Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

DFT study on the mechanism for the substitution of F^- into Al(Ⅲ) complexes in aqueous solution

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Contents

1. The structures of reactants, transition states and products with GP model

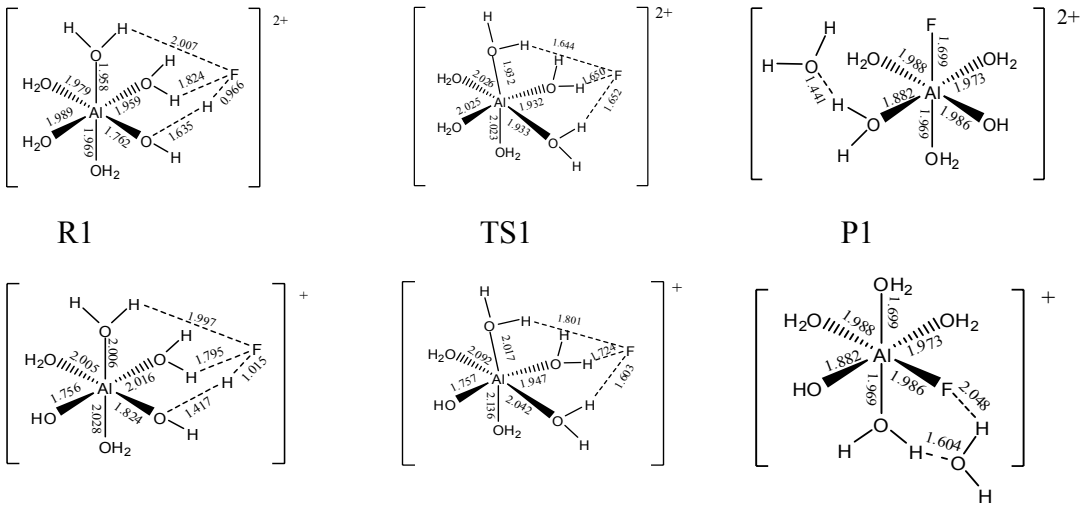

Fig. S1 The structures of reactants, transition states and products formed for substitution of a H_2O ligand of $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$ by F^- via the I_a mechanism. R1, TS1 and P1 corresponds to $Al(H_2O)_6^{3+}$. R2, TS2 and P2 corresponds to $Al(H_2O)_5(OH)^{2+}$.

2. Optimized geometry of reactant with PCM model

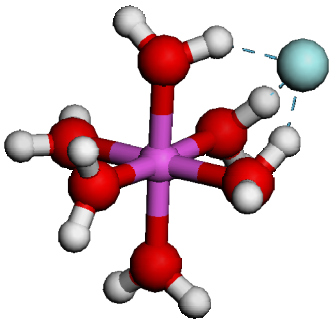

Fig. S2 Optimized geometry of reactant with PCM model for substitution of a H_2O ligand of $Al(H_2O)_6^{3+}$ by F^-.

