Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

The many-body expansion for aqueous systems revisited:

III. Hofmeister ion – water interactions

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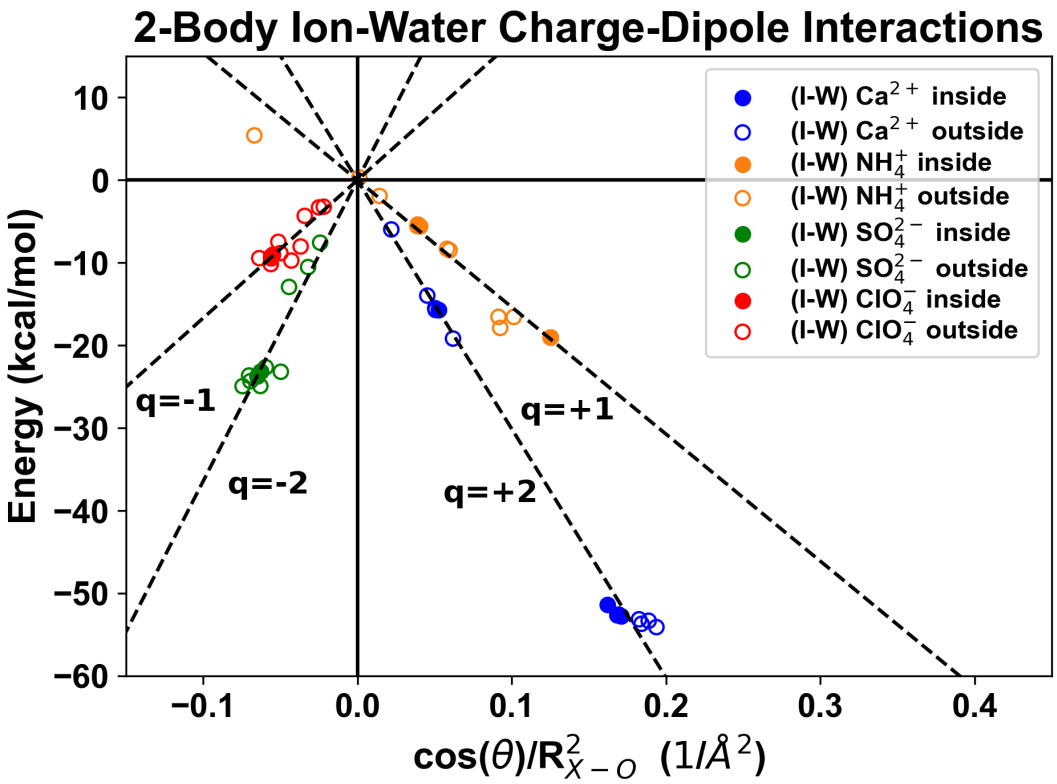

Figure FS1. Same as Figure 4 but not scaled for charge (x-axis is cos $(\theta)/R_{X-O}^2$). Note the emergence of the different lines for $q = -2, -1, +1, +2$.

