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A theoretical study of $[\mathrm{Be},(\mathrm{H_2O})_n]^{2+}$, $[\mathrm{BeOH},(\mathrm{H_2O})_{n-1}]^{+}$ and $[\mathrm{Be(OH)_2},(\mathrm{H_2O})_{n-2}]$ aggregates ($n = 1$–6). Incidence of the first hydration shells on the hydrolysis reactions of Be^{2+} and $BeOH^+$ systems

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Abstract

Ab initio results regarding the incidence of the first and part of the second hydration shell on the hydrolysis reaction of solvated Be^{2+} and $BeOH^+$ systems are presented. These results exhibit that the first shells strongly reduce the energy cost of the $Be^{2+} \rightarrow BeOH^+ + H^+$ reaction, however, this reaction remains strongly exothermic. For the $BeOH^+ \rightarrow Be(OH)_2 + H^+$ reaction, the first shells have considerably less incidence on it. This reaction is endothermic and its Helmholtz free energy cost is of the same order of magnitude as that experimentally reported in water. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Owing to their great importance in physical and biochemical systems, considerable efforts were devoted to study the interaction of monoatomic M^{n+} cations with water (from Li^+ to Cr^{3+}, cf. Refs. [1–11]). In particular, several studies focused on investigating the strength and the nature of the interaction of cations with their first hydration shell. However, as far as we know, no systematic study has been devoted to evaluate the properties of such interactions in the case of cation hydrolysed forms, $M(OH)_m^{(n-m)+}$, and therefore, to evaluate the incidence of first hydration shells on cation hydrolysis reactions. In the present Letter, we will present the theoretical results regarding the incidence of the first and part of the second hydration shell on the hydrolysis reactions of solvated Be^{2+} and $BeOH^+$ systems, using ab initio computations. The choice of beryllium arises from two of its properties.

In the gas phase, the cluster $[\mathrm{Be},(\mathrm{H_2O})_2]^{2+}$ is not stable and dissociates towards $BeOH^+ + H_3O^+$ [12], while in aqueous phase, Be^{2+} is known to be stable for pH values <6. In particular, Beyer et al. [12] showed that, in the gas phase, the hydrolysis reaction of $[\mathrm{Be},(\mathrm{H_2O})_2]^{2+}$ does not present an energetic barrier along its reaction pathway. Obviously, the first hydration shells in bulk phase have to play a pivotal role to explain such a difference of reactivity for Be systems.

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Another reason is that several polymer species of $BeOH^+$ are known to exist in liquid water, depending on the pH range of values considered. In particular, a cyclic $BeOH^+$ trimer has been experimentally observed [13] and this property is very close to that observed for the UO_2^{2+} ion [14]. Hence, the study of the reactivity of Be^{2+} in water can be considered as a starting point to theoretically investigate the properties of heavier hard cations, for which ab initio calculations are still computationally expensive [15,16].

One may wonder why we have chosen to investigate solvated $Be(OH)_2$ systems instead of BeO ones. Both previous species are possible products of the hydrolysis reaction of solvated $BeOH^+$ systems. However, our computations showed that $[Be(OH)_2, (H_2O)_n]$ aggregates are more stable than $[BeO, (H_2O)_{n+1}]$ ones for $n = 2$ [17], and, therefore, only solvated $Be(OH)_2$ systems were considered. Lastly, in the following, the $Be^{2+} \rightarrow BeOH^+ + H^+$ hydrolysis reaction is called HR1 and the $BeOH^+ \rightarrow Be(OH)_2 + H^+$ one, HR2.

