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About the Hydration of Mg++: A Quantum DFT Study#

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Abstract
The hydration of magnesium dication is studied using the DFT method BPW91/6–31G(d,p), which gives remarkable results for the reproduction of the infra–red spectrum of liquid water. The enthalpies and the Gibbs free energies of Mg++ hydration are computed using the standard and the cluster procedures, up to eight added molecules of water. The entropic contribution to the hydration phenomenon is discussed using frequency analyses.

Keywords. Hydration; magnesium cation; hydration shell; thermodynamics.

1 INTRODUCTION

A large number of studies have been devoted to the hydration of the magnesium dication (Mg++). As pointed out by Bock *et al*. [1], this hard divalent cation is generally found in a hexahydrated octahedral architecture and is implicated in a structural role, when associated with proteins. Among the divalent ions of biological interest, the absolute hardness η, as defined by Pearson, of magnesium (32.55 eV) is inferior to the hardest Be++ (67.84 eV) but superior to Ca++ (19.52 eV), Zn++ (10.88 eV), Cu++ (8.27 eV) and Fe++ (7.24 eV) [2,3].

The most recent theoretical studies for understanding the cation–water solvent interactions at the discrete molecular level, of the first and second shells of hydration, involve essentially the *ab initio* Hartree Fock, Density Functional Theory (DFT) and reaction field methods [1,4,5,6,7]. The water exchange reactions between the first and the second shells around cations is also of great interest (as seen in the review by Helm and Merbach [8] and Hartmann *et al*. [5] in the case of Zn++).

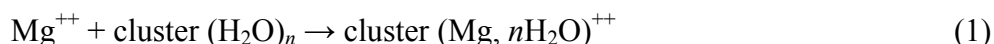As remarked by Markham *et al*., the cluster approach to compute the enthalpy ΔH and Gibbs free

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energy ΔG changes seems to be the best when combined with *ab initio* DFT methods.

When considering the reaction:

$$Mg^{++} + cluster\ (H_2O)_n \rightarrow cluster\ (Mg, nH_2O)^{++} \tag{1}$$

the computation takes into account both the ligation energies (water–ion interactions) and the water–water interactions.

Recently, Bour [9] has demonstrated that computations using the DFT method BPW91/6–31G(d,p), for a cluster of 214 water molecules, reproduce very well the Infra Red spectrum of liquid water; then the use of the PW91 exchange–correlation functional is preferable, for the dispersion forces are not well treated by the standard DFT procedures.

In this work, we have studied as a first step the hydration of Mg^{++} up to 8 water molecules, using the cluster approach and the DFT BPW91 at the same basis set level (6–31G(d,p)) with Bour [9].

2 MATERIALS AND METHODS

All computations have been conducted with the GAUSSIAN 98 [10], Gauss View [11] and Hyperchem [12] programs on local PC stations, using *ab initio* methods SCF Hartree–Fock and DFT BPW91 (Becke's 1988 exchange functional and Perdew–Wang's 1991 gradient–corrected correlation functional).

The different clusters were optimized using firstly RHF/6–31G* computations, then with the DFT Restricted BPW91 method at the 6–31G(d,p) basis set level. Optimization was done and frequency calculation was performed at the optimized geometry. This procedure allows to obtain the thermochemical properties of the water clusters and Mg^{++} hydrated clusters. By this way, the thermal correction to electronic energy (E$_{el}$) of a molecule (in hartree/particle) is [13,14,15]:

$$TCE = E_{trans} + E_{rot} + E_{vibr}(T) \tag{2}$$

where trans., rot. and vibr. indicate respectively the translational, rotational and vibrational motions,

with $\qquad E_{trans} = (3/2)\ k\ T;\ E_{rot} = (3/2)\ k\ T$ (nonlinear molecule)

and $\qquad E_{vibr}(T) = (1/2)\ k\ \sum_i \Theta_{Vi} + \sum_i \{k\Theta_{Vi}/[\exp(\Theta_{Vi}/T) - 1]\}$

with $i = 1, 2, ... m$

where *m* is the number of normal modes of harmonic vibrations ($m = 3n - 6$; n number of atoms), and Θ_{Vi} are the vibrational temperatures, related to the harmonic vibrational wave number ϖ_i (cm^{-1}) by the formula: $\Theta_{Vi} = (h\ c\ /\ k)\ \varpi_i$.

In this harmonic oscillator treatment, the zero–point vibrational energy is:

$$ZPE = (1/2)\ k\ \sum_i \Theta_{Vi} \tag{3}$$

Then, the resulting thermodynamic relations are (in hartree/particle) the thermal correction to enthalpy:

$$TCH = TCE + k\,T \tag{4}$$

and the thermal correction to the Gibbs free energy:

$$TCG = TCH - T\,S \tag{5}$$

where S, the computed entropy from the canonical partition functions, involves the three contributions: $S = S_{trans} + S_{rot} + S_{vibr}(T)$.

