emphasize that the simple models we pick by no means give the quantitatively accurate description of the ion effect. But we believe that the physical picture delivered in this work is correct.

The ion parameters are listed in Table S1. The cubical periodic boundary boxes were used in the simulations. The simulation boxes were constructed using the parameters in Table S2. The bond lengths and angles of water and SCN- were constrained at the equilibrium values (1.69 Å, 1.15 Å and 1.0 Å for the bond lengths of S-C, N-C and O-H; 109.47° and 180° for the bond angle of water and SCN⁻[9], respectively) by the SHAKE Algorithm [10]. The Lorentz-Berthelot rules [11] were used as the combination rule for the Lennard-Jones potential parameters. For each sample, a 5 ns NPT ensemble equilibration was carried out to obtain the proper size of the simulation box, followed by a 10 ns NVE ensemble simulation to calculate the dynamic properties. For each NPT simulation, the temperature is weakly coupled to a bath with the Nose-Hoover thermostats [12-13] at 298 K with the relaxation time of 0.1 ps. The weak coupling Berendsen scheme was used to control the system pressure at 1 atm with the coupling time constant of 1 ps [14]. The equation of motion was integrated using the velocity Verlet scheme [11] with a time step of 2 fs. The longrange Coulombic forces are calculated using the particle-mesh Ewald method [15]. The non-bonded van der Waals interactions are truncated at 12 Å using the switching function. Minimum image conditions [11] were used. All simulations are performed using the Tinker simulation code [16].

C. Details of *ab initio* MD simulation

We validate the physical picture provided by the classical model using the *ab initio* molecular dynamics simulations with the CP2K package [17]. Limited by the excessive computational expense, the *ab initio* simulations are only carried out in the 1M solutions and pure water.1M solutions have 2 ions (KSCN and NaSCN) and 120 water molecules, and the cube box size is 15.607 angstroms. The pure water is 120 water molecules, and the cube box size is 15.300 angstroms. The critical aspects of the CP2K simulation are based on the previous study [18].The Gaussian and augmented plane waves (GAPW) scheme is used, in which the electronic density is expanded in the form of plane waves with a cutoff of 280 Ry. In addition, Grimme's empirical dispersion corrections [19] are included. We choose revised Perdew-Burke-Ernzerhof as the exchange and correlation functional. Goedecker–Teter–Hutterpseudo-potentials [20] are used to treat the core electrons. Double-zeta split

valancebasis sets are used for all atomic kinds. The motion of nuclei follows Newton's equation of motion and is propagated based on the velocity Verlet algorithm [11] with a time step of 0.5fs. At each time step, the wave function is optimized based on the orbital transformation method, and the self-consistent field convergence criterion is set to 1.0×10^{-6} a.u. After using the Nosé–Hoover Thermostat [12-13] to run 15 ps for each system, we run 200 ps for each trajectory.

For the jump rotations, we calculate the hydrogen bond switching time correlation function (Fig.S4), since *ab initio* trajectories are too short to generate a converged jump time correlation function as in the classical simulation and the hydrogen bond switching time is the determining factor for jump contributions. The *ab initio* simulations also demonstrate that both Na^+ and K^+ accelerate the jump rotation. For the diffusive rotations, we calculate the diffusive rotational correlation function using all the hydrogen bonding water pairs (Fig.S4), which indicates that Na^+ slows down the diffusive rotation while K^+ slightly accelerates it. These observations are consistent with the results generated using the classical model.

The choice of XC functional is important for a proper description of water rotation. PBE functional, as pointed out by the reviewer, overstructures water and causes a too slow water rotational dynamics comparing to that observed in the experiments. revPBE functional [20] used herein is known to fairly speed up the rotation (comparing to PBE [21] as well as BLYP [22-24]) and has been applied extensively in the water dynamics simulation [25-32] Noticeably, recent reports suggested that incorporating vdW interactions into certain functionals might improve the liquid dynamics [24-28]. The study of the efficient and accurate description of vdW interaction is, however, still in a very early stage.

