## **Electronic Supplementary Information**

# Binary structure and dynamics of the hydrogen bonds in the

## hydration shell of ion

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#### **Consequences of the omission of molecular polarizabilities in the force fields.**

For the polarizabilities of the individual ions,<sup>1</sup> it can be seen that they are not important for the cations due to the lack of valent electron and for F<sup>-</sup> due to its high electronegativity which holds the valent electrons tightly.<sup>2</sup> Therefore, the only ion in this study that possesses a moderate polarizability is Cl<sup>-</sup>, which is 25.35 bohr<sup>3</sup> in aqueous solution.<sup>1</sup> Such polarization effects partially manifests in the coordination number of water in the first hydration shell of Cl<sup>+</sup>, as comparing the non-polarizable SPC/E model and the polarizable TIP4P/FQ model in Table 2. As of the structure and dynamics of water, Berne et al. found that the polarizable model strengthens HB, with an activation energy of breading HB ~0.2 kcal/mol higher than that of a non-polarizable model, and consequently results in a slower HB relaxation by 50% - 100%.<sup>3</sup> Despite the importance of the polarization effects, we think that the binary structure and dynamics of HB should not be altered even with a non-polarizable model, because the primary ion-water interaction is still the ionic charge and the permanent dipole of water. Jungwirth, Kunz and co-workers<sup>4</sup> found very similar structural properties for a protein in various aqueous solutions using a nonpolarizable or polarizable force field. On the other hand, it is notable that detailed study also demonstrated that the HB relaxation is more sensitive to the anisotropic local environment due to the many-body interactions imposed by the polarizable model,<sup>3</sup> which is of interest to investigate in further studies.

### Spatial distribution of the coordination water.

The difference between HD and HA in the hydration shells of different ions can be viewed more clearly by the iso-density spatial distribution of the coordination water. The iso-density surfaces of water  $O_2^D$  (blue) and water  $O_2^A$  (red) around  $O_1$  in the hydration shell of the different

cations and anions are presented in Fig. S6a-g in ESI, respectively. For the kosmotropic cations, such as Li<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, no  $O_2^A$  can be found at the lone electron pair regions of  $O_1$  at the given number density. Thus, the reduction of the HBs on  $O_1$  is evident due to the lack of HAs in the presence of a central cation. These iso-density distributions indicate that the lone electron pair regions of  $O_1$  behaves as a hydrophobic face in the sense that water molecules are mostly excluded from this region. Such induced hydrophobic face does not present in the neat water, in which the spatial distributions for various water models show distinctive pair of lobes around a central water molecule.<sup>5, 6</sup> For Na<sup>+</sup> and K<sup>+</sup>,  $O_2^A$  can be observed near the lone-pair regions of the central  $O_1$  in Fig. S6a and S6b, but remain less significant comparing to that in neat water (Fig. S6h). For Li<sup>+</sup>,  $Ca^{2+}$ ,  $Mg^{2+}$ , the probability of  $O_2^A$  is lower than the average in the bulk and thus not displayed. In contrast, the iso-density surface of  $O_2^D$  are quite stable around the central  $O_1$  water in the first hydration shell of the five hydrated cations. Moreover, the iso-density surface of  $O_2^D$  expands larger region than that of the neat water. For a hydrated anion, the trend reverses. Specifically, Fig. S6f and S6g reveal that the iso-density surface of  $O_2^D$  is less significant comparing to that of the neat water or cation, while the expansion of the iso-density surface of  $O_2^A$  is more significant comparing to that of cation, but less significant comparing to that of the neat water. Therefore, the HB of the coordination water shows asymmetric arrangement, due to the ion-specific effects that perturbs the balance of local water HBs that distinguish HD from HA. Specifically, a hydrated cation enhances HD and weakens HA, while a hydrated anion weakens HD and enhances HA. Such ion-specific effects is less significant for a hydrated anion, in agreement with **Fig. 3**.