It is to be noted also that, in our studied supermolecules, there are no internal rotation modes [16].In the ideal gas approximation, we obtain the total internal energy:

$$\mathbf{E} = E_{el} + TCE \tag{6}$$

the enthalpy:

$$\mathbf{H} = E_{el} + TCH$$
$$(\text{from } \mathbf{H} = \mathbf{E} + P\,V) \tag{7}$$

and the Gibbs free energy:

$$\mathbf{G} = E_{el} + TCG$$
$$(\text{from } \mathbf{G} = \mathbf{H} - T\,S) \tag{8}$$

The standard procedures for computing the energies of hydration are based on the reaction:

$$Mg^{++} + n\,H_2O \rightarrow (Mg, n\,H_2O)^{++} + \Delta H_1 \text{ (or } \Delta G_1) \tag{9}$$

In the cluster approach, a cluster of water containing n H_2O is symbolized by $(H_2O)_n$, and a cluster of hydrated Mg^{++} containing n H_2O is symbolized by $(Mg, nH_2O)^{++}$. Taking into account that Mg^{++} is hexahydrated, the structure of this cluster is $[(Mg, mH_2O)\,pH_2O]^{++}$ with m the number of the water molecules in the first hydration shell ($m = 1 \ldots 6$), p the number of water molecules in the second hydration shell, and $m + p = n$. In our modeling, $p = 1, 2$. Then, the Mg^{++} hydration reactions in the cluster procedure are:

$$Mg^{++} + (H_2O)n \rightarrow (Mg, n\,H_2O)^{++} + \Delta H_2 \text{ (or } \Delta G_2) \tag{10}$$
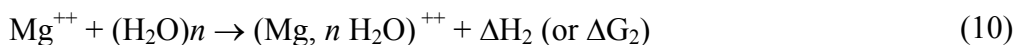
Reaction of successive binding water enthalpies or Gibbs free energy :

$$[Mg, (n-1)\,H_2O]^{++} + H_2O \rightarrow (Mg, n\,H_2O)^{++} + \Delta H_3 \text{ (or } \Delta G_3) \tag{11}$$
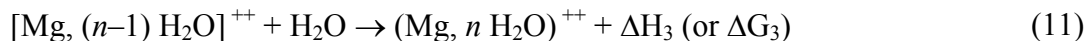
The resulting enthalpies (or Gibbs free energies) for Eqs. (9), (10), and (11) are:

$\Delta H_1 = H\,(Mg, n\,H_2O)^{++} - H\,(Mg^{++}) - n\,H\,(H_2O)$ for the standard procedure
$\Delta H_2 = H\,(Mg, n\,H_2O)^{++} - H\,(Mg^{++}) - H\,(H_2O)_n$ for the cluster
$\Delta H_3 = H\,(Mg, n\,H_2O)^{++} - H\,(H_2O) - H\,([Mg, (n-1)\,H_2O]^{++})$ approach

with the same procedure for obtaining ΔG_1, ΔG_2, and ΔG_3.

3 RESULTS AND DISCUSSION

Our calculated optimized structures of water clusters correspond to local minima (with no symmetry constraint) controlled by frequency analyses. The obtained *n*–mers are:

(*a*) a dimer with a structure close to those found by Xantheas and Dunning using an HF/MP2/aug–cc–pVDZ computation [17] with a distance between the two oxygens R(O–O) = 2.89 Å and a bend hydrogen bond δ $_{O–H–O}$ = 163.7.

(*b*) a cyclic trimer close to a perfect equilateral triangle with R(O–O) = 2.74 Å (corresponding to 2 hydrogen bonded water molecules) and 3 bended–hydrogen bonds with a δ angle which lies between 153.4° and 154.6°.

(*c*) a cyclic tetramer close to a square defined by R(O–O) = 2.68 Å and 4 bended hydrogen bonds with δ = 170.2°. This structure is remarkable from the electrostatic point of view because of the zero value of its dipole moment (see Table 1).

These trimer and tetramer structures are close to those described in Refs. [17] and [18]. Our $(H_2O)_5$ and $(H_2O)_6$ clusters differ from the cyclic pentamer and the S_6 cyclic structure defined by Xantheas and Dunning [17] and the $(H_2O)_8$ cluster differs from the octamers with S_4 and D_2d structures described by Tsai and Jordan [19] in their Monte Carlo simulation using the empirical TIP 3p potential and the standard Metropolis method.

For the $(H_2O)_5$ cluster we obtain a R(O–O) varying from 2.64 to 2.76 Å. For the $(H_2O)_6$ cluster the R(O–O) distances vary from 2.69 to 2.88 Å. For the $(H_2O)_7$ cluster we obtain a variation from 2.60 to 2.85 Å. And finally for the $(H_2O)_8$ cluster we observe that the distance R(O–O) varies from 2.59 to 2.84 Å.