A recent work reported by Nagata and co-workers demonstrates that the trend of water dynamics for different DFT functionals is observed for pure water as well as for aqueous solutions [24]. We can therefore estimate that relative water rotational speed (a certain concentration of electrolyte comparing to pure water) is less affected by the choice of functionals since the systematic affect is probably canceled out.

Furthermore, in the same work, Nagata also demonstrates that water rotation is less sensitive to the basis set.

D. Computation of the rotational correlation time: The second-order reorientation correlation function $C^{\alpha}(t)$ of a molecule or ion in a solution is described as a second-order Legendre polynomial[33-35] along a molecular axis α :

$$C(t) = \frac{1}{2} \left\langle 3[\mathbf{e}(t) \cdot \mathbf{e}(0)]^2 - 1 \right\rangle (S1)$$

Where **e** is a unit vector pointing along this axis. The rotational correlation times were calculated by fitting in the time interval of 0.5~5 ps for which $\ln(C^{\alpha}(t))$ decreases linearly [33].

We can, similarly, define the rotational correlation function C(t) for a specific subspecies from the Eq. S1, with only the requirement that the target water or SCN-belongs to this subspecies at t = 0, regardless of the following status of the target molecule at t > 0.

We also find that the tendency of frame rotation in *KSCN* and *NaSCN* solutions is more consistent with that of viscosity of solution with concentration for any exchange type than the average rotational time constant (Fig. 1 in main text). This suggests that the frame rotation of hydrogen bond pair can more reflect the mobility of global structures than its jump and average rotations. The jump rotation of water seems strongly dependent on its local environment. In concentrated solutions, the *SCN:W* and *SCN:SCN* hydrogen bond pairs cooperatively rotate more slowly than *W:W* and *W:SCN* hydrogen bond pairs. This shows that the anion can retard the frame rotation of water bound to it at higher concentration.

E. Extended Molecular Jump model

The Extended Molecular Jump model [33-34] was developed to describe the rearrangement of hydrogen bond network in the water solutions. The hydrogen bond breakage and reformation is motivated by a large amplitude angular jump of water O-H bond from one hydrogen bond acceptor to another. The water O-H reorientation

correlation function can be expressed by the product of two independent correlation functions,

$$C_{I}(t) = \langle P_{I}[\mathbf{u}_{OH}(0)\mathbf{u}_{OH}(t)] \rangle = \langle P_{I}[\widetilde{\mathbf{u}}_{OH}(0)\widetilde{\mathbf{u}}_{OH}(t)] \rangle \times \langle P_{I}[\mathbf{u}_{OX}(0)\mathbf{u}_{OX}(t)] \rangle$$
(S2)

Where \mathbf{u}_{OH} is the OH reorientation in the laboratory frame OX, $\mathbf{\tilde{u}}_{OH}$ is the OH orientation in the local OX frame, and \mathbf{u}_{OX} is the OX H-bond axis orientation in the laboratory frame. X is the hydrogen bond acceptor of OH, here referring to a sulfur or nitrogen atom of SCN⁻ or a water oxygen atom. The two independent correlation functions decay exponentially, the O-H bond rotational time τ_{EMJ} can therefore be expressed as

$$\frac{1}{\tau_{EMJ}} = \frac{1}{\tau_J} + \frac{1}{\tau_f} (S3)$$

The jump times, τ_J , can be derived from the Ivanov model as:

$$\tau_{J} = \tau_{0} \left\{ 1 - \frac{1}{5} \frac{\sin(5/2)\theta}{\sin(\theta/2)} \right\}^{-1} \qquad (S4)$$

 τ_0 here is the hydrogen bond switching time, θ is the amplitude of the jump angle, which is defined as the angle O^aO^{*}O^b (O^{*}: donor water oxygen, O^a: the oxygen of the old acceptor water, O^b: the oxygen of the new acceptor water) at the transition state. These two parameters can be obtained from MD simulations and are the intrinsic variables depending on the H-bond types. In pure water their values are 3.3 ps and 68 °, respectively [33].

