SUPPLEMENTARY MATERIALS

The Arrangement of First- and Second-Sphere Water Molecules in Divalent Magnesium Complexes: Results from Molecular Orbital and Density Functional Theory and from Structural Crystallography

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Running Title: Hydration shells of magnesium

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TABLE 1S. Total Molecular Energies (a.u.) of Various Divalent Magnesium Hydrates.

Structure	BP/DN** Optimized Geometry		B3LYP/6-311++G** Optimized Geometry	MP2(FULL)/6-311++G** Optimized Geometry
	BP/DN**	MP2(FC)/6-31+G*[a]		
		(MP2(FULL)/6-311++G**)[a]	(B3LYP/6-311++G**)[a]	(B3LYP/6-311++G**)	(MP2(FULL)/6-311++G**)
		[MP2(FULL)/6-311++G(2*d*,2*p*)][a]	[B3LYP/6-311++G(2*d*,2*p*)][a]	[B3LYP/6-311++G(2*d*,2*p*)][a]	[MP2(FULL)/6-311++G(2*d*,2*p*)][a]
				{B3LYP/6-311++G(3*df*,3*pd*)}[a]	{MP2(FULL)/6-311++G(3df,3pd)}[a]
					<CCSDT(FULL)/6-311++G(3*df*,3*pd*)>[a]
Mg^{2+}	-199.254451	-198.812134			
		(-198.948697)	(-199.241006)	(-199.241006)	(-198.948697)
		[-198.949797]	[-199.241006]	[-199.241006]	[-198.949797]
			{-199.241006}	{-198.958126}	
					<-198.959940>
$Mg[H_2O]^{2+}$	-275.858673	-275.151795			
		(-275.367868)	(-275.831132)	(-275.831306)	(-275.368268)
		[-275.391867]	[-275.834088]	[-275.834305]	[-275.392195]
				{-275.838525}	{-275.433461}
					<-275.449008>
$Mg[H_2O]_4^{2+}\cdot[H_2O]$	-582.057566[c]				
	-582.057355[b]	(-580.874038)[c]	(-581.995894)[c]	(-581.998018)[c]	(-580.876863)[c]
		(-580.870802)[b]	(-581.992952)[b]	[-582.008146][c]	[-580.987637][c]
		[-580.984690][c]	[-582.006028][c]	{-582.022923}[c]	{-581.154180}[c]
		[-580.980816][b]	[-582.003480][b]		
$Mg[H_2O]_5^{2+}$	-582.063220	–			
		(-580.884429)	(-582.000856)	(-582.003294)	(-580.887346)
		[-580.992830]	[-582.010426]	[-582.012971]	[-580.996032]
			{-582.027059}	{-581.162421}	

TABLE 1S (continued). Total Molecular Energies (hartree) of Various Divalent Magnesium Hydrates.

		BP/DN** Geometry		B3LYP/6-311++G** Geometry	MP2(FULL)/6-311++G** Geometry
Structure	BP/DN**	MP2(FC)/6-31+G*			
		(MP2(FULL)/6-311++G**)	(B3LYP/6-311++G**)	(B3LYP/6-311++G**)	(MP2(FULL)/6-311++G**)
		[MP2(FULL)/6-311++G(2*d*,2*p*)]	[B3LYP/6-311++G(2*d*,2*p*)]	[B3LYP/6-311++G(2*d*,2*p*)]	[MP2(FULL)/6-311++G(2*d*,2*p*)]
				{B3LYP/6-311++G(3*df*,3*pd*)}	{MP2(FULL)/6-311++G(3*df*,3*pd*)}
					<CCSDT(FULL)/6-311++G(3*df*,3*pd*)>
$Mg[H_2O]_6^{2+}$	-658.578813	-656.607656			
		(-657.233644)	(-658.507657)	(-658.508473)	(-657.234975)
		[-657.361773]	[-658.518176]	[-658.519202]	[-657.363768]
					{-658.535059}{-657.560728}
$Mg[H_2O]_4^{2+}\cdot[H_2O]_2$	-658.564237[c]				
	-658.555840[b]	(-657.204880)[c]	(-658.490410)[c]	(-658.501351)[c,f]	(-657.215885)[c,f]
	-	(-657.194671)[b]	(-658.479863)[b]	[-658.512817][c,f]	[-657.349119][c,f]
	-	[-657.336482][c]	[-658.500519][c]	{-658.529830}[c,f]	{-657.546285}[c,f]
	-	[-657.325235][b]	[-658.490954][b]		
$Mg[H_2O]_5^{2+}\cdot[H_2O]$	-658.574634[c]	–			
	-658.572176[b]	(-657.220598)[c]	(-658.501285)[c]	(-658.505060)[c,f]	(-657.225144)[c,f]
		(-657.215947)[b]	(-658.496607)[b]	[-658.516150][c,f]	[-657.356154][c,f]
		[-657.351233][c]	[-658.512256][c]	{-658.532782}[c,f]	{-657.553339}[c,f]
		[-657.346260][b]	[-658.508151][b]	-	-

TABLE 1S (continued). Total Molecular Energies (hartree) of Various Divalent Magnesium Hydrates.