The thermochemistry for these water clusters is reported in Table 1. We can note that the binding enthalpy for the water dimer $\Delta H_1 = \Delta H_2 = -5.66$ kcal mol^{-1} is comparable to the MP4 SDQ–(FC) / 6–31G* value (–5.0 kcal mol^{-1}) given in Ref. [4], but larger than the experimental value (–3.6 +/– 0.5 kcal mol^{-1}). This discrepancy is due to the level of used basis set, which not includes diffuse functions and no BSSE estimation [20]. The obtained magnesium–water clusters, which correspond to global minima (without any imaginary frequency) are represented in Figure 1.

The structures of dihydrated, tetrahydrated and hexahydrated magnesium are equivalent to those computed by Markham *et al*. [4]. Concerning the first coordination shell, our computed distances Mg–O are close but slightly longer than those obtained by Pavlov *et al*. [6] who have used the B3LYP DFT method with double ζ basis sets. We obtain for the different clusters: monohydrated 1.95 Å, dihydrated 1.97 Å, trihydrated 1.99 Å, tetrahydrated 2.03 Å, pentahydrated 2.06 – 2.11 Å, hexahydrated 2.12 Å.
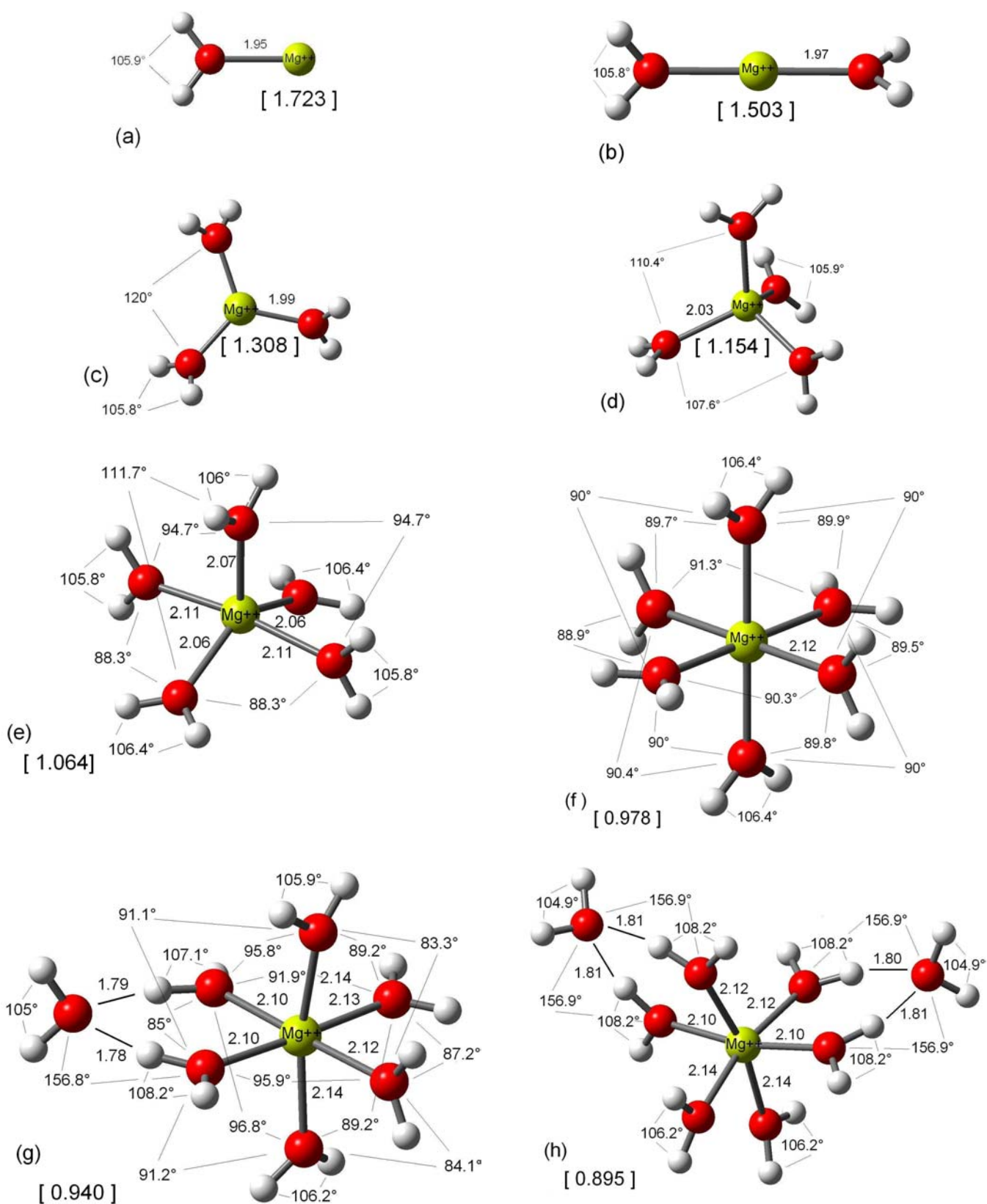
Figure 1. Structures of optimized Mg–Water clusters [Mg,nH2O] $^{++}$. (*a*) $n = 1$ to (*h*) $n = 8$. Bond lengths are in Ångstroms and angles in degrees. The Mulliken net charge of magnesium is presented in brackets.
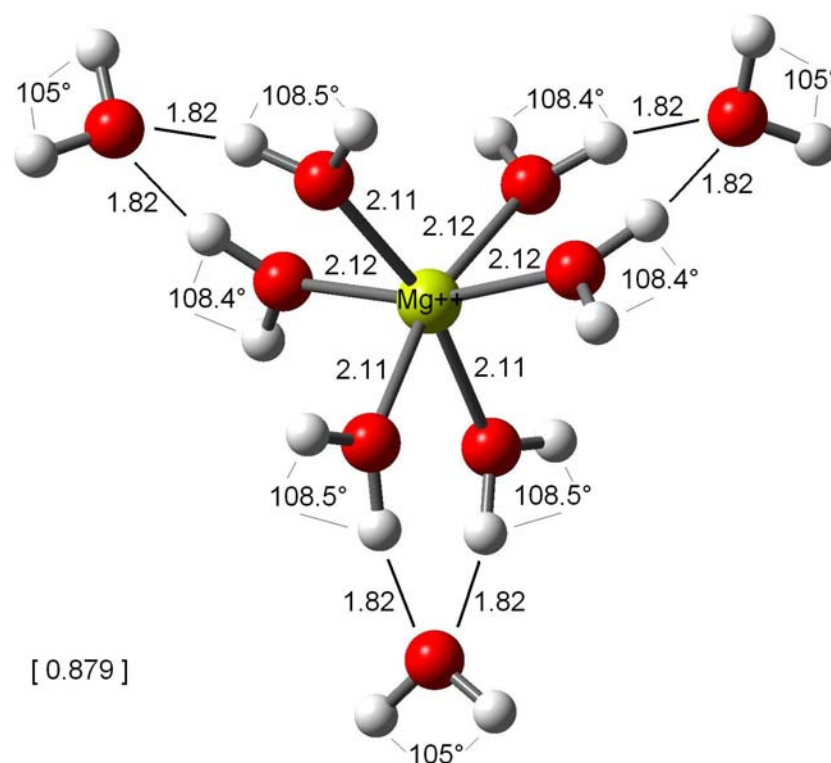
Figure 2. Molecular geometry of the optimised [(Mg,6H$_2$O)3H$_2$0]$^{++}$ cluster. Bond lengths are in Ångstroms and angles in degrees. The Mulliken net charge of magnesium is presented in brackets.