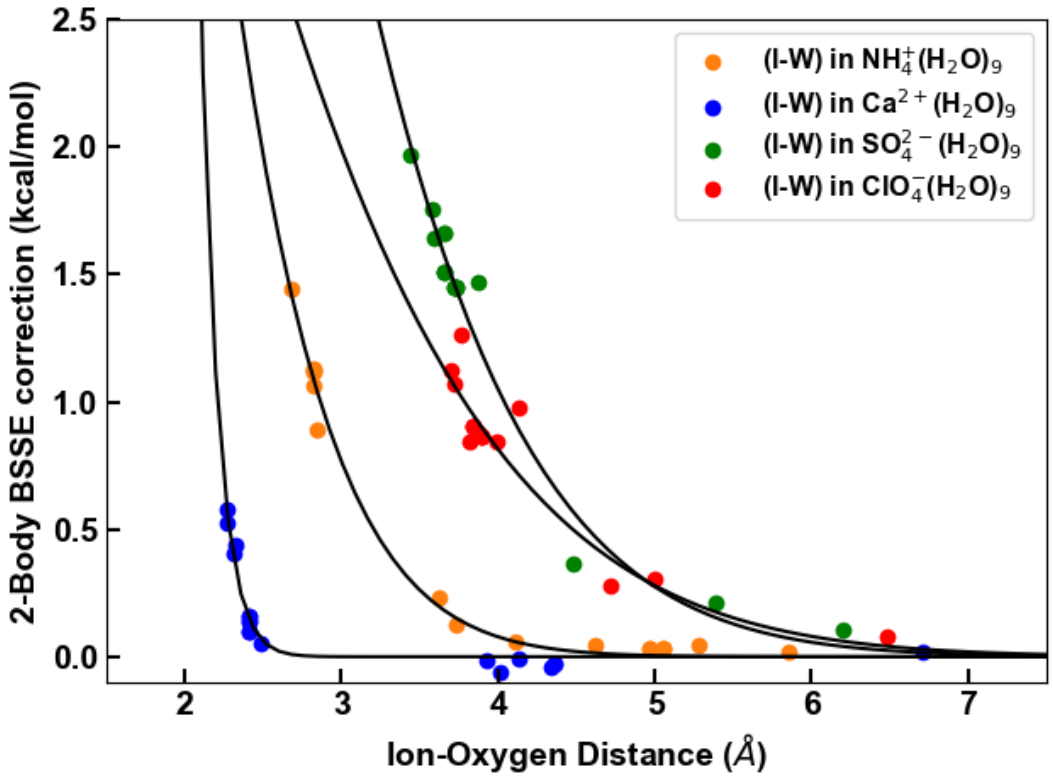

Figure FS2. Unscaled 2-B (I-W) and (W-W) contributions to the total BSSE correction for $Z^{+/-}(H_2O)_9$, where Z = Ca^{2+}, NH_4^+, SO_4^{2-}, ClO_4^- and their fits (solid lines) to Equation (8).