#### **Calculation of Hydrogen Bond Radial distribution functions.**

We constructed the radial distribution function  $g_{0_10}^{HB}(r)$  between the  $O_1$  water in the first hydration shell of an ion and other oxygen atoms of water. Here, an additional HB criterion is imposed on the otherwise regular RDF of  $g_{0_10}(r)$ . Since the distance cut-off in the HB criterion breaks  $g_{0_10}(r)$ , and thus causes a cusp in  $g_{0_10}^{HB}(r)$ , we adopted a longer cut-off of  $r_{00} < 4.0$  Å, instead of  $r_{00} < 3.5$  Å for judging the HB pair in this section, while  $\theta_{H00} < 30^{\circ}$  is retained. Moreover, in order to count the HB pairs between the successive layers starting from O1 instead of HB between the same layer, only the water pairs of  $r_{0_10'} - r_{0_10} > 0.8$  Å, in which 0' is assumed to be farther than 0 from  $O_1$ . In order to distinguish HD and HA,  $g_{O_1O}^{HB}(r)$  is further split to  $g_{0_10}^{\text{HD}}(r)$  and  $g_{0_10}^{\text{HA}}(r)$ , according to the oxygen whether it is  $O_2^{\text{D}}$  or  $O_2^{\text{A}}$  in the second hydration shell. It should be noted that such decomposition is only applied on HD or HA between water pairs between the first and second hydration shells, and beyond the second hydration shell, only the criterion of HB is applied. The so calculated  $g_{0_10}^{\text{HB}}(r)$ ,  $g_{0_10}^{\text{HD}}(r)$ , and  $g_{0_10}^{\text{HA}}(r)$  of different hydrated ions are shown in Fig. S10 in ESI. The cusp at  $r_{00} = 4.0$  Å is attributed to the distance criterion of HB. Despite a slightly loose HB criterion is adopted, it can be seen that it does not affect the HD and HA, of which the first minimum is located at 3.3 Å - 3.5 Å, which is below 4.0 Å.

Due the additional HB criterion, RDF's of HB, HD, and HA are not normalized to 1 for  $r \rightarrow \infty$  in the bulk water. For the neat water,  $g_{0_10}^{HB}(\infty) = 0.46$  by taking r = 9.0 Å as bulk, which may be interpreted as the probability of a randomly selected water 0 at large distance in the bulk to be successively connected to the  $O_1$  water in the first hydration shell via HBs. Furthermore,  $g_{0_10}^{HD}(r)$  or  $g_{0_10}^{HA}(r)$  at long distance also reflect the binary HB in the hydration shell of an ion, as can be

interpreted by the probability for a randomly selected water O at large distance to be successively connected to the  $O_2^D$  or  $O_2^A$  water in the second hydration shell of an ion via HBs. For example,  $g_{0_10}^{HD}(\infty)$  and  $g_{0_10}^{HA}(\infty)$  are 0.25 and 0.036 at r = 9.0 Å, respectively, from **Figs. S10b** and **S10c** in **ESI**, for  $O_1$  in the first hydration shell of Li<sup>+</sup>, and their ratio is close to the ratio of HD to HA, i.e.,  $\overline{N}_{HD}/\overline{N}_{HA}$ , in **Table S2** in **ESI**. Thus,  $g_{0_10}^{HD}(\infty)$  and  $g_{0_10}^{HA}(\infty)$  in the long distance correlates with the strength of the individual type of HB in the hydration layer, and also correlates with the height of the first peak. It can be seen from **Fig. S10c** in **ESI** that the sequence of both the limiting and peak values of  $g_{0_10}^{HA}(r)$  is K<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup> > Ca<sup>2+</sup> > Mg<sup>2+</sup>. For the anions, it can be seen that the sequence both the limiting and peak values of  $g_{0_10}^{HD}(r)$  is Cl<sup>-</sup> > F<sup>-</sup> from **Fig. S10e** in **ESI**. The above finding is in good agreement with the previous section for the binary HB in the hydration shell of ions.



**Fig. S1** (a) Radial distribution functions (solid lines) of ions ( $M = Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $F^-$ ,  $Cl^-$ ) and the oxygen ( $O_w$ ) of water, and the corresponding cumulative distribution functions (dashed lines). (b) Residence correlation functions of water in the first solvation shell of different ions.



**Fig. S2** Angular distributions of water dipole vector of  $O_1$ ,  $O_2^A$ ,  $O_2^D$ , with the vector of electric field induced by the cation. The notation of different oxygen is depicted in **Fig. 1a** in the main text.