2. Methodology

All computations were carried out using the GAUSSIAN-94 system of programs [18]. As shown by previous studies regarding cation/water interactions [1–11], a good agreement between experiment and theory is observed when using the MP2 level of theory and medium size basis sets, such as the 6-31+G(d,p) one. However, larger and more flexible basis sets, for instance the 6-311+G(2df,2p), are needed for a good description of hydrogen bonds (HBs) [19] and of anions, such as OH^- [20]. Hence, all structures considered in this Letter were first optimised at the MP2/6-31+G(d,p) level. A second series of optimisations at the MP2/6-311+G(2df,2p) level were then performed on the most stable structures previously obtained when they contain less than four OH^- or H_2O ligands. For greater clusters, energies were just refined at the previous level of theory.

Thermal corrections (at 298 K) were estimated using the harmonic approximation, from the frequencies computed at the MP2/6-31+G(d,p) level for small clusters as defined above, and at the HF/6-31G(d) level for greater ones (harmonic frequencies were, respectively, scaled by the classical factors 0.95 and 0.90 [21,22]). In Table 1, the enthalpic term H_n includes the vibrational, rotational, translational and PV contributions. The entropic $-TS_n$ terms reported in this table do not include the contribution of the asymmetric term, as defined in a previous paper [23], because our computations showed that it has quite no incidence on the energy cost of both HR1 and HR2.

Lastly, the binding energy (BE) corresponds to the difference in energy between a cluster and its subunits (i.e., H_2O, OH^-, Be^{2+} and H^+). The BE values discussed in the following correspond to results obtained at the MP2/6-311+G(2df,2p) level (it has to be noticed that the difference in BE between MP2/6-31+G(d,p) and MP2/6-311+G(2df,2p) results is at most 1%). Basis set superposition errors (BSSEs) [24] were estimated at the MP2/6-311+G(2df,2p) level (typical BSSE values for the systems here considered represent less than 3% of their BEs). Successive hydration energies $\Delta E_{n-1,n}$ corresponding to the reaction

$$[M, (H_2O)]_{n-1} + H_2O \xrightarrow{\Delta E_{n-1,n}} [M, (H_2O)_n] \quad (1)$$

have been also computed for $M = Be^{2+}$, $BeOH^+$ and $Be(OH)_2$. All structures discussed in this Letter correspond to minima.

3. Results

3.1. $[Be, (H_2O)_n]^{2+}$ aggregates ($n = 1$–6)

These aggregates have already been studied [10,11]. Hence, computations were just performed on the most stable $[Be, (H_2O)_n]^{2+}$ structures, as reported by earlier authors, at the levels of theory described in Section 2 (cf. Fig. 1, structures **1a**–**6a**, it has to be noticed that the first hydration shell of Be^{2+} is complete with four water molecules). Energy results are given in Table 1. For these clusters, BEs increase from about 140 ($n = 1$) towards 460 kcal mol^{-1} ($n = 6$), and R(Be–O) distance for water molecules of the first shell increases from 1.51 to 1.66 Å. All these results agree with earlier ones [10,11].

Table 1
Energy results for $[\mathrm{Be},(\mathrm{H_2O})_n]^{2+}$ systems ($n = 1$–6, structures **1a**–**6a**), $[\mathrm{BeOH},(\mathrm{H_2O})_n]^{+}$ systems ($n = 0$–5, structures **1b**–**6b**), and $[\mathrm{Be(OH)_2},(\mathrm{H_2O})_n]$ systems ($n = 0$–4, structures **2c**–**6c**)[a]

