Electronic Supplementary Information (ESI)

Initial hydration processes of magnesium chloride: size-selected anion photoelectron spectroscopy and *ab initio* calculations

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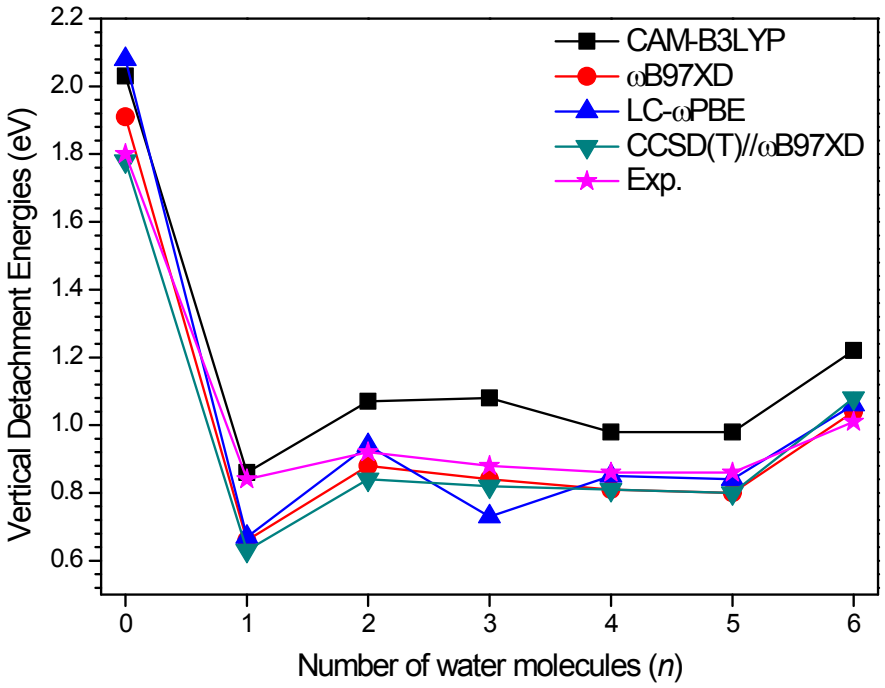
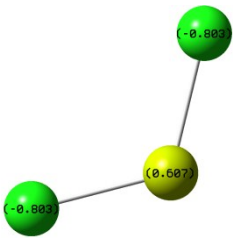
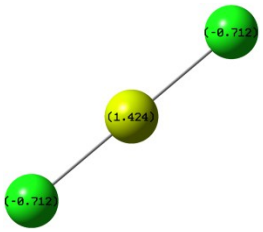
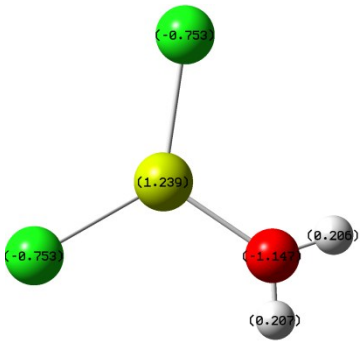
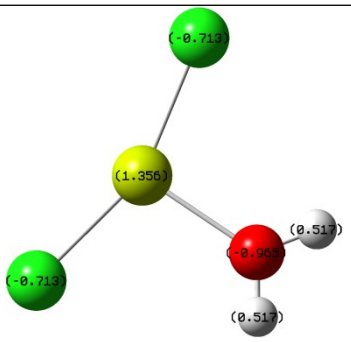
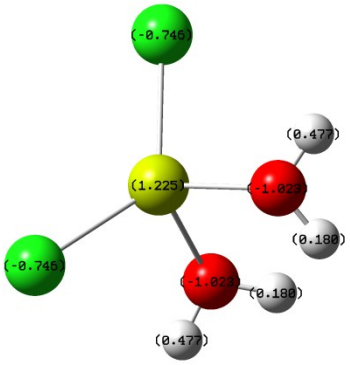
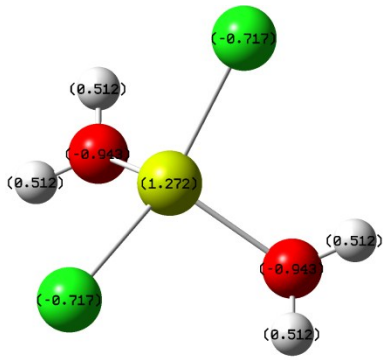
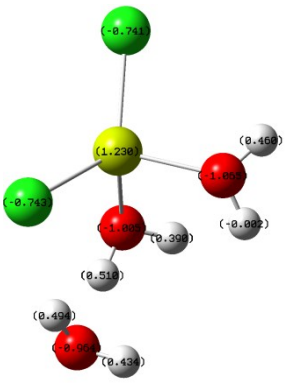
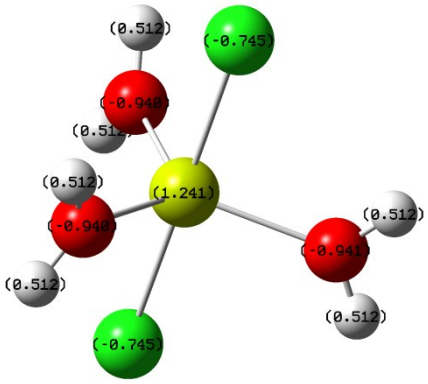