**Fig. S3** Two dimensional distributions,  $P(r_{MO_1}, \theta_{\mu \cdot E})$ , of different hydrated cations (M = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>), in which  $\theta_{\mu \cdot E}$  is the angle between the dipole  $\mu$  of the O<sub>1</sub> water in the first hydration shell with the electric field *E* from the hydrated cation M, and  $r_{MO_1}$  is the distance between O<sub>1</sub> and M. The cartoon depicts the arrangement of the O<sub>1</sub> water around a hydrated cation M in the first hydration shell represented by the brown dashed circles, with  $\mu$  and *E* represented by yellow arrow and black arrow, respectively.



**Fig. S4** (a) Angular distributions of water dipole vector of  $O_1$ ,  $O_2^A$ ,  $O_2^D$ , with the vector of electric field induced by the anion. The notation of different oxygen is depicted in **Fig. 1a** in the main text. Two dimensional distributions of O---O distance ( $r_{OO}$ ) and angle ( $\theta_{HOO}$ ) for donated hydrogen bond (HD) (b) and accepted hydrogen bond (HA) (c) in the case of Cl<sup>-</sup>.



**Fig. S5** Two dimensional distributions,  $P(r_{MO_1}, \theta_{\mu \cdot E})$ , of different anions (M = F<sup>-</sup>, Cl<sup>-</sup>), in which  $\theta_{\mu \cdot E}$  is the angle of dipole vector of the O<sub>1</sub> water in the first hydration shell with the vector of electric field *E* by the anion M, and  $r_{MO_1}$  is the distance between O<sub>1</sub> and M.



**Fig. S6** Iso-density distributions of  $O_2^D$  (blue) and  $O_2^A$  (red) water around  $O_1$  water in hydration shell of different cations, K<sup>+</sup> (a), Na<sup>+</sup> (b), Li<sup>+</sup> (c), Ca<sup>2+</sup> (d), Mg<sup>2+</sup> (e), F<sup>-</sup> (f), Cl<sup>-</sup> (g), compare to that in neat water (h), where the iso-density is 1.5 times higher than that in bulk, and subjected to the geometric criterion of hydrogen bond.



**Fig. S7** Angular distributions,  $P(\theta_{\mu \cdot E})$ , of the dipole ( $\mu$ ) on the three types of water molecules,  $O_1$ ,  $O_2^A$ ,  $O_2^D$  with the electric field (E) generated by Li<sup>+</sup> at different temperatures, 260 K, 280 K, 320 K, and 340 K. The notations of  $O_1$ ,  $O_2^A$ ,  $O_2^D$  are depicted in the inset of **Fig. 2a** in the main text.



**Fig. S8** Two dimensional distribution  $P(r_{00}, \theta_{H00})$  of HD between  $O_1$  and  $O_2^D$  (left column), and  $P(r_{00}, \theta_{H00})$  of HA between  $O_1$  and  $O_2^A$  (right column) t different temperatures, 260 K, 280 K, 320 K, and 340 K.



**Fig. S9** The average number of HB ( $\overline{N}_{HB}$ ), HD ( $\overline{N}_{HD}$ ), and HA ( $\overline{N}_{HA}$ ) of O<sub>1</sub> in the first hydration shell Li<sup>+</sup> at different temperatures, 260 K, 280 K, 320 K, and 340 K.



**Fig. S10** Radial distribution function of the O<sub>1</sub> water in the first hydration shell of different ions and other oxygen atoms of water, subjected to an additional HB criterion is of  $r_{00} < 4.0$  Å and  $\theta_{H00} < 30^{\circ}$ . Moreover, only the HB pairs between the successive layers starting from O<sub>1</sub>, instead of HB between the same layer, so that an addition condition  $r_{0_10'} - r_{0_10} > 0.8$  Å is imposed, in which O' is assumed to be farther than O from O<sub>1</sub>. (a)  $g_{0_10}^{HB}(r)$ , (b)  $g_{0_10}^{HD}(r)$ , (c)  $g_{0_10}^{HA}(r)$  of different hydrated cations; (d)  $g_{0_10}^{HB}(r)$ , (e)  $g_{0_10}^{HD}(r)$ , (f)  $g_{0_10}^{HA}(r)$  of different hydrated anions.  $g_{0_10}^{HB}(r)$  of the neat water is also depicted for comparison, and note that  $g_{0_10}^{HB}(r)$ ,  $g_{0_10}^{HD}(r)$ , and  $g_{0_10}^{HA}(r)$  are equivalent in the neat water.



