Electronic Supplementary Information (ESI)

The solvation effect on the rattling behaviour of the hydrated excess proton in water

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Contents

S1. Eight hydrated $^{*}H^{+}$ structures

In order to test different solvation environments, 1 to 6 explicit solvent water molecules (N_m' = 1~6) are added around the Zundel cation to construct different second hydration shell structures of $^{*}H^{+}$. For N_m' = 2, three different configurations labeled as N_m' = 2-*cis*, 2-*trans* and 2-Eigen respectively are investigated. In the N_m' = 2-*cis* configuration, the two explicit solvent water molecules are arranged in a *cis* way and form single hydrogen bonds with the inner-shell water molecules A and B. In the N_m' = 2-*trans* configuration, the two solvent water molecules are arranged in a *trans* way. In the N_m' = 2-Eigen configuration, the two explicit solvent water molecules form single hydrogen bonds with the same inner-shell water molecule (e.g., the water molecule A), and the molecule is actually the Eigen cation.

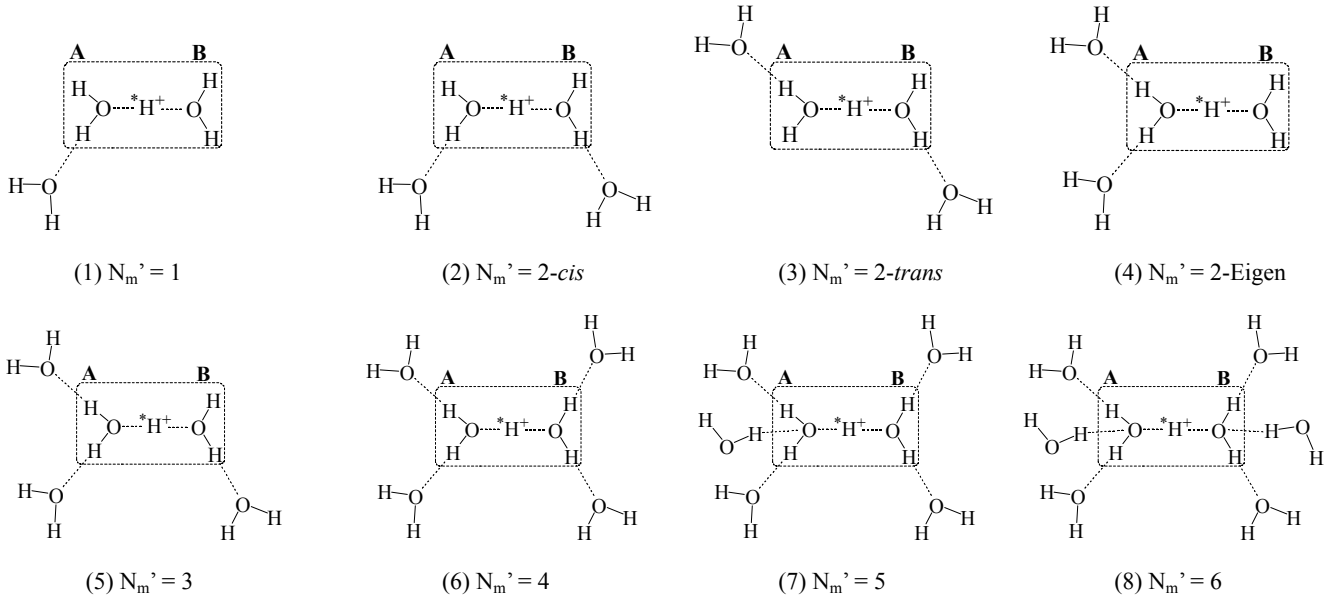


Fig. S1 The structural formulas of eight hydrated $^{*}H^{+}$ configurations.

S2. Calculation results in GP, GP-PCM, GP-SM, and GP-SM-PCM

Table S1 Summarization of the TS searching results for eight hydrated $^{*}H^{+}$ configurations in GP, GP-PCM, GP-SM, and GP-SM-PCM[a]

Model	N_m' = 0	N_m' = 1	N_m' = 2	N_m' = 3	N_m' = 4	N_m' = 5	N_m' = 6
GP	TS^0 is optimized into stable Zundel species without imaginary frequency. TS^* is not found	-	-	-	-	-	-
GP-PCM	TS^0 is optimized into stable Zundel species without imaginary frequency. TS^* is not found	-	-	-	-	-	-
GP-SM	-	TS^0 is optimized into stable Eigen-type species without imaginary frequency. TS^* is not found	2-*cis*: TS^0 is optimized into stable Zundel species without imaginary frequency. TS^* is not found 2-*trans*: TS^0 is optimized into stable Zundel species without imaginary frequency. TS^* is not found 2-Eigen: TS^0 is optimized into stable Eigen cation without imaginary frequency. TS^* is not found	TS^0 is optimized into stable Eigen-type species without imaginary frequency. TS^* is not found	TS^0 is optimized into stable Zundel species without imaginary frequency. TS^* is not found	TS^0 is optimized into stable Eigen-type species without imaginary frequency. TS^* is not found	TS^0 is optimized into stable Eigen-type species without imaginary frequency. TS^* is not found
GP-SM-PCM	-	TS^0 is optimized into stable Eigen-type species without imaginary frequency. TS^* is not found	**2-*cis*: TS^* for $^{*}H^{+}$ rattling is found and the complete reaction pathway is obtained** **2-*trans*: TS^* for $^{*}H^{+}$ rattling is found and the complete reaction pathway is obtained** 2-Eigen: TS^0 is optimized into stable Eigen cation without imaginary frequency. TS^* is not found	TS^0 is optimized into stable Eigen-type species without imaginary frequency. TS^* is not found	**TS^* for $^{*}H^{+}$ rattling is found and the complete reaction pathway is obtained**	TS^0 is optimized into stable Eigen-type species without imaginary frequency. TS^* is not found	**TS^* for $^{*}H^{+}$ rattling is found and the complete reaction pathway is obtained**

[a] The gas phase (GP) model only considers the inner-shell structure of $^{*}H^{+}$. The gas phase – polarizable continuum model (GP-PCM) uses PCM to model the bulk solvent on the basis of the GP cluster. The gas phase – supermolecule model (GP-SM) considers both the inner-shell structure of $^{*}H^{+}$ and its second hydration shell structure, and uses explicit solvent water molecule to model the short-range solute-solvent interaction. The gas phase – supermolecule model – polarizable continuum model (GP-SM-PCM) uses PCM to model the bulk solvent on the basis of the GP-SM cluster.

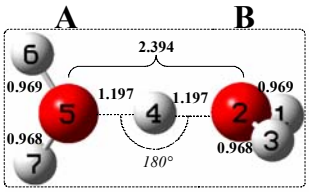


Fig. S2 Optimized geometry from TS searching in GP

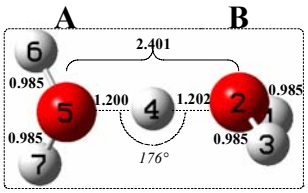
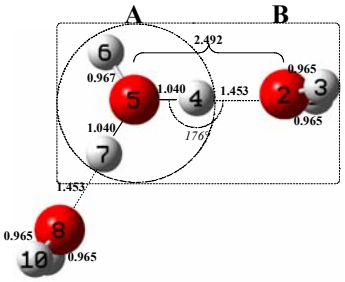
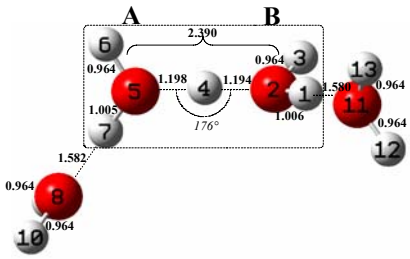


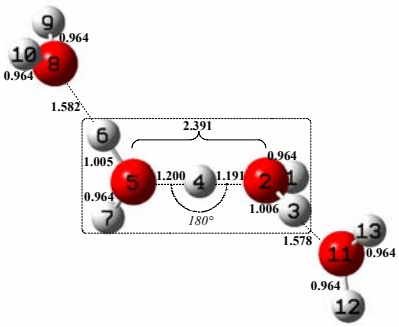
Fig. S3 Optimized geometry from TS searching in GP-PCM