Figure S1. Comparing the experimental VDEs to those ofthe lowest energy structures of $MgCl_2(H_2O)_n^-$ clusters calculated by different kinds of method.

We also carried out theoretical calculations by employing LC-ωPBE and CAM-B3LYP functionals to check the performance of ωB97XD functional. The results from the LC-ωPBE and CAM-B3LYP functionals are similar to those from the ωB97XD method. But those from the ωB97XD method are in slightly better agreement with experimental values.

0		
1		
2		
3		

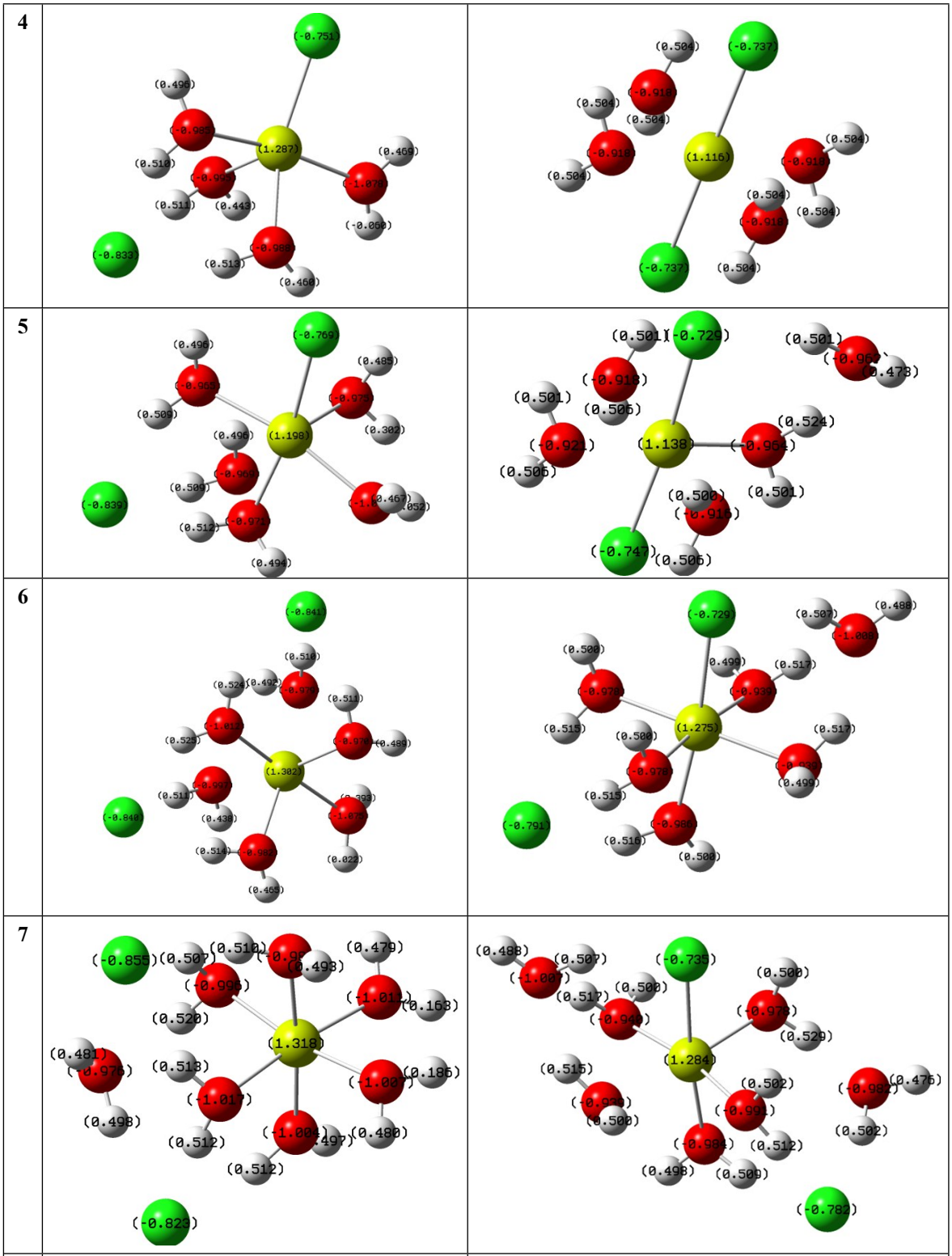


Figure S2. The NPA charge distributions (*e*) of the most stable isomer of $MgCl_2(H_2O)_{0\text{-}6}$ cluster anions and neutrals.