		BP/DN** Geometry		B3LYP/6-311++G** Geometry	MP2(FULL)/6-311++G** Geometry
Structure	BP/DN**	MP2(FC)/6-31+G*			
		(MP2(FULL)/6-311++G**)	(B3LYP/6-311++G**)	(B3LYP/6-311++G**)	(MP2(FULL)/6-311++G**)
		[MP2(FULL)/6-311++G(2*d*,2*p*)]	[B3LYP/6-311++G(2*d*,2*p*)]	[B3LYP/6-311++G(2*d*,2*p*)]	[MP2(FULL)/6-311++G(2*d*,2*p*)]
				{B3LYP/6-311++G(3*df*,3*pd*)}	{MP2(FULL)/6-311++G(3*df*,3*pd*)}
					<CCSDT(FULL)/6-311++G(3*df*,3*pd*)>
$Mg[H_2O]_6^{2+}\bullet[H_2O]$	-735.084616[b]	-732.852459[b]			
	-735.077844[c]	(-733.561240)[b]	(-734.998938)[b]	(-735.000437)[b]	(-733.563534)[b]
		(-733.553598)[c]	(-734.992328)[c]	(-735.002268)[c]	(-733.564986)[c]
		[-733.711235][b]	[-735.011395][b]	[-735.013019][b]	
		[-733.714054][c]	[-735.004115][c]	[-735.014439][c]	
				{-735.031279}[b]	
				{-735.032652}[c]	
$Mg[H_2O]_6^{2+}\bullet[H_2O]_{12}$	-1576.491133	-1571.435792			
(PSS)		(-1573.056535)	(-1576.283852)	–	–
		–	[-1576.319539]	–	–
				–	–
					–
$Mg[H_2O]_6^{2+}\bullet[H_2O]_{12}$	-1576.483101	–			
(PRA)		–	(-1576.284788)	–	
		–	[-1576.317700]	–	–
				–	–
$Mg[H_2O]_6^{2+}\bullet[H_2O]_{12}$	-1576.480951				
(PRB)		–	(-1576.279166)	–	–
		–	[-1576.316229]	–	–
		–		–	–
					–

TABLE 1S (continued). Total Molecular Energies (hartree) of Various Divalent Magnesium Hydrates.

		BP/DN** Geometry		B3LYP/6-311++G** Geometry	MP2(FULL)/6-311++G** Geometry
Structure	BP/DN**	MP2(FC)/6-31+G*			
		(MP2(FULL)/6-311++G**)	(B3LYP/6-311++G**)	(B3LYP/6-311++G**)	(MP2(FULL)/6-311++G**)
		[MP2(FULL)/6-311++G(2*d*,2*p*)]	[B3LYP/6-311++G(2*d*,2*p*)]	[B3LYP/6-311++G(2*d*,2*p*)]	[MP2(FULL)/6-311++G(2*d*,2*p*)]
				{B3LYP/6-311++G(3*df*,3*pd*)}	{MP2(FULL)/6-311++G(3*df*,3*pd*)}
					<CCSDT(FULL)/6-311++G(3*df*,3*pd*)>
$Mg[H_2O]_6^{2+}\bullet[H_2O]_{12}$	-1576.529137	-1571.504236			
(PRC)		(-1573.107541)	(-1576.333547)	(-1576.338646)[d]	
		[-1573.502046]	[-1576.363850]	[-1576.369771]	
				{-1576.411800}	–
$Mg[H_2O]_6^{2+}\bullet[H_2O]_{12}$	-1576.553527	-1571.522660			
(This work)		(-1573.121622)	(-1576.344683)	(-1576.350449)[d,e]	–
		[-1573.515334]	[-1576.374373]	–	–
				–	–
					–
H_2O	-76.471208	-76.209709			
		(-76.293662)	(-76.458370)	(-76.458531)	(-76.293950)
		[-76.317013]	[-76.461836]	[-76.462034]	[-76.317339]
		<-76.329302>		{-76.464510}	{-76.347480}
					<-76.361390>
$(H_2O)_2$ (dimer)	-152.949871	-152.430207			
		(-152.596442)	(-152.925602)	(-152.926350)	(-152.597670)
		[-152.642377]	[-152.931317]	[-152.931914]	[-152.643268]
		<-152.665665>		{-152.936663}	–
					–
$(H_2O)_3$ (cyclic)	-229.436612	-228.658571			
		(-228.905992)	(-229.399947)	(-229.401801)	(-228.909110)
		[-228.975164]	[-229.407762]	[-229.408843]	[-228.977104]
		<-229.011084>		{-229.415726}	–
					–

TABLE 1S (continued). Total Molecular Energies (hartree) of Various Divalent Magnesium Hydrates.

[a] The tight option in GAUSSIAN 94 or Gaussian 98 was used on these single point calculations.

[b] Second shell water molecule(s) bound to one first shell water molecule with a single hydrogen bond.

[c] Second shell water molecules(s) bound to two first shell water molecules with two hydrogen bonds.

[d] B3LYP/6-31G*//B3LYP/6-31G*: PRC -1575.588706 a.u.; Our structure - 1575.605181 a.u.