	n	ΔE	H_n	$-TS_n$	BSSE	BE	$\Delta E_{n-1,n}$
1a	1	−90.1528	0.0294	−0.0256	2.05	142.9	142.9
2a	2	−166.6566	0.0576	−0.0308	4.88	261.5	118.5
3a	3	−243.0998	0.0883	−0.0376	7.38	342.1	80.6
4a	4	−319.4962	0.1168	−0.0432	9.58	393.3	51.2
5a	5	−395.8618	0.1526	−0.0413	11.65	425.2	31.9
6a	6	−472.2242	0.1837	−0.0532	13.26	455.1	29.9
1b	0	−90.10539	0.0178	−0.0191	4.89	510.0	–
2b	1	−166.54822	0.0467	−0.0308	7.91	590.3	80.3
3b	2	−242.93755	0.0757	−0.0373	10.75	637.1	46.8
4b	3	−319.29678	0.1043	−0.0425	13.12	665.0	27.9
5b	4	−395.64376	0.1396	−0.0486	15.70	685.3	20.3
6b	5	−471.98692	0.1676	−0.0516	18.45	703.1	17.8
2c	0	−166.25033	0.0335	−0.0298	11.39	800.2	–
3c	1	−242.59444	0.0627	−0.0355	14.30	818.7	18.5
4c	2	−318.94241	0.1030	−0.0411	16.71	839.5	20.8
5c	3	−395.28120	0.1260	−0.0443	18.75	855.1	15.6
6c	4	−471.60435	0.1550	−0.0551	19.92	859.9	4.8

[a] ΔE: energies at the MP2/6-311 + G(2df,2p) level, in Hartree. Binding energies (BEs), basis set superposition error (BSSE, at the MP2/6-311 + G(2df,2p) level) and successive hydration energies $\Delta E_{n-1,n}$ (see text) in kcal mol^{-1}. Enthalpic (H_n) and entropic ($-TS_n$) contributions, in Hartree.

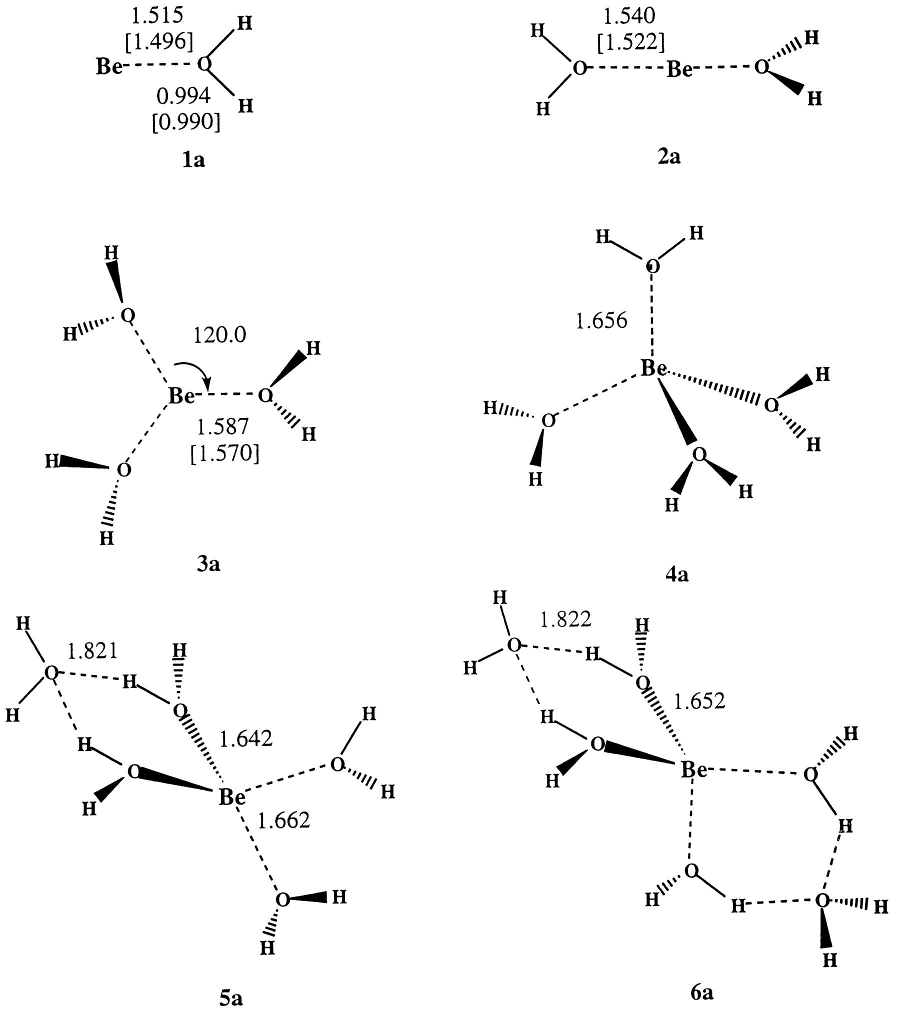
3.2. $[\mathrm{BeOH},(\mathrm{H_2O})_n]^{+}$ *aggregates* ($n = 1$–5)