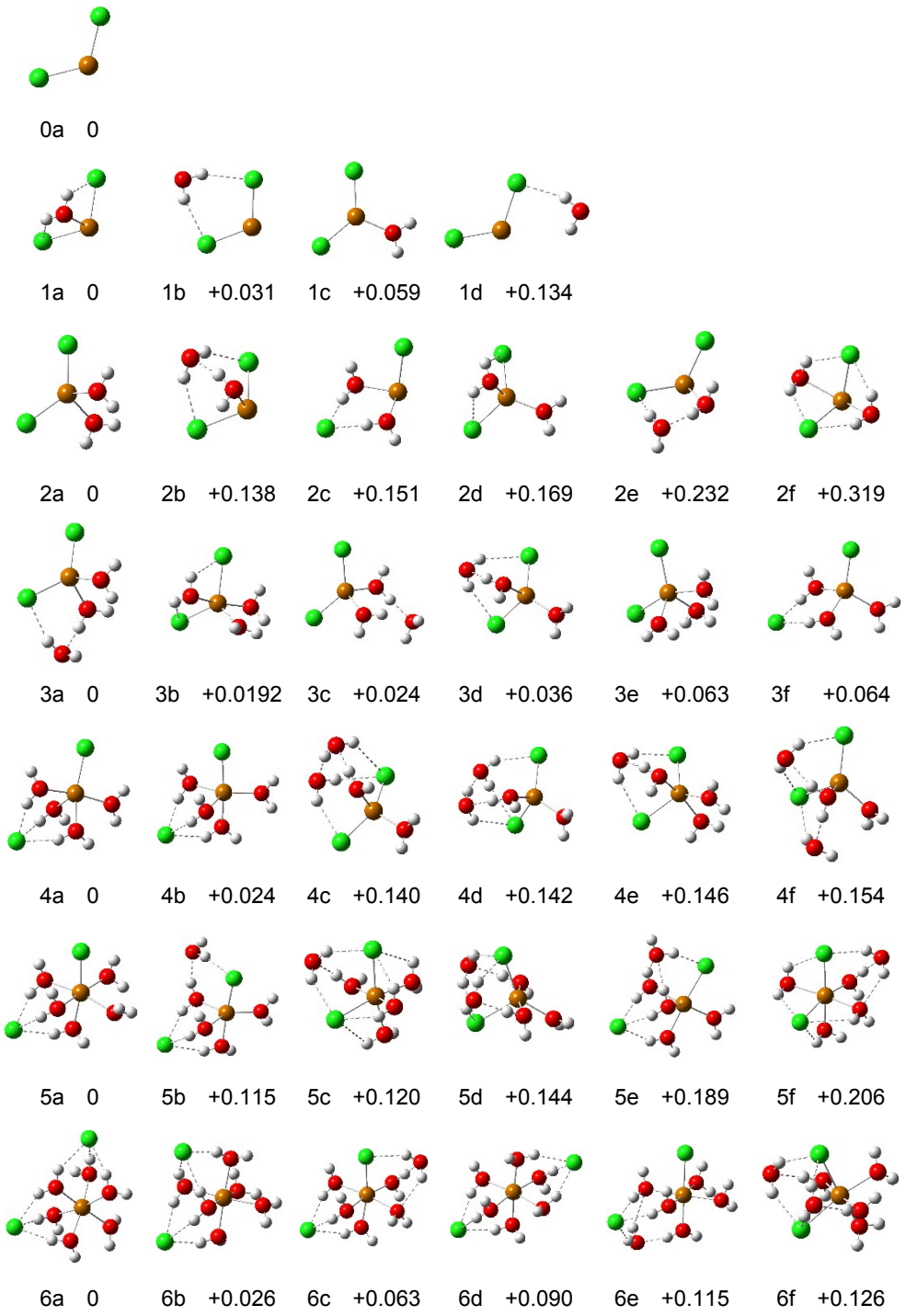


Figure S3. Typical low-lying isomers of $MgCl_2(H_2O)_n^-$ (n = 0-6) optimized at the ωB97XD/6-311++G(d,p) level of theory and their relative energies (eV).