The switching starts at the moment that H* hydrogen bonds to O^a and ends at the moment that H*hydrogen bonds to a new partner O^b. Two water molecules are considered to be hydrogen bonded if the distance between their oxygens $R_{OwOw} < 3.1$ Å, the distance between their oxygens $R_{OwHw} < 2.0$ Å and the angle $\theta_{HOwOw} < 20^{\circ}$ (O_w: water oxygen atom; H_w: water hydrogen atom). The hydrogen bond between water and SCN⁻ forms when the distance of water oxygen and sulfur or nitrogen atom $R_{OwN} < 3.1$ Å ($R_{OwS} < 3.3$ Å, the distance between their oxygens $R_{NHw} < 2.0$ Å ($R_{SHw} < 2.3$ Å) and the angle $\theta_{HOwN} < 20^{\circ}$ ($\theta_{HOwS} < 25^{\circ}$).

The hydrogen bond switching time τ_0 is calculated based on the Stable States Pictures (SSP) [33-34]. The H-bond switching process is that the labeled hydrogen switches its H-bond acceptor from O^a to O^b. The switching event begins with the Hbond state of O-H*...O^a and end with the product state that the H-bond O-H*...O^a is broken and O-H*...O^b has been formed. The switching correlation function is defined as [33-34]

$$C_0(t) = \langle n_R(0)n_P(t) \rangle$$
 (S5a)

 $n_{\rm R}(0)$ and $n_{\rm P}(t)$ are the probability for the system to be in the stable reactant and product states. $C_0(t)$ presents a forming probability of a stable product at time t, when the system is in the reactant state at t = 0. The hydrogen bond switching time τ_0 can be derived from its complementary correlation function:

$$(1 - C_0) = exp(-t/\tau_0)$$
(S5b)

at time range of 0.5~5 ps.

The total correlation function of OH reorientation after a fast libration can be expressed as [34],

$$C_{2}(t) = \langle u_{OH}(0) \mu_{OH}(t_{W-W}) \rangle_{W-W} \langle u_{OH}(0) \mu_{OH}(t_{W-SCN}) \rangle_{W-SCN} \langle u_{OH}(0) \mu_{OH}(t_{SCN-W}) \rangle_{SCN-W} \langle u_{OH}(0) \mu_{OH}(t_{SCN-SCN}) \rangle_{SCN-SCN}$$
(S6)

By assuming the mono-exponential form for the correlation function of each switching type, the total correlation function and be expressed as:

$$e^{-t/\tau_{EJM}} = e^{-t_{W-W}/\tau_{W-W}} e^{-t_{W-SCN}/\tau_{W-SCN}} e^{-t_{SCN-W}/\tau_{SCN-W}} e^{-t_{SCN-SCN}/\tau_{SCN-SCN}}$$
(S7)

here t_i is the "effective" time of the OH in a specific switching type *i*. The time *t* is the summation of four effective times, $t = t_{w-w} + t_{w-SCN} + t_{SCN-W} + t_{SCN-SCN}$. τ is the reorientational time for each switching type that can be decomposed into the contributions from jump and diffusive components:

$$e^{-t_i/\tau_i} = e^{-t_i/\tau_i^J} e^{-t_i/\tau_i^f}$$
(S8)

During the measurement from initial time 0, the hydrogen of water can stay in any state, which means the switching processes defined above. When the hydrogen atom of water is at state *i*, the time index of t_i will run, but other stop. If summation equation as before is used, the hydrogen always stays at one state. There is no exchange from one state to another state for one labeled hydrogen. Each rotation type can be decomposed into two decoupled part as in pure water, in which the hydrogen bond only exchange from water to water, W-W type jump. If all the rotation correlation functions can be described with the single exponential function after initial fast decay of correlation function, the total rotation time approximately can be expressed as the Eq. 3 in the previous work [34]

$$\tau_{EMJ} \cong A_{W-W}\tau_{W-W} + A_{W-SCN}\tau_{W-SCN} + A_{SCN-W}\tau_{SCN-W} + A_{SCN-SCN}\tau_{SCN-SCN}$$
(S9)

A_i is the fraction of water hydrogen at state *i* and equal to the ratio of the effective time and real evolution time t, $A_i = t_i/t$.