The most stable structures are given in Fig. 2 (structures **1b**–**6b**), and the energy results in Table 1. The isolated $\mathrm{BeOH^+}$ ion (**1b**) is linear, with an R(Be–O) distance of 1.34 Å. For $n = 1$–3, the most stable structures correspond to those where water molecules are directly bonded to the cationic centre (structures **2b**–**4b**). For $n = 1$–3, our computations also show that structures where water molecules are HB bonded to the first shell water molecules or to the hydroxyl group are from 20 to 60 kcal mol^{-1} less stable than those presented in Fig. 2 [17]. This is not surprising because the $\mathrm{Be^{2+}/H_2O}$ interaction energy is of 140 kcal mol^{-1} (cf. Section 3.1), while only of 30 kcal mol^{-1} for the $\mathrm{OH^-/H_2O}$ one [25]. For $n \geqslant 4$, the new molecules develop HB networks between the hydroxyl group and water molecules of the first shell (cf. structures **5b** and **6b**). Hence, the first hydration shell of $\mathrm{BeOH^+}$ is complete with three water molecules, and, if the $\mathrm{OH^-}$ ligand is also considered, the first shell of $\mathrm{Be^{2+}}$ under its $\mathrm{BeOH^+}$ form corresponds to a coordination number of four.

For water molecules of the first shell, the successive hydration energies $\Delta E_{n-1,n}$ of $\mathrm{BeOH^+}$ are from twice to three times smaller than those of $\mathrm{Be^{2+}}$ systems. For second shell molecules, those energies are of 20 kcal mol^{-1}, values smaller by 10 kcal mol^{-1} than those of $\mathrm{Be^{2+}}$ systems (cf. Table 1). Lastly, the R(Be–OH) distance increases as n increases (from 1.34 for $n = 1$ to 1.51 Å for $n = 5$ at the MP2/6-31 + G(d,p) level).

3.3. $[\mathrm{Be(OH)_2},(\mathrm{H_2O})_n]$ *aggregates* ($n = 0$–4)

The most stable structures for $[\mathrm{Be(OH)_2},(\mathrm{H_2O})_n]$ systems are shown in Fig. 3 (structures **2c**–**6c**), and energy results in Table 1. At the difference of the isolated $\mathrm{BeOH^+}$ ion, the isolated $\mathrm{Be(OH)_2}$ molecule (structure **2c**) is not linear (the ⟨Be–O–H⟩ angle is of 130° and the torsional ⟨H–O––O–H⟩ angle of about 100°). For $n = 1$, and whatever the level of theory considered, the most stable structure corresponds to that where the water molecule is directly bonded to the cationic centre (structure **3c**). For $n \geqslant 2$, the most stable structures correspond to those where the



1a **2a** **3a** **4a** **5a** **6a**

Fig. 1. Most stable $[\mathrm{Be},(\mathrm{H_2O})_n]^{2+}$ aggregates ($n = 1$–6), as obtained at the MP2/6-31 + G(d,p) and MP2/6-311 + G(2df,2p) (in brackets) levels (see text, distances in Å and angles in degree).

new water molecules develop HB networks between the water molecule of the first shell and the two hydroxyl groups. Hence, at the difference of solvated Be^{2+} and $BeOH^{+}$ systems, if we consider both water molecules and OH^{-} ligands, the first shell of Be^{2+} under its $Be(OH)_2$ form corresponds to a coordination number of three. It has also to be noticed that the hydrated $Be(OH)_2$ structures are planar when considering only heavy atoms, which is not the case for Be^{2+} and $BeOH^{+}$ (cf. Figs. 1–3).