3. The structural parameters at critical positions in IRC computation.

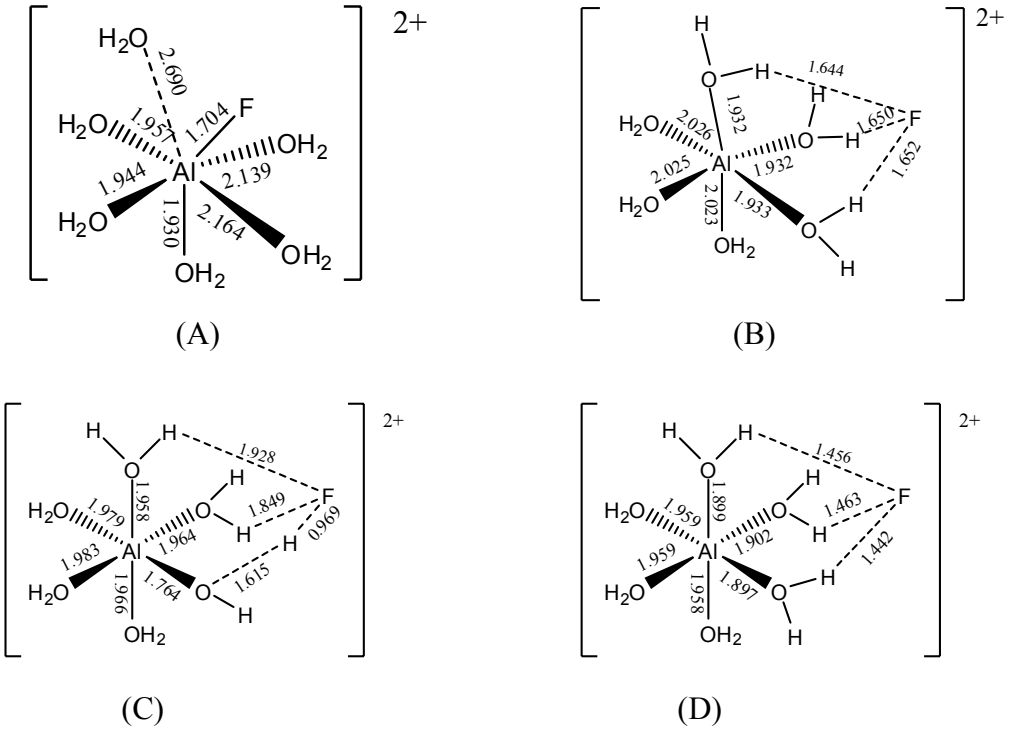

Fig. S3 The structural parameters at critical positions (A) s ≈ -9.0, (B) s ≈ 0, (C) s ≈ 6.1, (D) s ≈ 8.2 Bohr $(amu)^{1/2}$.

4. Natural population analysis (NPA) charges for reactants, transition states and products of the substitution reaction of $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$

Table S1 NPA charges (e) for the substitution reaction of $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5(OH)^{2+}$. R1, TS1 and P1 correspond to $Al(H_2O)_6^{3+}$. R2, TS2 and P2 correspond to $Al(H_2O)_5(OH)^{2+}$.

Species	q_{Al}	q_F	q_O	q_H
R1	1.941	-0.590	-0.993	0.549
TS1	1.911	-0.766	-0.962	0.552
P1	1.969	-0.746	-0.955	0.542
R2	1.927	-0.629	-1.019	0.529
TS2	1.901	-0.789	-0.986	0.528
P2	1.953	-0.770	-0.988	0.522

