Supplementary Material (ESI) for Chemical Communications

Supporting Information

Supermolecule density functional calculations on the water exchange of aquated Al(III) species in aqueous solution†

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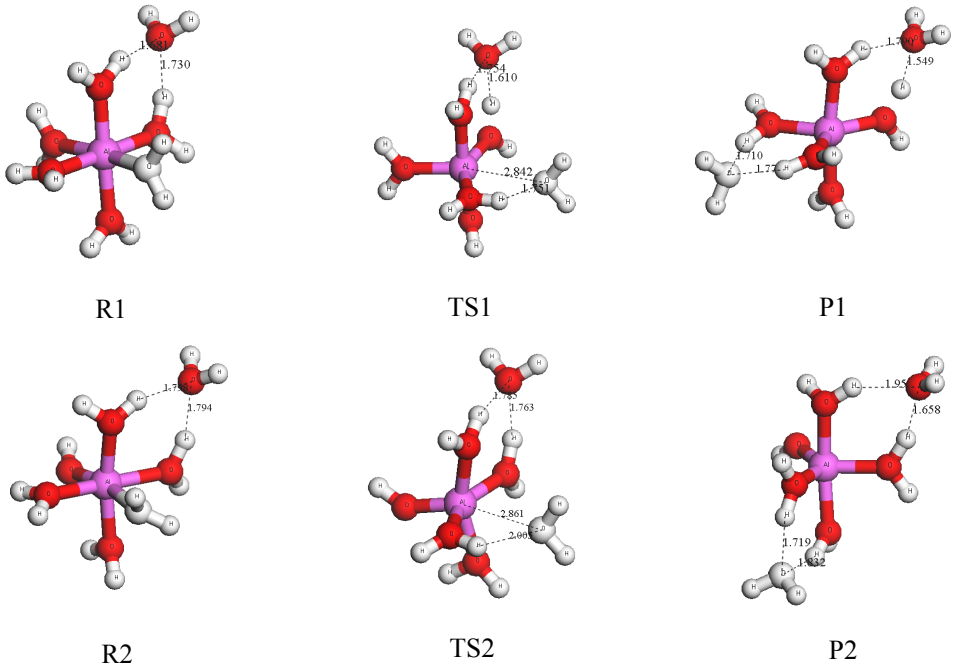
The structures and the selected structural parameters for the water exchange on $A(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ in the gas-phase reaction system, energies profiles of water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ for the gas-phase reaction system and supermolecular reaction system in aqueous solution, the technical details of the calculations and Cartesian coordinates of all supermolecular geometries optimized at B3LYP/6-311+G.**

1. Figure S1. Species involved in the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ for gas-phase reaction system optimized at B3LYP/6-311+G**



R1 TS1 P1

R2 TS2 P2

Figure S1. Species involved in the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ for gas-phase reaction system optimized at B3LYP/6-311+G**

2. The selected structural parameters for the water exchange on $A(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ in the gas-phase reaction system

Table S1 Selected Structural Parameters (Å) for the water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ in the gas-phase reaction system

complex	r(Al-O_I)	r(Al-O_L)	r(H-O_L)	r(Al-O_I)	∑r(Al-O)
R1	1.956,1.956,1.952,1.948,1.908,1.918			1.940	15.331
TS1	1.895,1.931,1.869,1.899,1.864	2.842	1.751	1.892	15.964
P1	1.903,1.960,1.847,1.866,1.871	3.490	1.710,1.773	1.889	16.622
R2	1.728,2.001,1.976,1.976,1.965,1.965			1.935	15.379
TS2	1.694,1.963,1.914,1.932,1.911	2.861	2.005	1.883	16.035
P2	1.687,1.889,1.965,1.883,1.956	3.761	1.719,1.832	1.876	16.902

3. Energies profiles of water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ for the gas-phase reaction system and supermolecular reaction system in aqueous solution