B3LYP/6-31+G*//B3LYP/6-31+G*: PRC -1575.705661 a.u.; Our structure - 1575.720352 a.u.

B3LYP/6-31+G**//B3LYP/6-31+G**: PRC -1575.893330 a.u.; Our structure - 1575.906534 a.u.; H_2O -76.434048 a.u.; Mg^{2+}-199.227433 a.u.; $Mg[H_2O]_6^{2+}$ = -658.350092 a.u.

[e] No symmetry was employed during the optimization of this structure and each cycle took several months to complete on a one processor R10000 SGI workstation. The total molecular energy listed here, -1576.350449 a.u., is for a partially optimized form.

[d] Optimizing the structures of $Mg[H_2O]_5^{2+}\bullet[H_2O]$ and $Mg[H_2O]_4^{2+}\bullet[H_2O]_2$ at the B3LYP/6-311++G** or MP2(FULL)/6-311++G** computational levels, starting from their optimized BP/DN** geometries in which the second-shell water molecules were hydrogen-bonded to only one inner-shell water molecule, regenerated the structures we found in which the second-shell water molecules were bonded to two inner-shell water molecules.

TABLE 2S. Thermal Corrections to 298 K, Σ (a.u.), Entropies, S(cal/mol-K), and Heat Capacities, C_V (cal/mol-K), Calculated at the B3LYP/6-311++G**//B3LYP/6-311++G** Computational Level.

Structure	Thermal Corrections Σ(a.u.)	Entropy S (cal/mol-K)	Heat Capacity C_V (cal/mol-K)
$Mg[H_2O]^{2+}$	0.027919[a]	56.368[a]	9.051[a]
$Mg[H_2O]_2^{2+}$	0.056018[b]	72.957[b]	18.348[b]
$Mg[H_2O]_3^{2+}$	0.084264[c]	91.060[c]	27.923[c]
$Mg[H_2O]_4^{2+}$	0.112343[d]	104.791[d]	38.025[d]
$Mg[H_2O]_4^{2+}\bullet[H_2O]$	0.140699[l,e]	112.807[l,e]	45.462[l,e]
$Mg[H_2O]_5^{2+}$	0.140493[f]	114.096[f]	48.040[f]
$Mg[H_2O]_4^{2+}\bullet[H_2O]_2$	0.169083[l]	121.227[l]	53.013[l]
$Mg[H_2O]_5^{2+}\bullet[H_2O]$	0.168863[l]	125.082[l]	55.914[l]
$Mg[H_2O]_6^{2+}$	0.168213[g]	118.266[g]	58.725[g]
$Mg[H_2O]_6^{2+}\bullet[H_2O]$	0.196046[k]	141.196[k]	67.885[k]
	0.196549[l]	137.640[l]	67.058[l]
$Mg[H_2O]_6^{2+}\bullet[H_2O]_{12}$ (PRC)	0.507061[h]	254.725[h]	161.771[h]
$Mg[H_2O]_6^{2+}\bullet[H_2O]_{12}$ (This Paper)	0.508188[i]	245.819[i]	156.632[i]
H_2O	0.024118[j]	45.088[j]	6.014[j]
$(H_2O)_2$	0.051977	68.939	15.973
$(H_2O)_3$	0.080192	81.236	24.269

[a] At the B3LYP/6-31+G**//B3LYP/6-31+G** computational level, Σ = 0.027857 a.u., S = 56.445 cal/mol-K, and C_V = 9.125 cal/mol-K; at the MP2(FULL)/6-311++G**//MP2(FULL)/6-311++G** level, Σ = 0.022656 a.u., S = 61.861 cal/mol-K, and C_V = 11.149 cal/mol-K.

TABLE 2S (continued). Thermal Corrections to 298 K, Σ (a.u.), Entropies, S(cal/mol-K), and Heat Capacities, C_V (cal/mol-K), Calculated at the B3LYP/6-311++G**//B3LYP/6-311++G** Computational Level.

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[b] At the MP2(FULL)/6-311++G**//MP2(FULL)/6-311++G** computational level, Σ = 0.056521 a.u., S = 72.836 cal/mol-K, and C_V = 18.561 cal/mol-K.

[c] At the MP2(FULL)/6-311++G** computational level,Σ=0.084923 a.u., S=92.023 cal/mol-K, and C_V =28.272 cal/mol-K.

[d] At the MP2(FULL)/6-311++G**//MP2(FULL)/6-311++G** computational level, Σ = 0.113379 a.u., S = 105.087 cal/mol-K, and C_V = 38.233 cal/mol-K.

[e] At the MP2(FULL)/6-311++G**//MP2(FULL)/6-311++G** computational level, Σ = 0.142167 a.u., S = 113.974 cal/mol-K, and C_V = 45.818 cal/mol-K.

[f] At the HF/6-311++G**//HF/6-31++G** computational level, Σ = 0.149332 a.u., S = 111.308 cal/mol-K, and C_V = 46.894 cal/mol-K; at the B3LYP/6-31+G**//B3LYP/6-31+G** level, Σ = 0.140341 a.u., S = 114.473 cal/mol-K, and C_V = 48.266 cal/mol-K; at the MP2(FULL)/6-311++G**//MP2(FULL)/6-311++G** level, Σ = 0.141751 a.u., S = 114.647 cal/mol-K and C_V = 48.355 cal/mol-K.