5. Optimized geometries of transition states using SM model

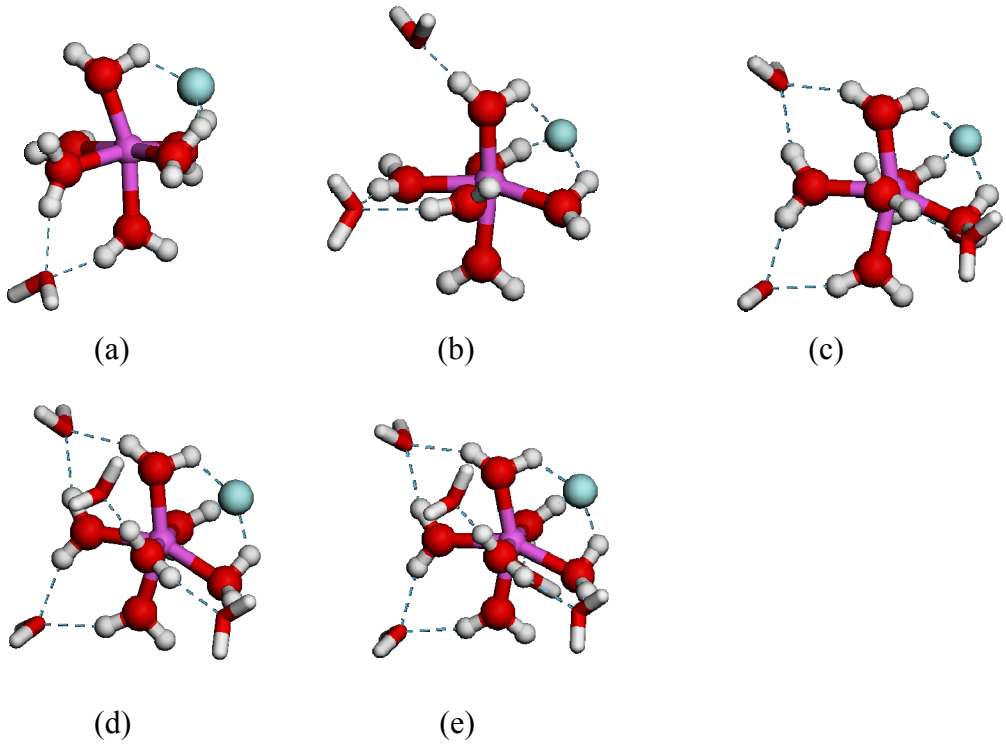

Fig. S4 Optimized geometries of transition states $\{[Al(H_2O)_5\ldots F(H_2O)]^{2+}\cdot nH_2O\}^{\neq}$ using SM model for substitution of a H_2O ligand of $Al(H_2O)_6^{3+}$ by F^- via the I_a mechanism with the different number of water molecules in the second solvent sphere. (a) n=1; (b) n=2; (c) n=3; (d) n=4; (e) n=5.

6. The atomic displacement in transition state.

Table S2 The atomic displacement in transition state.

No.	Atom	X	Y	Z	No.	Atom	X	Y	Z
1	O	-0.04	-0.11	-0.12	11	H	-0.04	0.37	-0.06
2	O	-0.05	-0.05	0.16	12	H	-0.19	0.19	0.08
3	O	0.05	0.02	0.00	13	H	-0.20	-0.16	0.13
4	O	0.05	-0.01	0.02	14	H	-0.04	-0.13	0.37
5	O	-0.05	0.16	-0.03	15	H	-0.04	-0.25	-0.30
6	Al	0.23	0.00	0.00	16	F	-0.32	0.00	0.00
7	H	0.01	-0.02	-0.04	17	H	-0.20	-0.03	-0.21
8	H	0.07	0.08	-0.04	18	H	0.05	-0.01	-0.02
9	H	0.01	0.05	0.00	19	H	0.07	-0.07	-0.05
10	H	0.07	0.00	0.09	20	H	0.01	-0.03	0.04

7. The summarized mechanism changeover induced by the spectator anion in previous study

Table S3 The mechanism changeover induced by the spectator anion in previous study.

Reaction	Mechanism	Activation parameters			$\Delta V^{\neq}$ (cm^3 mol^{-1})	k (s^{-1})	Ref.
		$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})			
$Al(H_2O)_6^{3+}+F^-$	I_a	96.3	82.9	71.6	-	1.79[a]	1
$Al(H_2O)_6(OH)^{2+}+F^-$	I_d	83.7	99.8	53.9	-	2201[a]	
$Fe^{3+}+Cl^-$	I_a	-	-	-	-4.5	-	2
$Fe(OH)^{2+}+Cl^-$	I_d	-	-	-	7.8	-	
$UO_2(OH_2)_5^{2+}+H_2O$	A	32.4[b]	-23.4[b]	39.3[b]	-2.9[b]	-	3
$UO_2(OH_2)_4L^{+/0}+H_2O$ ($L=F^-/OH^-/C_2O_4^{2-}$)	D	-	-	-	-	-	

[a] The obtained values according to the data in reference. [b] The computed values by *ab initio* method.

References

(1) B. J. Plankey and H. H. Patterson, *Inorg. Chem*. 1989, **28**, 4331.
(2) B. B. Hasinoff. *Can. J. Chem*. 1976, **54**, 1820.
(3) F. P. Rotzinger. *Chem. Eur. J*. 2007, **13**, 800.