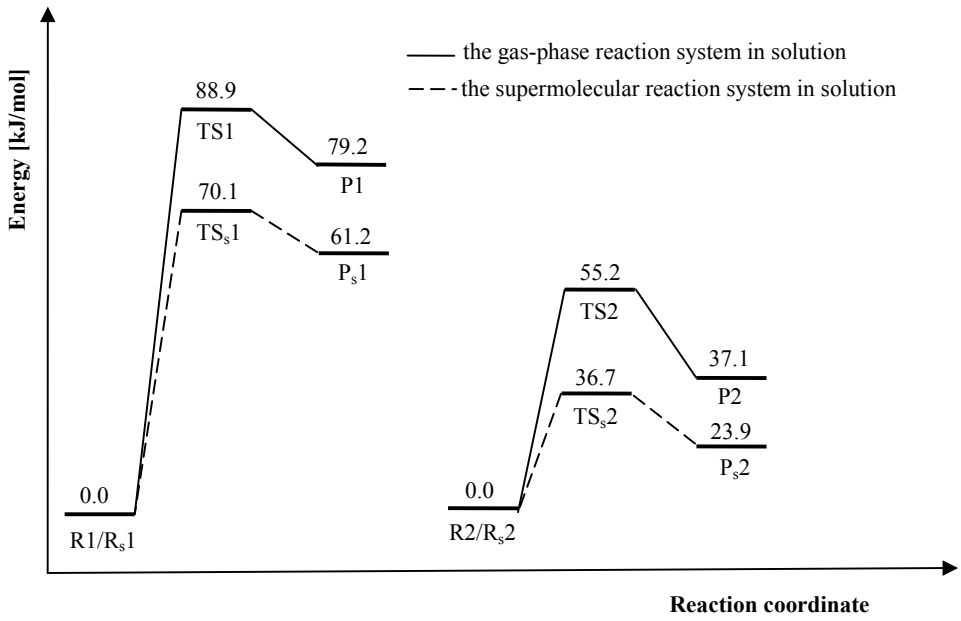


Figure S2. Energies profiles for water exchange on $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ for the gas-phase reaction system and supermolecular reaction system in aqueous solution

4. The technical details of the calculations

(1) The two models proposed in the present study are defined as follows:

(a) The gas-phase model. The gas-phase model in the gas phase did not consider the solvent effect. The energy calculations (ΔE(g)) for the gas-phase model in the gas phase were performing on the

optimized structures (R1, R2, TS1, TS2, P1 and P2) of the gas-phase reaction system. The gas-phase model in the aqueous solution did not consider the explicit solvent water effect. The energy calculations (ΔE(aq)) for the gas-phase model in the aqueous solution were performing single-point energy calculations with PCM method on the optimized structures (R1, R2, TS1, TS2, P1 and P2) of the gas-phase reaction system.

(b) The supermolecular model. The supermolecular model in the gas phase only considers the explicit solvent water effects but does not consider the bulk water effects. The energy calculations ($\Delta E_s(g)$) for the supermolecular model in the gas phase were performing on the optimized structures (R_s1, R_s2, TS_s1, TS_s2, P_s1 and P_s2) of the supermolecular reaction system. The supermolecular model in aqueous solution not only considers the explicit solvent water effects but also considers the bulk water effects. The energy calculations ($\Delta E_s(aq)$) for the supermolecular model in the aqueous solution were performing single-point energy calculations with PCM method on the optimized structures (R1, R2, TS1, TS2, P1 and P2) of the supermolecular reaction system.

(2) The detailed optimization for the reactants, transition states and products in the gas-phase reaction system and supermolecular reaction system.

*All the structures in the gas-phase reaction system were fully optimized at B3LYP/6-311+G** level, and then for the supermolecular reaction system based on the optimized structures in the gas-phase reaction system the additional six water molecules were added and re-optimized at the same level. For the transition states TS1 and TS2, we found them with TS method using G03 program. For the transition states TS_s1 and TS_s2, we using the optimized transition states of the gas-phase reaction system, and added additional six water molecules, and then re-optimized with TS method using G03 program. For the products P1 and P2 in the gas-phase reaction system, we used the optimized geometries of the transition states TS1 and TS2 and moved the water leaving molecules far from the center Al atom, and then optimized to products P1 and P2. For the products P_s1 and P_s2 in the supermolecular reaction system, we used the optimized geometries of the products P1 and P2 of gas-phase reaction system and added additional six water molecules, and then optimized to the products P_s1 and P_s2.*