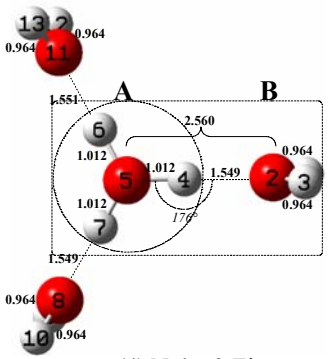
(1) N_m' = 1



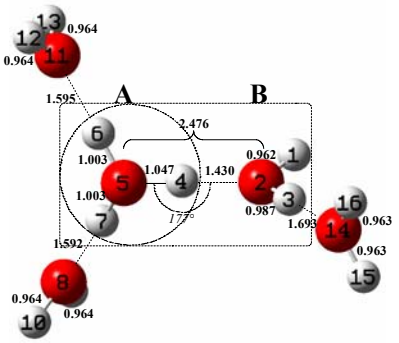
(2) N_m' = 2-*cis*



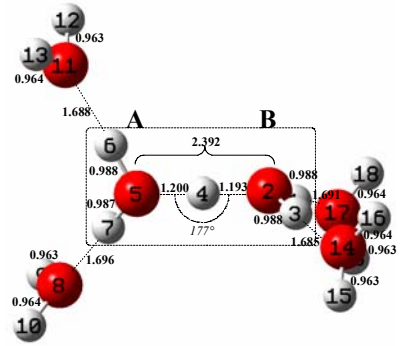
(3) N_m' = 2-*trans*



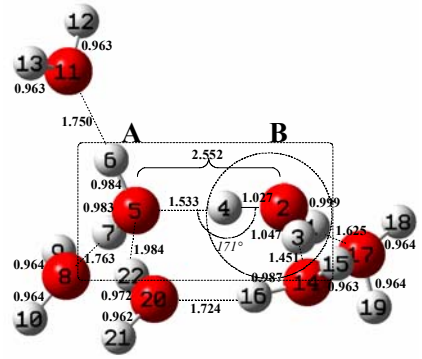
(4) N_m' = 2-Eigen



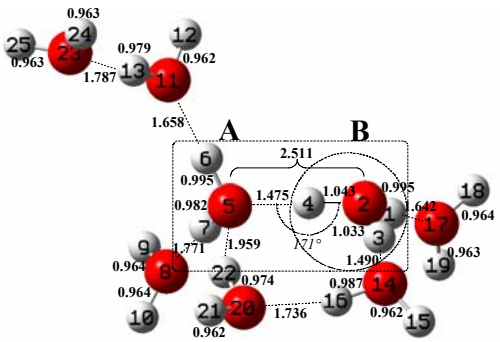
(5) N_m' = 3



(6) N_m' = 4

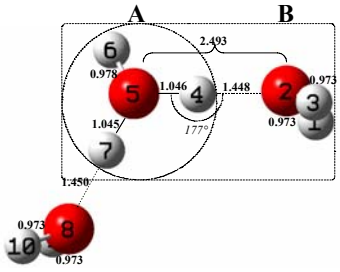


(7) N_m' = 5

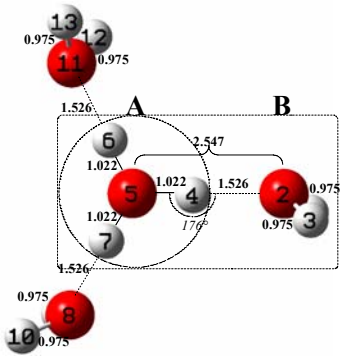


(8) N_m' = 6

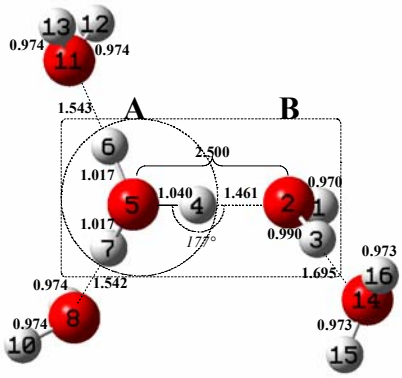
Fig. S4 Optimized geometries from TS searching in GP-SM.



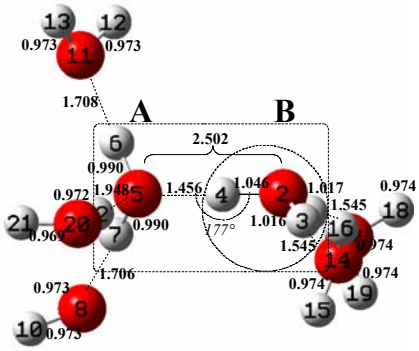
(1) N_m' = 1



(2) N_m' = 2-Eigen



(3) N_m' =3



(4) N_m' = 5

Fig. S5 Optimized geometries of the four hydrated $^{*}H^{+}$ structures with asymmetrical solvation environments from TS searching in GP-SM-PCM (N_m' = 1, 2-Eigen, 3, and 5).

Table S2 Structural parameters of the final optimized geometries from TS searching in GP, GP-PCM, GP-SM, and GP-SM-PCM