8. The computational details of transmission coefficient

As an important kinetic parameter, transmission coefficient (κ) can relate the theoretical to experimental data by Eq. S1,[1] where k_{ex} is experimental rate constant and k_{TST} is transition state rate constant. k_{ex} is determined by a rich variety of experimental techniques and the relationship between the experimental activation parameters ($\Delta H_e^{\neq}$, $\Delta S_e^{\neq}$, $\Delta G_e^{\neq}$) and k_{ex} is expressed by Eyring equation,[2] where $\Delta H_e^{\neq}$, $\Delta S_e^{\neq}$, $\Delta G_e^{\neq}$ represent experimental activation enthalpy, activation entropy, activation free energy respectively and k_b, T, h, R are Boltzmann's constant, absolute temperature, Planck's constant and the gas constant respectively. k_{TST} is obtained from theoretical computation.[3] According to the transition state theory, k_{TST} can be expressed by Eyring equation (Eq. S3) as well. $\Delta H_c^{\neq}$, $\Delta S_c^{\neq}$ and $\Delta G_c^{\neq}$ represent computational activation activation enthalpy, activation entropy, activation free energy respectively.

$$k_{ex} = \kappa\, k_{TST} \qquad \text{(S1)}$$

$$k_{ex} = \frac{k_b T}{h}\exp\left(-\frac{\Delta G_e^{\neq}}{RT}\right) = \frac{k_b T}{h}\exp\left(\frac{\Delta S_e^{\neq}}{R} - \frac{\Delta H_e^{\neq}}{RT}\right) \qquad \text{(S2)}$$

$$k_{TST} = \frac{k_b T}{h} \exp\left(-\frac{\Delta G_c^{\neq}}{RT}\right) = \frac{k_b T}{h} \exp\left(\frac{\Delta S_c^{\neq}}{R} - \frac{\Delta H_c^{\neq}}{RT}\right) \qquad \text{(S3)}$$

In previous studies κ is assumed to be unity,[4] thereby $k_{ex} = k_{TST}$. However, people recently have realized that κ actually deviates from unity more or less.[3,5] According to this viewpoint, the computed activation parameters should not be compared directly with the experimental activation parameters and they are linked by Eq. S1. Thus κ is crucial to establish the relation of experiment and theory. In previous work κ is obtained by two approaches: one is based on Eq. S1 with the known kex and k_{TST}; the other is molecular dynamics, by which κ can be observed directly. According to the Garcia-Viloca's view,[6] the transmission coefficient κ includes three factors, namely, recrossing factor, tunneling factor and non-equilibrium factor where the recrossing and non-equilibrium factors are found important for reaction in aqueous solution. In previous molecular dynamics study,[6d] the absence of non-equilibrium factor gives rise to the large error in k_{ex} compared with the measured values. If the static calculation is employed to observe k_{TST}, the yielding κ by Eq. S1 include not only recrossing factor but also nonequilibrium factor.[6a,6b] Although the current DFT errors prevent the accurate computation of transmission coefficients, the computation by static method is still a potential approach to obtain κ in case of overcoming the errors.

Reference

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3 (a) Z. S. Qian, H. Feng, X. Y. Jin, W. J. Yang, Y. J. Wang and S. P. Bi, *Environ. Sci. Technol.*, 2009, **43**, 9281; (b) Z. S. Qian, H. Feng, Z. J. Zhang, W. J. Yang, M. Wang, Y. J. Wang and S. P. Bi, *Geochim. Cosmochim. Acta*, 2009, **73**, 1588; (c) J. R. Rustad and A. G. Stack, *J. Am. Chem. Soc.* 2006, **128**, 14778; (d) J. W. Wang, J. R. Rustad and W. H. Casey, *Inorg. Chem*. 2007, **46**, 2962.

4 Y. Inada, A. M. Mohammed, H. H. Loeffler and S. Funahashi, *Helv. Chim. Acta*, 2005, **88**, 461.

5 (a) W. H. Casey and J. R. Rustad, *Annu. Rev. Earth Planet. Sci.* 2007, **35**, 21; (b) Z. S. Qian, H. Feng, W. J. Yang and S. P. Bi, *J. Am. Chem. Soc.*, 2008, **130**, 14402.