5 Cartesian coordinates of all supermolecular geometries optimized at B3LYP/6-311+G**

R_s1

O	0.53581900	1.73368500	-0.32472100
O	-1.18832000	-1.64002000	-0.75748800
O	-1.86095900	0.78504900	0.13167500
O	0.36117600	-0.62006500	1.22712100
O	1.39159000	-0.73321400	-1.22236600
O	-0.67580100	0.40001300	-2.39596600
Al	-0.20606800	0.00531600	-0.47320900
H	-2.17216800	-1.66171900	-0.68376500
H	0.38964600	-1.58394300	1.40162200
H	0.50133600	-0.11365400	2.09578600

H	1.58083400	-0.65123700	-2.16648100
H	2.17106200	-1.22652400	-0.79005100
H	-1.08641800	-0.23015400	-3.00746300
H	-0.70683100	1.27966900	-2.79993900
H	-1.96263800	1.72390800	0.41940600
H	-2.72982400	0.31993400	0.10076500
H	1.48821800	2.04123800	-0.52286500
H	0.03026900	2.48674000	0.05824500
H	-0.82755100	-2.46304700	-0.34160900
H	1.54798400	0.85973300	3.83671600
O	0.68603500	0.63746800	3.45894800
H	0.09129500	0.51876000	4.21241500
H	-0.54677700	-3.93073400	1.53767500
O	0.00123900	-3.40345400	0.93584600
H	0.74335200	-3.98345400	0.70670300
H	-1.79555000	4.12397000	0.23624100
O	-1.40848100	3.38758300	0.73535900
H	-1.37246300	3.69859700	1.65315700
H	-4.50116000	-0.94728700	-0.98640200
O	-3.84530500	-1.04277200	-0.27758500
H	-4.33292600	-1.45070700	0.45522800
O	2.89046400	2.61307300	-0.84648700
H	3.12153500	3.07295300	-1.66541500
H	3.54504700	2.88902500	-0.19075800
O	3.32943500	-2.14129300	-0.27457100
H	4.02928800	-1.84420200	0.32278500
H	3.73818000	-2.80541200	-0.84838300

TS_s1

O	0.62484200	1.65384600	-0.01765100
O	-1.40361400	-1.52061700	-0.39681000
O	-1.80925100	0.92195700	0.33949500
O	0.51253100	-0.80503400	1.37159600
O	0.92070600	-0.59620800	-1.45134800
O	-1.02101500	0.52422800	-2.80698200
Al	-0.23565500	-0.00992600	-0.12281500
H	-2.38546300	-1.46243200	-0.33140600
H	0.38402100	-1.77112500	1.51375400
H	1.08126400	-0.41729600	2.13765900
H	0.59858800	-0.38008600	-2.34837500
H	1.79658500	-1.13746900	-1.48328200

H	-1.61109800	-0.01521900	-3.35313500
H	-0.97054800	1.37319400	-3.26931400
H	-1.83798200	1.89196400	0.55630900
H	-2.71877500	0.52976200	0.31604200
H	1.57878000	1.89366900	-0.30195400
H	0.18316800	2.46037800	0.32534900
H	-1.10963700	-2.40895900	-0.08278800
H	2.82518700	-0.13957400	3.44823600
O	1.89984500	0.09701500	3.29651200
H	1.52601600	0.30273000	4.16456300
H	-0.74735100	-3.93151600	1.78545700
O	-0.21898400	-3.47060300	1.11491600
H	0.41004500	-4.13671200	0.79736800
H	-1.58846200	4.21198200	0.29576100
O	-1.29282800	3.48415100	0.86497800
H	-1.33956300	3.83424000	1.76847100
H	-4.62538900	-0.52362200	-0.65718000
O	-3.97708400	-0.65502800	0.05276300
H	-4.49638000	-0.95878700	0.81416400
O	2.99938400	2.32903100	-0.68808300
H	3.22122600	2.76738400	-1.52120900
H	3.64866600	2.63814600	-0.04129800
H	3.93428300	-1.62039800	-1.50279800
O	3.04014800	-1.97873200	-1.58664600
H	3.10888200	-2.74327000	-2.17571200