Table 1. Thermochemistry of clusters (H2O)*n* (R BPW91/6–31G(d,p) computations) (T = 298.15 K, P = 1 atm)

Number of water molecules	H Hartree	G Hartree	Eel Hartree	S cal/molK	μ D	ΔH$_1$ kcal/mol	ΔH$_2$ kcal/mol	ΔG$_1$ kcal/mol	ΔG$_2$ kcal/mol
1 H$_2$O	−76.386667	−76.408126	−76.41134052	45.164	2.0260	0	0	0	0
2 H$_2$O	−152.782353	−152.813635	−152.83347807	65.838	1.8101	−5.66	−5.66	1.64	1.64
3 H$_2$O	−229.191157	−229.226878	−229.27148812	75.182	1.4159	−19.55	−13.89	−1.57	−3.21
4 H$_2$O	−305.601174	−305.642768	−305.70859473	87.541	0.0001	−34.20	−14.65	−6.44	−4.87
5 H$_2$O	−381.999163	−382.047353	−382.13407719	101.424	4.0843	−41.31	−7.11	−4.22	−2.22
6 H$_2$O	−458.398072	−458.452320	−458.56176614	114.176	2.0105	−48.99	−7.68	−2.24	−1.98
7 H$_2$O	−534.807221	−534.864912	−534.99833798	121.422	6.2276	−63.10	−14.11	−5.04	−2.80
8 H$_2$O	−611.209940	−611.276469	−611.42822796	140.023	3.3729	−73.17	−10.07	−7.19	−2.15

The second shell of hydration is initiated with the structures [(Mg, 6H$_2$O) H$_2$O]$^{++}$ and [(Mg, 6H$_2$O) 2 H$_2$O]$^{++}$. We can observe on Figures 1(g) and 1(h) that the water molecules belonging to the second shell are hydrogen bounded to two water molecules of the first shell. This structure was obtained also by Markham *et al*. [4] for the [(Mg, 6H$_2$O) 2H$_2$O]$^{++}$ cluster. Figure 2 represents the structure of the cluster with 3H$_2$O in the second shell. We observe also in this case the presence of double hydrogen bonds to three water molecules of the first shell. It is to be noted that the distances between the oxygen atoms of the water molecules belonging to the first shell and the oxygen atoms of water molecules of the second shell are ~2.75 Å, in agreement with those reported by Pavlov *et al*. [6] and very closed to the experimental value (2.76 Å).