6 M. Garcia-Viloca, J. Gao, M. Karplus and D. G. Truhlar, *Science* 2004, **303**, 186.

9. Cartesian coordinates of all the structures

$[Al(H_2O)_6]^{3+} \cdot F^-$

O	-0.75993500	-0.36458600	-1.42946700
O	-0.69194900	1.57918700	0.45552700
O	1.60525100	1.18631900	-0.97986400
O	1.44827100	-1.56381000	-0.51316200
O	-0.78037800	-1.06015300	1.17932900
Al	0.30924200	-0.01903800	-0.07228300
H	1.35042200	2.08996100	-1.22833600
H	2.28722100	0.89262500	-1.60447700
H	1.14871800	-2.14395600	-1.23277700
H	2.22763500	-1.95618800	-0.09024300
H	-1.74192800	-0.87010700	1.06600800
H	-0.69378500	-2.01261000	1.33918400
H	-0.58488400	2.16207300	1.22257400
H	-1.63900000	1.57038400	0.20455800
H	-2.29372100	-0.25272400	-0.87509600
F	-2.83535000	-0.00932800	-0.11269100
H	-0.66634900	-0.16257900	-2.36447000
O	1.49391500	0.25503900	1.48929800
H	2.30650100	0.78399800	1.51120100
H	1.27577800	-0.02539300	2.39249600

$\{[Al(H_2O)_5\ldots F(H_2O)]^{2+}\}^{\neq}$

O	0.71809900	-1.04125400	-1.42867200
O	0.71378700	-0.71215100	1.61788000
O	-1.37196900	-1.51765100	0.29695000
O	-1.37342800	0.49925500	-1.46093300
O	0.71488200	1.75801300	-0.18798700
Al	-0.06464400	-0.00013800	-0.00078000
H	-1.14545400	-2.28064400	0.85200200
H	-2.12599500	-1.75853000	-0.26229700
H	-1.15214700	0.39906600	-2.40034400
H	-2.12637800	1.10486600	-1.38619100
H	1.69169700	1.55603700	-0.17740000
H	0.50651200	2.53797400	-0.72190000
H	0.50593400	-0.63755100	2.56020900
H	1.69053100	-0.61748200	1.43546800
H	1.69447300	-0.92992100	-1.25862000
F	2.21316900	0.00102500	0.00409700
H	0.51209100	-1.89710800	-1.83109100
O	-1.38091000	1.01323100	1.15933000
H	-2.13252700	0.64381000	1.64712500
H	-1.16057500	1.87650600	1.54376000

$[Al(H_2O)_5F]^{2+} \cdot H_2O$

O	-0.58995700	-1.97220700	0.08990700

O	3.30370700	0.00169500	-0.12292100
O	1.13259300	-0.06939800	1.08985300
O	-1.61747300	0.02372900	1.47949800
O	-1.94316700	0.06602000	-1.23016500
Al	-0.36875100	-0.00281900	-0.04265200
H	2.07862200	-0.06220800	0.63337600
H	1.20887400	-0.09182900	2.05206300
H	-1.97912200	-0.75998300	1.92117800
H	-1.91387800	0.82067300	1.94540000
H	-1.75016900	0.07384400	-2.18286400
H	-2.90042500	0.11590800	-1.09026700
H	4.22195300	-0.05974800	0.17040700
H	3.27963800	-0.02877300	-1.08845200
H	-1.05832900	-2.47582500	-0.59452300
F	0.58164600	-0.01783700	-1.45088700
H	0.17182400	-2.50869500	0.36183300
O	-0.44746200	1.97488700	0.14064000
H	0.34224300	2.44360500	0.45479900
H	-0.84821700	2.53239200	-0.54498400