The successive hydration energies $\Delta E_{n-1,n}$ for $Be(OH)_2$ systems are considerably smaller as compared to those of Be^{2+} and $BeOH^{+}$ systems, respectively, by a factor six and three (cf. Table 1). This is not surprising because of the total electrostatic charges of each systems (respectively, 2+, 1+ and 0). In particular, for $n = 4$, the $\Delta E_{n-1,n}$ value is of the same order of magnitude as the water dimer BE (respectively, −4.8 and −5.4 kcal mol^{-1}). It has to be noticed that the BE of the structure corresponding to the **6c** one, where all the water molecules not interacting with hydroxyl hydrogens have been removed is of −8.3, 10.4 kcal mol^{-1} smaller than the BE of structure **2c**.

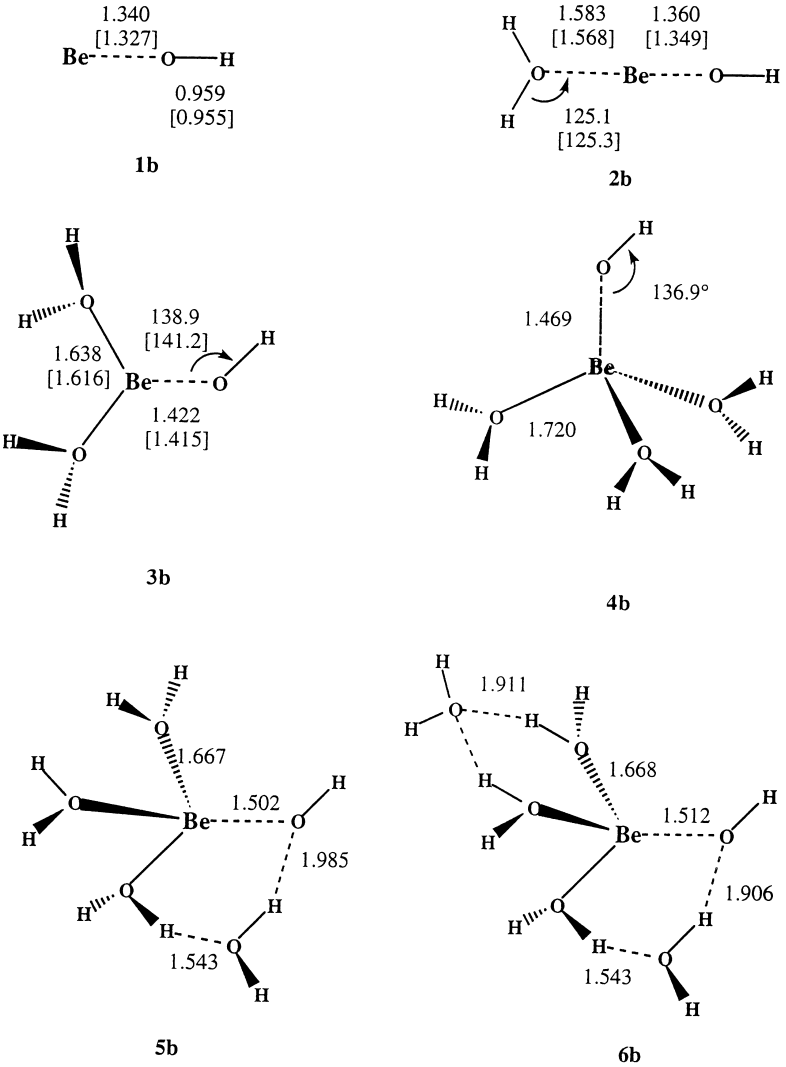


Fig. 2. Most stable $[BeOH,(H_2O)_n]^+$ aggregates ($n = 0$–5), as obtained at the MP2/6-31 + G(d,p) and MP2/6-311 + G(2df,2p) (in brackets) levels (see text, distances in Å and angles in degree).

