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

Superatomic nature of alkaline earth metal-water complexes: The cases of $Be(H_2O)_4^{0,+}$ and $Mg(H_2O)_6^{0,+}$

Isuru R. Ariyarathna and Evangelos Miliordos*

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849-5312, USA

* E-mail: emiliord@auburn.edu

Table S1. Optimal geometries (Cartesian coordinates in Å) of H_2O and $Mg(H_2O)_{n=1-6}^+$ at MP2 and C-MP2.

		MP2				C-MP2		
H_2O	O	-0.000000	0.000000	0.118137	O	0.000000	-0.000000	0.118137
	H	-0.000000	0.757376	-0.472549	H	-0.000000	0.757376	-0.472549
	H	0.000000	-0.757376	-0.472549	H	-0.000000	-0.757376	-0.472549
$Mg(H_2O)_1^+$	Mg	-0.991536	-0.000042	-0.000179	Mg	-0.983107	-0.000021	0.000000
	O	1.073209	-0.000152	0.000171	O	1.063256	-0.000075	-0.000001
	H	1.655051	0.773114	0.000385	H	1.644960	0.773429	0.000004
	H	1.657710	-0.771392	0.000387	H	1.646279	-0.772577	0.000004
$Mg(H_2O)_2^+$	Mg	0.000037	0.965657	0.000019	Mg	0.000032	0.956170	-0.000002
	O	1.477693	-0.514271	0.004704	O	1.466204	-0.508859	0.004687
	O	-1.477708	-0.514240	-0.004731	O	-1.466217	-0.508832	-0.004692
	H	-2.381241	-0.359183	-0.311363	H	-2.368491	-0.353228	-0.314991
	H	-1.513439	-1.320475	0.526674	H	-1.504223	-1.312818	0.530152
	H	2.381418	-0.359195	0.310755	H	2.368646	-0.353215	0.314473
	H	1.512936	-1.320937	-0.526077	H	1.503787	-1.313253	-0.529571
$Mg(H_2O)_3^+$	Mg	-0.000105	0.000035	0.915850	Mg	0.000017	-0.000000	0.905477
	O	0.834208	-1.497560	-0.330818	O	1.521755	-0.759858	-0.327201
	O	-1.714111	0.026438	-0.330905	O	-1.418968	-0.937910	-0.327141
	O	0.880022	1.471107	-0.330833	O	-0.102803	1.697777	-0.327197
	H	1.076899	2.363294	-0.017719	H	-0.444438	2.544134	-0.011144
	H	1.548092	1.271105	-0.998859	H	0.562899	1.911584	-0.993406
	H	-2.585142	-0.249111	-0.017569	H	-1.981056	-1.656980	-0.011033
	H	-1.875095	0.704726	-0.999177	H	-1.937069	-0.468321	-0.993299
	H	0.327231	-1.976190	-0.999000	H	1.374079	-1.443257	-0.993439
	H	1.508331	-2.114121	-0.017428	H	2.425516	-0.887233	-0.011095
$Mg(H_2O)_4^+$	Mg	-0.000334	-0.010068	-0.678384	Mg	-0.000012	-0.014237	-0.659730
	O	-0.000274	-1.301573	0.994509	O	-0.000017	-1.296441	0.996164
	O	2.160237	-0.199020	-0.429005	O	2.138909	-0.189236	-0.442186
	O	-2.160833	-0.197835	-0.428648	O	-2.138936	-0.189179	-0.442171
	O	0.001428	1.653003	0.646517	O	0.000071	1.634070	0.653285
	H	0.000807	1.632205	1.610907	H	0.000009	1.611389	1.617736
	H	0.000597	2.582318	0.388858	H	0.000023	2.563597	0.396196
	H	-0.774114	-1.836216	1.208006	H	-0.774110	-1.832766	1.205060
	H	0.774088	-1.835379	1.208224	H	0.774081	-1.832762	1.205056
	H	-2.755981	0.447313	-0.024749	H	-2.737117	0.459248	-0.047608
	H	-2.598203	-0.475577	-1.245293	H	-2.563364	-0.465351	-1.266372
	H	2.597547	-0.478429	-1.245109	H	2.563342	-0.465474	-1.266361
	H	2.754806	0.447975	-0.027213	H	2.737065	0.459257	-0.047694

$Mg(H_2O)_5^+$	Mg	0.000000	0.000000	0.438630	Mg	0.000000	0.000000	0.414429
	O	0.000000	2.130461	0.105340	O	0.000000	2.110227	0.117931
	O	-0.000000	-2.130461	0.105340	O	-0.000000	-2.110227	0.117931
	O	2.128429	-0.001184	0.433364	O	2.104168	-0.000912	0.433542
	O	-2.128429	0.001184	0.433364	O	-2.104168	0.000912	0.433542
	O	0.000000	0.000000	-1.680992	O	0.000000	0.000000	-1.683177
	H	-0.000599	0.777538	-2.249089	H	-0.000444	0.777776	-2.251103
	H	0.000599	-0.777538	-2.249089	H	0.000444	-0.777776	-2.251103
	H	-0.765437	2.592182	0.473805	H	-0.765789	2.565788	0.493754
	H	0.764341	2.592634	0.475501	H	0.764741	2.566121	0.495474
	H	-2.544299	0.000780	1.307260	H	-2.508822	0.000516	1.313196
	H	-2.837125	-0.002037	-0.224920	H	-2.820581	-0.001877	-0.216969
	H	-0.764341	-2.592634	0.475501	H	-0.764741	-2.566121	0.495474
	H	0.765437	-2.592182	0.473805	H	0.765789	-2.565788	0.493754
	H	2.837125	0.002037	-0.224920	H	2.820581	0.001877	-0.216969
	H	2.544299	-0.000780	1.307260	H	2.508822	-0.000516	1.313196

$Mg(H_2O)_6^+$	Mg	0.000000	0.000000	0.000000	Mg	0.000000	0.000000	0.000000
	O	-2.086171	0.000000	0.000000	O	-2.066618	0.000000	0.000000
	O	0.000000	0.000000	2.086166	O	0.000000	0.000000	2.066615
	O	0.000000	0.000000	-2.086166	O	0.000000	0.000000	-2.066615
	O	2.086171	-0.000000	0.000000	O	2.066618	-0.000000	0.000000
	O	0.000000	2.086166	0.000000	O	0.000000	2.066615	0.000000
	O	-0.000000	-2.086166	0.000000	O	-0.000000	-2.066615	0.000000
	H	0.000000	-2.661305	-0.779136	H	0.000000	-2.641536	-0.779384
	H	-0.000000	-2.661305	0.779136	H	-0.000000	-2.641536	0.779384
	H	0.779136	-0.000000	-2.661305	H	0.779383	-0.000000	-2.641536
	H	-0.779136	0.000000	-2.661305	H	-0.779383	0.000000	-2.641536
	H	-2.661311	0.779136	0.000000	H	-2.641539	0.779383	0.000000
	H	-2.661311	-0.779136	-0.000000	H	-2.641539	-0.779383	-0.000000
	H	0.000000	2.661305	0.779136	H	0.000000	2.641536	0.779384
	H	0.000000	2.661305	-0.779136	H	0.000000	2.641536	-0.779384
	H	-0.779136	-0.000000	2.661305	H	-0.779383	-0.000000	2.641536
	H	0.779136	-0.000000	2.661305	H	0.779383	-0.000000	2.641536
	H	2.661311	0.779136	0.000000	H	2.641539	0.779383	0.000000
	H	2.661311	-0.779136	0.000000	H	2.641539	-0.779383	0.000000

Table S2. Harmonic vibrational frequencies (cm^{-1}) at the DFT/B3LYP level for $Mg(H_2O)_{n=1-6}^{+}$.