Figures 1 and 2 show also the evolution of the Mulliken net charge on magnesium cation. At our

basis set level, we observe a continuous decrease of the charge with the number of water molecules around the magnesium; in the case of the hexahydrated structure (Figure 1f) about half of the dicationic charge was transferred to water molecules. This type of magnesium charge variation was also observed by Pavlov *et al.* [6] in their B3LYP / 6–311+G(2d,2p) computations.

Table 2. Thermochemistry of clusters (Mg^{++}, nH$_2$O) (R BPW91/6–31G(d,p) computations) (T = 298.15 K, P = 1 atm)

No. of H$_2$O	H Hartree	G Hartree	Eel Hartree	S cal/mol K	ΔH_1 kcal/mol	ΔH_2 kcal/mol	ΔH_3 kcal/mol	ΔG_1 kcal/mol	ΔG_2 kcal/mol	ΔG_3 kcal/mol
0 H$_2$O	–199.218209	–199.235058	–199.22056907	35.46	—	—	—	—	—	—
1 H$_2$O	–275.742305	–275.769858	–275.77067554	57.99	–86.24	–86.24	–86.24	–79.49	–79.49	–79.49
2 H$_2$O	–352.249411	–352.286100	–352.30540379	77.22	–161.82	–156.16	–75.58	–147.33	–148.98	–67.84
3 H$_2$O	–428.733156	–428.776549	–428.81692022	91.33	–222.73	–203.18	–60.92	–198.99	–197.42	–51.66
4 H$_2$O	–505.197814	–505.247992	–505.30915153	105.61	–271.67	–237.47	–48.94	–238.72	–232.28	–39.73
5 H$_2$O	–581.635776	–581.691815	–581.77461345	117.94	–303.86	–262.55	–32.19	–261.12	–256.90	–22.40
6 H$_2$O	–658.068274	–658.129200	–658.23450302	128.23	–332.62	–283.63	–28.76	–279.48	–277.25	–18.36
7 H$_2$O	–734.494029	–734.560846	–734.68792860	140.63	–357.15	–294.05	–24.53	–294.24	–289.20	–14.76
8 H$_2$O	–810.920390	–810.991312	–811.14231548	149.27	–382.06	–308.89	–24.91	–308.26	–301.07	–14.02

The thermochemistry of our *n*–hydrated divalent magnesium structures is reported in Table 2. We have reported there the energies of magnesium hydration obtained with the standard procedure (ΔH_1 and ΔG_1) and with the cluster procedure (ΔH_2 and ΔG_2). ΔH_3 and ΔG_3 are the values for the successive binding water enthalpies or Gibbs free energies, in a cluster procedure. The first line in Table 2 (0 H$_2$O) corresponds to the Mg^{++} energetic and entropic properties.

The results presented by Pavlov *et al*. [6] concern only the standard procedure and only internal energy variations during the magnesium hydration. Thus a direct comparison with our results is not possible. For instance, in the case of the hexahydrated magnesium, they found (with our notations): $\Delta E_1 = -303.9$ kcal mol^{-1} and $\Delta E_3 = -24.5$ kcal mol^{-1}. But our results may be compared with those obtained by Markham *et al*. [4] for a number of water molecules *n* = 2, 4, 6, 8, using *ab initio* Hartree Fock MP2 computations. The correspondence between their results and ours is $\Delta H_{298} = \Delta H_2$ and $\Delta G_{298} = \Delta G_2$. For the hexahydrated magnesium, they found $\Delta G_{298} = -266.7$ kcal mol^{-1}, using a MP2 (FULL)/6–311++G** computation and $\Delta G_{298} = -286.5$ kcal mol^{-1} when using the MP4 SDQ(FC)/6–31G* procedure. Our $\Delta G_2 = -277.2$ kcal mol^{-1} value is situated between these two results. Another fact emphasized by Markham *et al*. [4] was to compare the ΔG_2 values as *n* increases with the experimental one: $\Delta G_{exp} = -439.7$ kcal mol^{-1}. They observed that for an MP2 (FULL)/6–311++G** computation, in the case of hexahydrated magnesium, the first shell of hydration accounts for 61% of the ΔG_2 experimental value (in our case, this value is 63%). Then, when two water molecules are added in the second shell, they account for:

$$[\Delta G_2^{(Mg,\,8H2O)++} - \Delta G_2^{(Mg,\,6H2O)++} / \Delta G_{exp} - \Delta G_2^{(Mg,\,6H2O)++}]\,\%.$$