The contribution of the jump rotation is determined by the hydrogen bond switching time and the jump angle from Eq. S4. The average value was adopted from previous work by Laage *et al*. Here an integration value from 0 to 180° is used as in Eq. S10, given that the distribution of jump angle is not symmetrical around the average value.

$$\langle \tau^{J} \rangle = \int_{0}^{\pi} \tau^{J}(\theta) p(\theta) d\theta$$
 (S10)

 $p(\theta)$ is the possibility of jump angle θ . This treatment is more reasonable, since $p(\theta)$ is not symmetrical around the average value. The hydrogen bond switching time is 3.3 ps for our work and in ref. S14.bby fitting the complementary correlation function Eq. S5 with single exponential function.

F. Details of the rotational time constant decomposition

Since the rotation of a water molecule in pure water as well as in the ionic solutions is closely related to the hydrogen bond switching, we can group the simulated hydrogen bond switching events into different types and rationalize the ion effects on each one of them. We first dissect the trajectories of tagged water molecule into a group of successive fragments. Each fragment starts at the moment that the previous switching finishes and the tagged water molecule (the hydrogen bond donor) forms the hydrogen bond with the current hydrogen bond acceptor, and it ends at the moment that the current switching completes and the tagged water molecule forms the hydrogen bond with the next hydrogen bond acceptor. The tagged water molecule can form the hydrogen bond either with another water molecule or with a SCN^{-} anion. We therefore categorize these fragments into four groups: from water to water (W:W), from water to SCN^{-} (W:SCN), from SCN^{-} to water (SCN:W) and from SCN^{-} to SCN^{-} (SCN:SCN). Their populations at different concentrations are presented in the supporting materials (Table S3).

Using a similar treatment as in [34], the difference between the rotational time constants of water at a certain concentration c and in pure water can be decomposed as:

$$\begin{split} & \left\langle \tau_{RP}(c) \right\rangle - \tau_{RP}^{Bulk} = \delta \tau_P + \delta \tau_{WW}^J + \delta \tau_{WW}^f + \delta \tau_{WSCN}^J + \delta \tau_{SCNW}^f + \delta \tau_{SCNW}^f + \delta \tau_{SCNW}^f + \delta \tau_{SCNSCN}^f + \delta \tau_{SCNSCN}^{f} + \delta \tau_{SCN$$

in which P_{ij} is the population of the hydrogen bond switching from i to j. $\tau_{ij}^{\alpha\beta}$ is the reorientation time of the hydrogen bond switching from i to j with the jump and frame contributions determined at concentration α and β , respectively. α and β stand for either the concentration c or the pure water. Note that for a anion related $\tau_{ij}^{\alpha\beta}$ containing a bulk term (either *i* or *j* is "SCN", and either α or β is "b"), the bulk

term was calculated in an infinitely dilute solution (in practice a 0.1M solution). The contributions from all the terms in Eq.S11 are presented in Fig S2.

The first term $\delta \tau_p$ (pale-blue bar in Fig.S2) represents the contribution from replacing the *W*:*W* type of hydrogen bond switching in pure water with the anion related types (*SCN*:*W*, *W*:*SCN* and *SCN*:*SCN*) in solution, assuming that each type has a concentration independent contribution to the overall rotation. $\delta \tau_p$ is always negative since the hydrogen bond between water and *SCN*-anion is weaker than the water-water ones. Each of the remaining eight terms in the first line of Eq.S11 describes how the jump or diffusive rotation of the tagged water molecule, during a certain type of hydrogen bond switching, is affected by the presence of the ions.

G. Further remarks on the free energy profiles along the average jump path

To study the effects of cations and anions separately, we select a dilute solution (0.1M) and inspect five types of the water-to-water hydrogen bond switchings: (1) No ion is adjacent to either donor or acceptor. (2) One cation in the first solvation shell of donor. (3) One anion in the first solvation shell of acceptor. (4) One cation in the first solvation shell of acceptor. The situation when a cation and an anion are bound to the same water molecule is not considered here because the probability of this condition is negligibly small in the dilute solutions (0.03% for KSCN and 0.02% for NaSCN in the 0.1M solution). Table S4 in the supporting information gives the jump rotational times of the donor water molecule during all these types of hydrogen bond switchings.