$Mg(H_2O)_1^+$	$Mg(H_2O)_2^+$	$Mg(H_2O)_3^+$	$Mg(H_2O)_4^+$	$Mg(H_2O)_5^+$	$[Mg(H_2O)_6^+$
345.2	56.8	80.6	67.7	41.8	57.5
386.3	97.0	81.0	84.3	78.8	57.5
505.5	192.6	108.1	89.8	80.4	57.5
1652.5	336.4	146.5	100.7	84.4	100.4
3709.1	349.1	147.8	107.2	84.5	100.4
3789.1	352.4	264.7	137.4	110.4	100.4
	367.8	321.3	168.6	122.9	130.1
	472.1	321.5	205.4	129.9	130.1
	517.0	325.6	225.4	170.3	130.1
	1645.8	341.1	263.2	204.2	162.6
	1649.9	365.1	315.1	204.3	162.6
	3712.9	365.3	318.4	208.2	162.6
	3713.9	468.7	327.8	231.1	195.2
	3798.7	469.0	338.0	246.0	195.2
	3799.1	506.4	351.4	247.4	199.0
		1638.0	358.8	258.8	199.0
		1638.0	361.5	298.3	199.1
		1640.3	426.5	301.2	244.8
		3712.3	444.5	307.7	244.8
		3712.4	473.8	361.0	244.9
		3712.7	503.8	380.7	249.0
		3803.1	1619.0	400.2	249.0
		3803.5	1619.5	409.5	309.2
		3803.7	1623.8	440.0	318.7
			1628.8	479.5	379.1
			3655.2	485.5	379.1
			3659.3	489.0	379.1
			3690.8	1578.7	460.7
			3729.7	1580.8	460.7
			3754.4	1608.1	460.7
			3755.0	1608.3	463.4
			3793.1	1613.6	463.4
			3823.7	3523.8	463.4
				3549.2	1593.6
				3615.2	1593.6
				3631.7	1597.1
				3638.6	1597.1
				3639.6	1597.1
				3668.5	1599.3
				3714.8	3594.4
				3715.1	3594.4
				3763.6	3595.5
					3595.5
					3595.5
					3663.9
					3699.7
					3699.8
					3699.8
					3700.2
					3700.3
					3700.3

Table S3. Optimal geometries (Cartesian coordinates in Å) of $Mg(H_2O)_{n=1-6}$ at MP2 and C-MP2.

		MP2				C-MP2		
$Mg(H_2O)_1$	Mg	-1.344997	0.000007	0.000090	Mg	-1.640298	-0.001062	-0.000283
	O	1.496590	0.000042	-0.000791	O	1.286655	0.000760	0.000086
	H	2.083950	0.763014	0.002624	H	1.873837	0.763368	0.000480
	H	2.083290	-0.763438	0.002622	H	1.874240	-0.761537	0.000482
$Mg(H_2O)_1@H_2O$	Mg	1.754559	-0.544601	0.002698	Mg	1.698592	-0.566657	0.002126
	O	-2.165092	-0.376657	-0.074959	O	-2.119715	-0.383099	-0.079219
	H	-2.680368	-0.533759	0.722495	H	-2.650032	-0.544878	0.707526
	O	0.166016	1.094274	0.080158	O	0.182728	1.127509	0.084417
	H	0.170058	1.862878	-0.502496	H	0.198185	1.880874	-0.517708
	H	-0.733135	0.708369	0.023729	H	-0.717737	0.744852	0.026181
	H	-1.818663	-1.243205	-0.317697	H	-1.717630	-1.236248	-0.283092
$Mg@3(H_2O)$	Mg	2.650717	-0.011021	-0.003842	Mg	-2.586004	-0.000372	-0.000325
	O	-1.013495	-0.788106	-1.387160	O	0.972910	-1.509455	-0.526698
	O	-1.001717	-0.803311	1.381289	O	0.972005	1.211165	-1.043848
	O	-0.978316	1.602603	0.009768	O	0.971382	0.298660	1.570897
	H	-1.506424	2.377098	-0.197681	H	1.504628	0.230883	2.366442
	H	-1.078573	1.001040	-0.748347	H	1.061864	-0.556527	1.115785
	H	-1.535945	-0.998758	2.154698	H	1.504799	1.934632	-1.382313
	H	-1.080046	0.156002	1.238982	H	1.061436	1.244652	-0.075581
	H	-1.104641	-1.142905	-0.485781	H	1.062813	-0.687734	-1.039863
	H	-1.554750	-1.349722	-1.946937	H	1.506131	-2.164397	-0.983379
$Mg(H_2O)_4$	Mg	-0.021827	0.005594	-0.699218	Mg	-0.000054	-0.018721	-0.678356
	O	-0.099252	-1.231304	1.073266	O	-0.000180	-1.155638	1.142735
	O	2.132661	-0.355603	-0.437570	O	2.158314	-0.272143	-0.428253
	O	-2.211821	-0.125198	-0.385694	O	-2.158492	-0.271667	-0.428138
	O	0.273506	1.625016	0.688369	O	0.000684	1.638198	0.624034
	H	-0.155668	1.568724	1.558779	H	-0.000705	1.654797	1.594341
	H	-0.015730	2.465606	0.297308	H	-0.000578	2.551531	0.304497
	H	-0.937842	-1.709738	1.134186	H	-0.775668	-1.730366	1.206569
	H	0.602825	-1.893728	1.127663	H	0.775013	-1.730766	1.206522
	H	-2.424769	-0.514600	-1.256914	H	-2.579508	0.607230	-0.414370
	H	-2.578355	0.778369	-0.446642	H	-2.368969	-0.622326	-1.313209
	H	2.443736	-0.544299	-1.338310	H	2.369010	-0.622113	-1.313527
	H	2.566966	0.479259	-0.192424	H	2.579444	0.606670	-0.413565
$Mg(H_2O)_5$	Mg	0.017353	0.014040	-0.154204	Mg	0.011075	0.014961	-0.173794
	O	0.100184	-1.976504	-0.714036	O	0.232703	-1.965251	-0.664424
	O	0.009577	2.040414	-0.587631	O	-0.142312	2.029733	-0.542695
	O	2.108485	0.143440	-0.231237	O	2.067662	0.285910	-0.264395
	O	-2.065269	-0.081546	-0.433426	O	-2.040852	-0.224381	-0.433325
	O	-0.251540	-0.161293	1.881640	O	-0.206838	-0.166697	1.849533
	H	0.460793	-0.688537	2.318812	H	0.542507	-0.653038	2.273827
	H	-0.292822	0.689150	2.373733	H	-0.299926	0.673926	2.350388
	H	-0.731047	-2.477715	-0.649457	H	-0.557932	-2.522774	-0.561916
	H	0.767096	-2.491855	-0.216501	H	0.943743	-2.406055	-0.154564
	H	-2.504380	0.550528	-1.027058	H	-2.521544	0.348823	-1.054162
	H	-2.512407	0.019933	0.428882	H	-2.492091	-0.112530	0.426405
	H	-0.589880	2.578196	-0.030598	H	-0.795416	2.508073	0.008642
	H	0.895972	2.428783	-0.466241	H	0.708584	2.482513	-0.393869
	H	2.487870	-0.068889	0.653380	H	2.478060	0.005641	0.588530
	H	2.599076	-0.424159	-0.856977	H	2.578219	-0.178632	-0.955312
$Mg(H_2O)_6$	Mg	-0.000034	-0.000027	0.008216	Mg	-0.000038	-0.000010	0.004131
	O	1.145893	-1.244297	-1.250485	O	-0.644742	1.549829	-1.239508