We found in our case 14.7%, a result in agreement with those obtained by Markham *et al*. (14%). Because the Gibbs free energy involves the entropic contribution T S, it is interesting to understand the entropy variation versus the n added water molecules in a water cluster or around the magnesium dication. Tables 3 and 4 show the results obtained for the (H$_2$O)n and (Mg, nH$_2$O)$^{++}$

clusters, with the translational, rotational and vibrational contributions (with all vibrational modes taken into account) to the total entropy S. For all *n*, we observe that: S([Mg,*n*H$_2$O]$^{++}$) < S (Mg^{++}) + S ([H$_2$O]*n*). The variation of these entropic contributions, plotted as a function of n added molecules in the clusters, is shown in Figure 3. It is to be noted that our results for the total entropy values and for *n* = 2, 4, 6, 8, are comparable to those obtained by Markham *et al.* [4] using an *ab initio* calculation at the RHF/6–31G* level; the only discrepancy concerns the hexahydrated magnesium for which these authors have found S = 115.9 kcal mol^{-1}.

Table 3. Entropy of clusters (H2O)*n* (R BPW91/6–31G(d,p) computations) (T = 298.15 K, P = 1 atm)

Number of water molecules	S cal/mol K	S_{trans} cal/mol K	S_{rot} cal/mol K	S_{vib} cal/mol K	Vibrational modes	Stretching and bending vibrations	Intermolecular vibrations
1 H$_2$O	45.164	34.609	10.549	0.007	3	3	0
2 H$_2$O	65.866	36.675	21.149	8.042	12	6	6
3 H$_2$O	75.182	37.883	24.925	12.374	21	9	12
4 H$_2$O	87.541	38.741	24.925	21.955	30	12	18
5 H$_2$O	101.424	39.406	28.167	33.851	39	15	24
6 H$_2$O	114.176	39.949	29.077	45.149	48	18	30
7 H$_2$O	121.422	40.409	29.940	51.073	57	21	36
8 H$_2$O	140.023	40.807	31.051	68.165	66	24	42

Table 4. Entropy of clusters (Mg++, *n*H2O) (R BPW91/6–31G(d,p) computations) (T = 298.15 K, P = 1 atm)

| Number of water molecules	S cal/mol K	S_{trans} cal/mol K	S_{rot} cal/mol K	S_{vib} cal/mol K	Vibrational modes	Stretching and bending vibrations	Intermolecular vibrations
0 H$_2$O	35.462	35.462	0	0	—	—	—
1 H$_2$O	57.991	37.132	19.293	1.566	6	3	3
2 H$_2$O	77.218	38.196	22.475	16.548	15	6	9
3 H$_2$O	91.328	38.978	26.501	25.849	24	9	15
4 H$_2$O	105.608	39.597	27.613	38.397	33	12	21
5 H$_2$O	117.943	40.110	28.411	49.423	42	15	27
6 H$_2$O	128.228	40.547	29.068	58.613	51	18	33
7 H$_2$O	140.628	40.928	30.139	69.560	60	21	39
8 H$_2$O	149.267	41.266	31.072	76.929	69	24	45

Figures 3a and 3b show clearly the weight of the three contributions to the total entropy S_{tot}. For our water clusters, the vibrational entropy becomes a predominant contribution when *n* ≥ 6 molecules. In the case of the hydrated magnesium clusters, we obtain the same result for *n* ≥ 5. And as soon as *n* = 3 we observe that $S_{vib} \approx S_{rot}$ and when *n* = 4 $S_{vib} \approx S_{trans}$. To explain this behaviour, it has to be reminded that S_{trans} depends only on the mass of the cluster, while S_{rot} depends on the 3 rotation temperatures which are related to the structure of the cluster (3 principal moments of inertia and rotational symmetry number). For all *n*, we have $S_{trans} > S_{rot}$. The vibrational contribution S_{vib} depends on the vibrational modes in the clusters and in particular the most important contribution comes from the low frequency vibration modes which correspond to the intermolecular movements (libration of water molecules and translations of Mg^{++} along the O–O axis of two ligated H$_2$O) with vibrational temperatures inferior to 900K.