4. Incidence of the first hydration shells on HR1 and HR2

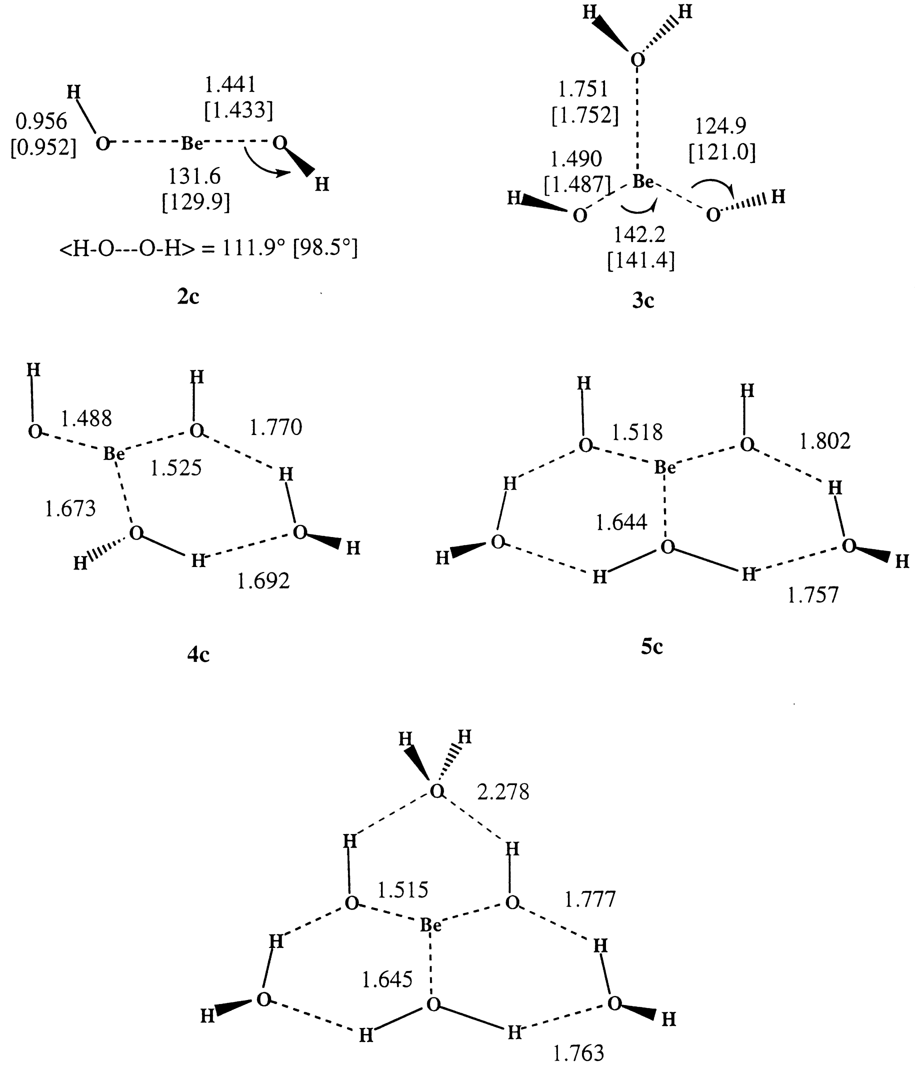
To estimate the incidence of the first (and part of the second) hydration shell on HR1 and HR2, these reactions have been considered as follows

$$[M,(H_2O)_n]^{m+} + (H_2O)_n \overset{\Delta G_n}{\rightarrow} [MOH,(H_2O)_{n-1}]^{(m-1)+} + H_{2n+1}O_n^+ \qquad (2)$$

where M^{m+} corresponds to Be^{2+} or $BeOH^+$. ΔG_n corresponds to the Helmholtz free energy cost of the reaction. In the case of $n \rightarrow \infty$, Eq. (2) can be written as follows

$$M^{m+}(aq) \overset{\Delta G(aq)}{\rightarrow} MOH^{(m-1)+} + H^+(aq). \qquad (3)$$