O	0.506216	1.614957	-1.249274	O	-1.020069	-1.330796	-1.242025
O	-0.758986	-1.612342	1.128409	O	1.245312	1.243773	1.125013
O	-1.017118	1.462176	1.129776	O	0.456893	-1.701419	1.122458
O	1.774520	0.148295	1.130490	O	-1.699929	0.454020	1.125913
O	-1.650408	-0.368667	-1.251188	O	1.662377	-0.215338	-1.242605
H	-2.356860	-0.848376	-0.788539	H	2.491523	-0.011114	-0.779702
H	-2.075066	0.389062	-1.679120	H	1.798844	-1.069145	-1.678844
H	-1.223497	-1.308496	1.939503	H	1.538635	0.813049	1.958416
H	-0.089453	-2.252330	1.456968	H	0.853999	2.096436	1.416175
H	0.702690	-1.990808	-1.679326	H	0.026581	2.095617	-1.674683
H	1.914142	-1.616289	-0.787176	H	-1.236032	2.165087	-0.775468
H	1.993861	1.048089	1.459250	H	-2.240694	-0.312120	1.418394
H	1.742438	-0.405824	1.941592	H	-1.473873	0.924789	1.958624
H	1.374800	1.604299	-1.677138	H	-1.828558	-1.021273	-1.676146
H	0.443975	2.466135	-0.785736	H	-1.257128	-2.151400	-0.779547
H	-1.905960	1.201790	1.458372	H	1.391091	-1.788250	1.413379
H	-0.521600	1.712099	1.940928	H	-0.062666	-1.742113	1.955847

Table S4. Harmonic vibrational frequencies (cm^{-1}) at the DFT/B3LYP level for $Mg(H_2O)_{n=1-6}$.

$Mg(H_2O)$	$Mg(H_2O)_1$@ H_2O	$Mg@3H_2O^a$	$Mg(H_2O)_4$	$Mg(H_2O)_5$	$Mg(H_2O)_6$
83.1	27.5	13.4	57.9	38.8	83.2
105.7	98.9	13.6	79.8	51.6	86.3
216.1	161.7	41.0	86.1	63.3	86.9
1604.2	194.3	122.3	92.2	71.3	103.9
3703.0	228.7	123.9	107.7	76.4	118.5
3819.7	244.5	181.6	113.6	117.0	118.7
	309.4	188.2	146.8	122.4	125.6
	458.7	188.5	176.5	129.4	132.6
	748.2	220.2	191.7	138.9	133.0
	1618.1	365.1	264.1	154.2	148.0
	1633.4	365.7	271.1	156.2	148.3
	3461.6	519.4	286.1	175.5	153.6
	3758.2	527.2	294.6	201.4	202.0
	3777.8	527.2	300.0	247.8	202.6
	3864.1	787.2	335.6	258.6	249.6
		1643.1	369.5	280.0	249.9
		1643.2	385.8	310.1	257.9
		1664.9	411.5	346.0	289.5
		3614.2	441.6	353.2	290.7
		3670.6	455.4	388.6	292.9
		3670.7	504.3	412.9	310.6
		3917.6	1554.4	417.2	319.4
		3917.8	1564.9	474.4	321.2
		3918.4	1573.3	482.2	321.9
			1583.4	491.9	386.8
			3493.1	493.1	387.9
			3527.9	543.9	388.9
			3553.2	1523.7	503.7
			3572.0	1532.0	507.5
			3627.4	1542.9	511.3
			3636.6	1545.2	511.9
			3645.0	1565.3	515.8
			3746.6	3360.0	516.5
				3388.3	1546.6
				3388.4	1546.9
				3403.1	1555.5
				3434.1	1566.3
				3435.7	1566.3
				3448.6	1568.1
				3468.6	3422.4
				3600.5	3422.6
				3697.3	3457.5
					3509.2
					3509.5
					3511.3
					3565.0

	3565.3
	3592.7
	3657.9
	3658.6
	3659.1

[a]*Obtained from MP2(FC) because this molecule is not stable under B3LYP*

Table S5. Optimal geometry (Cartesian coordinates in Å) of $Mg(H_2O)_6$ under C_s symmetry.

$Mg(H_2O)_6$ (C_s)			
Mg	-0.006003	0.011129	0.000000
O	2.092472	-0.049096	0.000000
O	0.265945	2.076332	0.000000
O	-0.146213	-2.065110	0.000000
O	-0.146213	-0.050257	2.099561
O	-2.080113	0.333555	0.000000
O	-0.146213	-0.050257	-2.099561
H	1.157548	2.454181	0.000000
H	0.656865	-2.626787	0.000000
H	-0.372430	2.801200	0.000000
H	-0.918648	-2.660727	0.000000
H	-2.557185	0.000859	0.776101
H	-2.557185	0.000859	-0.776101
H	2.488097	-0.502728	0.775618
H	2.488097	-0.502728	-0.775618
H	0.365039	0.594853	2.617905
H	0.365039	0.594853	-2.617905
H	0.119729	-0.924355	2.442375
H	0.119729	-0.924355	-2.442375

Table S6. Optimal geometries (Cartesian coordinates in Å) of $Be(H_2O)_{n=1-4}^{+/0}$ at MP2: Be, N: cc-pVTZ, H: aug-cc-pVTZ.