0.169771 a.u., S = 120.220 cal/mol-K, and C_V = 59.038 cal/mol-K.

[g] At the B3LYP/6-31+G**//B3LYP/6-31+G** computational level, Σ = 0.168079 a.u., S = 118.644 cal/mol-K, and C_V = 58.938 cal/mol-K; at the MP2(FULL)/6-311++G** level, Σ =

[h] At the B3LYP/6-31+G**//B3LYP/6-31+G** computational level, Σ = 0.507291 a.u. and S = 254.675 cal/mol-K; at the B3LYP/6-31+G*//B3LYP/6-31+G* level, Σ = 0.505248 a.u. and S = 251.455 cal/mol-K.

[i] These values were calculated at the B3LYP/6-31+G**//B3LYP/6-31+G** computational level. For comparison, we note that at the B3LYP/6-31+G*//B3LYP/6-31+G* computational level, Σ = 0.506343 a.u. and S = 243.387 cal/mol-K; at the B3LYP/6-31G*//B3LYP/6-31G* level, Σ = 0.507016 a.u. and S = 235.886 cal/mol-K.

TABLE 2S (continued). Thermal Corrections to 298 K, Σ (a.u.), Entropies, S(cal/mol-K), and Heat Capacities, C_V (cal/mol-K), Calculated at the B3LYP/6-311++G**//B3LYP/6-311++G** Computational Level.

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[j] At the B3LYP/6-31+G**//B3LYP/6-31+G** computational level, Σ = 0.024119 a.u., S = 45.100 cal/mol-K, and C_V = 6.014 cal/mol-K; at the MP2(FULL)/6-311++G**//MP2(FULL)/6-311++G** level, Σ=0.024539 a.u., S=45.080 cal/mol-K, and C_V = 6.009 cal/mol-K.

[k] Second-shell water molecule hydrogen-bonded to only one first-shell water molecule.

[l] Second-shell water molecule hydrogen-bonded to two first-shell water molecules.

TABLE 3S. Calculated Geometrical Parameters for the Water Dimer and (Cyclic) Water Trimer.

Parameter	Computational Level		
	BP/DN**	B3LYP/6-311++G** (B3LYP/6-31+G**)	MP2(FULL)/6-311++G**
A. Dimer			
O---H (Å)	1.917	1.933 (1.918)	1.946
O---O (Å)	2.887	2.900 (2.887)	2.910
<O-H---O(°)	169.4	174.9 (173.6)	176.8
B. (Cyclic) Trimer			
O---H (Å)	1.856	1.912 (1.904)	1.933
O---O (Å)	2.768	2.783 (2.778)	2.797
<O-H---O(°)	151.4	147.2 (147.2)	147.0

TABLE 4S. Calculated Binding Enthalpies, ΔH°_{298} (kcal/mol), of the Water Dimer and Trimer (Cyclic).

		BP/DN** Optimized Geometry[a]		B3LYP/6-311++G** Optimized Geometry[a]	MP2(FULL)/6-311++G** Optimized Geometry[b]
Structure	BP/DN**	MP2(FC)/6-31+G* (MP2(FULL)/6-311++G**) [MP2(FULL)/6-311++G(2d,2p)]	(B3LYP/6-311++G**) [B3LYP/6-311++G(2d,2p)]	(B3LYP/6-311++G**) [B3LYP/6-311++G(2d,2p)] {B3LYP/6-311++G(3df,3pd)}	(MP2(FULL)/6-311++G** [MP2(FULL)/6-311++G(2d,2p)] <CCSDT(FULL)/6-311++G(3df,3pd)>
	ΔH°_{298}	ΔH°_{298}	ΔH°_{298}	ΔH°_{298}	ΔH°_{298}
$(H_2O)_2$	+2.9	+3.9 (+4.0) [+3.5]	(+3.8) [+3.0]	(+4.1) [+3.2] {+3.0}	(+4.3) [+3.6] <+3.6>
$(H_2O)_3$ (cyclic)	+10.8	+14.8 (+12.0) [+11.5]	(+11.9) [+10.3]	(+12.8) [+10.6] {+10.3}	(+13.4) [+12.1] —

[a] Thermal corrections used to obtain ΔH°_{298} were obtained from B3LYP/6-311++G** frequency analyses with no scaling.

[b] Thermal corrections used to obtain ΔH°_{298} were obtained from MP2(FULL)/6-311++G** frequency analyses with no scaling.

TABLE 5S. Unscaled Calculated Frequencies, ν (cm^{-1}), and IR Intensities, I (KM/mol), of $Mg[H_2O]_6^{2+}$.