For each type of these water-to-water switchings, we present the time evolution of the free energy variation along the average jump path in Fig.S3 (details given in "*method*" section in main context). Time origin is chosen to be the moment that θ =0, where θ is the angle between the projection of the O*H* vector on the O*O^aO^b plane and the bisector of the O^aO*O^b angle (inset of the left panel of Fig.S3). Most of the water-to-water jump types (except when, occasionally, the cation is next to the acceptor water in the *NaSCN* solution) have the free energy barrier significantly higher than the overall SCN-to-water jump. On the other hand, for a water-to-water jump, when an anion is adjacent to either the donor or the acceptor water molecules, the rotation of this water molecule is not much affected. The transition free energy barriers for the water-to-water jumps with a cation in the vicinity, however, are more significantly lowered.

These observations suggest that: (1) the SCN⁻ anion affects the jump rotation mainly through the formation of the SCN-Water hydrogen bond, which is weaker than the Water-Water hydrogen bond. The non-direct-hydrogen-bonding effect of the anion on the jumps is negligible; (2) although the sodium and potassium cations don't form hydrogen bond with the water molecules, they can still considerably affect the jump rotation of water.

H. Distortion of the cation hydration shell structures

Fig.5 in main context gives the hydrogen bonding configuration between the cation bound water molecule i and a nearby water molecule j which forms the hydrogen bond with i. *NaSCN* solution has this configuration more deviated from the non-ion case, which, however, doesn't suggest a more distorted ion hydration shell structure. As a demonstration, in Fig.S5 we calculate the relative orientation between the dipole of water molecule i and the vector pointing from cation to the oxygen of water i as in Fig. 4 and 5 of ref. 2. Which is an indicator of how distorted the ion hydration shell structure is. Despite the different force fields used, our results are very similar to what were reported therein, and both results suggest a more distorted hydration shell structure in the *KSCN* solution. Our simulation result is therefore consistent with what's reported in the literature. This is also consistent with the experimental observation that potassium causes the water O-H stretch shifts further to the blue side compared with sodium.

In fact, these two quantities are related: the angle between the dipole of water molecule i and the ion-oxygen (i) vector is smaller for sodium, which results from a stronger orientation restriction effect of sodium on the water molecule i. The

hydrogen bonding configuration between water i and j therefore becomes more distorted for sodium.

I. Correlation between the diffusive rotation and the hydrogen bond switching

Stokes-Einstein relation suggests that the diffusive rotation of water molecules is proportional to viscosity in the dilute solutions (ref.51-53 and ref.27 in the main context, also demonstrated in figure S5). Since the amplitude of viscosity is, based on the Eyring's model (ref.27 and ref.53 in the main context), determined by the ratio $\tilde{\tau}/L^2$ between the time ($\tilde{\tau}$) and length (*L*) of the "excited" hoppings of the molecules, the value of diffusive rotation time constant τ_{W-W}^f in the bulk should be proportional to the same physical quantity as well.

To identify whether these excited hoppings are simply the hydrogen bond switchings, we calculate the average hydrogen bond switching length L_{HB} and the switching time $\tilde{\tau}_{HB}$ (section J of the supporting materials). A good correlation is observed between $\tilde{\tau}_{HB} / L_{HB}^2$ and τ_{W-W}^f (Fig.S8), which suggests that the "hopping" is indeed the hydrogen bond switching. The diffusive rotation of bulk water is therefore controlled by the hydrogen bond switching processes.

J. Correlation between the calculated viscosity and diffusive rotation

We calculated the viscosities based on the simulation trajectories using the Green-Kubo method [36-37], the shear viscosity is obtained by integrating the auto correlation function of the off-diagonal elements of the viscous pressure tensor $P_{\alpha\beta}$ given by

$$P_{\alpha\beta} = \left\langle \frac{1}{V} \left(\sum_{i} p_{i\alpha} p_{i\beta} + \sum_{i} \sum_{j>i} r_{ij\alpha} F_{ij\beta} \right) \right\rangle$$
(S10)