	$Be(H_2O)_n^+$ (Doublet ground state)				$Be(H_2O)_n$ (Singlet ground state)			
n=1	Be	-1.202809	-0.000014	-0.000001	Be	-1.266490	0.000045	0.037726
	O	0.368678	-0.000009	0.000000	O	0.429148	0.000018	-0.101459
	H	0.930801	0.793759	0.000002	H	0.816662	0.785929	0.330455
	H	0.931007	-0.793627	0.000002	H	0.816119	-0.786251	0.330310
n=2	Be	0.000002	-0.806557	0.000072	Be	0.000000	0.871507	0.073475
	O	-1.328823	0.110433	0.000087	O	1.291072	-0.131924	-0.098267
	O	1.328824	0.110430	-0.000183	O	-1.291072	-0.131924	-0.098267
	H	-1.472790	1.067894	-0.000838	H	1.231902	-1.024128	0.328429
	H	1.472746	1.067898	0.001328	H	-1.231902	-1.024129	0.328426
	H	2.187250	-0.338216	-0.000464	H	-2.044644	0.336507	0.310761
	H	-2.187229	-0.338252	0.000452	H	2.044644	0.336509	0.310759
n=3	Be	-0.000118	0.000034	0.643277	Be	0.000025	-0.000005	0.609093
	O	-1.496562	-0.306472	-0.089734	O	-0.805622	-1.301563	-0.125736
	H	-2.179849	-0.618596	0.520221	H	-0.982590	-1.870980	0.650636
	H	-1.905771	0.359623	-0.661598	H	-1.684585	-1.019285	-0.456880
	O	1.013718	-1.142761	-0.089468	o	1.530016	-0.046925	-0.125770
	H	1.625943	-1.577866	0.520629	H	2.111669	0.084951	0.650496
	O	0.482909	1.449202	-0.089766	o	-0.724336	1.348470	-0.125812
	H	1.265432	1.470446	-0.660177	H	-0.040301	1.968956	-0.455954
	H	0.553021	2.197309	0.519967	H	-1.129887	1.785921	0.650381
	H	0.641179	-1.830807	-0.660408	H	1.725133	-0.949394	-0.456501
n=4	Be	-0.005133	-0.000350	0.018191	Be	0.000401	-0.060002	0.000442
	O	-0.385061	1.544202	0.438089	O	0.033594	0.866983	-1.361251
	H	0.134738	1.926613	1.178956	H	0.823855	1.475213	-1.284419
	H	-1.327506	1.743919	0.618678	H	-0.772173	1.459955	-1.353413
	O	-1.329426	-0.642726	-0.717532	O	-1.351751	-0.998957	-0.087099
	H	-1.241498	-1.265809	-1.460214	H	-1.580676	-1.419896	0.766569
	O	1.195709	0.062223	-1.116725	O	1.356343	-0.993102	0.091709
	H	1.419917	0.893094	-1.565091	H	1.586021	-1.417004	-0.760299
	H	2.011608	-0.449327	-0.993669	H	2.118200	-0.392311	0.307231
	H	-2.084416	-0.927930	-0.165757	H	-2.115883	-0.402235	-0.306139
	O	0.534199	-0.960053	1.230737	O	-0.037523	0.873614	1.357184
	H	1.154557	-0.541390	1.876318	H	0.764936	1.470888	1.346825
	H	-0.170231	-1.406936	1.761465	H	-0.831187	1.477095	1.277531

Table S7. Harmonic vibrational frequencies (cm^{-1}) at the DFT/B3LYP level for $Be(H_2O)_{n=1-4}$.

$Be(H_2O)_1^+$	$Be(H_2O)_2^+$	$Be(H_2O)_3^+$	$Be(H_2O)_4^+$	$Be(H_2O)_1$	$Be(H_2O)_2$	$Be(H_2O)_3$	$Be(H_2O)_4$
368.1	66.4	132.4	84.9	371.8	223.6	104.9	114.7
665.7	243.0	133.3	104.9	523.1	238.1	108.1	147.1
833.9	252.9	217.7	124.7	544.6	250.3	186.9	173.9
1642.2	327.5	217.9	167.0	1532.5	370.1	202.5	180.8
3626.9	340.0	251.3	177.1	3429.8	374.8	202.8	199.5
3696.3	591.9	294.4	217.4	3519.7	578.7	243.7	221.0
	596.5	421.2	233.1		591.8	460.2	237.9
	801.5	422.0	242.1		683.9	461.5	246.5
	846.4	425.9	252.1		734.2	467.2	247.1
	1631.9	497.1	255.2		1488.0	483.1	464.8
	1646.7	587.6	293.8		1497.4	581.3	506.4
	3618.4	587.6	354.6		3078.6	581.6	511.9
	3619.5	711.8	380.7		3098.2	680.2	565.4
	3748.3	712.3	472.2		3552.4	699.0	577.6
	3748.9	748.6	593.5		3572.4	699.5	605.7
		1627.7	608.0			1528.2	657.0
		1627.8	608.3			1528.3	662.6
		1629.6	670.1			1528.7	742.2
		3637.1	763.4			3364.9	780.7
		3639.1	767.2			3365.2	794.6
		3639.3	785.8			3400.6	830.1
		3755.9	1527.7			3463.7	1452.4
		3758.4	1557.8			3485.9	1478.1
		3758.5	1566.9			3486.0	1514.3
			1597.9				1516.9
			3248.9				3094.7
			3291.6				3122.4
			3341.3				3126.8
			3420.8				3142.9
			3471.5				3160.9
			3491.9				3243.8
			3554.4				3407.8
			3611.8				3440.6

Table S8. Electronic energies and optimal structures (Cartesian Coordinates in Å) of the intermediates and transition states for the reaction of H_2 release from $Be(NH_3)_4$ and $Be(H_2O)_4$

$Be(NH_3)_4 \rightarrow Be(NH_2)_2(NH_3)_2 + H_2$							
$Be(NH_3)_4$				TS1			
Be	0.000051	0.000203	-0.000047	Be	0.101686	-0.000008	0.058059
N	-0.838132	-0.824007	-1.262618	N	1.854509	-0.000023	0.161018
N	-1.089225	1.059675	0.816569	N	-0.495430	-1.385113	-0.807472
N	0.629672	-1.151659	1.119291	N	-0.495379	1.385054	-0.807582
N	1.297690	0.916030	-0.673203	N	-0.738984	0.000072	1.456010
H	-1.618824	-1.385487	-0.900051	H	2.357228	-0.000882	-0.729248
H	-0.220582	-1.464633	-1.776819	H	2.155157	-0.816079	0.694883
H	-1.232337	-0.169942	-1.950345	H	2.155291	0.816966	0.693374
H	-0.626676	1.569926	1.579341	H	-0.290623	-2.274356	-0.352163
H	-1.879081	0.549758	1.231639	H	-0.293269	-1.489442	-1.798896
H	-1.486138	1.763417	0.181465	H	-1.521473	-1.204187	-0.691195
H	1.823551	1.422602	0.049996	H	-0.293228	1.489302	-1.799017
H	0.962611	1.615975	-1.346950	H	-0.290543	2.274329	-0.352345
H	1.969754	0.318089	-1.170181	H	-0.829784	-0.818090	2.048135
H	1.138414	-0.698564	1.888728	H	-0.829748	0.818289	2.048063
H	1.284089	-1.803772	0.669126	H	-1.521431	1.204168	-0.691277
H	-0.115021	-1.718453	1.543961	H	-2.077330	0.000093	0.683626
Int1				TS2			
Be	0.350487	-0.000358	0.047371	Be	0.337277	-0.000114	0.083227
N	-0.400776	-1.360125	-0.810502	N	-0.422087	1.381243	-0.830513
N	-0.399197	1.361225	-0.809564	N	-0.669527	-0.000750	1.466817
N	1.930800	-0.000943	0.153566	N	1.920613	-0.000409	0.178445
N	-0.733922	-0.000211	1.494763	N	-0.422815	-1.380137	-0.832113
H	-0.070687	-1.463505	-1.762790	H	-0.169250	2.251833	-0.378480
H	-1.413649	-1.069814	-0.816056	H	-1.434747	1.233528	-0.737479
H	-0.322923	-2.268765	-0.369342	H	-0.183135	1.474657	-1.809772
H	-0.068432	1.464536	-1.761628	H	-0.616837	0.808583	2.074439
H	-0.320199	2.269533	-0.367938	H	-0.617374	-0.810919	2.073371
H	-1.412249	1.072472	-0.815840	H	-1.777292	-0.000032	0.879587
H	2.498182	0.812428	0.331535	H	2.430040	-0.001740	1.046725
H	2.497865	-0.815009	0.329317	H	2.585770	0.000193	-0.577907
H	-0.641704	-0.813614	2.091729	H	-0.183816	-1.472575	-1.811454
H	-0.640942	0.812801	2.092143	H	-0.170486	-2.251375	-0.381047
H	-2.602068	0.000438	-0.391178	H	-2.619877	0.000677	0.149659
H	-1.683480	0.000311	1.052719	H	-1.435398	-1.232001	-0.739001
Int2				Prod			
Be	0.208036	0.009047	0.215018	Be	0.000021	0.000123	0.217408
N	-0.766797	1.226675	-0.823402	N	-1.406622	-0.413447	-0.947392
N	-0.849089	-0.747299	1.172708	N	1.406579	0.412567	-0.947791
N	1.490884	0.809734	0.759744	N	-0.417367	1.353324	0.977778
N	0.792588	-1.239265	-1.044542	N	0.417402	-1.352418	0.978959
H	-0.924421	1.913444	-0.094669	H	-1.763112	0.265853	-1.608769
H	-1.670555	0.855527	-1.089157	H	-2.113099	-0.558621	-0.235313
H	-0.352813	1.704739	-1.614287	H	-1.266278	-1.298801	-1.417540