Mode	Sym	HF/6-311++G**		B3LYP/6-311++G**		B3LYP/6-31+G**		MP2(FULL)/6-311++G**	
		ν	I	ν	I	ν	I	ν	I
δ-OMgO	F_u	100.5	2.75	95.6	3.48	95.4	4.36	98.2	6.41
δ-OMgO	F_g	136.3		121.4		118.8		99.7	
δ-OMgO	F_u	166.2	0.52	155.0	1.21	154.0	2.02	157.4	3.38
τ-HOH	E_u	230.9		211.6		216.9		192.5	
ν-MgO	E_g	253.4		249.1		249.3		269.2	
τ-HOH	F_g	299.9		284.9		288.2		243.9	
ν-MgO	A_g	319.7		313.9		314.7		321.9	
ω-HOH	F_u	388.4	1.94	378.0	16.17	372.9	32.08	391.3	222.50
ω-HOH	F_g	455.1		410.0		397.5		384.9	
τ-HOH	A_u	433.1		426.5		434.5		409.7	
ν-MgO	F_u	488.7	309.43	438.7	297.25	423.6	318.76	422.0	181.42
ρ-HOH	F_g	589.8		542.9		537.0		549.2	
ρ-HOH	F_u	607.9	653.66	566.4	528.92	567.0	511.61	579.5	437.90
δ-HOH	F_u	1793.3	315.18	1664.0	276.84	1655.5	298.8	1671.8	261.4
δ-HOH	E_g	1794.0		1664.7		1656.0		1673.4	
δ-HOH	A_g	1799.0		1670.1		1662.4		1677.7	

Table 5S (continued). Unscaled Calculated Frequencies, ν (cm^{-1}), and IR Intensities, I (KM/mol), of $Mg[H_2O]_6^{2+}$.

ν_s-OH	E_g	4068.9		3774.7		3771.7		3824.4	
ν_s-OH	F_u	4070.7	280.30	3775.7	210.98	3772.6	203.82	3825.2	221.1
ν_s-OH	A_g	4079.3		3781.7		3778.2		3830.8	
ν_{as}-OH	F_g	4146.6		3849.8		3861.0		3917.7	
ν_{as}-OH	F_u	4147.2	484.66	3850.2	384.74	3861.6	395.51	3918.1	405.07

TABLE 6S. Selected Mg-O and Mg-H (Å) Distances for Our Form of $Mg[H_2O]_6^{2+} \bullet [H_2O]_{12}$ Obtained From the B3LYP/6-31+G** Optimization.

	Mg-O (inner shell)	Mg-H (inner shell)	Mg-H (inner shell)	Mg•••O (outer shell)	Mg•••H (outer shell)	Mg•••H (outer shell)
O1	2.098	2.768	2.778			
O2	2.099	2.780	2.771			
O3	2.098	2.770	2.775			
O4	2.098	2.778	2.768			
O5	2.099	2.771	2.780			
O6	2.098	2.775	2.770			
O7				4.145	4.151	5.043
O8				4.119	4.035	4.998
O9				4.144	4.146	5.044
O10				4.113	4.026	4.992
O11				4.140	4.146	5.039
O12				4.119	4.035	4.998
O13				4.145	4.151	5.043
O14				4.119	4.035	4.998
O15				4.144	4.146	5.044
O16				4.113	4.027	4.993
O17				4.140	4.147	5.040
O18				4.119	4.035	4.998
Average	2.098	2.774	2.774	4.130	4.090	5.019

TABLE 7S. Unscaled Calculated Frequencies, ν (cm^{-1}), and IR Intensities, I (KM/mol), of our Form of $Mg[H_2O]_6^{2+} \bullet [H_2O]_{12}$ Obtained at the B3LYP/6-31+G** Computational Level.

ν	I	ν	I	ν	I
37.3	2.1	156.7	9.7	369.0	18.4
39.9	2.3	158.5	10.9	370.4	
45.7		167.0		370.7	17.9
49.4		177.8		371.6	
51.4		179.3		376.3	5.3
53.4	24.0	181.0	13.6	382.6	
69.6	1.5	184.2	26.1	391.6	12.0
70.4	1.9	185.7	34.8	415.2	123.9
83.6	1.7	189.0		415.4	
90.4		195.1		416.1	135.5
90.8		225.5	21.3	419.4	
98.5		227.4	16.1	425.6	
101.7		227.8	50.3	428.9	6.4
102.9		228.7		430.5	5.2
108.4		229.6		446.2	11.5
109.9		249.2	11.8	457.6	
118.8		260.7		466.0	41.7
127.7		262.9		467.7	41.6
136.7		267.3		468.7	
138.9		271.3	7.0	471.8	
139.7		272.3	6.3	475.7	125.4

TABLE 7S (continued). Unscaled Calculated Frequencies, ν (cm^{-1}), and IR Intensities, I (KM/mol), of our Form of $Mg[H_2O]_6^{2+} \bullet [H_2O]_{12}$ obtained at the B3LYP/6-31+G** Computational Level.