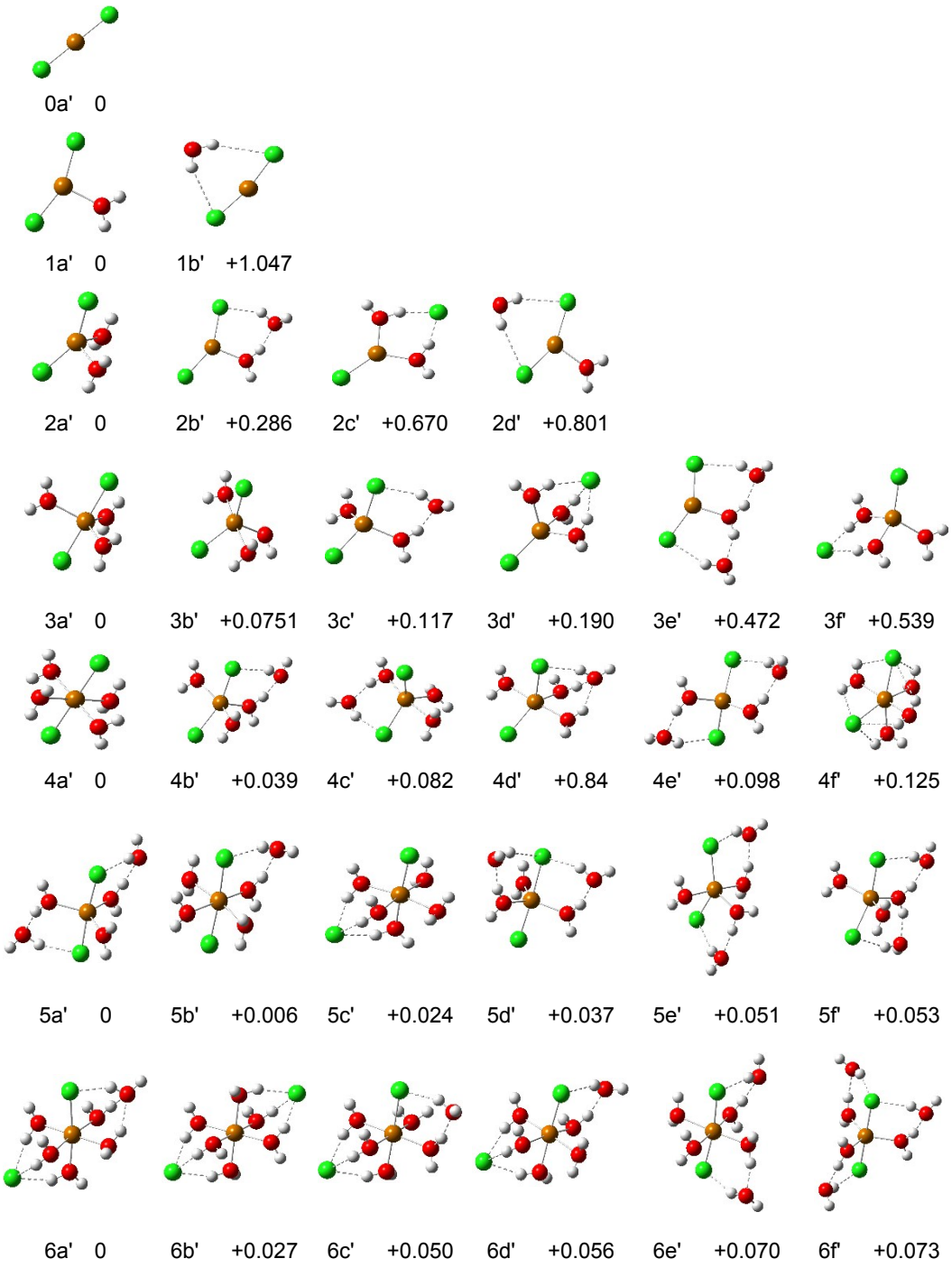


Figure S4. Typical low-lying isomers of $MgCl_2(H_2O)_n$ (n = 0-6) neutrals obtained at the ωB97XD/6-311++G(d,p) level of theory and their relative energies (eV).

Table S1. The absolute energies and the zero point energies (in Hartrees) of the most stable isomers of $MgCl_2(H2O)_n^-$ (n=0-7) and the neutrals calculated with ωB97XD/6-311++G(d,p) level of theory. CCSD(T) /6-311++G(d,p) single point energies based on ωB97XD/6-311++G(d,p) geometry were also listed.

	Anion			Neutral		
n	CCSD(T)	ωB97XD	ZPE	CCSD(T)	ωB97XD	ZPE
0	-1119.15702	-1120.685862	0.001841	-1119.123911	-1120.645046	0.002356
1	-1195.465495	-1197.134379	0.02404	-1195.45148	-1197.118977	0.027793
2	-1271.785953	-1273.600255	0.050576	-1271.774993	-1273.587909	0.052946
3	-1348.094252	-1350.054967	0.076428	-1348.090103	-1350.048915	0.076898
4	-1424.407376	-1426.516793	0.102424	-1424.406491	-1426.507496	0.103444
5	-1500.721906	-1502.975077	0.128661	-1500.715793	-1502.964142	0.129521
6	-1577.030904	-1579.433614	0.153989	-1577.026536	-1579.421059	0.155811
7	–	-1655.889119	0.179429	–	-1655.880317	0.182449