Where $p_{i\alpha}$ and $p_{i\beta}$ are the α and β components of the momentum of particle *i*, $r_{ij\alpha}$ is α component of vector the distance between the particles *i* and *j* of, and $F_{ij\alpha}$ is the α

component of the force of their interaction. To improve the statistics, we averaged the autocorrelation functions over all independent off-diagonal tensor elements as:

$$\eta = \frac{V}{3kT} \int_0^\infty \left[\left(P_{xy}(0) P_{xy}(t) \right) + \left\langle P_{xz}(0) P_{xz}(t) + \left\langle P_{yz}(0) P_{yz}(t) \right) \right\rangle \right] dt$$
(S11)

Calculated viscosities at a series of concentrations are presented in Fig S5 and compared with the frame rotation time constants. A strong correlation is observed.

As discussed in the main context, the viscosity can be related to the excited "hopping" of the molecules in the system (Eyring model). Since the hoppings in the dilute solution are simply the hydrogen bond switchings, the hopping amplitude is calculated (using a similar treatment as in ref. 34) as following: when the hydrogen bond exchanges, the labeled molecule is considered as hopping from one "dynamical basin" to another. We define the center of the *k*'th basin, $\overline{R}(n)_k$, to be the running average of the molecular center-of-mass $\overline{R}(n)$ during the waiting time between two successful hydrogen bond switching processes. And the waiting time is the period from initial moment of hydrogen bond formation to the last moment that thishydrogen bond is intact. If the wait process contains n snapshots along the MD trajectory, then

$$\overline{R}(n)_k = \frac{(n-1)\overline{R}(n-1)_k + R(n)}{n} \tag{1}$$

When the hydrogen bond exchanges, the labeled molecule is supposed to hops into a new basin, the running index *n* is updated to 1. The hopping time is then defined as the waiting time by counting the time frame, while the jump length is defined as the average distance between two consecutive basin centers, $\langle \overline{R}_{k+1} - \overline{R}_k \rangle$.

K. Figures and Tables





(B)







Fig. S1 (A) FTIR spectra of NaSCN and KSCN aqueous solutions (HOD, 1 wt% D2O in H2O) in the OD stretch region with various concentrations

(B) Left: waiting time dependent parallel (P_1) and perpendicular (P_{\perp}) data at around 2510 cm⁻¹. Right: transient absorption spectra in the OD frequency region of HOD solution at 0.1 ps.

(C) Left: waiting time dependent parallel (P_1) and perpendicular (P_{\perp}) data at around 2520 cm⁻¹. Right: transient absorption spectra in the OD frequency region of HOD solutions at 0.1 ps.

(D) Left: waiting time dependent parallel (P_1) and perpendicular (P_{\perp}) data at around 2520 cm⁻¹. Right: transient absorption spectra in the OD frequency region of HOD solutions at 0.1 ps.



Fig S2 Ion effects on the jump and diffusive rotations of different hydrogen bond switching types. The decomposition of the differences of the rotational time constants between the solution and pure water in the *KSCN*(left), and *NaSCN* (middle) and $Mg(SCN)_2$ solutions calculated using eq.1. The overall difference is dominantly decided by the ion effect on the jump (blue) and diffusive (brick-red) rotations during the processes that the tagged hydrogen bond donor water switches from one hydrogen bond acceptor water molecule to another (*W:W*). The simulation of $Mg(SCN)_2$ is carried out using the same procedure as those of *KSCN* and *NaSCN*, using the force field model of magnesium cation as introduced in [38]



Fig.S3 Time evolutions of the free energy variation during the jump. The free energy profiles are calculated for the 0.1MKSCN and NaSCN solutions, with the time origin chosen to be the moment that the hydrogen bond switching event happens (main context). Upper): Free energy profiles of five water-to-water jump types as well as the overall SCN-to-water jump. Middle) and Lower): Free energy profiles of the water-to-water jumps, decomposed into contributions along the radial (middle) and angular (lower) coordinates.



Figure S4the hydrogen bond switching correlation function of Eq. S5 and the frame correlation functions, generated by the *ab initio* MD simulations, of water in KSCN and NaSCN solutions at 1 M comparing to that in pure water. The jump rotation in the solutions (yellow) is accelerated compared with that in pure water(light blue). On the other hand, the diffusive rotation is accelerated in KSCN, while retarded in NaSCN solution.