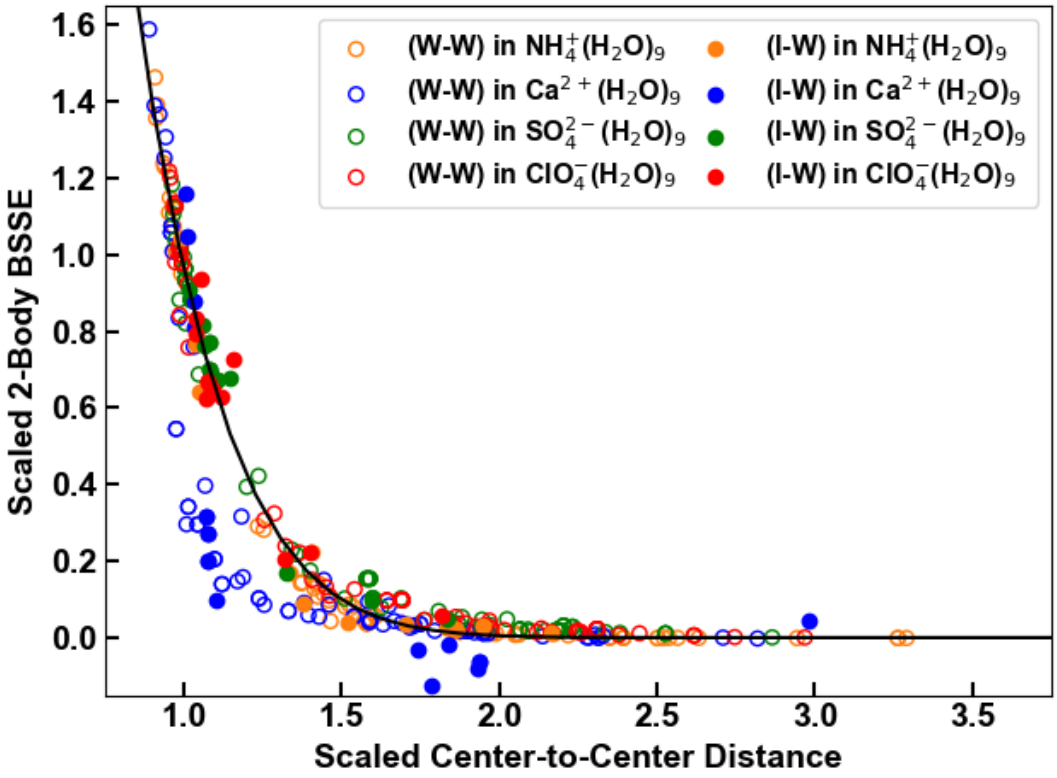

Figure FS3. Scaled 2-B (I-W) and (W-W) contributions to the total BSSE correction for $Z^{+/-}(H_2O)_9$, where Z = Ca^{2+}, NH_4^+, SO_4^{2-}, ClO_4^- and their fit (solid line, excluding calcium) to Equation (8). These points are comprised of 288 water dimer and 72 ion-water pairs. The points from NH_4^+, SO_4^{2-}, ClO_4^- fit to a nearly identical trend (equation (8), a = 12.62, b = 1.25 and R^2 = 0.9888) whereas the points from Ca^{2+} decay more quickly (equation (8), a = 141.22, b = 1.99 and R^2 = 0.8957).

Table TS1. Magnitude (kcal/mol) of BSSE-uncorrected MB terms at the MP2/aVDZ level of theory. The numbers in parentheses correspond to the percentage of the total energy.

	$Ca^{2+}(H_2O)_9$		$NH_4^+(H_2O)_9$		$SO_4^{2-}(H_2O)_9$		$ClO_4^-(H_2O)_9$	
k	**Ion Inside**	**Ion Outside**	**Ion Inside**	**Ion Outside**	**Ion Inside**	**Ion Outside**	**Ion Inside**	**Ion Outside**
1-B	0.81 (-0.3)	3.42 (-1.2)	0.41 (-0.4)	3.83 (-2.8)	3.24 (-1.6)	5.11 (-2.6)	1.08 (-1.0)	2.58 (-2.3)
2-B	-387.36 (124.2)	-306.33 (106.3)	-121.09 (105.6)	-128.76 (95.8)	-236.97 (118.7)	-215.03 (110.0)	-113.18 (107.2)	-112.56 (99.7)
3-B	85.84 (-27.5)	11.08 (-3.8)	4.40 (-3.8)	-8.09 (6.0)	40.62 (-20.3)	16.44 (-8.4)	8.88 (-8.4)	-1.36 (1.2)
4-B	-12.24 (3.9)	4.78 (-1.7)	1.74 (-1.5)	-2.25 (1.7)	-7.69 (3.9)	-3.38 (1.7)	-2.72 (2.6)	-2.76 (2.4)
5-B	2.38 (-0.8)	-0.38 (0.1)	-0.12 (0.1)	1.70 (-1.3)	1.21 (-0.6)	2.18 (-1.1)	0.65 (-0.6)	1.67 (-1.5)
6-B	-2.53 (0.8)	-1.03 (0.4)	0.02 (-0.0)	-1.41 (1.0)	-0.02 (0.0)	-1.08 (0.6)	-0.40 (0.4)	-0.76 (0.7)
7-B	1.66 (-0.5)	0.47 (-0.2)	-0.01 (0.0)	0.87 (-0.6)	-0.03 (0.0)	0.35 (-0.2)	0.20 (-0.2)	0.30 (-0.3)
8-B	-0.46 (0.1)	-0.07 (0.0)	0.001 (-0.0)	-0.39 (0.3)	-0.03 (0.0)	-0.08 (0.0)	-0.05 (0.0)	-0.08 (0.1)
9-B	0.03 (-0.0)	0.02 (0.0)	0.001 (-0.0)	0.10 (-0.1)	-0.001 (0.0)	0.02 (-0.0)	0.001 (-0.0)	0.02 (-0.0)
10-B	0.000 (0.0)	-0.007 (0.0)	0.000 (0.0)	-0.01 (0.0)	0.006 (-0.0)	-0.004 (0.0)	0.002 (-0.0)	-0.003 (0.0)
Total	**-311.86**	**-288.05**	**-114.65**	**-134.43**	**-199.66**	**-195.47**	**-105.55**	**-112.95**

Table TS2. Decomposition of the MBE (1-B to 10-B) terms into ion-water (I-W-…-W) and water-water (W-W-…-W) contributions (kcal/mol). Parentheses indicate the percentage of each contribution to the total magnitude of the MB terms listed in Table TS1.