P_s1

O	1.53265900	-0.74350800	-0.41760100
O	-2.01542700	0.53462000	-0.33965600
O	-0.78821700	-1.55926000	-1.23143300
O	0.32348200	1.61790300	-0.70409700
O	-0.29956000	-0.33394700	1.60033600
O	-2.17283000	0.42039300	3.20196500
Al	-0.20788500	-0.10268500	-0.20088300
H	-2.76352300	-0.02298000	-0.65775500
H	-0.32559400	2.36096500	-0.75139900
H	1.24476600	1.96688200	-0.93895700
H	-1.06118300	-0.03963200	2.20875500
H	0.40924600	-0.77968200	2.18235900
H	-2.02890800	1.08580100	3.88864100
H	-2.86889200	-0.16060000	3.53779800

H	-0.18056500	-2.27208200	-1.57572300
H	-1.73535200	-1.73020400	-1.47194000
H	2.42174300	-0.33360700	-0.06910300
H	1.72344300	-1.57722800	-0.89650600
H	-2.25441100	1.49259100	-0.38186000
H	2.91772700	3.46063000	-0.87421100
O	2.68365900	2.61449100	-1.28558400
H	2.94961700	2.69985500	-2.21387100
H	-2.25487600	3.63130900	-1.46528400
O	-1.90572800	3.21810800	-0.65957200
H	-2.08025100	3.85751200	0.04884100
H	1.38112000	-3.99147700	-1.53245500
O	1.24558700	-3.10776900	-1.90919500
H	1.54594200	-3.17367200	-2.82953000
H	-4.04762400	-2.08336100	-1.05273100
O	-3.45993700	-1.47181400	-1.52428000
H	-3.87918200	-1.33441000	-2.38886700
O	3.64759100	0.33349700	0.38605000
H	4.41110100	-0.09784400	0.79327800
H	3.96676300	1.08608400	-0.13193300
H	1.33038700	-2.33491900	3.49546600
O	1.44848000	-1.45050000	3.12256500
H	1.96292300	-0.95273800	3.77246500

R_s2

O	-1.13322800	0.32129100	2.34914800
O	0.29355600	-0.53264100	-1.10494000
O	0.47389400	1.67643100	0.72472900
O	-1.94039800	1.04805200	-0.21608700
O	-1.63670200	-1.51826100	0.52623400
O	0.94157200	-0.94490400	1.47633200
Al	-0.41070500	-0.02278300	0.43363700
H	1.05154800	-0.12009600	-1.53236800
H	-2.71655500	0.61433700	-0.63175300
H	-1.84513300	1.96759100	-0.53755500
H	-1.32207900	-2.27450500	-0.07408400
H	-2.56511600	-1.37775100	0.25472800
H	1.73868300	-1.43423300	1.12997600
H	0.91020400	-1.02698400	2.43620600
H	0.12251200	2.48201200	0.29837100
H	1.48465500	1.69891800	0.63932800

H	-1.85556400	-0.18191200	2.74741100
H	-1.06891900	1.18028400	2.78596800
H	-4.86805800	-0.57098500	-0.59982300
O	-3.94726200	-0.68549500	-0.87278000
H	-3.97960500	-1.15595300	-1.71801700
H	-0.21327800	-2.23461200	-1.66954100
O	-0.84382400	-2.93838900	-1.40665400
H	-0.53361100	-3.80147800	-1.69822000
H	-1.47641400	4.37162500	-0.20250400
O	-1.06974200	3.62086200	-0.65773800
H	-0.81677900	3.95472000	-1.52963100
H	3.15863300	0.98800800	-3.01750100
O	3.04083200	0.48915900	-2.19850200
H	3.56252100	-0.31537600	-2.31558000
H	3.69283800	2.24082800	0.62384600
O	3.01108400	1.62822800	0.32618800
H	3.23109100	1.32772200	-0.57882800
H	3.14687100	-3.22262500	0.66350500
O	3.12612800	-2.26353100	0.76984400
H	3.97344100	-2.01978100	1.16260300