H	-0.844178	-0.588509	2.168593	H	2.112933	0.559052	-0.235858
H	-1.256655	-1.656272	1.015010	H	1.266108	1.297128	-1.419391
H	-3.293995	-0.237539	0.185504	H	1.763299	-0.267715	-1.608033
H	1.862879	0.678179	1.686457	H	1.025804	-2.090125	0.661448
H	1.991429	1.569486	0.326532	H	0.213751	-1.512608	1.952344
H	1.458802	-0.848979	-1.699335	H	-0.213877	1.514283	1.951070
H	1.310533	-1.842720	-0.416362	H	-1.025567	2.090877	0.659527
H	-3.909451	-0.124384	-0.230771				
H	0.123184	-1.808077	-1.549143				

$Be(H_2O)_4 \rightarrow Be(OH)_2(H_2O)_2 + H_2$

$Be(H_2O)_4$				TS1			
Be	-0.000000	0.048414	0.000000	Be	0.097702	-0.042360	0.011418
O	0.032392	-0.868476	-1.351877	O	-0.779378	-0.211141	1.402153
H	-0.763812	-1.464398	-1.392756	H	-0.710072	0.471157	2.093423
H	0.840171	-1.449839	-1.383232	O	1.738968	-0.120857	0.270459
O	1.342539	0.983006	-0.021434	H	2.102494	-0.943602	-0.108986
H	1.542450	1.443354	0.818975	O	-0.474012	-1.112408	-0.993873
O	-1.342540	0.983005	0.021438	H	-0.634776	-2.015453	-0.674998
H	-1.542447	1.443362	-0.818967	H	-1.579136	-0.570748	-1.038659
H	-2.143970	0.457835	0.272544	H	2.215199	0.631330	-0.126899
H	2.143968	0.457839	-0.272548	O	-0.290018	1.379197	-0.693165
O	-0.032391	-0.868481	1.351874	H	-1.282462	1.108804	-0.954022
H	-0.840172	-1.449841	1.383230	H	-0.350637	2.177305	-0.137197
H	0.763810	-1.464406	1.392747	H	-1.715892	-0.167686	1.017079

Intermediate				Prod			
Be	-0.143875	-0.000099	0.222887	Be	-0.000000	-0.000043	0.219834
O	0.782761	-1.072833	0.780845	O	-0.009476	-1.408149	0.797533
H	0.774908	-1.293842	1.708892	H	-0.008810	-1.570528	1.737164
O	0.861871	1.011443	-0.817649	O	1.370536	-0.007856	-0.909898
H	0.657983	1.901955	-0.507906	H	1.870077	0.771981	-0.639100
O	-1.133758	-0.844062	-0.998693	O	-1.370539	0.008040	-0.909891
H	-0.998185	-1.774988	-0.786241	H	-1.870178	-0.771789	-0.639255
H	-2.024225	-0.596134	-0.719982	H	-1.861458	0.793528	-0.639740
H	1.784839	0.814888	-0.612243	H	1.861549	-0.793337	-0.639903
O	-1.138356	0.981378	0.832722	O	0.009480	1.407980	0.797765
H	-1.252317	1.069144	1.775375	H	0.008818	1.570201	1.737424
H	3.036082	-0.544215	0.093984				
H	3.616270	-0.183824	-0.221232				

Table S9. Harmonic vibrational frequencies (cm^{-1}) of the intermediates and transition states for the reaction of H_2 release from $Be(NH_3)_4$ and $Be(H_2O)_4$.

$Be(NH_3)_4 \rightarrow Be(NH_2)_2(NH_3)_2 + H_2$						
$Be(NH_3)_4$	TS1	Int1 $BeNH_2(NH_3)_3..H$	TS2	Int2 $Be(NH_3)_2(NH_2)_2...H_2$	Product $Be(NH_3)_2(NH_2)_2$	H_2
168.3	1464.6i	97.6	1119.6i	22.8	56.5	4408.3
170.6	85.4	176.0	95.0	72.7	63.7	
170.7	172.2	202.3	186.6	84.2	125.5	
170.8	179.2	249.1	199.8	113.1	168.2	
177.7	232.1	255.8	226.5	132.9	175.6	
177.9	239.0	301.6	246.9	151.9	181.0	
231.0	266.4	309.9	256.9	173.1	218.1	
231.8	282.9	321.3	278.5	189.0	239.8	
232.1	316.6	323.5	281.2	192.8	255.0	
465.2	374.4	335.9	303.0	224.7	277.8	
609.6	462.2	443.2	318.4	241.7	284.9	
609.9	570.7	471.7	431.7	260.8	354.6	
610.3	575.9	478.8	435.8	286.9	363.7	
630.7	596.7	522.0	523.4	321.4	530.9	
631.1	620.2	525.7	551.7	366.7	554.1	
631.4	646.2	546.1	555.3	380.1	624.4	
732.1	678.4	619.0	571.8	452.2	648.0	
732.1	691.8	718.1	616.8	511.1	650.8	
870.7	727.6	743.6	687.9	532.9	719.1	
870.8	756.3	766.8	733.5	557.9	857.6	
871.0	829.3	816.3	782.6	626.2	1056.3	
1293.4	894.8	879.1	818.5	652.0	1182.6	
1298.6	921.2	906.0	884.6	652.8	1191.6	
1298.7	973.3	1064.6	1048.7	727.9	1587.1	
1298.8	1270.9	1267.2	1221.2	858.9	1592.0	
1581.4	1271.2	1283.0	1235.7	1050.2	1639.1	
1581.4	1276.0	1343.8	1373.8	1187.4	1643.5	
1593.5	1586.4	1595.7	1509.2	1196.6	1653.5	
1593.6	1601.5	1632.0	1591.7	1588.0	1663.5	
1593.6	1606.9	1633.5	1619.9	1591.7	3488.1	
1602.1	1609.6	1665.2	1633.6	1640.8	3490.1	
1602.1	1619.2	1673.1	1648.6	1646.3	3584.8	
1602.1	1621.8	1699.1	1668.1	1655.2	3585.3	
3238.9	1632.8	1700.0	1675.4	1666.3	3603.3	
3238.9	2935.2	2816.2	1687.0	3488.4	3603.4	
3239.0	2952.3	2872.2	3291.2	3490.7	3613.6	
3282.2	3353.0	2993.5	3313.9	3571.0	3614.4	
3320.2	3422.6	3529.3	3514.7	3584.3	3657.0	
3320.3	3431.9	3531.1	3548.7	3602.0	3657.4	
3320.5	3464.1	3531.5	3549.0	3603.8		
3329.4	3477.2	3586.7	3589.3	3611.3		