	$Ca^{2+}(H_2O)_9$				$NH_4^+(H_2O)_9$			
	Ion Inside		**Ion Outside**		**Ion Inside**		**Ion Outside**	
k	**I-W**	**W-W**	**I-W**	**W-W**	**I-W**	**W-W**	**I-W**	**W-W**
1-B	0.00 (0.0)	0.81 (100.0)	0.00 (0.0)	3.42 (100.0)	0.13 (31.7)	0.28 (68.3)	0.88 (23.0)	2.95 (77.0)
2-B	-399.56 (103.1)	12.20 (-3.1)	-286.44 (93.5)	-19.89 (6.5)	-107.88 (89.1)	-13.21 (10.9)	-73.46 (57.0)	-55.31 (43.0)
3-B	88.05 (102.6)	-2.21 (-2.6)	8.45 (76.3)	2.63 (23.7)	1.30 (29.5)	3.10 (70.5)	3.88 (-48.0)	-11.97 (148.0)
4-B	-12.10 (98.9)	-0.14 (1.1)	5.08 (106.1)	-0.29 (-6.1)	1.76 (101.1)	-0.01 (0.6)	0.10 (-4.4)	-2.35 (104.4)
5-B	2.10 (88.2)	0.28 (11.8)	-0.55 (144.7)	0.17 (-44.7)	-0.12 (98.4)	-0.002 (1.6)	0.92 (54.4)	0.77 (45.6)
6-B	-2.38 (94.4)	-0.14 (5.6)	-1.02 (99.0)	-0.01 (1.0)	0.01	0.002	-1.00 (70.9)	-0.41 (29.1)
7-B	1.63 (97.6)	0.04 (2.4)	0.51 (108.5)	-0.04 (-8.5)	-0.01	0.000	0.70 (80.5)	0.17 (19.5)
8-B	-0.46	0.009	-0.10	0.03	0.001	-0.001	-0.34 (87.2)	-0.05 (12.8)
9-B	0.03	-0.003	0.03	-0.007	0.001	0.000	0.09	0.007
10-B	0.000	0.000	-0.007	0.000	0.000	0.000	-0.01	0.000
Total	**-322.69 (103.5)**	**10.83 (-3.5)**	**-274.05 (95.1)**	**-13.99 (4.9)**	**-104.80 (91.4)**	**-9.84 (8.6)**	**-68.23 (50.8)**	**-66.2 (49.2)**