Table S2. Stepwise water binding energies (WBE, in $kJmol^{-1}$) of Lowest energy structures of $MgCl_2(H_2O)_n^-$ (*n* = 1-7) clusters and their neutrals. The WBE is calculated as WBE = [$E(MgCl_2(H_2O)_{n-1})$ + $E(H_2O)$] - $E(MgCl_2(H_2O)_n)$

n	Anion		Neutral	
	CCSD(T)	ωB97XD	CCSD(T)	ωB97XD
1	58	42	108	109
2	89	88	97	96
3	57	59	75	75
4	70	77	78	69
5	74	68	59	64
6	59	69	64	64
7	–	61	–	71

Table S3 The Cartesian atomic coordinates of the typical low-lying isomers of $MgCl_2(H2O)_n^-$ (n = 0-7) clusters and the neutrals calculated with ωB97XD/6-311++G(d,p) level of theory.

0a

	X	Y	Z
Mg	0.000000	0.000000	0.890118
Cl	0.000000	2.004408	-0.314159
Cl	0.000000	-2.004408	-0.314159

0a'

	X	Y	Z
Mg	0.000000	0.000000	0.000593
Cl	0.000000	2.187442	-0.000209
Cl	0.000000	-2.187442	-0.000209

1a

	X	Y	Z
Mg	-0.000103	0.222382	0.000035
Cl	2.039646	-0.769362	0.000074
Cl	-2.040437	-0.768098	0.000015
O	0.001343	2.228413	-0.000319
H	0.786977	2.819620	0.000876
H	-0.783032	2.821302	-0.000270

1a'

	X	Y	Z
Mg	-0.000103	0.222382	0.000035
Cl	2.039646	-0.769361	0.000074
Cl	-2.040437	-0.768099	0.000015
O	0.001342	2.228413	-0.000319
H	0.786976	2.819620	0.000876
H	-0.783033	2.821302	-0.000270

2a

	X	Y	Z
Mg	0.000078	0.055708	-0.000002
Cl	2.041254	-0.970474	0.250156
Cl	-2.040957	-0.970813	-0.250255
O	0.554075	1.519581	-1.387817
H	0.249953	2.431931	-1.184727
H	1.515233	1.580225	-1.471468
O	-0.554627	1.519195	1.388011
H	-0.250917	2.431695	1.185010
H	-1.515848	1.579323	1.471333

2a'

	X	Y	Z
Mg	0.000002	0.000024	-0.049464
Cl	-2.186397	-0.000014	-0.640530
Cl	2.186350	-0.000024	-0.640717
O	0.000030	-1.728177	1.117069
H	-0.783354	-2.284118	1.125517
H	0.783404	-2.284133	1.125463
O	0.000049	1.728215	1.117022
H	0.783430	2.284158	1.125509
H	-0.783335	2.284154	1.125557

3a

	X	Y	Z
Mg	0.464966	0.006200	0.034386
Cl	-1.071478	1.738559	0.281309
Cl	2.690162	0.233578	-0.450546
O	-0.600970	-1.319193	-1.163562
H	-0.491740	-2.240385	-0.880032
H	-1.567688	-1.142357	-1.082867
O	0.453953	-1.278572	1.658911
H	-0.244869	-1.969040	1.728333
H	1.281559	-1.720421	1.895670
O	-3.117103	-0.605858	-0.426554
H	-2.771001	0.248372	-0.114865
H	-3.190517	-1.147915	0.367803

3a'

	X	Y	Z
Mg	0.000028	-0.006590	0.393748
Cl	2.071987	0.014163	-0.824964
Cl	-2.072031	0.013167	-0.824883
O	0.000574	-2.151606	-0.019151
H	0.775893	-2.207303	-0.591452
H	-0.775345	-2.207712	-0.590606
O	-0.000625	2.150362	0.048306
H	-0.776084	2.222149	-0.522133
H	0.775293	2.222641	-0.521451
O	0.000104	-0.038393	2.412418
H	-0.777781	-0.041313	3.007892
H	0.778016	-0.056905	3.007579