Figure S5 The calculated relative viscosity η/η_0 (calculated using the Green-Kubo model, see section I of the supporting material) and frame rotational times of water with EJM model.



Figure.S6 *Left:* Distributions of angles between the cation-oxygen vector and the water dipole vector in the cation first solvation shell. *right:* the radial distribution functions of cation(Z)-water (oxygen or hydrogen) as the function of a reduce abscissa, $r^* = r/r_{ZO}^1$, r_{ZO}^1 is the first maximum of $g_{ZO}(r)$ [2].



Figure. S7 the reorientation correlation functions $C_2(t)$ (A), the frame reorientation(B) and the hydrogen bond switching correlation functions(C) from water-to-water in pure water, KSCN and NaSCN solutions at 0.5M and 2 M, as well as the hydrogen bond switching correlation functions of water-to-water jump at different environments (Bulk, CBA, CBD, ADA, ABD, the definitions in main text) (D) in KSCN and NaSCN solutions at 0.5 M.

Table S1Theforce field parameters

	Atom	<i>q</i> (e)	σ (Å)	ε(kJ·mol ⁻¹)
SPC/E	Ow	-0.8476	3.166	0.650
Water	Hw	0.4238	0.000	
	S	-0.56	3.52	1.52
SCN ⁻ [9]	С	0.14	3.35	0.43
	Ν	-0.58	3.31	0.31
K+		+1.0	3.33	0.42
Na ⁺		+1.0	2.58	0.42
Mg ²⁺		+2.0	1.6445	3.661

Table S2The details of the simulation boxes (*C*: concentration with unit mol/kg, $N_{\rm I}$: the number of KSCN (NaSCN), $N_{\rm w}$: Number of water, *L*: the length of box with unit Å)

/			
С	NI	N _w	L
KSCN			
0.1	5	2500	42.35
0.2	10	2500	42.42
0.3	15	2500	42.50
0.4	20	2500	42.56
0.5	12	1176	32.87
1	24	1176	33.16
2	46	1154	33.48
2.5	56	1122	33.48
5	110	1090	34.51
10	200	1000	35.76
15	264	848	36.15
NaSCN			
0.1	5	2500	42.34
0.2	10	2500	42.38
0.3	15	2500	42.44
0.4	20	2500	42.49
0.5	12	1176	32.83
1	24	1154	32.98
2	46	1154	33.25
2.5	56	1122	33.22
5	110	1090	33.85
10	200	1000	34.77
15	352	848	34.78

Table S3 The populations of four types of hydrogen bond exchanges in

KSCN and NaSCN solutions

C (mol/Kg)	0	0.5	1	2	2.5	5	10	15
KSCN								
P_{W-W}	1.00	0.93	0.88	0.78	0.73	0.58	0.42	0.32
P_{W-SCN}		0.03	0.05	0.09	0.11	0.16	0.20	0.21
P _{SCN-W}		0.03	0.05	0.09	0.11	0.16	0.20	0.21
P _{SCN-SCN}		0.01	0.02	0.04	0.05	0.10	0.17	0.25
NaSCN								
P_{W-W}		0.93	0.87	0.77	0.71	0.54	0.36	0.26
P_{W-SCN}		0.03	0.05	0.09	0.12	0.17	0.21	0.21
P _{SCN-W}		0.03	0.05	0.09	0.12	0.18	0.23	0.25
P _{SCN-SCN}		0.01	0.02	0.04	0.06	0.11	0.20	0.27

Table S4 The jump rotational times of five types of the W-W exchange fragments

	KSCN 0.1 M	NaSCN0.1 M	KSCN 0.5 M	NaSCN0.5 M
$ au_J^{PWB}(ps)$	4.18	4.20	4.06	4.09
τ _J ^{CBD} (ps)	3.67	3.84	3.58	3.79
τ _J ^{CBA} (ps)	3.76	3.00	3.73	2.86
τ _J ^{ABD} (ps)	4.16	4.15	4.02	4.07
τ _J ^{ABA} (ps)	4.09	4.09	4.00	4.02

in KSCN and NaSCN solutions

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