$[Al(H_2O)_5OH]^{2+} \cdot F^-$

O	0.62161700	0.55166000	1.44743700
O	0.89593800	0.81747700	-1.18337500

O	-1.33053000	1.75274400	0.02257200
O	-1.67864100	-0.68152900	1.18655100
O	0.70473200	-1.69280000	0.05269300
Al	-0.38634100	-0.02833300	-0.19964100
H	-1.01435500	2.43976400	-0.58137300
H	-2.29624800	1.79051000	0.05376400
H	-1.43242000	-1.07071500	2.03530500
H	-2.30624800	-1.25862300	0.72071600
H	1.67445300	-1.58624200	0.05060400
H	0.46170800	-2.40344200	-0.55655100
H	0.90107900	0.79329800	-2.14403400
H	2.14389300	0.47945600	-0.60409100
H	1.59632500	0.50048300	1.33162200
F	2.79069000	0.06999700	0.06312900
H	0.40852100	1.40576000	1.84488300
O	-1.53358100	-0.82262800	-1.26518000
H	-1.66676100	-0.75127300	-2.20924500

$\{[Al(H_2O)_4OH\ldots F(H_2O)]^+\}^{\ddagger}$

O	-0.35812900	0.09596200	-1.74050500
O	-0.94020700	1.65559300	0.72512900
O	1.39343000	1.55716200	-0.41321400
O	1.78827100	-0.99598700	-0.54359900

O	-0.62465800	-1.91462000	0.20375500
Al	0.07247200	-0.02282300	0.15417200
H	1.24086000	2.46115900	-0.11100000
H	2.34448700	1.39525200	-0.45394700
H	1.72299700	-1.69319000	-1.21005300
H	2.19428300	-1.37164600	0.25350300
H	-1.59214200	-1.79086400	0.10831800
H	-0.44899400	-2.29797800	1.07567700
H	-0.95278000	1.92988400	1.65073400
H	-1.83884200	1.29165800	0.48881100
H	-1.34588100	0.07803300	-1.72606000
F	-2.15814200	-0.11199300	-0.21738800
H	-0.01911400	0.79109200	-2.31809300
O	0.77555000	-0.35694700	1.72920300
H	0.90220700	0.18194200	2.50820900

$[Al(H_2O)_4F(OH)]^+ \cdot H_2O$

O	0.05195800	0.84824900	1.65411500
O	-3.18215200	0.03563800	-0.12752000
O	-1.02957000	-1.28665700	0.38169200
O	1.69781000	-1.08139900	0.93761800
O	1.85934500	1.33037800	-0.39772900
Al	0.36626800	-0.02544800	-0.16054400

H	-1.96018700	-0.94980000	0.20138500
H	-0.95427400	-2.19661400	0.06981600
H	2.39686400	-0.67656100	1.46719700
H	2.11065700	-1.64817500	0.26189600
H	1.61661900	2.26261700	-0.48416400
H	2.31083100	1.07056000	-1.21620900
H	-4.10045500	-0.09859800	-0.38428800
H	-2.79619000	0.72715500	-0.68671800
H	-0.62883600	1.53465400	1.59848600
F	-0.79021400	1.13745300	-0.74561600
H	-0.15665200	0.29275800	2.41762200
O	1.07651400	-0.98388300	-1.46165100
H	0.72083800	-1.12284300	-2.33960500

10. Frequencies of all the structures

$[Al(H_2O)_6]^{3+} \cdot F^-$

60.6738	131.9240	148.6212	162.1262	177.4094	185.2566	216.2098
232.7244	245.3854	257.5564	261.8701	284.7297	307.9233	317.3176
321.6313	328.8758	355.0243	382.3006	394.4846	427.4321	439.7986
454.0840	486.2430	503.6078	507.5521	515.2319	577.3141	652.3525
659.7053	670.3801	697.1713	704.7606	745.0946	761.6366	829.7207
899.9230	1028.1491	1650.5776	1658.4581	1670.6170	1672.7553	
1685.1714						
3234.4739	3475.4466	3603.2491	3722.3415	3729.2690	3735.4099	
3779.8798	3787.3222	3799.0096	3804.3104	3809.0850	3888.4723	