ν	I	ν	I	ν	I
141.6		293.3		530.3	2.6
144.2	12.6	295.2		537.0	
145.6	13.0	339.9		541.6	
545.4		837.2	174.9	3447.4	
552.9	28.8	864.4		3461.3	1433.5
557.9	63.9	886.3	533.1	3464.0	1425.9
572.3		887.6	552.6	3482.0	
573.3	23.0	911.6		3482.8	
573.5	555.6	912.4		3496.8	3.4
579.6	466.6	921.8		3519.7	1446.6
583.3	448.1	1635.3		3521.7	
587.7		1636.6	334.0	3522.3	
635.1	122.9	1637.4	346.9	3532.9	146.4
638.0	98.7	1642.7		3534.4	134.8
639.2	149.7	1643.1		3536.9	
640.6		1646.4	13.0	3597.3	1553.8
644.1		1666.1	23.7	3598.4	1487.6
653.2		1667.7		3598.9	
707.4		1667.9		3599.6	
748.9	600.6	1673.7	165.2	3602.9	932.4
759.8	521.7	1676.7	145.7	3613.2	
759.8		1680.0		3667.7	54.6

TABLE 7S (continued). Unscaled Calculated Frequencies, ν (cm^{-1}), and IR Intensities, I (KM/mol), of our Form of $Mg[H_2O]_6^{2+} \bullet [H_2O]_{12}$ at the B3LYP/6-31+G** Computational Level.

ν	I	ν	I	ν	I
761.5	509.3	1681.3	30.6	3667.8	1.1
763.5		1682.5	14.4	3672.5	1.0
796.7		1684.4		3674.1	9.7
810.2	666.4	1685.9		3674.4	2568.3
827.5		1698.0		3676.1	2518.8
828.7		1700.7	232.7	3848.1	
835.8	180.6				

TABLE 8S. Calculated Mg-O Infrared Breathing Frequencies (cm^{-1}).

Level	$Mg[H_2O]^{2+}$	$Mg[H_2O]_2^{2+}$	$Mg[H_2O]_3^{2+}$	$Mg[H_2O]_4^{2+}$	$Mg[H_2O]_5^{2+}$	$Mg[H_2O]_6^{2+}$	$Mg[H_2O]_6^{2+}\bullet[H2O]_{12}$	
	ν	ν	ν	ν	ν	ν	ν(PRC)	ν(This Work)
HF/6-311++G**	560.2	411.4	387.2	364.2	341.1	319.7	-	-
B3LYP/6-311++G**	550.0	406.0	380.5	357.8	335.4	313.9	344.4	-
(B3LYP/6-31+G**)	(555.5)	(403.3)	(381.7)	(358.7)	(336.7)	(314.7)	(343.8)	(339.9)
MP2(FULL)/6-311++G**	542.7	401.2	378.0	357.8	339.2	321.9	-	-

Deposited Figures

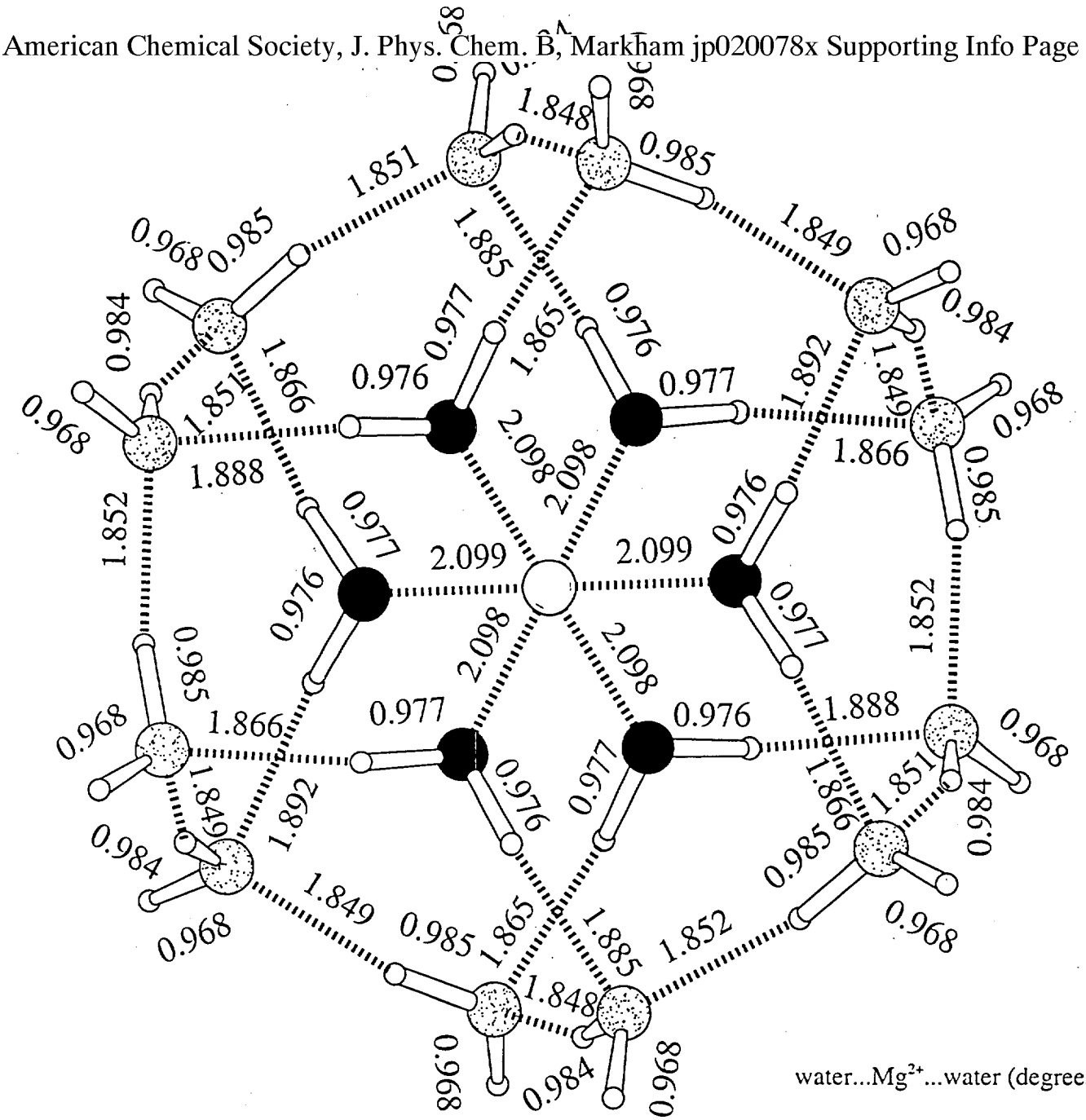
Figure 1S. Model of $Mg[H_2O]_6^{2+} \bullet [H_2O]_{12}$.