Bond length or distance (Å)								Bond angle (°)	Dihedral angle (°)
$r(^*H^+\cdots O_I)^a$	$r(^*H^+\cdots O_{II})^b$	$r(O_I\text{-}H)^c$	$r(O_{II}\text{-}H)^d$	$r(O_I\cdots O_I)^e$	$r(O_I\cdots O_{II})^f$	$r(H_D\text{-}O_A)^g$	δ^h	∠O5-H4-O2	
				GP					
H4-O5 = 1.197 H4-O2 = 1.197	-	O5-H6 = 0.969 O5-H7 = 0.968 O2-H1 = 0.969 O2-H3 = 0.968	-	O5-O2 = 2.394	-	-	1.000	180	D(H6-O5-O2-H1) = -94.9 D(H6-O5-O2-H3) = 117 D(H7-O5-O2-H1) = 53.2 D(H7-O5-O2-H3) = -95.1
				GP-PCM					
H4-O5 = 1.200 H4-O2 = 1.202	-	O5-H6 = 0.985 O5-H7 = 0.985 O2-H1 = 0.985 O2-H3 = 0.985	-	O5-O2 = 2.401	-	-	1.002	176	D(H6-O5-O2-H1) = -88.3 D(H6-O5-O2-H3) = 148 D(H7-O5-O2-H1) = 35.4 D(H7-O5-O2-H3) = -88.1
				GP-SM					
				(1) N_m' = 1					
H4-O5 = 1.040 H4-O2 = 1.453	H4-O8 = 3.132	O5-H6 = 0.967 O5-H7 = 1.040 O2-H1 = 0.965 O2-H3 = 0.965	O8-H9 = 0.965 O8-H10 = 0.965	O5-O2 = 2.492	O5-O8 = 2.492	H7-O8 = 1.453	1.397	176	D(H6-O5-O2-H1) = -69.3 D(H6-O5-O2-H3) = 108 D(H7-O5-O2-H1) = 69.6 D(H7-O5-O2-H3) = -113
				(2) N_m' = 2-*cis*					
H4-O5 = 1.198 H4-O2 = 1.194	H4-O8 = 3.360 H4-O11 = 3.364	O5-H6 = 0.964 O5-H7 = 1.005 O2-H1 = 1.006 O2-H3 = 0.964	O8-H9 = 0.964 O8-H10 = 0.964 O11-H12 = 0.964 O11-H13 = 0.964	O5-O2 = 2.390	O5-O8 = 2.587 O2-O11 = 2.585	H1-O11 = 1.580 H7-O8 = 1.582	1.003	176	D(H6-O5-O2-H1) = 92.9 D(H6-O5-O2-H3) = -51.6 D(H7-O5-O2-H1) = -122 D(H7-O5-O2-H3) = 93.2
				(3) N_m' = 2-*trans*					
H4-O5 = 1.200 H4-O2 = 1.191	H4-O8 = 3.385 H4-O11 = 3.370	O5-H6 = 1.005 O5-H7 = 0.964 O2-H1 = 0.964 O2-H3 = 1.006	O8-H9 = 0.964 O8-H10 = 0.964 O11-H12 = 0.964 O11-H13 = 0.964	O5-O2 = 2.391	O5-O8 = 2.587 O2-O11 = 2.583	H3-O11 = 1.578 H6-O8 = 1.582	1.008	180	D(H6-O5-O2-H1) = 93.3 D(H6-O5-O2-H3) = 122 D(H7-O5-O2-H1) = 53.1 D(H7-O5-O2-H3) = -91.7
				(4) N_m' = 2-Eigen					
H4-O5 = 1.012 H4-O2 = 1.549	H4-O8 = 3.138 H4-O11 = 3.131	O5-H6 = 1.012 O5-H7 = 1.012 O2-H1 = 0.964 O2-H3 = 0.964	O8-H9 = 0.964 O8-H10 = 0.964 O11-H12 = 0.964 O11-H13 = 0.964	O5-O2 = 2.560	O5-O8 = 2.559 O5-O11 = 2.563	H6-O11 = 1.551 H7-O8 = 1.549	1.531	176	D(H6-O5-O2-H1) = -74.4 D(H6-O5-O2-H3) = 109 D(H7-O5-O2-H1) = 65.8 D(H7-O5-O2-H3) = -111
				(5) N_m' = 3					
H4-O5 = 1.047 H4-O2 = 1.430	H4-O8 = 3.206 H4-O11 = 3.189 H4-O14 = 3.681	O5-H6 = 1.003 O5-H7 = 1.003 O2-H1 = 0.962 O2-H3 = 0.987	O8-H9 = 0.964 O8-H10 = 0.964 O11-H12 = 0.964 O11-H13 = 0.964 O14-H15 = 0.963 O14-H16 = 0.963	O5-O2 = 2.476	O5-O8 = 2.594 O5-O11 = 2.596 O2-O14 = 2.680	H3-O14 = 1.693 H6-O11 = 1.595 H7-O8 = 1.592	1.366	177	D(H6-O5-O2-H1) = -49.7 D(H6-O5-O2-H3) = 114 D(H7-O5-O2-H1) = 86.9 D(H7-O5-O2-H3) = -110
				(6) N_m' = 4					
H4-O5 = 1.200 H4-O2 = 1.193	H4-O8 = 3.429 H4-O11 = 3.419 H4-O14 = 3.406 H4-O17 = 3.401	O5-H6 = 0.988 O5-H7 = 0.987 O2-H1 = 0.988 O2-H3 = 0.988	O8-H9 = 0.963 O8-H10 = 0.964 O11-H12 = 0.963 O11-H13 = 0.964 O14-H15 = 0.963 O14-H16 = 0.964 O17-H18 = 0.964 O17-H19 = 0.963	O5-O2 = 2.392	O5-O8 = 2.683 O5-O11 = 2.675 O2-O14 = 2.672 O2-O17 = 2.677	H1-O17 = 1.691 H3-O14 = 1.685 H6-O11 = 1.688 H7-O8 = 1.696	1.006	177	D(H6-O5-O2-H1) = -109 D(H6-O5-O2-H3) = 112 D(H7-O5-O2-H1) = 31.4 D(H7-O5-O2-H3) = -108
				(7) N_m' = 5					
H4-O5 = 1.533 H4-O2 = 1.027	H4-O8 = 3.661 H4-O11 = 3.635 H4-O14 = 2.926 H4-O17 = 3.184 H4-O20 = 3.187	O5-H6 = 0.984 O5-H7 = 0.983 O2-H1 = 0.999 O2-H3 = 1.047	O8-H9 = 0.964 O8-H10 = 0.964 O11-H12 = 0.963 O11-H13 = 0.963 O14-H15 = 0.963 O14-H16 = 0.987 O17-H18 = 0.964 O17-H19 = 0.964 O20-H21 = 0.962 O20-H22 = 0.972	O5-O2 = 2.552	O5-O8 = 2.744 O5-O11 = 2.734 O5-O20 = 2.887 O2-O14 = 2.491 O2-O17 = 2.623	H1-O17 = 1.625 H3-O14 = 1.451 H6-O11 = 1.750 H7-O8 = 1.763 H16-O20 = 1.724 H22-O5 = 1.984	1.493	171	D(H6-O5-O2-H1) = -126 D(H6-O5-O2-H3) = 108 D(H7-O5-O2-H1) = 2.30 D(H7-O5-O2-H3) = -124
				(8) N_m' = 6					
H4-O5 = 1.475 H4-O2 = 1.043	H4-O8 = 3.604 H4-O11 = 3.523 H4-O14 = 2.924 H4-O17 = 3.228 H4-O20 = 3.200 H4-O23 = 5.862	O5-H6 = 0.995 O5-H7 = 0.982 O2-H1 = 0.995 O2-H3 = 1.033	O8-H9 = 0.964 O8-H10 = 0.964 O11-H12 = 0.962 O11-H13 = 0.979 O14-H15 = 0.962 O14-H16 = 0.987 O17-H18 = 0.964 O17-H19 = 0.963 O20-H21 = 0.962 O20-H22 = 0.974 O23-H24 = 0.963 O23-H25 = 0.963	O5-O2 = 2.511	O5-O8 = 2.751 O5-O11 = 2.653 O5-O20 = 2.872 O2-O14 = 2.510 O2-O17 = 2.635 O2-O23 = 6.653	H1-O17 = 1.642 H3-O14 = 1.490 H6-O11 = 1.658 H7-O8 = 1.771 H13-O23 = 1.787 H16-O20 = 1.736 H22-O5 = 1.959	1.414	171	D(H6-O5-O2-H1) = -115 D(H6-O5-O2-H3) = 117 D(H7-O5-O2-H1) = 13.8 D(H7-O5-O2-H3) = -114
				GP-SM-PCM					
				(1) N_m' = 1					
H4-O5 = 1.046 H4-O2 = 1.448	H4-O8 = 3.076	O5-H6 = 0.978 O5-H7 = 1.045 O2-H1 = 0.973 O2-H3 = 0.973	O8-H9 = 0.973 O8-H10 = 0.973	O5-O2 = 2.493	O5-O8 = 2.495	H7-O8 = 1.450	1.384	177	D(H6-O5-O2-H1) = -88.2 D(H6-O5-O2-H3) = 142 D(H7-O5-O2-H1) = 39.1 D(H7-O5-O2-H3) = -91.2
				(2) N_m' = 2-Eigen					
H4-O5 = 1.022 H4-O2 = 1.526	H4-O8 = 3.071 H4-O11 = 3.108	O5-H6 = 1.022 O5-H7 = 1.022 O2-H1 = 0.975 O2-H3 = 0.975	O8-H9 = 0.975 O8-H10 = 0.975 O11-H12 = 0.975 O11-H13 = 0.975	O5-O2 = 2.547	O5-O8 = 2.547 O5-O11 = 2.547	H6-O11 = 1.526 H7-O8 = 1.526	1.493	176	D(H6-O5-O2-H1) = -89.8 D(H6-O5-O2-H3) = 141 D(H7-O5-O2-H1) = 38.3 D(H7-O5-O2-H3) = -90.5
				(3) N_m' = 3					
H4-O5 = 1.040 H4-O2 = 1.461	H4-O8 = 3.098 H4-O11 = 3.133 H4-O14 = 3.633	O5-H6 = 1.017 O5-H7 = 1.017 O2-H1 = 0.970 O2-H3 = 0.990	O8-H9 = 0.974 O8-H10 = 0.974 O11-H12 = 0.974 O11-H13 = 0.974 O14-H15 = 0.973 O14-H16 = 0.973	O5-O2 = 2.500	O5-O8 = 2.559 O5-O11 = 2.559 O2-O14 = 2.685	H3-O14 = 1.695 H6-O11 = 1.543 H7-O8 = 1.542	1.405	177	D(H6-O5-O2-H1) = -84.8 D(H6-O5-O2-H3) = 142 D(H7-O5-O2-H1) = 43.6 D(H7-O5-O2-H3) = -89.5
				(4) N_m' = 5					
H4-O5 = 1.456 H4-O2 = 1.046	H4-O8 = 3.512 H4-O11 = 3.528 H4-O14 = 3.149 H4-O17 = 3.100 H4-O20 = 3.634	O5-H6 = 0.990 O5-H7 = 0.990 O2-H1 = 1.017 O2-H3 = 1.016	O8-H9 = 0.973 O8-H10 = 0.973 O11-H12 = 0.973 O11-H13 = 0.973 O14-H15 = 0.974 O14-H16 = 0.974 O17-H18 = 0.974 O17-H19 = 0.974 O20-H21 = 0.969 O20-H22 = 0.972	O5-O2 = 2.502	O5-O8 = 2.694 O5-O11 = 2.698 O5-O20 = 2.919 O2-O14 = 2.560 O2-O17 = 2.561	H1-O17 = 1.545 H3-O14 = 1.545 H6-O11 = 1.708 H7-O8 = 1.706 H22-O5 = 1.948	1.392	177	D(H6-O5-O2-H1) = -93.5 D(H6-O5-O2-H3) = 138 D(H7-O5-O2-H1) = 29.6 D(H7-O5-O2-H3) = -99.1

[a] $r(^*H^+\cdots O_I)$ is the distance between $^*H^+$ and the inner-shell coordination water O atom. [b] $r(^*H^+\cdots O_{II})$ is the distance between $^*H^+$ and the second-shell solvent water O atom. [c] $r(O_I\text{-}H)$ is the covalent O-H bond length of the inner-shell coordination water molecule. [d] $r(O_{II}\text{-}H)$ is the covalent O-H bond length of the second-shell solvent water molecule. [e] $r(O_I\cdots O_I)$ is the distance between the inner-shell coordination water O atoms. [f] $r(O_I\cdots O_{II})$ is the distance between the inner-shell and second-shell water O atoms. [g] $r(H_D\text{-}O_A)$ is hydrogen bond length, in which H_D and O_A are the proton donating H atom and the proton accepting O atom, respectively. [h] δ is defined as $\delta = r(^*H^+\cdots O_I)_{longer} / r(^*H^+\cdots O_I)_{shorter}$.