3329.5	3488.3	3597.8	3592.6	3613.1	
3357.8	3513.6	3598.8	3606.5	3641.1	
3357.9	3516.0	3598.9	3606.9	3656.9	
3358.0	3584.4	3655.7	3664.8	4292.1	

$Be(H_2O)_4 \rightarrow Be(OH)_2(H_2O)_2 + H_2$

$Be(H_2O)_4$	TS1	Intermediate $Be(OH)_2(H_2O)_2$...H_2	Product $Be(OH)_2(H_2O)_2$
110.4	1465.5i	43.4	32.5
154.4	86.1	68.6	152.4
182.8	172.7	155.2	182.2
194.1	192.5	172.8	216.2
206.3	237.8	182.1	223.6
223.7	259.1	211.1	283.7
243.8	291.2	229.3	285.9
246.7	312.7	242.8	325.5
250.7	372.0	284.9	325.7
476.5	425.0	289.2	398.6
521.6	479.2	327.6	409.0
531.9	520.2	338.5	575.7
594.5	607.9	401.1	612.2
607.0	628.4	413.3	617.5
615.9	650.2	431.0	666.4
669.6	677.3	565.9	672.3
678.1	693.4	596.0	696.8
754.7	696.6	616.7	863.3
805.5	759.5	649.0	1147.0
811.4	839.1	673.2	1599.1
835.3	923.5	684.9	1605.7
1458.3	1042.5	708.8	3778.1
1492.6	1226.1	866.8	3780.0
1538.6	1451.9	1140.6	3874.6
1539.4	1519.9	1600.6	3876.0
3123.9	1575.2	1607.5	3969.9
3150.6	2114.6	3765.6	3971.4
3183.8	2877.4	3777.4	
3210.5	3555.4	3862.6	
3273.4	3595.8	3874.4	
3316.0	3620.0	3963.1	
3513.6	3634.9	3970.5	
3533.4	3674.2	4290.0	

Table S10. Electronic states, electronic configurations, and vertical excitation energies (eV) at CASSCF, CASPT2, and C-CASPT2 of sixteen excited states of $Mg(H_2O)_6^+$ using the following basis sets, Mg, N: TZ, H: DATZ and Mg, N: TZ, H: DAQZ.

		Mg, N: TZ, H: DATZ[a]			Mg, N: TZ, H: DAQZ[b]		
Config.	State (T_h)	CASSCF	CASPT2	C-CASPT2	CASSCF	CASPT2	C-CASPT2
1^2S ($1s^1$)	1^2A_g	0.00	0.00	0.00	0.00	0.00	0.00
1^2P ($1p^1$)	1^2T_u	0.82	1.03	1.03	0.82	1.03	1.04
		0.82	1.03	1.03	0.82	1.03	1.04
		0.82	1.03	1.03	0.82	1.03	1.04
1^2D ($1d^1$)	1^2E_g	1.65	1.92	1.93	1.65	1.92	1.93
		1.65	1.92	1.93	1.65	1.93	1.93
	1^2T_g	1.80	2.21	2.21	1.80	2.21	2.22
		1.80	2.21	2.21	1.80	2.21	2.22
		1.80	2.21	2.21	1.80	2.21	2.22
2^2S ($2s^1$)	2^2A_g	2.55	2.95	2.96	2.55	2.96	2.97
2^2P ($2p^1$)	2^2T_u	2.61	2.98	2.99	2.60	2.98	2.99
		2.61	2.98	2.99	2.60	2.98	2.99
		2.61	2.98	2.99	2.60	2.98	2.99
1^2F ($1f^1$)	1^2A_u	2.78	3.24	3.25	2.76	3.23	3.24
	3^2T_u	2.87	3.35	3.36	2.85	3.34	3.35
		2.87	3.35	3.36	2.85	3.34	3.35
		2.87	3.35	3.36	2.85	3.34	3.35
	4^2T_u	2.96	3.42	3.43	2.95	3.42	3.43
		2.96	3.42	3.43	2.95	3.42	3.43
		2.96	3.42	3.43	2.95	3.42	3.43
2^2D ($2d^1$)	2^2E_g	3.34	3.81	3.83	3.33	3.81	3.82
		3.34	3.81	3.83	3.33	3.81	3.82
	2^2T_g	3.40	3.96	3.97	3.40	3.96	3.97
		3.40	3.96	3.97	3.40	3.96	3.97
		3.40	3.96	3.97	3.40	3.96	3.97
3^2S ($3s^1$)	3^2A_g	3.76	4.25	4.27	3.73	4.24	4.25
1^2G ($1g^1$)	3^2T_g	3.82	4.33	4.34	3.76	4.30	4.32
		3.82	4.33	4.34	3.76	4.30	4.32
		3.82	4.33	4.34	3.76	4.30	4.32
	3^2E_g	3.85	4.35	4.37	3.80	4.32	4.34
		3.85			3.80		
	4^2T_g	3.98	4.54	4.55	3.90	4.48	4.50
		3.98	4.54	4.55	3.90	4.48	4.50
		3.98	4.54	4.55	3.90	4.48	4.50
	4^2A_g	3.99			3.90		

[a]TZ and DATZ stands for cc-pVTZ and d-aug-cc-pVTZ

[b]TZ and DAQZ stands for cc-pVTZ and d-aug-cc-pVQZ

Table S11. Electronic states, electronic configurations, and vertical excitation energies (eV) at CASSCF, CASPT2, and C-CASPT2 of sixteen excited states of $Mg(H_2O)_6^+$ using the following basis sets, Mg, N: TZ, H: TATZ and Mg, N: TZ, H: TAQZ.

		Mg, N: TZ, H: TATZ[a]			Mg, N: TZ, H: TAQZ[b]		
Config.	State (T_h)	CASSCF	CASPT2	C-CASPT2	CASSCF	CASPT2	C-CASPT2
1^2S ($1s^1$)	1^2A_g	0.00	0.00	0.00	0.00	0.00	0.00
1^2P ($1p^1$)	1^2T_u	0.82	1.03	1.03	0.82	1.02	1.00
		0.82	1.03	1.03	0.82	1.02	1.02
		0.82	1.03	1.03	0.82	1.03	1.02
1^2D	1^2E_g	1.65	1.92	1.93	1.65	1.92	1.93
($1d^1$)		1.65	1.92	1.93	1.65	1.93	1.93
	1^2T_g	1.79	2.21	2.21			
		1.79	2.21	2.21			
		1.79	2.21	2.21			
2^2S ($2s^1$)	2^2A_g	2.54	2.94	2.96	2.54	2.95	2.96
2^2P ($2p^1$)	2^2T_u	2.60	2.97	2.98	2.59	2.89	2.87
		2.60	2.97	2.98	2.59	2.91	2.88
		2.60	2.97	2.98	2.59	2.92	2.90
1^2F ($1f^1$)	1^2A_u	2.72	3.21	3.22	2.72	3.21	3.21
	3^2T_u	2.80	3.31	3.32	2.80	3.30	3.28
		2.80	3.31	3.32	2.80	3.30	3.30
		2.80	3.31	3.32	2.80	3.31	3.30
	4^2T_u	2.94	3.40	3.41	2.94	3.40	3.39
		2.94	3.40	3.41	2.94	3.40	3.40
		2.94	3.40	3.41	2.94	3.40	3.40
2^2D	2^2E_g	3.33	3.79	3.80	3.33	3.80	3.81
($2d^1$)		3.33	3.79	3.81	3.33	3.80	3.81
	2^2T_g	3.39	3.94	3.95			
		3.39	3.94	3.95			
		3.39	3.94	3.95			
3^2S ($3s^1$)	3^2A_g	3.61	4.17	4.18	3.61	4.17	4.18
1^2G ($1g^1$)	3^2T_g	3.63	4.20	4.22			
		3.63	4.20	4.22			
		3.63	4.20	4.22			
	3^2E_g	3.65	4.21	4.23	3.65	4.22	4.24
		3.65			3.65		
	4^2T_g	3.69	4.30	4.32			
		3.69	4.30	4.32			
		3.69	4.30	4.32			
	4^2A_g	3.73			3.73		