(a) Bond and hydrogen bond distances.

(b) Some distances and angles.

(c) Mg•••H distances for first coordination shell.

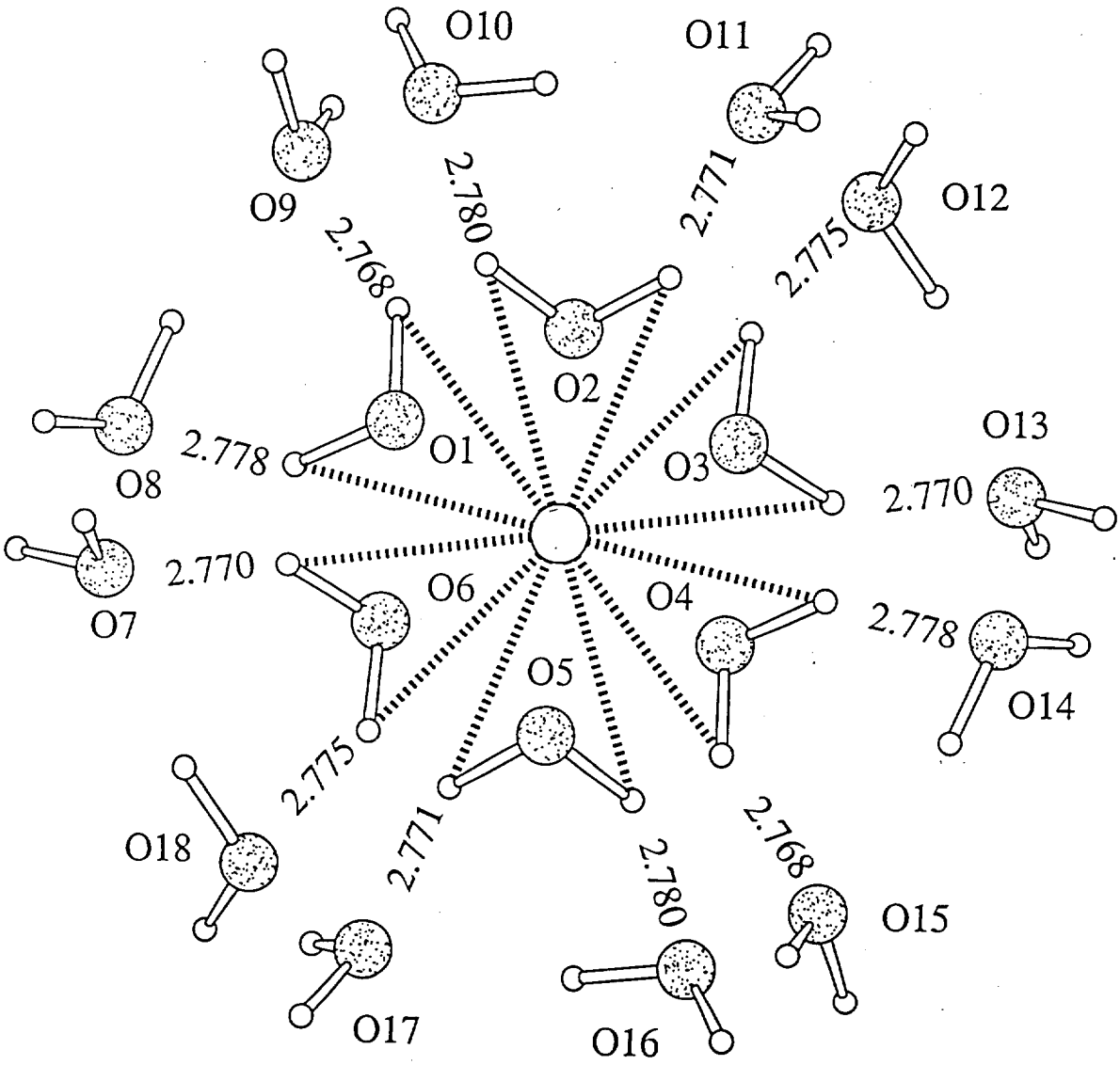
(d) Mg•••O distances for second coordination shell.