	$SO_4^{2-}(H_2O)_9$				$ClO_4^-(H_2O)_9$			
	Ion Inside		**Ion Outside**		**Ion Inside**		**Ion Outside**	
k	**I-W**	**W-W**	**I-W**	**W-W**	**I-W**	**W-W**	**I-W**	**W-W**
1-B	0.58 (17.9)	2.66 (82.1)	0.93 (18.2)	4.18 (81.8)	0.11 (10.3)	0.96 (89.7)	0.76 (29.5)	1.82 (70.5)
2-B	-223.44 (94.3)	-13.53 (5.7)	-185.54 (86.3)	-29.48 (13.7)	-90.86 (80.3)	-22.33 (19.7)	-71.32 (63.4)	-41.24 (36.6)
3-B	46.59 (114.7)	-5.97 (-14.7)	19.71 (119.9)	-3.27 (-19.9)	15.35 (172.9)	-6.47 (-72.9)	6.16 (-452.9)	-7.52 (552.9)
4-B	-7.12 (92.6)	-0.57 (7.4)	-1.94 (57.3)	-1.45 (42.7)	-2.25 (82.7)	-0.47 (17.3)	-1.05 (38.0)	-1.71 (62.0)
5-B	0.65 (53.3)	0.57 (46.7)	1.27 (58.3)	0.91 (41.7)	0.26 (39.4)	0.40 (60.6)	0.92 (55.1)	0.75 (44.9)
6-B	0.28	-0.31	-0.76 (70.4)	-0.32 (29.6)	-0.16 (40.0)	-0.24 (60.0)	-0.48 (63.2)	-0.28 (36.8)
7-B	-0.13	0.10	0.27 (75.0)	0.09 (25.0)	0.10 (52.6)	0.09 (47.4)	0.20 (66.7)	0.10 (33.3)
8-B	-0.02	-0.004	-0.06	-0.02	-0.03	-0.01	-0.05	-0.03
9-B	0.003	-0.004	0.02	0.003	0.003	-0.001	0.01	0.005
10-B	0.006	0.000	-0.004	0.000	0.002	0.000	-0.003	0.000
Total	**-182.60 (91.5)**	**-17.06 (8.5)**	**-166.10 (85.0)**	**-29.37 (15.0)**	**-77.48 (73.4)**	**-28.07 (26.6)**	**-64.84 (57.4)**	**-48.11 (42.6)**

Table TS3. Least-mean-squares fitted parameters for the 2-B contribution to the total BSSE correction via equation (8). These fits correspond to the unscaled (I-W) BSSE corrections in Figure FS2.

System	*a*	*b*	x^2	R^2
$Ca^{2+}(H_2O)_9$	82643.96	1.40	0.023	0.967
$NH_4^+(H_2O)_9$	35.33	0.54	0.042	0.992
$ClO_4^-(H_2O)_9$	11.13	0.32	0.174	0.886
$SO_4^{2-}(H_2O)_9$	25.06	0.36	0.143	0.989

Table TS4. Cartesian coordinates of the aqueous ionic clusters optimized at the MP2/aVDZ level of theory.

$Ca^{2+}(H_2O)_9$ ion inside		
O	-0.03401470	2.38203492	-0.53809149
H	0.76167746	2.90055005	-0.72696050
H	-0.71340449	3.03643609	-0.32011223
O	4.11334421	0.11902460	1.25212914
H	4.79850669	-0.56772484	1.24987432
H	4.54522675	0.87896755	1.67283178
O	0.03401470	-2.38203492	-0.53809149
H	-0.76167746	-2.90055005	-0.72696050
H	0.71340449	-3.03643609	-0.32011223
O	-2.28580328	-0.42982134	-0.84906205
H	-3.08344113	-0.38258890	-0.28415281
H	-2.60595992	-0.46883183	-1.76054513
O	1.40458315	-0.44305392	1.71611538
H	2.37509119	-0.32401541	1.76065310
H	1.15198424	-0.84271584	2.55954920
O	2.28580328	0.42982134	-0.84906205
H	2.60595992	0.46883183	-1.76054513
H	3.08344113	0.38258890	-0.28415281
O	0.00000000	0.00000000	-2.68192605
H	0.15345193	-0.75182769	-3.27338633
H	-0.15345193	0.75182769	-3.27338633
O	-1.40458315	0.44305392	1.71611538
H	-2.37509119	0.32401541	1.76065310
H	-1.15198424	0.84271584	2.55954920
O	-4.11334421	-0.11902460	1.25212914
H	-4.54522675	-0.87896755	1.67283178
H	-4.79850669	0.56772484	1.24987432
Ca	0.00000000	0.00000000	-0.19776074

$Ca^{2+}(H_2O)_9$ ion outside			
Ca	-0.67021412	1.70269630	0.13940692
O	0.20084704	-2.33354517	-0.05688644
H	-0.56133079	-2.46998149	-0.64475609
H	0.75524001	-3.14882190	-0.14649850
O	-2.21585911	-1.86571801	-1.79357745
H	-2.08529684	-2.12800072	-2.71927829
H	-3.01430481	-2.34998891	-1.52735671
O	-2.27399835	0.84374682	-1.30525021
H	-2.30824771	-0.11579457	-1.54050896