Table S3 Structural parameters of the optimized reactant (R), transition state (TS*), and product (P) configurations in the four $^*H^+$ rattling pathways in GP-SM-PCM (N_m' = 2-*cis*, 2-*trans*, 4, and 6)

Species	Bond length or distance (Å)								Bond angle (°)	Dihedral angle (°)
	r($^*H^+\cdots O_I$)[a]	r($^*H^+\cdots O_{II}$)[b]	r(O_I-H)[c]	r(O_{II}-H)[d]	r($O_I\cdots O_I$)[e]	r($O_I\cdots O_{II}$)[f]	r(H_D-O_A)[g]	δ[h]	∠O5-H4-O2	
					(a) N_m' = 2-*cis*					
R	H4-O5 = 1.112 H4-O2 = 1.309	H4-O8 = 3.140 H4-O11 = 3.407	O5-H6 = 0.976 O5-H7 = 1.027 O2-H1 = 1.000 O2-H3 = 0.972	O8-H9 = 0.975 O8-H10 = 0.975 O11-H12 = 0.973 O11-H13 = 0.973	O5-O2 = 2.421	O5-O8 = 2.533 O2-O11 = 2.627	H1-O11 = 1.629 H7-O8 = 1.507	1.177	177	D(H6-O5-O2-H1) = -92.6 D(H6-O5-O2-H3) = 137 D(H7-O5-O2-H1) = 34.4 D(H7-O5-O2-H3) = -95.5
TS*	H4-O5 = 1.200 H4-O2 = 1.200	H4-O8 = 3.260 H4-O11 = 3.260	O5-H6 = 0.974 O5-H7 = 1.011 O2-H1 = 1.011 O2-H3 = 0.974	O8-H9 = 0.974 O8-H10 = 0.974 O11-H12 = 0.974 O11-H13 = 0.974	O5-O2 = 2.399	O5-O8 = 2.580 O2-O11 = 2.580	H1-O11 = 1.570 H7-O8 = 1.570	1.000	177	D(H6-O5-O2-H1) = -93.9 D(H6-O5-O2-H3) = 138 D(H7-O5-O2-H1) = 34.2 D(H7-O5-O2-H3) = -93.9
P	H4-O5 = 1.309 H4-O2 = 1.112	H4-O8 = 3.408 H4-O11 = 3.140	O5-H6 = 0.972 O5-H7 = 1.000 O2-H1 = 1.027 O2-H3 = 0.976	O8-H9 = 0.973 O8-H10 = 0.973 O11-H12 = 0.975 O11-H13 = 0.975	O5-O2 = 2.421	O5-O8 = 2.627 O2-O11 = 2.532	H1-O11 = 1.507 H7-O8 = 1.629	1.177	177	D(H6-O5-O2-H1) = -95.4 D(H6-O5-O2-H3) = 138 D(H7-O5-O2-H1) = 34.5 D(H7-O5-O2-H3) = -92.5
					(b) N_m' = 2-*trans*					
R	H4-O5 = 1.113 H4-O2 = 1.308	H4-O8 = 3.183 H4-O11 = 3.436	O5-H6 = 1.027 O5-H7 = 0.976 O2-H1 = 0.972 O2-H3 = 1.000	O8-H9 = 0.975 O8-H10 = 0.975 O11-H12 = 0.973 O11-H13 = 0.973	O5-O2 = 2.420	O5-O8 = 2.534 O2-O11 = 2.629	H3-O11 = 1.629 H6-O8 = 1.508	1.175	176	D(H6-O5-O2-H1) = -83.0 D(H6-O5-O2-H3) = 147 D(H7-O5-O2-H1) = 44.2 D(H7-O5-O2-H3) = -85.6
TS*	H4-O5 = 1.200 H4-O2 = 1.200	H4-O8 = 3.299 H4-O11 = 3.300	O5-H6 = 1.011 O5-H7 = 0.974 O2-H1 = 0.974 O2-H3 = 1.011	O8-H9 = 0.974 O8-H10 = 0.974 O11-H12 = 0.974 O11-H13 = 0.974	O5-O2 = 2.398	O5-O8 = 2.582 O2-O11 = 2.582	H3-O11 = 1.571 H6-O8 = 1.571	1.000	176	D(H6-O5-O2-H1) = -80.8 D(H6-O5-O2-H3) = 148 D(H7-O5-O2-H1) = 43.8 D(H7-O5-O2-H3) = -84.4
P	H4-O5 = 1.308 H4-O2 = 1.113	H4-O8 = 3.437 H4-O11 = 3.184	O5-H6 = 1.000 O5-H7 = 0.972 O2-H1 = 0.976 O2-H3 = 1.027	O8-H9 = 0.973 O8-H10 = 0.973 O11-H12 = 0.975 O11-H13 = 0.975	O5-O2 = 2.420	O5-O8 = 2.629 O2-O11 = 2.534	H3-O11 = 1.508 H6-O8 = 1.629	1.175	176	D(H6-O5-O2-H1) = -85.4 D(H6-O5-O2-H3) = 147 D(H7-O5-O2-H1) = 44.4 D(H7-O5-O2-H3) = -82.8
					(c) N_m' = 4					
R	H4-O5 = 1.086 H4-O2 = 1.354	H4-O8 = 3.164 H4-O11 = 3.201 H4-O14 = 3.534 H4-O17 = 3.510	O5-H6 = 1.008 O5-H7 = 1.008 O2-H1 = 0.987 O2-H3 = 0.987	O8-H9 = 0.974 O8-H10 = 0.974 O11-H12 = 0.974 O11-H13 = 0.974 O14-H15 = 0.973 O14-H16 = 0.973 O17-H18 = 0.973 O17-H19 = 0.973	O5-O2 = 2.439	O5-O8 = 2.591 O5-O11 = 2.591 O2-O14 = 2.703 O2-O17 = 2.702	H1-O17 = 1.716 H3-O14 = 1.716 H6-O11 = 1.584 H7-O8 = 1.584	1.247	177	D(H6-O5-O2-H1) = -89.0 D(H6-O5-O2-H3) = 138 D(H7-O5-O2-H1) = 39.4 D(H7-O5-O2-H3) = -93.0
TS*	H4-O5 = 1.200 H4-O2 = 1.200	H4-O8 = 3.314 H4-O11 = 3.346 H4-O14 = 3.346 H4-O17 = 3.314	O5-H6 = 0.996 O5-H7 = 0.996 O2-H1 = 0.996 O2-H3 = 0.996	O8-H9 = 0.973 O8-H10 = 0.973 O11-H12 = 0.973 O11-H13 = 0.973 O14-H15 = 0.973 O14-H16 = 0.973 O17-H18 = 0.973 O17-H19 = 0.973	O5-O2 = 2.398	O5-O8 = 2.645 O5-O11 = 2.646 O2-O14 = 2.646 O2-O17 = 2.645	H1-O17 = 1.650 H3-O14 = 1.650 H6-O11 = 1.650 H7-O8 = 1.650	1.000	177	D(H6-O5-O2-H1) = -90.9 D(H6-O5-O2-H3) = 139 D(H7-O5-O2-H1) = 38.9 D(H7-O5-O2-H3) = -90.9
P	H4-O5 = 1.354 H4-O2 = 1.086	H4-O8 = 3.510 H4-O11 = 3.533 H4-O14 = 3.201 H4-O17 = 3.164	O5-H6 = 0.987 O5-H7 = 0.987 O2-H1 = 1.008 O2-H3 = 1.008	O8-H9 = 0.973 O8-H10 = 0.973 O11-H12 = 0.973 O11-H13 = 0.973 O14-H15 = 0.974 O14-H16 = 0.974 O17-H18 = 0.974 O17-H19 = 0.974	O5-O2 = 2.439	O5-O8 = 2.702 O5-O11 = 2.704 O2-O14 = 2.591 O2-O17 = 2.591	H1-O17 = 1.584 H3-O14 = 1.584 H6-O11 = 1.716 H7-O8 = 1.716	1.247	177	D(H6-O5-O2-H1) = -93.0 D(H6-O5-O2-H3) = 138 D(H7-O5-O2-H1) = 39.6 D(H7-O5-O2-H3) = -88.8
					(d) N_m' = 6					
R	H4-O5 = 1.070 H4-O2 = 1.402	H4-O8 = 3.091 H4-O11 = 3.140 H4-O14 = 3.501 H4-O17 = 3.459 H4-O20 = 3.569 H4-O23 = 3.649	O5-H6 = 1.022 O5-H7 = 1.022 O2-H1 = 0.993 O2-H3 = 0.993	O8-H9 = 0.975 O8-H10 = 0.975 O11-H12 = 0.975 O11-H13 = 0.975 O14-H15 = 0.973 O14-H16 = 0.973 O17-H18 = 0.973 O17-H19 = 0.973 O20-H21 = 0.970 O20-H22 = 0.966 O23-H24 = 0.971 O23-H25 = 0.969	O5-O2 = 2.472	O5-O8 = 2.554 O5-O11 = 2.553 O5-O20 = 3.094 O2-O14 = 2.679 O2-O17 = 2.679 O2-O23 = 2.943	H1-O17 = 1.687 H3-O14 = 1.687 H6-O11 = 1.532 H7-O8 = 1.533 H22-O5 = 2.130 H24-O2 = 1.972	1.310	178	D(H6-O5-O2-H1) = -97.9 D(H6-O5-O2-H3) = 138 D(H7-O5-O2-H1) = 26.3 D(H7-O5-O2-H3) = -97.6
TS*	H4-O5 = 1.204 H4-O2 = 1.205	H4-O8 = 3.250 H4-O11 = 3.296 H4-O14 = 3.297 H4-O17 = 3.247 H4-O20 = 3.598 H4-O23 = 3.604	O5-H6 = 1.005 O5-H7 = 1.005 O2-H1 = 1.005 O2-H3 = 1.005	O8-H9 = 0.974 O8-H10 = 0.974 O11-H12 = 0.974 O11-H13 = 0.974 O14-H15 = 0.974 O14-H16 = 0.974 O17-H18 = 0.974 O17-H19 = 0.974 O20-H21 = 0.970 O20-H22 = 0.968 O23-H24 = 0.968 O23-H25 = 0.970	O5-O2 = 2.408	O5-O8 = 2.615 O5-O11 = 2.614 O5-O20 = 3.017 O2-O14 = 2.615 O2-O17 = 2.614 O2-O23 = 3.017	H1-O17 = 1.611 H3-O14 = 1.611 H6-O11 = 1.610 H7-O8 = 1.611 H22-O5 = 2.049 H24-O2 = 2.049	1.001	178	D(H6-O5-O2-H1) = -97.4 D(H6-O5-O2-H3) = 138 D(H7-O5-O2-H1) = 26.5 D(H7-O5-O2-H3) = -97.6
P	H4-O5 = 1.402 H4-O2 = 1.070	H4-O8 = 3.459 H4-O11 = 3.480 H4-O14 = 3.140 H4-O17 = 3.090 H4-O20 = 3.631 H4-O23 = 3.572	O5-H6 = 0.993 O5-H7 = 0.993 O2-H1 = 1.022 O2-H3 = 1.022	O8-H9 = 0.973 O8-H10 = 0.973 O11-H12 = 0.973 O11-H13 = 0.973 O14-H15 = 0.975 O14-H16 = 0.975 O17-H18 = 0.975 O17-H19 = 0.975 O20-H21 = 0.969 O20-H22 = 0.971 O23-H24 = 0.966 O23-H25 = 0.970	O5-O2 = 2.472	O5-O8 = 2.678 O5-O11 = 2.679 O5-O20 = 2.941 O2-O14 = 2.552 O2-O17 = 2.554 O2-O23 = 3.094	H1-O17 = 1.533 H3-O14 = 1.532 H6-O11 = 1.687 H7-O8 = 1.687 H22-O5 = 1.970 H24-O2 = 2.129	1.310	178	D(H6-O5-O2-H1) = -101 D(H6-O5-O2-H3) = 135 D(H7-O5-O2-H1) = 22.6 D(H7-O5-O2-H3) = -102