Deposited Figure 1S(a)

water...Mg^{2+}...water (degrees)

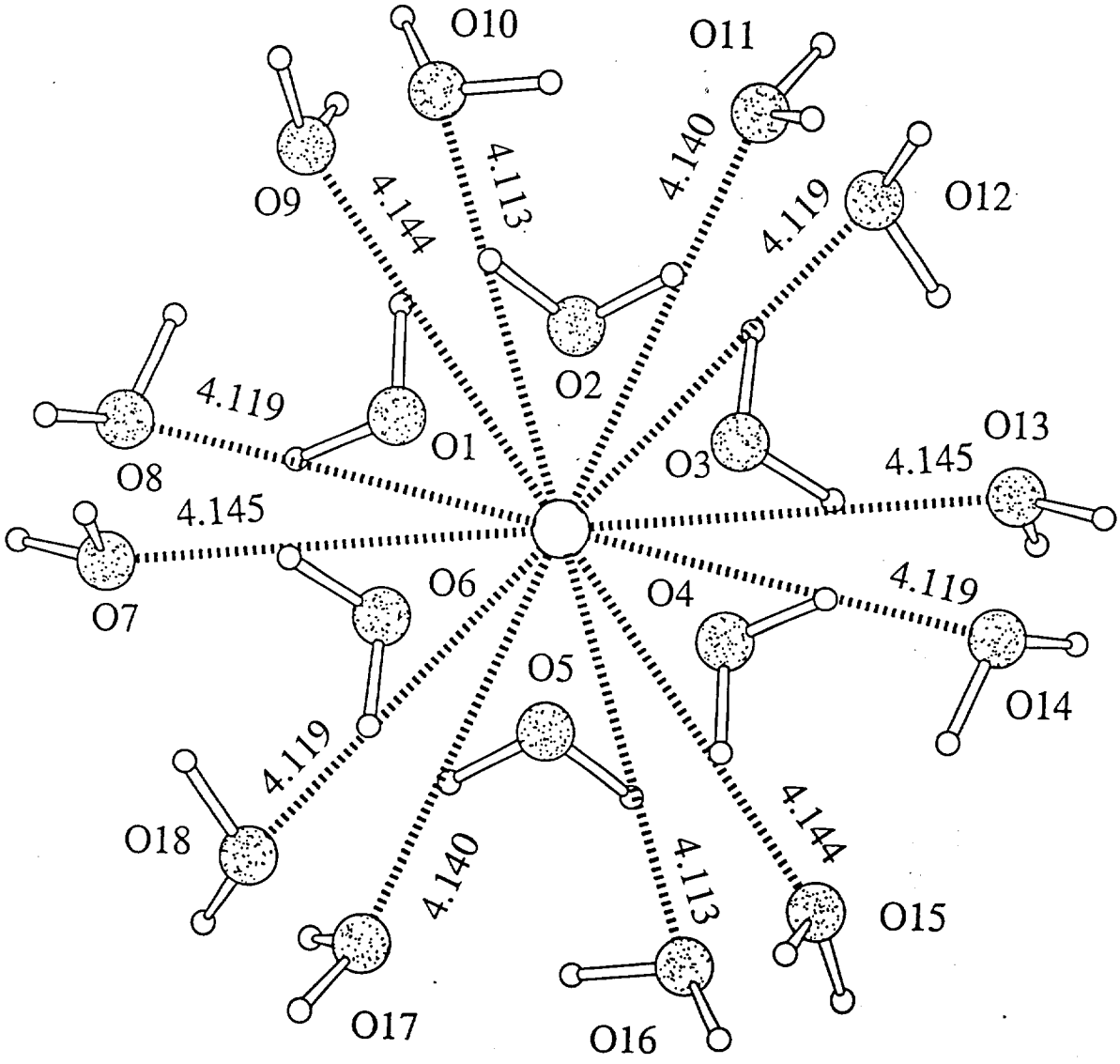
O1—Mg^{2+}—O2	88.5
O1—Mg^{2+}—O3	91.4
O1—Mg^{2+}—O4	180.0
O1—Mg^{2+}—O5	91.5
O1—Mg^{2+}—O6	88.6
O2—Mg^{2+}—O3	88.3
O2—Mg^{2+}—O4	91.5
O2—Mg^{2+}—O5	180.0
O2—Mg^{2+}—O6	91.7
O3—Mg^{2+}—O4	88.6
O3—Mg^{2+}—O5	91.7
O3—Mg^{2+}—O6	180.0
O4—Mg^{2+}—O5	88.5
O4—Mg^{2+}—O6	91.4
O5—Mg^{2+}—O6	88.3



water H—O—H angle (degrees)

O1	109.7	O7	107.2	O13	107.2
O2	109.8	O8	107.0	O14	107.0
O3	109.7	O9	107.2	O15	107.2
O4	109.7	O10	107.0	O16	107.0
O5	109.8	O11	107.2	O17	107.2
O6	109.7	O12	107.0	O18	107.0

Deposited Figure 1S(b)



Deposited Figure 1S(c)