**Fig. S11** The time evolution of several distances of a randomly selected  $O_1$  water in the first hydration shell of K<sup>+</sup> from MD simulation. The inset depicts the atomic pairs for which the distance are monitored over 10 ps time window, starting from an arbitrary time 0. The horizonal gray line denotes the first minimum in the Radial distribution function of K<sup>+</sup> the oxygen of water from **Fig. S1**, and the horizonal cyan line denotes distance criterion of HB. This trajectory may or may not be representative.



**Fig. S12** The continuous hydrogen bond correlation function of HD  $C_{c,HD}(t)$  (a), and HA  $C_{c,HA}(t)$  (b) for the case of Li<sup>+</sup> at the different temperatures.

	$\tau_{R^{a}}$ (ps)	Previous simulations
Li <sup>+</sup>	56.7	33.3, <sup>b</sup> 54.5 <sup>c</sup>
$Na^+$	16.7	9.9, <sup>b</sup> 19.8 <sup>c</sup>
$\mathrm{K}^+$	7.7	4.8, <sup>b</sup> 9.4 <sup>c</sup>
$Mg^+$	d	
$Ca^+$	746.9	700 <sup>c</sup>
F-	22.6	$20.3,^{b}23.7^{c}$
Cl-	11.0	$4.5,^{b} 14.0^{c}$

**Table S1.** Residence time  $(\tau_R)$  of water in the first shell of different ions.

 ${}^{a}\tau_{R}$  is fitted by  $R(t) = \exp(-t/\tau_{R})$  at large *t*, in which is R(t) given by **Fig. S1b**; <sup>*b*</sup>MD simulation with one ion and either 64 or 125 waters;<sup>7</sup> <sup>*c*</sup>MD simulation with one ion and 215 SPC/E waters;<sup>8</sup> <sup>*d*</sup>The coordination water in the first hydration shell of Mg<sup>2+</sup> almost has not changed during MD simulation.

**Table S2.** The average number of HB ( $\overline{N}_{HB}$ ), HD ( $\overline{N}_{HD}$ ), and HA ( $\overline{N}_{HA}$ ) of the O<sub>1</sub> water in first shell of different ions, and the coefficient  $\gamma_{HD}$  and  $\gamma_{HA}$ , which give the relative ratios of HD and HA with  $\gamma_{HD} + \gamma_{HA} = 1$ .

	$\overline{N}_{ m HB}$	Previous results of $\overline{N}_{\rm HB}$	${ar N}_{ m HD}$	$\overline{N}_{ m HA}$	$\gamma_{ m HD}$	$\gamma_{ m HA}$
Li <sup>+</sup>	2.02	$1.97^{a,b}$	1.80	0.22	0.89	0.11
$Na^+$	2.29	$2.27^{a,b}$	1.75	0.54	0.76	0.24
$\mathrm{K}^+$	2.55	$2.59^{a}$	1.77	0.78	0.69	0.31
$Mg^+$	1.90		1.89	0.01	0.99	0.01
$Ca^+$	1.88		1.80	0.08	0.96	0.04
F-	2.58	$2.54^{a,b}$	0.88	1.70	0.34	0.66
Cl	2.61	$2.65^{a,b}$	0.91	1.70	0.35	0.65
$H_2O$	3.57	3.51 <sup><i>a</i>,<i>b</i></sup>	1.79	1.79	0.50	0.50

<sup>a</sup>MD simulation;<sup>9</sup> <sup>b</sup>MD simulation.<sup>10</sup>

**Table S3.** Average number of HB ( $\overline{N}_{HB}$ ), HD ( $\overline{N}_{HD}$ ), and HA ( $\overline{N}_{HD}$ ) of O<sub>1</sub> in the first hydration shell of Li<sup>+</sup> at different temperatures.

	$\overline{N}_{ m HB}$	$\overline{N}_{ m HD}$	$\overline{N}_{ m HD}$
260K	2.10	1.89	0.21
280K	2.06	1.84	0.22
300K	2.02	1.80	0.22
320K	1.99	1.77	0.22
340K	1.95	1.73	0.22

**Table S4.** The distance of the free energy minima  $(r^*)$ , maxima  $(r^{\ddagger})$ , and free energy barrier<sup>*a*</sup>  $\Delta G^{\ddagger} = G(r^{\ddagger}) - G(r^*)$  of HB, HD, and HA of the  $O_1 - O_2$  pair, in which  $O_1$  denotes the water in the first hydration shell and  $O_2$  denotes  $O_2^{\rm D}$  or  $O_2^{\rm A}$  in the second hydration shell, with different hydrated ions, as well as the corresponding  $r^*$ ,  $r^{\ddagger}$ , and  $\Delta G^{\ddagger}$  of HB in the neat water.