[a] r($^*H^+\cdots O_I$) is the distance between $^*H^+$ and the inner-shell coordination water O atom. [b] r($^*H^+\cdots O_{II}$) is the distance between $^*H^+$ and the second-shell solvent water O atom. [c] r(O_I-H) is the covalent O-H bond length of the inner-shell coordination water molecule. [d] r(O_{II}-H) is the covalent O-H bond length of the second-shell solvent water molecule. [e] r($O_I\cdots O_I$) is the distance between the inner-shell coordination water O atoms. [f] r($O_I\cdots O_{II}$) is the distance between the inner-shell and second-shell water O atoms. [g] r(H_D-O_A) is hydrogen bond length, in which H_D and O_A are the proton donating H atom and the proton accepting O atom, respectively. [h] δ is defined as δ= r($^*H^+\cdots O_I$)$_{longer}$/ r($^*H^+\cdots O_I$)$_{shorter}$.

S3. Testing results with BLYP, ωB97X-D, and M06-2X density functionals

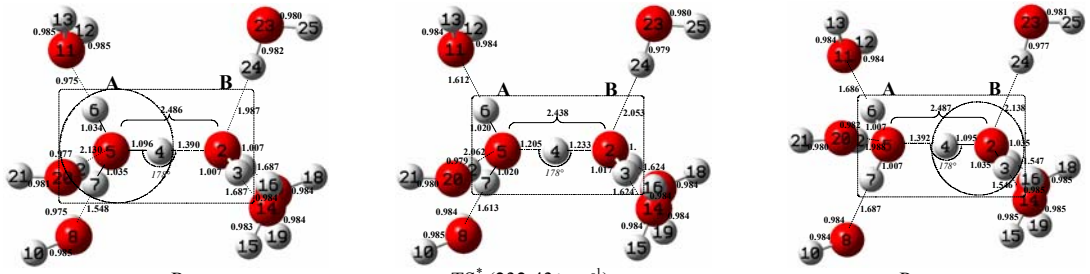
In order to verify the phenomenon of hydrogen bond length changing in the proton rattling pathway with N_m' = 6, additional computations on the N_m' = 6 pathway with other density functionals and implicit solvation model are conducted. The tested methods include BLYP/6-311++G(d,p)-PCM, ωB97X-D/6-311++G(d,p)-PCM, and M06-2X/6-311++G(d,p)-SMD. The testing results are listed in Fig. S6, Table S4, and Table S5. The detailed modeling results are as follows:

(a) BLYP/6-311++G(d,p)-PCM. The optimized R, TS* and P configurations and the thermodynamics parameters are very close to the B3LYP/6-311++G(d,p)-PCM results, and the concerted hydrogen bond length changing can be observed;

(b) ωB97X-D/6-311++G(d,p)-PCM. The optimized R, TS* and P configurations are similar to those obtained by B3LYP/6-311++G(d,p)-PCM. Although there exist differences in specific structural and thermodynamic parameters (for instance, the second-shell hydrogen bond lengths are longer and the activation energies are higher for the ωB97X-D/6-311++G(d,p)-PCM method), the concerted hydrogen bond length changing can be found during R→TS*→P;

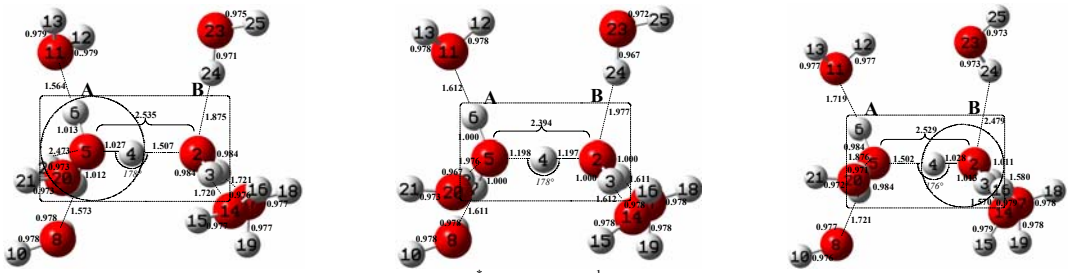
(c) M06-2X/6-311++G(d,p)-SMD. The optimized R, TS* and P configurations are different from those obtained by B3LYP/6-311++G(d,p)-PCM in that additional hydrogen bonds are formed between the second-shell solvent water molecules. Whereas, the kinetic proton rattling process and the thermodynamic parameters are similar to the B3LYP/6-311++G(d,p)-PCM results, and the concerted hydrogen bond length changing also exists in the proton rattling pathway.

In general, the phenomenon of the concerted hydrogen bond length changing during the proton rattling in the N_m' = 6 pathway is verified by different computational methods. It suggests that the modeled proton rattling pathway obtained with the B3LYP/6-311++G(d,p)-PCM method is reliable.



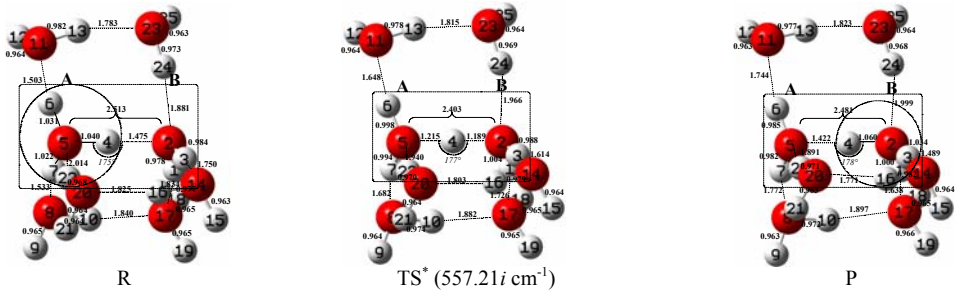
R TS* (232.43*i* cm^{-1}) P

(a) BLYP/6-311++G(d,p)-PCM



R TS* (496.24*i* cm^{-1}) P

(b) ωB97X-D/6-311++G(d,p)-PCM



R TS* (557.21*i* cm^{-1}) P

(c) M06-2X/6-311++G(d,p)-SMD

Fig. S6 Optimized reactant (R), transition state (TS*), and product (P) configurations in the $^*H^+$ rattling pathways with N_m' = 6 obtained by the BLYP, ωB97X-D, and M06-2X density functionals.