H	-3.03008970	1.24376879	-1.75913608
O	-1.25084759	0.97203606	2.21079034
H	-1.80715093	1.26083331	2.94708834
H	-0.87101943	0.07997647	2.47318548
O	3.21949799	1.88093666	-0.83751867
H	3.64416289	1.95005753	-1.70755286
H	3.96141723	1.92009846	-0.21277058
O	0.93987736	3.30914237	-0.30588970
H	1.84422046	2.97833039	-0.52061130
H	1.00055234	4.27536983	-0.30552511
O	0.94423207	0.19186150	-0.35848038
H	0.85451543	-0.79685154	-0.30016820
H	1.87002554	0.41486167	-0.56108465
O	-0.10164026	-1.33301647	2.55894189
H	-0.10130687	-1.90592199	3.33766998
H	-0.06156275	-1.91462300	1.77511754
O	1.70430295	-4.56457660	-0.21801813
H	2.40859384	-4.79096875	-0.84066051
H	1.57534058	-5.36283223	0.31272710

$NH_4^+(H_2O)_9$ ion inside

N	0.18231854	-0.19063081	0.14139222
H	0.48464987	-0.86815184	-0.58131753
H	0.95167223	-0.04105538	0.81849667
H	-0.64690789	-0.56311103	0.63776948
H	-0.06014000	0.70979513	-0.30937971
O	1.00637115	-2.03982788	-1.82890977
H	1.69333164	-1.88612476	-2.49411949
H	0.67243727	-2.92987647	-2.01423336
O	2.28076131	0.21734213	1.98822152
H	2.62107172	-0.44294713	2.60971154
H	2.79563226	1.01813661	2.16620836
O	-0.47899676	2.26531673	-1.08810613
H	-0.88374028	3.02609083	-0.64601003
H	-0.38571430	2.53369401	-2.01401915
O	-2.08003219	-1.20272730	1.49716224
H	-2.95861569	-1.33070415	1.11017884
H	-2.17244793	-1.47061424	2.42330425
O	3.04397219	-1.48996687	-3.70094247
H	2.92109150	-1.30388697	-4.64344861
H	3.92920827	-1.87734823	-3.63509623
O	3.69834974	2.61508733	2.43535939
H	4.62049612	2.78873706	2.19549440
H	3.52540161	3.18724995	3.19743680
O	-0.18092911	2.92651994	-3.81439228

H	0.46069088	3.54964270	-4.18599021
H	-0.92713491	2.93687552	-4.43173581
O	-4.58772420	-1.55980204	0.25512783
H	-5.37617914	-1.01338388	0.38857959
H	-4.92650659	-2.43302937	0.00866523
O	-2.23572476	-1.93147987	4.21807206
H	-2.31505884	-2.83168407	4.56647073
H	-2.65370732	-1.36677561	4.88473789

$NH_4^+(H_2O)_9$ ion outside

H	-2.90191463	1.69394429	-1.43152441
H	-1.41950336	0.83830313	-1.31173726
H	-1.88222318	1.97823148	-0.11392955
H	-2.67615745	0.49825030	-0.25773816
N	-2.23630971	1.27064292	-0.78491971
O	-0.83690003	2.78882848	1.13163332
H	-0.06761287	3.04162255	0.56173011
H	-1.00521637	3.54026115	1.71562176
O	1.04520273	3.04930281	-0.73638345
H	1.64839738	2.28474103	-0.84411966
H	1.55150746	3.82525010	-1.00902999
O	-0.94319455	-2.63196604	-0.95864259
H	-1.23055327	-3.34272282	-1.54783370
H	-0.11519094	-2.96478007	-0.52422927
O	2.32394905	0.59505097	-1.03196591
H	3.12329326	0.41379086	-1.54468460
H	2.42933731	0.10195819	-0.18512712
O	1.39655675	-3.21880745	0.19373635
H	1.64369372	-4.01275811	0.68446505
H	1.76043400	-2.46295807	0.69956042
O	-2.49951031	-1.13136675	0.71387118
H	-2.04908073	-1.80816011	0.15485681
H	-3.17436040	-1.61099013	1.21328493
O	-0.24954895	0.14062445	2.01949060
H	-1.04251397	-0.34205280	1.72351593
H	-0.44622674	1.08443695	1.87289097
O	-0.25433523	-0.07632413	-1.97743162
H	0.68031791	0.11226059	-1.76017977
H	-0.38750943	-1.02173933	-1.76696021
O	2.14196035	-0.78197025	1.33107308
H	1.26993915	-0.42962842	1.65847092
H	2.75298273	-0.69756988	2.07577147