$\{[Al(H_2O)_5 \ldots F(H_2O)]^{2+}\}^{\neq}$

-251.3648	92.2699	97.6725	180.6491	205.2032	206.1152	217.6309
250.6371	252.4023	269.8744	272.7017	300.5647	303.2471	307.1789
326.4850	330.7300	380.3762	383.9104	389.6013	414.9666	458.5348
461.8851	477.4706	499.5976	519.8646	521.3138	523.4340	647.5118
649.8994	673.5074	693.5402	734.9385	735.6114	826.0733	833.7193
916.3251	1528.9403	1532.8601	1595.0721	1658.4592	1658.5495	
1664.4665						
3260.7161	3270.0981	3332.9688	3736.2228	3736.5876	3741.6215	
3797.6300	3798.2231	3802.1928	3815.6342	3815.8711	3816.4043	

$[Al(H_2O)_5F]^{2+} \cdot H_2O$

30.3833 60.1134 140.7229 149.8446 154.6808 162.8518 192.8816

207.8674 213.4967 223.3829 232.6436 242.8305 267.2532 278.8752

302.8748 318.5065 334.5646 351.6034 386.9098 397.1161 429.0181

448.5656 454.7252 481.9625 484.6487 508.1225 543.6001 565.9195

579.8293 656.6268 680.2875 682.2678 736.0767 798.7343 929.0363

1036.2402 1617.9976 1642.9146 1652.5379 1674.3581 1677.5454

1736.3006

2360.9729 3721.3282 3735.7091 3737.4279 3743.5031 3781.1292

3801.7078 3802.5275 3814.6710 3819.1124 3831.2385 3873.5013

$[Al(H_2O)_5OH]^{2+} \cdot F^-$

93.0213 130.0183 145.4762 153.5448 181.4740 193.7895 221.5146

229.2180 258.9027 276.5451 277.0701 286.8194 291.4235 309.8788

321.0048 356.2140 383.1305 402.2381 411.2238 424.2982 440.9175

472.9752 529.3336 560.6825 578.3064 611.3067 629.5403 672.6093

685.9939 701.3060 716.2949 773.2769 818.9736 877.7831

1142.1918 1312.9324 1602.4453 1624.1490 1633.1277 1666.7109

2377.7551 3507.9117 3650.3601 3722.1457 3765.0295 3822.7083

3833.0592 3852.1691 3854.1640 3887.4302 3956.4172

$\{[Al(H_2O)_4OH\ldots F(H_2O)]^+\}^{\ddagger}$

-238.0200 70.0165 97.0310 132.7617 173.2426 182.0595 211.4537

221.5835 233.6492 253.4176 272.4364 289.3955 298.3984 313.1582

318.3176 333.7930 361.4394 386.3426 395.0515 413.7403 432.0163

451.7283 485.5788 500.9946 586.3703 604.1096 627.2891 646.4873

677.5129 701.4202 703.1733 745.0457 795.9376 823.4147 947.3385

1565.0910 1605.3032 1620.7193 1622.7868 1641.8890 3249.7385

3437.3923

3576.3789 3736.4550 3787.8689 3794.7310 3831.3203 3839.7319

3841.6188 3883.9670 3961.3416

$[Al(H_2O)_4F(OH)]^+ \cdot H_2O$

30.3732 98.6981 128.1992 141.6582 156.1337 160.1965 184.2888

208.3645 224.1115 251.5646 253.9941 266.5540 275.3362 287.5658

302.2583 304.6109 333.3414 363.0495 371.9147 390.5453 421.5563

445.4958 462.2498 534.1746 543.5146 584.2524 599.3285 629.3472

662.7429 671.6217 696.7589 729.7853 745.2437 836.2766 1021.7850

1591.3803 1629.9228 1642.1775 1656.9676 1692.3818 3059.6125

3689.9511 3740.7451 3741.9989 3763.0268 3835.7250 3839.7824

3841.4292 3846.7520 3888.3385 3937.5690