Table S4 Thermodynamic parameters for the $^*H^+$ rattling pathways with N_m' = 6 obtained by the BLYP, ωB97X-D, and M06-2X density functionals[a]

No.	species	$\Delta E_{elect(0K)}$ (kJ mol^{-1})	$\Delta E_{ZPE(0K)}$ (kJ mol^{-1})	$\Delta E_{0(0K)}$ (kJ mol^{-1})	ΔE_{298} (kJ mol^{-1})	ΔH_{298} (kJ mol^{-1})	ΔS_{298} (J mol^{-1} K^{-1})	ΔG_{298} (kJ mol^{-1})	τ_{TS} (fs)[b]
(a) BLYP/6-311++G(d,p)-PCM	TS*	1.3	-4.2	-3.0	-4.7	-4.7	-11.7	-1.2	143
	P	0.3	-0.4	-0.1	0.4	0.4	7.4	-1.9	
(b) ωB97X-D/6-311++G(d,p)-PCM	TS*	13.6	-3.0	10.6	7.2	7.2	-33.2	17.1	67
	P	-0.4	0.1	-0.3	-0.7	-0.7	-13.8	3.4	
(c) M06-2X/6-311++G(d,p)-SMD	TS*	3.6	-6.3	-2.7	-4.0	-4.0	-8.8	-1.3	60
	P	1.9	1.1	3.0	2.3	2.3	-9.9	5.2	

[a] The thermodynamic values are relative to R. [b] $\tau_{TS} = 1/(c|\nu^{\neq}|)$, where c is the speed of light and $\nu^{\neq}$ is the imaginary frequency of TS*.

Table S5 Structural parameters of the optimized reactant (R), transition state (TS*), and product (P) configurations in the $^*H^+$ rattling pathways with N_m' = 6 obtained by the BLYP, ωB97X-D, and M06-2X density functionals

Species	Bond length or distance (Å)								Bond angle (°)	Dihedral angle (°)
	$r(^*H^+\cdots O_I)^a$	$r(^*H^+\cdots O_{II})^b$	$r(O_I\text{-}H)^c$	$r(O_{II}\text{-}H)^d$	$r(O_I\cdots O_I)^e$	$r(O_I\cdots O_{II})^f$	$r(H_D\text{-}O_A)^g$	δ^h	∠O5-H4-O2	
				(a) BLYP/6-311++G(d,p)-PCM						
R	H4-O5 = 1.096 H4-O2 = 1.390	H4-O8 = 3.128 H4-O11 = 3.182 H4-O14 = 3.501 H4-O17 = 3.451 H4-O20 = 3.606 H4-O23 = 3.688	O5-H6 = 1.034 O5-H7 = 1.035 O2-H1 = 1.007 O2-H3 = 1.007	O8-H9 = 0.985 O8-H10 = 0.985 O11-H12 = 0.985 O11-H13 = 0.985 O14-H15 = 0.983 O14-H16 = 0.984 O17-H18 = 0.984 O17-H19 = 0.984 O20-H21 = 0.981 O20-H22 = 0.977 O23-H24 = 0.982 O23-H25 = 0.980	O5-O2 = 2.486	O5-O8 = 2.582 O5-O11 = 2.580 O5-O20 = 3.105 O2-O14 = 2.692 O2-O17 = 2.692 O2-O23 = 2.969	H1-O17 = 1.687 H3-O14 = 1.687 H6-O11 = 1.547 H7-O8 = 1.548 H22-O5 = 2.130 H24-O2 = 1.987	1.268	178	D(H6-O5-O2-H1) = -97.6 D(H6-O5-O2-H3) = 140 D(H7-O5-O2-H1) = 25.3 D(H7-O5-O2-H3) = -97.2
TS*	H4-O5 = 1.205 H4-O2 = 1.233	H4-O8 = 3.256 H4-O11 = 3.310 H4-O14 = 3.335 H4-O17 = 3.281 H4-O20 = 3.633 H4-O23 = 3.656	O5-H6 = 1.020 O5-H7 = 1.020 O2-H1 = 1.017 O2-H3 = 1.017	O8-H9 = 0.984 O8-H10 = 0.985 O11-H12 = 0.984 O11-H13 = 0.984 O14-H15 = 0.984 O14-H16 = 0.984 O17-H18 = 0.984 O17-H19 = 0.984 O20-H21 = 0.980 O20-H22 = 0.979 O23-H24 = 0.979 O23-H25 = 0.980	O5-O2 = 2.438	O5-O8 = 2.631 O5-O11 = 2.630 O5-O20 = 3.040 O2-O14 = 2.640 O2-O17 = 2.640 O2-O23 = 3.034	H1-O17 = 1.624 H3-O14 = 1.624 H6-O11 = 1.612 H7-O8 = 1.613 H22-O5 = 2.062 H24-O2 = 2.055	1.023	178	D(H6-O5-O2-H1) = -96.9 D(H6-O5-O2-H3) = 141 D(H7-O5-O2-H1) = 25.6 D(H7-O5-O2-H3) = -96.9
P	H4-O5 = 1.392 H4-O2 = 1.095	H4-O8 = 3.444 H4-O11 = 3.507 H4-O14 = 3.177 H4-O17 = 3.117 H4-O20 = 3.690 H4-O23 = 3.614	O5-H6 = 1.007 O5-H7 = 1.007 O2-H1 = 1.035 O2-H3 = 1.035	O8-H9 = 0.984 O8-H10 = 0.984 O11-H12 = 0.984 O11-H13 = 0.984 O14-H15 = 0.985 O14-H16 = 0.985 O17-H18 = 0.985 O17-H19 = 0.985 O20-H21 = 0.980 O20-H22 = 0.982 O23-H24 = 0.977 O23-H25 = 0.981	O5-O2 = 2.487	O5-O8 = 2.692 O5-O11 = 2.692 O5-O20 = 2.969 O2-O14 = 2.579 O2-O17 = 2.580 O2-O23 = 3.113	H1-O17 = 1.547 H3-O14 = 1.546 H6-O11 = 1.686 H7-O8 = 1.687 H22-O5 = 1.988 H24-O2 = 2.138	1.271	178	D(H6-O5-O2-H1) = -83.0 D(H6-O5-O2-H3) = 154 D(H7-O5-O2-H1) = 39.3 D(H7-O5-O2-H3) = -83.7
				(b) ωB97X-D/6-311++G(d,p)-PCM						
R	H4-O5 = 1.027 H4-O2 = 1.507	H4-O8 = 3.048 H4-O11 = 3.090 H4-O14 = 3.556 H4-O17 = 3.503 H4-O20 = 3.488 H4-O23 = 3.397	O5-H6 = 1.013 O5-H7 = 1.012 O2-H1 = 0.984 O2-H3 = 0.984	O8-H9 = 0.978 O8-H10 = 0.978 O11-H12 = 0.979 O11-H13 = 0.979 O14-H15 = 0.977 O14-H16 = 0.976 O17-H18 = 0.977 O17-H19 = 0.977 O20-H21 = 0.973 O20-H22 = 0.973 O23-H24 = 0.971 O23-H25 = 0.975	O5-O2 = 2.535	O5-O8 = 2.583 O5-O11 = 2.577 O5-O20 = 3.282 O2-O14 = 2.704 O2-O17 = 2.703 O2-O23 = 2.843	H1-O17 = 1.721 H3-O14 = 1.720 H6-O11 = 1.564 H7-O8 = 1.573 H22-O5 = 2.473 H24-O2 = 1.875	1.467	178	D(H6-O5-O2-H1) = -94.9 D(H6-O5-O2-H3) = 143 D(H7-O5-O2-H1) = 24.9 D(H7-O5-O2-H3) = -97.1
TS*	H4-O5 = 1.198 H4-O2 = 1.197	H4-O8 = 3.221 H4-O11 = 3.254 H4-O14 = 3.252 H4-O17 = 3.224 H4-O20 = 3.393 H4-O23 = 3.342	O5-H6 = 1.000 O5-H7 = 1.000 O2-H1 = 1.000 O2-H3 = 1.000	O8-H9 = 0.978 O8-H10 = 0.978 O11-H12 = 0.978 O11-H13 = 0.978 O14-H15 = 0.978 O14-H16 = 0.978 O17-H18 = 0.978 O17-H19 = 0.978 O20-H21 = 0.973 O20-H22 = 0.967 O23-H24 = 0.967 O23-H25 = 0.972	O5-O2 = 2.394	O5-O8 = 2.610 O5-O11 = 2.612 O5-O20 = 2.936 O2-O14 = 2.612 O2-O17 = 2.610 O2-O23 = 2.932	H1-O17 = 1.611 H3-O14 = 1.612 H6-O11 = 1.612 H7-O8 = 1.611 H22-O5 = 1.976 H24-O2 = 1.977	1.001	178	D(H6-O5-O2-H1) = -102 D(H6-O5-O2-H3) = 135 D(H7-O5-O2-H1) = 21.0 D(H7-O5-O2-H3) = -102
P	H4-O5 = 1.502 H4-O2 = 1.028	H4-O8 = 3.524 H4-O11 = 3.554 H4-O14 = 3.107 H4-O17 = 3.092 H4-O20 = 3.401 H4-O23 = 3.440	O5-H6 = 0.984 O5-H7 = 0.984 O2-H1 = 1.011 O2-H3 = 1.013	O8-H9 = 0.977 O8-H10 = 0.976 O11-H12 = 0.977 O11-H13 = 0.977 O14-H15 = 0.979 O14-H16 = 0.979 O17-H18 = 0.978 O17-H19 = 0.978 O20-H21 = 0.972 O20-H22 = 0.971 O23-H24 = 0.973 O23-H25 = 0.973	O5-O2 = 2.529	O5-O8 = 2.703 O5-O11 = 2.703 O5-O20 = 2.844 O2-O14 = 2.582 O2-O17 = 2.589 O2-O23 = 3.269	H1-O17 = 1.580 H3-O14 = 1.570 H6-O11 = 1.719 H7-O8 = 1.721 H22-O5 = 1.876 H24-O2 = 2.479	1.461	176	D(H6-O5-O2-H1) = -97.5 D(H6-O5-O2-H3) = 141 D(H7-O5-O2-H1) = 25.5 D(H7-O5-O2-H3) = -96.4
				(c) M06-2X/6-311++G(d,p)-SMD						
R	H4-O5 = 1.040 H4-O2 = 1.475	H4-O8 = 2.881 H4-O11 = 2.921 H4-O14 = 3.308 H4-O17 = 3.217 H4-O20 = 3.006 H4-O23 = 3.004	O5-H6 = 1.031 O5-H7 = 1.022 O2-H1 = 0.978 O2-H3 = 0.984	O8-H9 = 0.965 O8-H10 = 0.964 O11-H12 = 0.964 O11-H13 = 0.982 O14-H15 = 0.963 O14-H16 = 0.977 O17-H18 = 0.965 O17-H19 = 0.965 O20-H21 = 0.964 O20-H22 = 0.968 O23-H24 = 0.973 O23-H25 = 0.963	O5-O2 = 2.513	O5-O8 = 2.545 O5-O11 = 2.524 O5-O20 = 2.946 O2-O14 = 2.718 O2-O17 = 2.782 O2-O23 = 2.838	H1-O17 = 1.831 H3-O14 = 1.750 H6-O11 = 1.503 H7-O8 = 1.533 H22-O5 = 2.014 H24-O2 = 1.881 H13-O23 = 1.784 H16-O20 = 1.825 H10-O17 = 1.840	1.418	175	D(H6-O5-O2-H1) = -118 D(H6-O5-O2-H3) = 129 D(H7-O5-O2-H1) = -1.1 D(H7-O5-O2-H3) = -114
TS*	H4-O5 = 1.215 H4-O2 = 1.189	H4-O8 = 2.997 H4-O11 = 3.127 H4-O14 = 3.079 H4-O17 = 3.092 H4-O20 = 3.035 H4-O23 = 3.020	O5-H6 = 0.998 O5-H7 = 0.994 O2-H1 = 1.004 O2-H3 = 0.988	O8-H9 = 0.964 O8-H10 = 0.974 O11-H12 = 0.964 O11-H13 = 0.978 O14-H15 = 0.964 O14-H16 = 0.979 O17-H18 = 0.965 O17-H19 = 0.965 O20-H21 = 0.964 O20-H22 = 0.970 O23-H24 = 0.969 O23-H25 = 0.964	O5-O2 = 2.403	O5-O8 = 2.651 O5-O11 = 2.632 O5-O20 = 2.887 O2-O14 = 2.607 O2-O17 = 2.697 O2-O23 = 2.910	H1-O17 = 1.726 H3-O14 = 1.614 H6-O11 = 1.648 H7-O8 = 1.682 H22-O5 = 1.940 H24-O2 = 1.966 H13-O23 = 1.815 H16-O20 = 1.803 H10-O17 = 1.882	1.022	177	D(H6-O5-O2-H1) = -117 D(H6-O5-O2-H3) = 126 D(H7-O5-O2-H1) = -0.9 D(H7-O5-O2-H3) = -117
P	H4-O5 = 1.422 H4-O2 = 1.060	H4-O8 = 3.056 H4-O11 = 3.267 H4-O14 = 2.933 H4-O17 = 3.020 H4-O20 = 3.012 H4-O23 = 3.030	O5-H6 = 0.985 O5-H7 = 0.982 O2-H1 = 1.034 O2-H3 = 1.000	O8-H9 = 0.963 O8-H10 = 0.972 O11-H12 = 0.963 O11-H13 = 0.977 O14-H15 = 0.964 O14-H16 = 0.982 O17-H18 = 0.965 O17-H19 = 0.966 O20-H21 = 0.963 O20-H22 = 0.971 O23-H24 = 0.968 O23-H25 = 0.964	O5-O2 = 2.481	O5-O8 = 2.719 O5-O11 = 2.711 O5-O20 = 2.842 O2-O14 = 2.515 O2-O17 = 2.629 O2-O23 = 2.935	H1-O17 = 1.638 H3-O14 = 1.489 H6-O11 = 1.744 H7-O8 = 1.772 H22-O5 = 1.891 H24-O2 = 1.999 H13-O23 = 1.823 H16-O20 = 1.771 H10-O17 = 1.897	1.342	177	D(H6-O5-O2-H1) = -115 D(H6-O5-O2-H3) = 127 D(H7-O5-O2-H1) = -1.9 D(H7-O5-O2-H3) = -120