Hence, the ΔG_n values have to tend toward the Helmholtz free energy cost $\Delta G(aq)$ of the hydrolysis reaction in aqueous phase. To numerically



2c **3c** **4c** **5c** **6c**

Fig. 3. Most stable $[Be(OH)_2, (H_2O)_n]$ aggregates ($n = 0$–4), as obtained at the MP2/6-31 + G(d,p) and MP2/6-311 + G(2df,2p) (in brackets) levels (see text, distances in Å and angles in degree).

estimate the ΔG_n values, the results reported in Table 1 are needed, as well as the energy costs corresponding to the protonation reaction of small $(H_2O)_n$ aggregates ($n = 1$–6). These values were taken from Ref. [26], and correspond to computations performed at the MP4(sdtq)/6-311 + G(2df,p) level (from the results of Ref. [26], the difference in BE for protonated water aggregates between the MP2/6-311 + G(d,p) level and the CCSD(T)/6-311 + G(2df,p) one is less than 1%, incertitude of the same order of magnitude as our one, cf. Section 2). ΔH and $-T\Delta S$ values corresponding, respectively, to the reaction $[M, (H_2O)_n]^{m+} \rightarrow [MOH, (H_2O)_{n-1}]^{(m-1)+} + H^+$ ($M = Be^{2+}$ and $BeOH^+$) and to the protonation reaction of small water aggregates needed to compute the Helmholtz free energy of HR1 and HR2 are listed in Tables 2 and 3. These values were computed

Table 2
Estimate of the Helmholtz free energy cost ΔG_n of the hydrolysis reaction HR1 defined in Eq. (2), in the case $M^{m+} = Be^{2+a}$

n	ΔE(Be)	$\Delta E(H^+)$	ΔH(Be)	$\Delta H(H^+)$	$-T\Delta S$(Be)	$-T\Delta S(H^+)$	ΔG_n
1	29.75	−172.06	−7.28	8.47	4.1	−1.01	−138.03
2	67.82	−201.68	−6.84	6.34	0.8	1.6	−131.96
3	101.56	−214.55	−7.91	6.96	0.1	−1.4	−115.32
4	125.14	−222.20	−7.84	6.21	0.4	−3.3	−101.59
5	136.82	−227.47	−8.16	6.53	−4.6	0.5	−96.38
6	148.89	−231.17	−10.10	6.53	1.0	−4.5	−89.36

[a] $\Delta E(\mathrm{Be}), \Delta H(\mathrm{Be})$ and $T\Delta S$(Be): energy (at the MP2/6-311 + G(2df,2p) level), enthalpic and entropic costs of the reaction $[\mathrm{Be}, (\mathrm{H_2O})_n]^{2+} \rightarrow [\mathrm{BeOH}, (\mathrm{H_2O})_{n-1}]^{+} + \mathrm{H}^+$. $\Delta E(\mathrm{H}^+), \Delta H(\mathrm{H}^+)$ and $T\Delta S(\mathrm{H}^+)$: energy, enthalpic and entropic costs of the proton solvation reaction: $(\mathrm{H_2O})_n + \mathrm{H}^+ \rightarrow \mathrm{H}_{2n+1}\mathrm{O}_n^+$ (taken from Ref. [16]). All results in kcal mol^{-1}.