(a)   Entropy for (H2O)$_n$

(b)   Entropy for (Mg,nH2O)$^{++}$
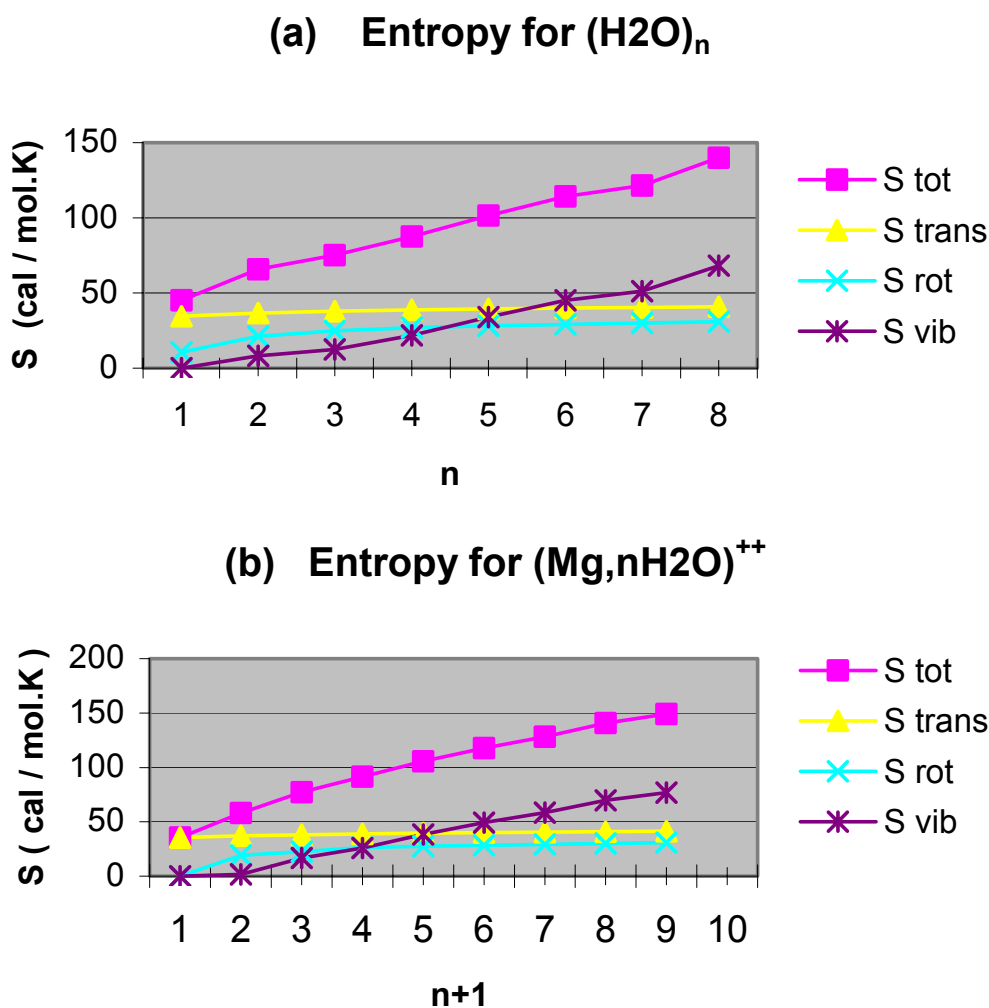
Figure 3. Entropy contributions for: (*a*) water clusters, (*b*) hydrated magnesium clusters.

Figures 4a and 4b show the vibrational spectra obtained respectively for $(H_2O)_6$ and $(Mg, 6H_2O)^{++}$ clusters. We observe that in the case of the water cluster the IR spectrum is composed of large bands corresponding to the stretching (3102.6 to 3782.7 cm^{-1}) and the bending (1637.3 to 1726.6 cm^{-1}) of water, and in the low frequency domain to the intermolecular movements (32.6 to 1053.6 cm^{-1}). This spectrum is, even with only 6 molecules of water, similar to the IR spectrum of liquid water.

The corresponding spectrum for the hexahydrated–magnesium is not composed of large bands but of sharp peaks: H_2O stretching (~3700 and 3800 cm^{-1}), H_2O bending (~1630 cm^{-1}) and librations of water molecules and translations of Mg along an O–O axis (~350, 390 and 550 cm^{-1}). This drastic difference between the IR spectra of water clusters and Mg–hydrated complexes is due to the strong structuration of water molecules around the dication, in the inner shell of hydration.

(*a*)