[a] $r(^*H^+\cdots O_I)$ is the distance between $^*H^+$ and the inner-shell coordination water O atom. [b] $r(^*H^+\cdots O_{II})$ is the distance between $^*H^+$ and the second-shell solvent water O atom. [c] $r(O_I\text{-}H)$ is the covalent O-H bond length of the inner-shell coordination water molecule. [d] $r(O_{II}\text{-}H)$ is the covalent O-H bond length of the second-shell solvent water molecule. [e] $r(O_I\cdots O_I)$ is the distance between the inner-shell coordination water O atoms. [f] $r(O_I\cdots O_{II})$ is the distance between the inner-shell and second-shell water O atoms. [g] $r(H_D\text{-}O_A)$ is hydrogen bond length, in which H_D and O_A are the proton donating H atom and the proton accepting O atom, respectively. [h] δ is defined as $\delta = r(^*H^+\cdots O_I)_{longer}/\ r(^*H^+\cdots O_I)_{shorter}$.

S4. Cartesian coordinates of the reaction species in the $^{*}H^{+}$ rattling pathways (Å)

(a) N_m' = 2-*cis*

R				TS				P			
H	1.41298800	0.40130300	0.91435600	H	1.40904300	0.41242800	0.91946700	H	1.43062900	0.43190400	0.94138100
O	1.08610100	-0.43650800	0.47734200	O	1.09496400	-0.44725500	0.48933900	O	1.12373100	-0.44918300	0.51174200
H	1.78624100	-0.77072600	-0.10773100	H	1.78020200	-0.76868800	-0.12315500	H	1.79483400	-0.76495600	-0.12215600
H	-0.10879900	-0.41442700	-0.05753300	H	0.00012200	-0.41808200	-0.00000300	H	0.10907100	-0.41413700	0.05758600
O	-1.12326800	-0.44996700	-0.51240400	O	-1.09491900	-0.44748400	-0.48943600	O	-1.08617500	-0.43666300	-0.47682200
H	-1.79460700	-0.76595000	0.12115000	H	-1.78009400	-0.76914100	0.12300300	H	-1.78620300	-0.77013700	0.10880300
H	-1.43020600	0.43113800	-0.94186600	H	-1.40920500	0.41211800	-0.91949800	H	-1.41316900	0.40053900	-0.91488000
O	-1.78536200	1.72201600	-1.63421000	O	-1.79317800	1.74845000	-1.64971400	O	-1.83877600	1.76941900	-1.68860600
H	-2.25522500	2.39731200	-1.11093400	H	-2.23021700	2.44320700	-1.12513300	H	-2.23540200	2.48652500	-1.16328600
H	-2.27158900	1.64532600	-2.47589300	H	-2.31166700	1.66914000	-2.47060600	H	-2.40311200	1.67865500	-2.47658300
O	1.83801700	1.77057800	1.68757000	O	1.79275600	1.74861800	1.64971900	O	1.78487400	1.72214500	1.63493900
H	2.40087000	1.67978700	2.47660500	H	2.31110100	1.66930500	2.47070300	H	2.27107600	1.64479200	2.47658700
H	2.23620600	2.48702200	1.16253000	H	2.22981300	2.44345000	1.12524900	H	2.25465800	2.39799700	1.11229200