4a

	X	Y	Z
Mg	0.699651	0.150306	-0.104642
Cl	2.657947	-1.067487	0.065432
Cl	-3.043667	-0.315937	0.119154
O	1.629400	1.994773	-0.018625
H	1.206673	2.867984	0.159843
H	2.567320	2.077922	0.198624
O	-0.493870	0.542992	1.568156
H	-1.431760	0.333807	1.344417

4a'

	X	Y	Z
Mg	0.000007	0.001652	0.000146
Cl	2.378877	-0.006820	0.005642
Cl	-2.379103	0.006395	-0.006876
O	0.004893	-0.971060	-1.918831
H	0.790283	-0.748845	-2.426669
H	-0.770996	-0.738748	-2.436568
O	0.014693	1.920979	-0.969015
H	-0.759121	2.444238	-0.742399

H	-0.467613	1.463395	1.863292
O	-0.424575	-1.572777	-0.478209
H	-0.094439	-2.389964	-0.098808
H	-1.388858	-1.464246	-0.290166
O	-0.701734	1.042857	-1.389465
H	-1.605494	0.752588	-1.131717
H	-0.698178	2.010290	-1.382595

H	0.802098	2.423928	-0.742529
O	-0.015018	-1.919434	0.969416
H	-0.804751	-2.419070	0.743414
H	0.756485	-2.444934	0.740444
O	-0.003927	0.968783	1.920808
H	0.773006	0.734602	2.436250
H	-0.788364	0.742092	2.428271

5a

	X	Y	Z
Mg	0.577924	0.253366	-0.002983
Cl	2.044479	-1.619801	-0.152422
Cl	-0.647086	-0.526605	-1.555933
O	-1.585792	-0.551386	-1.259914
H	-0.405753	-1.429322	-1.784298
H	1.779406	1.048394	1.598832
O	2.221206	1.858408	1.309790
H	2.488593	0.397731	1.681365
H	1.763175	1.485533	-1.223868
O	2.393222	1.107116	-1.854247
H	1.641887	2.415414	-1.498204
H	-0.898827	1.738740	0.195874
O	-0.893931	2.520139	-0.369994
H	-1.795145	1.341095	0.124662
H	-0.612619	-0.782364	1.430112
O	-1.563638	-0.734022	1.180636
H	-0.378615	-1.715321	1.392305
H	-3.228567	-0.260188	0.008514

5a’

	X	Y	Z
Mg	-0.307526	0.100756	-0.002150
Cl	-2.445179	-1.013701	0.035418
Cl	1.709486	1.414024	-0.033454
O	-0.643651	0.484094	-2.102744
H	-1.238869	-0.196935	-2.432060
H	0.155848	0.465162	-2.634761
O	0.648387	-1.701645	-0.492264
H	1.601291	-1.801288	-0.275662
H	0.174544	-2.502332	-0.260523
O	-1.402077	1.922259	0.432131
H	-1.027278	2.695305	0.001774
H	-2.307883	1.812072	0.126023
O	-0.199814	-0.227397	2.118143
H	-1.095270	-0.450133	2.395600
H	0.077297	0.550009	2.609226
O	3.232665	-1.318983	0.001609
H	3.991677	-1.369216	0.583613
H	2.781653	-0.483847	0.224170