$SO_4^{2-}(H_2O)_9$ ion inside

S	0.00000000	-0.00000000	-0.59461648
O	1.45152438	-0.00086739	-1.08877596
O	-0.72651337	-1.25662329	-1.08877596
O	0.00000000	0.00000000	0.96337313
O	-0.72501101	1.25749069	-1.08877596
O	-2.63232864	-0.50305014	1.88730102
H	-1.68695646	-0.37629483	1.64494688
H	-2.97460127	-0.99514853	1.11782859
O	0.22854183	-3.67113826	-0.00586527
H	-0.19242089	-2.87343557	-0.40060255
H	0.58137035	-3.30561078	0.82831319
O	-3.53348316	-1.15011640	-0.88399614
H	-3.64364786	-0.18350106	-0.79771192
H	-2.56834445	-1.22131871	-1.06251067
O	3.06502808	2.03349216	-0.00586527
H	2.58467864	1.27007641	-0.40060255
H	2.57205774	2.15628689	0.82831319
O	1.75181852	-2.02813841	1.88730102
H	1.16935911	-1.27279973	1.64494688
H	2.34912455	-2.07850600	1.11782859
O	0.88051012	2.53118855	1.88730102
H	0.62547672	3.07365454	1.11782859
H	0.51759734	1.64909456	1.64494688
O	2.76277160	-2.48502798	-0.88399614
H	1.98074051	-3.06374108	-0.79771192
H	2.34186526	-1.61359218	-1.06251067
O	-3.29356991	1.63764610	-0.00586527
H	-3.15342809	1.14932390	0.82831319
H	-2.39225775	1.60335916	-0.40060255
O	0.77071156	3.63514439	-0.88399614
H	0.22647919	2.83491090	-1.06251067
H	1.66290735	3.24724213	-0.79771192

$SO_4^{2-}(H_2O)_9$ ion outside

O	1.21797968	-0.49966788	1.11320746
S	1.26813101	-1.23103751	-0.25395744
O	1.49573967	-2.72329446	-0.02564417
O	2.36208424	-0.63347501	-1.12877590
O	-0.12070806	-1.03909450	-0.94375297
H	-1.69196617	1.46131074	0.67848716
O	-1.33483925	2.34653829	0.44191659
H	-0.36598146	2.24089981	0.58195772
H	-0.59340318	0.40275268	-1.83934557
O	-0.97511472	1.24100733	-2.20581994
H	-1.15255838	1.75441813	-1.38931021

H	-1.44604860	-3.11694523	-0.04089329
O	-0.95510586	-3.74778604	0.50822501
H	-0.02283752	-3.47054413	0.29426272
H	-0.83065339	-2.59394705	2.10924496
O	-0.73242990	-1.80065886	2.67339773
H	0.03256191	-1.35011179	2.24081805
H	-1.38609183	-0.60471738	0.10452801
O	-2.15182402	-0.34462591	0.68721664
H	-1.88563601	-0.76640381	1.53114226
H	0.97122484	1.83783871	-2.27516437
O	1.90853535	1.91019770	-2.01296107
H	2.11679637	0.97333005	-1.76245503
H	1.70970333	2.23784050	-0.17206956
O	1.45257054	2.19369999	0.77529491
H	1.45892110	1.21622870	0.95653816
H	-0.64703004	4.00312003	1.81029368
O	0.17924954	4.37510189	2.15922197
H	0.81929562	3.72389593	1.81072339
H	-3.43934712	-0.11995096	-0.84973866
O	-3.72593391	0.14161238	-1.74338273
H	-2.89846244	0.51321220	-2.10302059