(b) N_m' = 2-*trans*

R				TS				P			
H	1.36831700	0.21211500	0.95105100	H	1.36871500	0.24772100	0.92091500	H	1.39809400	0.28130400	0.89446600
O	1.08806400	-0.57600800	0.45641700	O	1.10798400	-0.56841600	0.45830700	O	1.15127600	-0.55656300	0.45978000
H	1.82213800	-0.82550800	-0.17516300	H	1.83799300	-0.82503400	-0.19279800	H	1.87706100	-0.82581900	-0.21487400
H	-0.12100800	-0.52159400	-0.04006200	H	-0.00003000	-0.52639100	-0.00009200	H	0.12072000	-0.52369300	0.04012400
O	-1.15148600	-0.55364500	-0.45968000	O	-1.10789700	-0.56867800	-0.45841400	O	-1.08806400	-0.57829300	-0.45626400
H	-1.87702500	-0.82400200	0.21485700	H	-1.83782400	-0.82539300	0.19277300	H	-1.82218900	-0.82577500	0.17601600
H	-1.39827100	0.28484300	-0.89316300	H	-1.36879500	0.24733900	-0.92114400	H	-1.36759900	0.20925800	-0.95223300
O	-2.98559100	-1.23654800	1.15056900	O	-3.00645100	-1.23674900	1.15883000	O	-3.04482100	-1.24168100	1.16925200
H	-2.94228000	-0.91779400	2.07092300	H	-2.95760800	-0.93873500	2.08490900	H	-2.99662300	-0.95825400	2.09920600
H	-3.18835000	-2.18879000	1.20220000	H	-3.24525600	-2.18042600	1.19430800	H	-3.30643900	-2.17893800	1.19305300
O	3.04367300	-1.24284200	-1.16904800	O	3.00678300	-1.23603300	-1.15891800	O	2.98619600	-1.23402700	-1.15172600
H	2.99203000	-0.96371600	-2.10011900	H	2.95659700	-0.94018100	-2.08561700	H	2.94253400	-0.91520400	-2.07202800
H	3.30821400	-2.17935900	-1.18938700	H	3.24754400	-2.17928100	-1.19249300	H	3.19456400	-2.18505100	-1.20328700

(c) N_m' = 4

R				TS				P			
H	1.39858100	0.36760000	0.89175500	H	1.40165000	0.37263200	0.90768600	H	1.46140100	0.39528000	0.93625700
O	1.08472300	-0.44545200	0.42828500	O	1.10657000	-0.46818100	0.46242000	O	1.17328100	-0.46733300	0.50111300
H	1.80259300	-0.77061500	-0.16603100	H	1.80983100	-0.78404200	-0.16841000	H	1.85940000	-0.78691700	-0.16494900
H	-0.16601500	-0.42559700	-0.08914100	H	0.00008400	-0.43621000	-0.00007600	H	0.16830800	-0.42553700	0.09009900
O	-1.17073900	-0.46684300	-0.50073600	O	-1.10646100	-0.46831400	-0.46256100	O	-1.08235800	-0.44537800	-0.42723500
H	-1.85695800	-0.78841700	0.16431200	H	-1.80962500	-0.78427900	0.16832000	H	-1.80008400	-0.76936800	0.16789500
H	-1.45897400	0.39712000	-0.93321200	H	-1.40171500	0.37245800	-0.90777800	H	-1.39608000	0.36718300	-0.89166300
O	-1.83456500	1.74564900	-1.67363300	O	-1.80190900	1.76137200	-1.70429800	O	-1.84360800	1.78031200	-1.75632400
H	-2.21921500	2.46660000	-1.14368500	H	-2.15631200	2.50350700	-1.18397500	H	-2.17590400	2.54210500	-1.25121800
H	-2.39193100	1.67476000	-2.46925300	H	-2.38846200	1.68076400	-2.47674900	H	-2.46133900	1.67590800	-2.50031000
O	-2.98341500	-1.30318600	1.15121400	O	-3.00813600	-1.31929700	1.16910400	O	-3.06553000	-1.34724300	1.17356300
H	-2.92545600	-1.03941600	2.08695500	H	-2.96195700	-1.07853000	2.11088400	H	-3.02558600	-1.14505600	2.12401400
H	-3.16875300	-2.25931300	1.15551700	H	-3.21782800	-2.26945000	1.15197400	H	-3.29009100	-2.29200400	1.12027900
O	3.06891700	-1.35189100	-1.16844400	O	3.00849700	-1.31884400	-1.16908900	O	2.98507300	-1.29832300	-1.15465100
H	3.03387900	-1.14698200	-2.11850500	H	2.96144200	-1.07949500	-2.11118800	H	2.92520700	-1.03285900	-2.08979300
H	3.28937100	-2.29770300	-1.11673000	H	3.21940300	-2.26870500	-1.15072000	H	3.17158400	-2.25421000	-1.16108100
O	1.84578600	1.78252300	1.75366200	O	1.80141900	1.76158700	1.70429600	O	1.83724300	1.74185500	1.68044700
H	2.46300800	1.68014800	2.49835100	H	2.38766400	1.68106000	2.47698900	H	2.39514200	1.66876000	2.47549100
H	2.17843000	2.54293200	1.24670000	H	2.15598700	2.50371300	1.18407200	H	2.22150000	2.46433100	1.15229500

(d) N_m' = 6

R				TS				P			
H	-1.36608700	0.71763600	-0.74607500	H	-1.35559000	0.72879900	-0.72134100	H	1.40879300	0.16489900	0.86093400
O	-1.09154100	-0.23273600	-0.66281000	O	-1.09878200	-0.23924000	-0.64066200	O	1.09334800	-0.61879200	0.28571900
H	-1.80721600	-0.71113600	-0.16850300	H	-1.81645900	-0.72676900	-0.13398600	H	1.76754500	-0.80632000	-0.45890300
H	0.18189700	-0.40398500	-0.10259800	H	-0.00642300	-0.38746200	-0.15367300	H	0.11285000	-0.44253200	-0.10625000
O	1.15422900	-0.57149100	0.31281900	O	1.08391200	-0.57884500	0.31936200	O	-1.17167700	-0.25762600	-0.63556400
H	1.85504600	-0.71781000	-0.41646200	H	1.78887900	-0.72214200	-0.38231500	H	-1.87627500	-0.74803500	-0.13726100
H	1.43442000	0.19817800	0.92416700	H	1.37637500	0.16721300	0.92577600	H	-1.44718500	0.69447900	-0.69019700
O	1.78241400	1.34037100	1.88530400	O	1.76424200	1.35643300	1.94104900	O	-1.81672000	2.33451700	-0.83448000
H	2.18240800	2.14338000	1.50398600	H	2.13188300	2.17458000	1.56195300	H	-2.06962400	2.82062200	-0.03055600
H	2.32064400	1.11825500	2.66716700	H	2.33829900	1.13571900	2.69606600	H	-2.46925100	2.59251400	-1.50854100
O	2.96675900	-0.95696900	-1.44297800	O	2.96626100	-0.97298800	-1.45123500	O	-3.10098200	-1.59214900	0.65878800
H	3.01050500	-0.36318300	-2.21482300	H	3.01828400	-0.38146400	-2.22301900	H	-3.09773500	-1.60783300	1.63146600
H	3.07736900	-1.86075900	-1.79113300	H	3.08568800	-1.87398000	-1.80084700	H	-3.26957200	-2.51055900	0.38544500
O	-3.05235700	-1.53347500	0.61794400	O	-3.01078700	-1.50621100	0.61459900	O	2.84165700	-1.11339600	-1.50688700
H	-3.06704500	-1.53133400	1.59065700	H	-3.06130700	-1.45320800	1.58549200	H	2.91619700	-0.51800400	-2.27496400
H	-3.22148900	-2.45577900	0.35836700	H	-3.15200100	-2.44395400	0.39350800	H	2.88643600	-2.01988000	-1.86254100
O	-1.73440300	2.35356400	-0.93410800	O	-1.67277900	2.29879500	-0.89527200	O	1.80833400	1.33186600	1.77093100
H	-2.32995600	2.60288700	-1.66204500	H	-2.21108900	2.57017900	-1.66008600	H	2.38982800	1.13069200	2.52705300
H	-2.05617700	2.84336900	-0.15751600	H	-2.03898100	2.77946000	-0.13174600	H	2.18439700	2.12507900	1.34709200
O	0.99990500	-3.10834800	2.07787300	O	1.01214600	-3.07979100	2.00465300	O	-1.18807000	-1.29741700	-3.38626800
H	1.89510200	-3.28887800	2.40537600	H	1.91268700	-3.21005600	2.34027000	H	-2.08671800	-1.16213900	-3.72376800
H	1.09534900	-2.32168500	1.52476300	H	1.06275300	-2.27549000	1.46783900	H	-1.20751100	-0.94850100	-2.48011500
O	-1.09779800	-1.34338200	-3.38800400	O	-1.11732200	-1.36759600	-3.43871500	O	0.96399000	-3.13295000	2.08395900
H	-1.11466400	-0.97165500	-2.49093700	H	-1.13625700	-0.99984800	-2.54314300	H	1.04403000	-2.34075500	1.53628300
H	-1.99167700	-1.19780500	-3.73383000	H	-2.01610600	-1.23676500	-3.77886000	H	1.86382500	-3.30234700	2.40462800