(*b*)
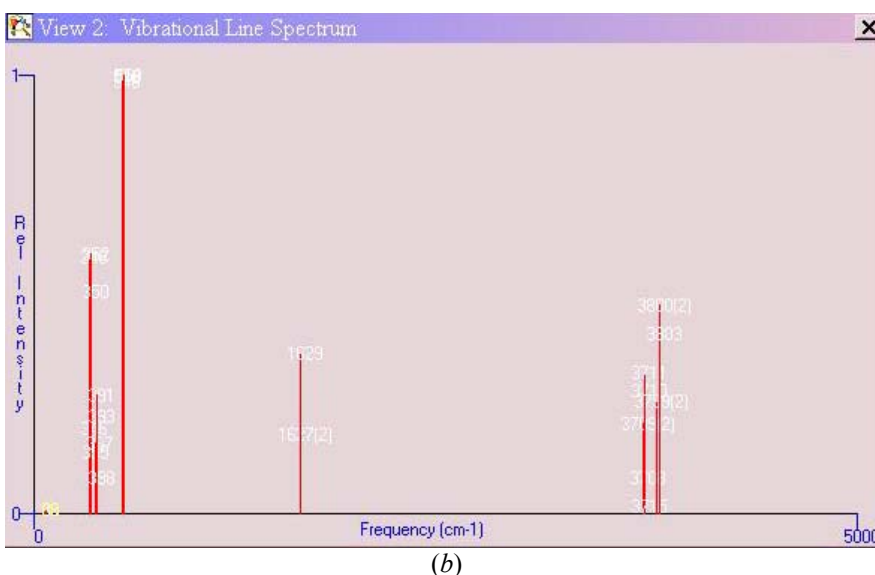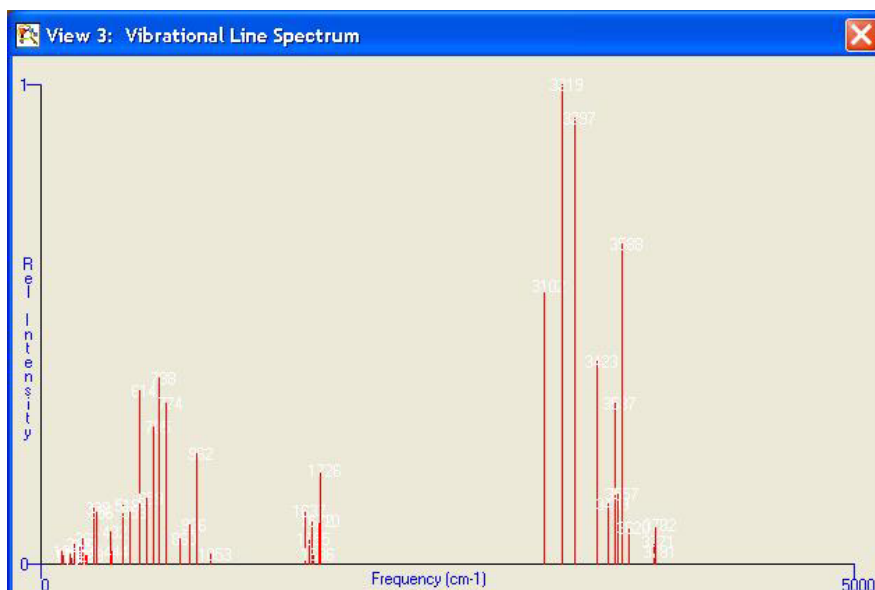
Figure 4. Vibrational line spectra for clusters with 6 water molecules: (*a*) water cluster $(H_2O)_6$, (*b*) hydrated magnesium cluster $[Mg,6H_2O]^{++}$.

Concerning the monohydrated metallic cations, Chang [21] has recently related linear correlations between the water binding electronic energy and the $|E(HOMO–H_2O) – E(LUMO–$ metal $Z+)|$ computed with DFT (BPW) and coupled cluster (CCSD(T)) methods. It seems that these methods are not very well suited to the reproduction of the frontier orbitals of magnesium dication or H_2O. When we observe their results, the HOMO of water is situated at ~ -7.3 eV; this value is far from the ionization potential of water which is 12.6 eV [2]. The same remark is valid in the case of metallic cations LUMOs, because the ionization potential and the hardness of these species ($\eta \sim |E_{LUMO} - E_{HOMO}|/2$) are not well computed using the DFT methods. An *ab initio* Hartree–Fock method is better to reproduce the frontier orbitals properties.

4 CONCLUSIONS

This study presents an investigation for the magnesium hydration up to 8 added molecules of water, using the DFT computations (OPT+FREQ) – RBPW91 / 6–31G(d,p).

Our results show that the cluster procedure for obtaining the enthalpies or the Gibbs free energies of hydration is preferable to the standard one. Our results are close to those obtained by Markham *et al.* [4] in their *ab initio* Hartree–Fock MP2 (FULL)/6–311++G** and MP4SDQ(FC)/6–31G* computations.

Our obtained vibrational spectra for $(Mg,6H_2O)^{++}$ and $(H_2O)_6$ clusters show a drastic difference in the low frequency domain which concerns the intermolecular movements. The entropy contributions may be, as remarked by Pavlov *et al*. [6], an important factor for stabilizing the hexahydrated form of Mg^{++}.

Work is in progress to introduce the effect of diffuse functions in the used basis sets for DFT BPW91 computations, in order to get a better approach of the experimental values of the dipole moment and the polarizabilities of the water molecule, for better taking into account the contribution of the dispersion forces.

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