[a]TZ and TATZ stands for cc-pVTZ and t-aug-cc-pVTZ

[b]TZ and TAQZ stands for cc-pVTZ and t-aug-cc-pVQZ

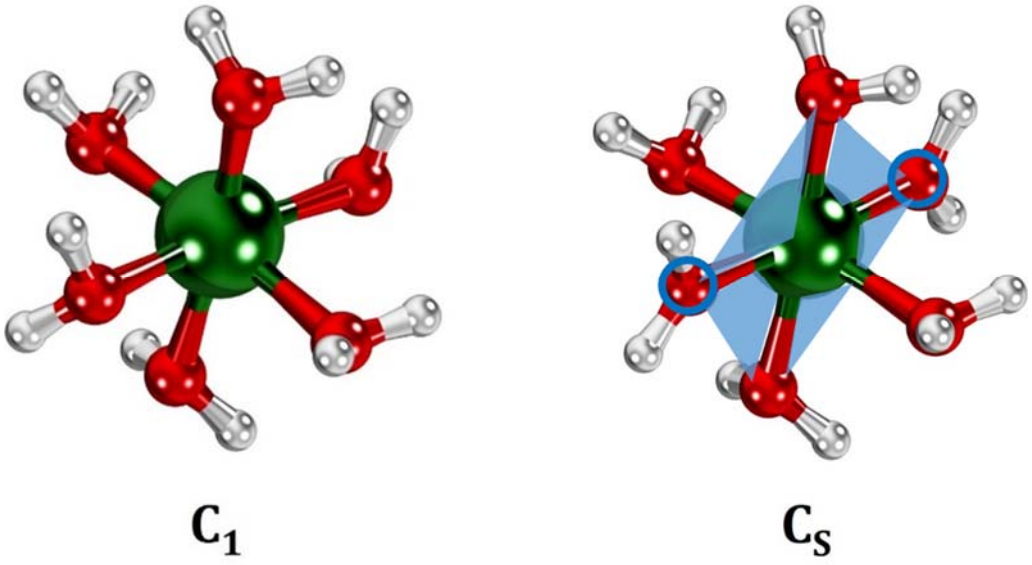

Figure S1. Optimized $Mg(H_2O)_6$ under (C_1) and (C_s) point groups. Two water ligands (encircled in blue) were rotated to create the depicted plane of symmetry.

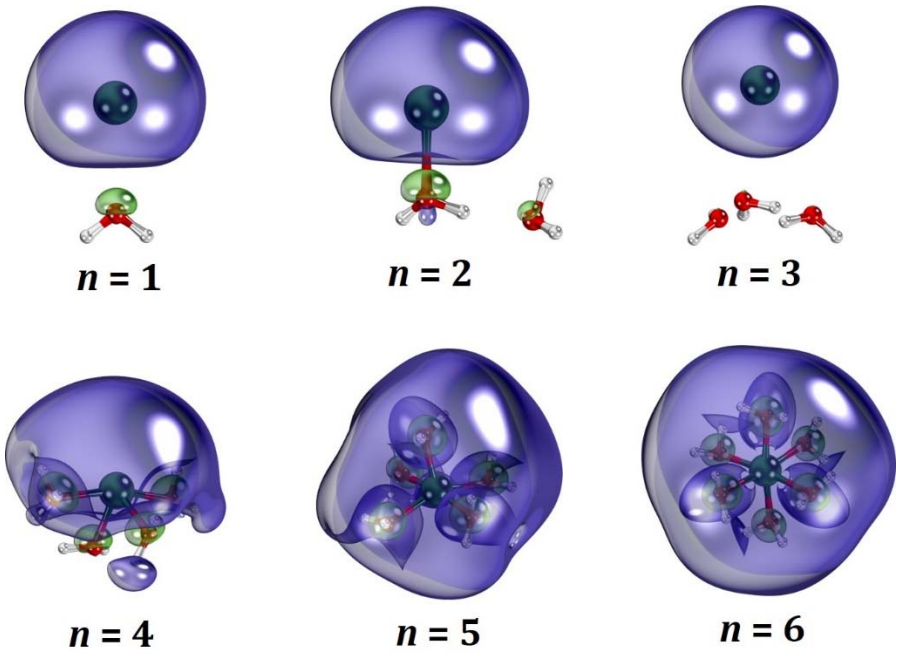

Figure S2. Contours of the highest occupied molecular orbital (HOMO) of $Mg(H_2O)_{n=1-6}$ of their singlet ground states. Note that one and two water ligands in $Mg(H_2O)_{2,3}$ populate the second solvation shell.

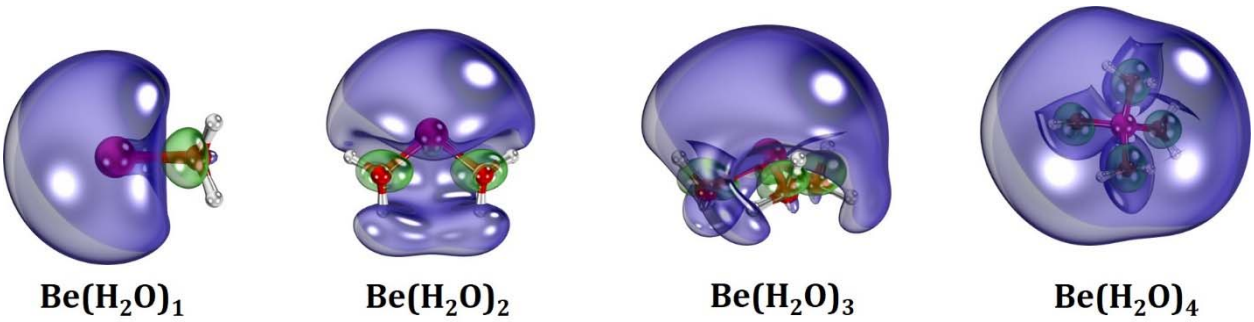

Figure S3. Contours of the highest occupied molecular orbital (HOMO) of $Be(H_2O)_n$ of their singlet ground states.