$ClO_4^-(H_2O)_9$ ion inside

Cl	0.00000000	0.00000000	-0.68699979
O	1.41695761	0.00063831	-1.17984485
O	-0.70792601	-1.22744044	-1.17984485
O	0.00000000	0.00000000	0.82978920
O	-0.70903160	1.22680213	-1.17984485
O	-2.78491486	-0.59952545	1.88595428
H	-1.82911976	-0.59119680	1.71652552
H	-3.14106404	-1.06516125	1.10372872
O	0.35212831	-3.77172006	0.11713970
H	-0.20898597	-3.07960887	-0.26792308
H	0.69797648	-3.34198853	0.92495513
O	-3.72727459	-1.13535286	-0.80781407
H	-3.80533233	-0.16386812	-0.72238311
H	-2.83803803	-1.24227330	-1.18162364
O	3.09034124	2.19081209	0.11713970
H	2.77151250	1.35881727	-0.26792308
H	2.54525873	2.27545963	0.92495513
O	1.91166170	-2.11204429	1.88595428
H	1.42655133	-1.28846578	1.71652552
H	2.49298873	-2.18766063	1.10372872
O	0.87325316	2.71156974	1.88595428
H	0.64807532	3.25282188	1.10372872

H	0.40256844	1.87966258	1.71652552
O	2.84688172	-2.66023805	-0.80781407
H	2.04458012	-3.21358041	-0.72238311
H	2.49485925	-1.83667638	-1.18162364
O	-3.44246954	1.58090797	0.11713970
H	-3.24323521	1.06652890	0.92495513
H	-2.56252653	1.72079159	-0.26792308
O	0.88039288	3.79559092	-0.80781407
H	0.34317878	3.07894968	-1.18162364
H	1.76075221	3.37744853	-0.72238311

$ClO_4^-(H_2O)_9$ ion outside

O	1.66636734	-0.03145681	1.34667349
Cl	1.68338717	-0.91838825	0.13587299
O	1.95638387	-2.32723270	0.53663927
O	2.69129501	-0.43376801	-0.85781046
O	0.29750862	-0.86683457	-0.51435696
H	-2.04721427	1.51341523	0.88709363
O	-1.80564674	2.25221369	0.30071538
H	-0.84325149	2.37548646	0.46731589
H	-0.65800557	0.27415063	-1.69789444
O	-1.23468762	0.92860289	-2.13179477
H	-1.53528588	1.47091100	-1.36715063
H	-2.00501379	-2.72462596	-1.03954078
O	-1.30399898	-3.37754783	-0.82457063
H	-0.49772125	-2.85320832	-0.95806960
H	-1.11364247	-3.30220992	1.03790098
O	-0.91221699	-3.04636879	1.96548311
H	0.04381834	-2.88647525	1.92982998
H	-1.02983049	-0.44701104	0.79143738
O	-1.85863100	-0.44916071	1.30812323
H	-1.73955582	-1.28172253	1.81050155
H	0.59954501	1.76851763	-2.37306993
O	1.50597712	2.02825300	-2.11976129
H	1.93631636	1.18127396	-1.90625001
H	1.20876237	2.59217687	-0.40371878
O	0.93445991	2.68395358	0.53700436
H	1.28394232	1.87187082	0.94615621
H	-1.46002491	4.39784773	1.21620433
O	-0.71497127	4.95599904	1.48487014
H	0.04231785	4.38220446	1.28053071
H	-2.88833863	-0.91168210	-0.25123561
O	-3.13470178	-1.22306129	-1.14611113
H	-2.74093303	-0.54373576	-1.72128100