6a

	X	Y	Z
Mg	-0.013352	0.749877	-0.092564
Cl	3.083632	-1.477616	0.009794
Cl	-3.027548	-1.540322	0.004035
O	-1.638615	0.803806	-1.431461
H	-2.242530	0.062360	-1.190276
H	-2.176822	1.604203	-1.438563
O	-1.423803	0.569935	1.520613
H	-2.071521	-0.127377	1.255748
H	-1.934706	1.372405	1.683850
O	-0.004606	-1.297645	-0.276738
H	0.807824	-1.823527	-0.208464
H	-0.823808	-1.819652	-0.214044
O	1.437906	0.616947	1.479753
H	2.108492	-0.056049	1.211093
H	1.002443	0.276946	2.265434
O	1.624070	0.782386	-1.416737
H	2.131869	1.595765	-1.421897
H	2.244306	0.054228	-1.173688
O	0.063394	2.842723	0.049113
H	-0.722175	3.394790	-0.158344
H	0.416670	3.227109	0.868481

6a’

	X	Y	Z
Mg	0.006973	0.312290	0.003853
Cl	2.147327	0.493094	1.146222
Cl	-2.137080	0.459199	-1.166099
O	0.869274	1.402620	-1.640315
H	1.596957	1.961375	-1.353705
H	0.223104	1.954655	-2.088972
O	-0.518613	2.236954	0.867635
H	-1.476307	2.308859	0.918112
H	-0.163570	2.329830	1.755877
O	0.423469	-1.520399	-0.929838
H	-0.029932	-1.653405	-1.764445
H	1.371193	-1.752822	-1.039827
O	-0.819662	-0.616324	1.715531
H	-0.179274	-1.126522	2.215175
H	-1.613431	-1.172425	1.554246
O	-3.018788	-1.821439	0.778525
H	-3.907953	-1.737771	1.123758
H	-2.969637	-1.218737	0.013879
O	3.092288	-1.728147	-0.843311
H	3.088561	-1.007305	-0.187067
H	3.578662	-2.448309	-0.441169

7a

	X	Y	Z
Mg	-0.653334	-0.859759	-0.045204
Cl	2.642725	0.839477	-0.821963
Cl	-1.814346	2.737204	0.217589
O	-0.414168	0.578596	-1.589059

7a’

	X	Y	Z
Mg	0.448670	-0.053090	0.146883
Cl	2.020435	0.963898	-1.459439
Cl	-3.425934	-1.024396	-0.357339
O	-0.649381	-0.833714	-1.456987

H	0.532548	0.820567	-1.632046	H	-1.620311	-0.958959	-1.300157
H	-0.865043	1.396240	-1.293659	H	-0.528671	-0.420644	-2.314370
O	-2.514949	-0.112795	0.555891	O	-0.406820	1.846786	0.347504
H	-3.265864	-0.430480	0.050098	H	-1.386875	1.959972	0.428563
H	-2.512643	0.880891	0.507760	H	-0.094086	2.436291	-0.343392
O	1.166119	-1.712470	-0.634578	O	-1.024903	-0.808937	1.401981
H	1.523466	-2.368262	-0.032186	H	-0.869074	-1.459274	2.086329
H	1.851135	-1.000712	-0.752444	H	-1.912222	-0.984195	0.998803
O	-0.703797	-2.348831	1.475912	O	1.677185	0.391621	1.837330
H	-1.124929	-2.082571	2.301536	H	2.616999	0.224890	1.653982
H	-1.112136	-3.209916	1.236596	H	1.588267	1.312530	2.093073
O	0.266539	0.576926	1.219757	O	1.517712	-1.917026	0.163807
H	1.135025	0.795717	0.823577	H	2.477946	-1.777553	0.207314
H	-0.248440	1.406236	1.158823	H	1.331295	-2.395858	-0.647524
O	-1.742658	-2.199903	-1.290029	O	3.873469	-0.492545	0.430514
H	-2.026466	-3.048029	-0.883004	H	3.563805	0.060245	-0.320736
H	-1.309663	-2.441334	-2.117162	H	4.829872	-0.529289	0.395836
O	3.166752	0.084445	1.369131	O	-3.048132	1.901349	0.505736
H	3.717691	0.337709	0.624870	H	-3.675166	2.500865	0.101140
H	3.672164	-0.470260	1.967847	H	-3.325380	0.996261	0.244707