TS_s2

O	-1.33745000	0.09015200	2.66862600
O	0.55032800	-0.47909000	-1.32841200
O	0.44074800	1.63066400	0.67034300
O	-1.86828500	0.97472800	-0.30149900
O	-1.46605400	-1.57281000	0.15174000
O	0.80460600	-0.86294500	1.46663100
Al	-0.28957600	-0.05565300	0.14017100
H	1.31713100	-0.02156200	-1.69165500
H	-2.70733800	0.56891200	-0.61647100
H	-1.88907900	1.95210900	-0.38616500
H	-1.13628800	-2.28435000	-0.49998300
H	-2.41906700	-1.47111000	-0.02616200
H	1.55012700	-1.52479100	1.37393500
H	0.44757100	-0.85796400	2.36714000
H	0.03566100	2.47790800	0.40797600
H	1.45207600	1.73083800	0.65059100
H	-2.03075400	-0.47879900	3.02702500
H	-1.32855300	0.87533100	3.23058800
H	-4.82727600	-0.60567500	-0.48842500

O	-3.95205600	-0.65559800	-0.89711200
H	-4.10030000	-0.97897700	-1.79726200
H	0.08947300	-2.20316900	-2.01847400
O	-0.56078600	-2.89806600	-1.79327900
H	-0.24682600	-3.76067200	-2.08305800
H	-1.74447800	4.27695700	0.31706100
O	-1.31756600	3.64757000	-0.28104100
H	-1.15590800	4.13640400	-1.10016400
H	3.26627800	1.42273300	-2.96646000
O	3.21966700	0.83226800	-2.20295800
H	3.86516200	0.13653500	-2.38469700
H	3.63910400	2.35103000	0.81160600
O	2.97602700	1.79016500	0.39486900
H	3.27148900	1.56307200	-0.50914500
H	2.68310400	-3.53987500	1.38293600
O	2.77210900	-2.57935400	1.38089400
H	3.64289200	-2.38287300	1.74662300

P_s2

O	-1.50319800	-2.79186300	2.09710700
O	-0.45247100	1.69519800	0.10052800
O	-1.36612800	-0.78417600	-0.74361400
O	1.03208200	-0.59005400	-1.71293000
O	1.97408300	0.76928500	0.31355800
O	0.34720000	-1.08760800	1.27930700
Al	0.22500500	0.11273600	-0.13343900
H	-1.37055000	1.96532600	-0.01810700
H	1.98432300	-0.45774400	-1.94075100
H	0.56239300	-1.12100600	-2.39648800
H	2.01655200	1.77177700	0.51746200
H	2.79544100	0.49969800	-0.12819500
H	1.04117900	-1.04215400	1.99528400
H	-0.36787800	-1.72396100	1.55902300
H	-1.42129200	-1.34686400	-1.53484400
H	-2.29898500	-0.52952000	-0.43270600
H	-1.36573500	-3.74222000	2.18983700
H	-2.17912400	-2.55160400	2.74221400
H	4.35374300	-0.76295700	-1.87233900
O	3.67293800	-0.07619900	-1.85330100
H	4.02301400	0.65557600	-2.38101700
H	0.74956000	3.17624500	0.50064600

O	1.71858800	3.25632100	0.58310500
H	1.93477200	3.92347500	1.24340100
H	-0.61024500	-2.98575700	-3.35340000
O	-0.70031500	-2.03225400	-3.21674900
H	-1.07017100	-1.68369300	-4.04022800
H	-3.61558600	3.25983200	-0.73994000
O	-3.32619800	2.72049000	0.00775200
H	-3.52879900	3.24377300	0.79447500
H	-4.51367800	-0.43792000	0.05956900
O	-3.65173600	-0.00935200	0.08991700
H	-3.77981200	0.96041500	0.06799600
H	2.62512100	-1.86774400	3.52172600
O	2.12207300	-1.09679100	3.23422600
H	2.17536000	-0.45251500	3.94983100