	$r^{HB,*}$	$r^{HB,\ddagger}$	$\Delta G^{HB,\ddagger}$	$r^{HD,*}$	$r^{HD,\ddagger}$	$\Delta G^{HD,\ddagger}$	$r^{HA,*}$	$r^{HA,\ddagger}$	$\Delta G^{HA,\ddagger}$
Li <sup>+</sup>	2.74	3.38	2.37	2.74	3.38	2.69	2.86	3.48	1.06
$Na^+$	2.76	3.38	2.35	2.74	3.38	2.45	2.76	3.40	2.14
$K^+$	2.74	3.38	2.60	2.74	3.38	2.59	2.74	3.38	2.62
$Mg^+$	2.70	3.34	3.30	2.70	3.34	3.39	<sup>b</sup>	b	b
$Ca^+$	2.74	3.38	2.43	2.74	3.36	2.61	2.88	3.48	0.54
F-	2.74	3.38	2.55	2.76	3.38	2.19	2.74	3.38	2.78
Cl-	2.74	3.38	2.58	2.74	3.38	2.39	2.74	3.38	2.69
$H_2O$	2.74	3.38	2.56	C	C	<sup>C</sup>	C	<sup>C</sup>	c

<sup>*a*</sup>Unit in  $k_BT$ , in which  $k_B$  is Boltzmann constant and T = 300 K; <sup>*b*</sup>The probability to form HA in the hydration shell of Mg<sup>2+</sup> is extremely rare, and there is essentially no free energy barrier of HA, as shown in **Fig. 5** in the main text; <sup>*c*</sup>Same as HB, because HB, HD, and HA are equivalent in the neat water.

**Table S5.** The reorientation relaxation time  $(\tau_r)$ , HB relaxation time  $(\tau_{HB})$ , HD relaxation time  $(\tau_{HD})$  and HA relaxation time  $(\tau_{HA})$  of the  $O_1 - O_2$  pair, in which  $O_1$  denotes the water in the first hydration shell and  $O_2$  denotes  $O_2^D$  or  $O_2^A$  in the second hydration shell, with different hydrated ions, as well as the corresponding relaxation time in the neat water.

	$\tau_r^a$ (ps)	$ au_{\scriptscriptstyle \mathrm{HB}}\mathrm{(ps)}$	Previous results of $\tau_{HB}$ (ps)	$ au_{ ext{HD}} ( ext{ps})$	$ au_{\text{HA}}$ (ps)
Li <sup>+</sup>	6.6	0.60	$0.52,^{b}0.53^{c}$	0.65	0.18
$Na^+$	2.7	0.49	$0.44,^{b} 0.46^{c}$	0.54	0.29
$\mathrm{K}^+$	2.0	0.55	$0.48^{b}$	0.56	0.41
$Mg^+$	30.0	1.11		1.11	f
$Ca^+$	21.0	0.67		0.69	0.13
F-	3.5	0.62	$0.55,^b 0.60^c$	0.61	0.64
Cl	2.3	0.61	$0.56,^{b} 0.58^{c}$	0.64	0.59
$H_2O$	2.1	0.53	$0.54,^{b} 0.55,^{c} 0.50,^{d} 0.56^{e}$	g	g

 ${}^{a}\tau_{r}$  is fitted by  $P_{2}(t) = \exp(-t/\tau_{r})$  at large *t*, in which is  $P_{2}(t)$  given by **Fig. 6a** in the main text;  ${}^{b}$ MD simulation;  ${}^{9}$   ${}^{c}$ MD simulation;  ${}^{10}$   ${}^{d}$ Experimental measurement;  ${}^{11}$   ${}^{e}$ Experimental measurement;  ${}^{12}$   ${}^{f}$ The probability to form HA in the hydration shell of Mg<sup>2+</sup> is extremely rare;  ${}^{g}$ Same as HB, because HB, HD, and HA are equivalent in the neat water.

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