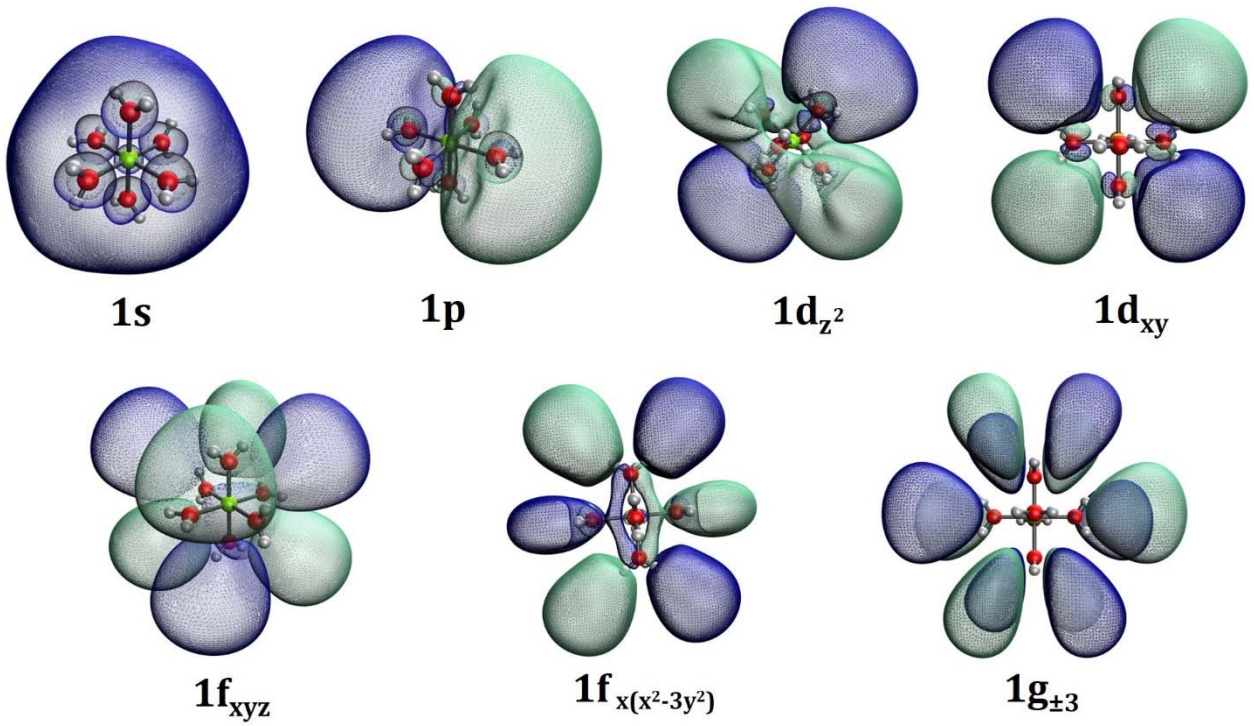

Figure S4. Dyson orbitals from EOM-EA-CCSD for $Mg(H_2O)_6^+$.

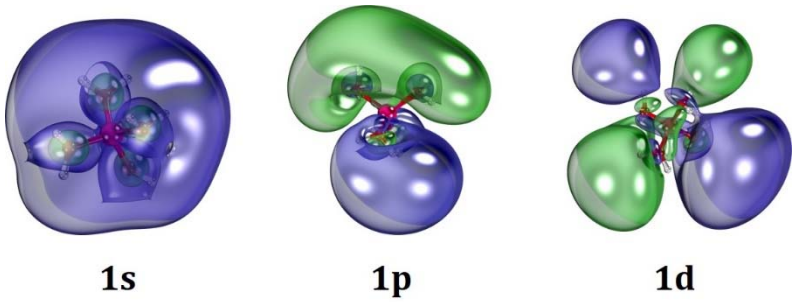

Figure S5. Selected outer orbitals of $Be(H_2O)_4^+$.

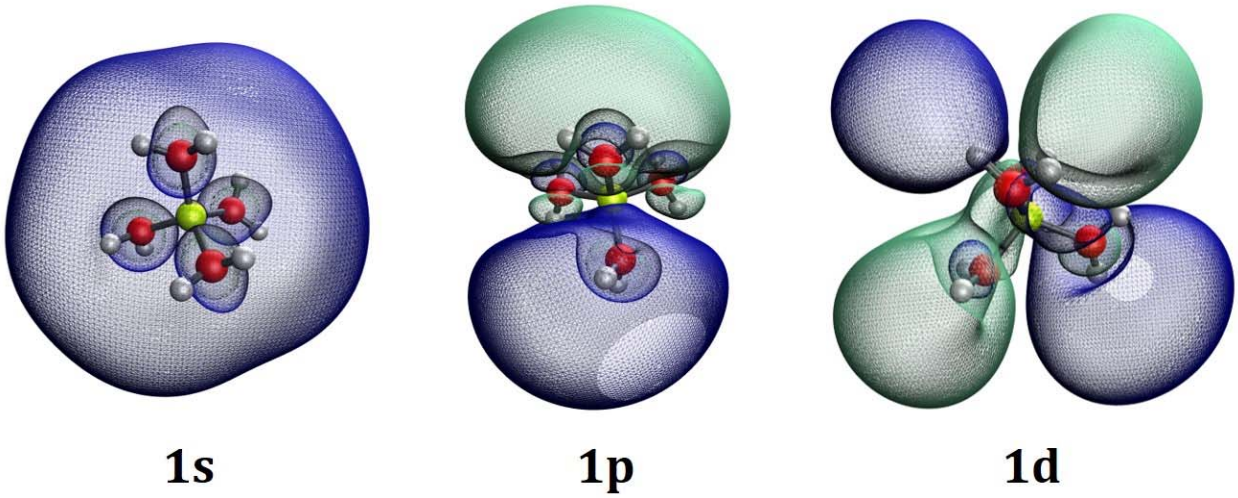

Figure S6. Dyson orbitals from EOM-EA-CCSD for $Be(H_2O)_4^+$.

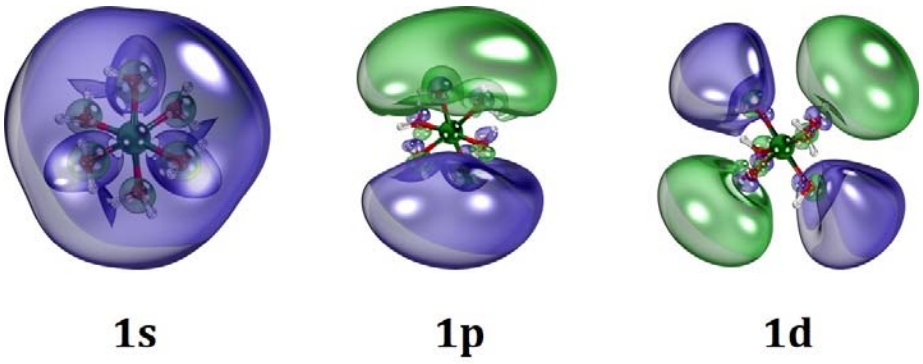

Figure S7. Selected outer orbitals of $Mg(H_2O)_6$ under C_s symmetry.

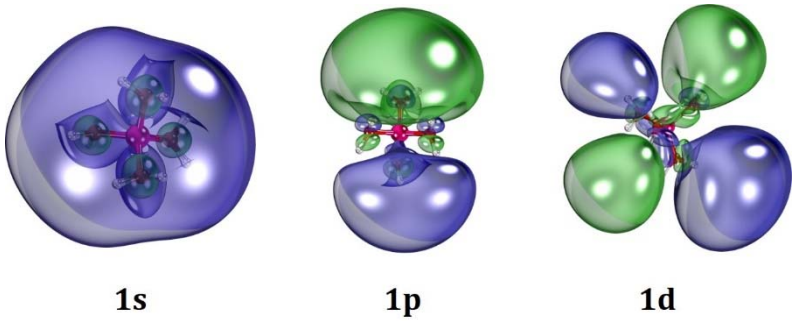

Figure S8. Selected outer orbitals of $Be(H_2O)_4$.