Table 3
Estimate of the Helmholtz free energy cost ΔG_n of the hydrolysis reaction HR2 defined in Eq. (2), in the case $M^{m+} = BeOH^{+a}$

n	ΔE(BeOH)	$\Delta E(H^+)$	ΔH(BeOH)	$\Delta H(H^+)$	$-T\Delta S$(BeOH)	$-T\Delta S(H^+)$	ΔG_n
1	186.93	−172.06	−8.28	8.47	0.6	−1.01	14.64
2	215.30	−201.68	−8.16	6.34	1.1	1.6	14.50
3	222.37	−214.55	−8.00	6.96	0.9	−1.4	6.29
4	227.01	−222.20	−8.53	6.21	2.7	−3.3	1.88
5	240.07	−231.17	−7.91	6.53	−2.2	−4.5	9.51

[a] $\Delta E(\mathrm{BeOH}), \Delta H(\mathrm{BeOH})$ and $T\Delta S$(BeOH): energy (at the MP2/6-311 + G(2df,2p) level), enthalpic and entropic costs of the reaction $[\mathrm{BeOH}, (\mathrm{H_2O})_n]^{+} \rightarrow [\mathrm{Be(OH)_2}, (\mathrm{H_2O})_{n-1}] + \mathrm{H}^+$. $\Delta E(\mathrm{H}^+), \Delta H(\mathrm{H}^+)$ and $T\Delta S(\mathrm{H}^+)$: energy, enthalpic and entropic costs of the proton solvation reaction: $(\mathrm{H_2O})_n + \mathrm{H}^+ \rightarrow \mathrm{H}_{2n+1}\mathrm{O}_n^+$ (taken from Ref. [16]). All results in kcal mol^{-1}.

from results summarised in Table 1 and from values taken in Ref. [26].

4.1. *Hydrolysis of* Be^{2+}

ΔG_n values corresponding to Eq. (2), are given in Table 2. As observed and whatever the value of n, HR1 is strongly exothermic, but the ΔG_n values decrease as n increases, from about −138 to −89 kcal mol^{-1}, for n varying from 1 to 6. However, it has to be noticed that molecules of the first shell have stronger incidence on the ΔG_n values than those of the second: the variation of ΔG_n values is of 37 kcal mol^{-1} for $n = 1$–4, and only of 12 kcal mol^{-1} for $n = 4$–6. As observed in Table 1 and as previously discussed in Section 3.2, the successive solvation $\Delta E_{n-1,n}$ energies of Be^{2+} are stronger than those of $BeOH^+$, by a mean factor of 2.3. However, the difference in $\Delta E_{n-1,n}$ between Be^{2+} and $BeOH^+$ systems decreases with n, in particular for $n \geqslant 4$, explaining the strongest incidence of the first shell water molecules on the ΔG_n values.

All these results exhibit that the first hydration shells considerably lower the reaction ΔG_n energy cost of HR1. However, the ΔG_n values are still far from the ΔG(aq) derived from experimental results in liquid water. For instance ΔG_6 is of 89 kcal mol^{-1}, while ΔG(aq) is estimated at +7.4 kcal mol^{-1} [27]. Hence, hydration shells of a greater order than the second have also to play an important role to explain the bulk result, as shown by Peslherbe et al. [28,29] in the case of the Na^+ solvation process.

4.2. *Hydrolysis of* $BeOH^+$

ΔG_n values for the hydrolysis of $BeOH^+$ are given in Table 3. As observed and whatever the value of n, the reaction is endothermic and ΔG_n values are considerably smaller than in the case of HR1 (by a factor of seven to ten). An other difference with HR1 arises from the fact that no clear trend is observed for the HR2 ΔG_n values: they decrease between $n = 1$ and 4, and increase for $n = 5$. For $n = 1$–5, the mean ΔG_n value is of

9 kcal mol^{-1}, with a standard error of the mean of 5 kcal mol^{-1}, value to be compared with the variation of the ΔG_n value in the case of HR1: 49 kcal mol^{-1} between $n = 1$ and 6 (cf. Section 4.1). It has to be noticed that the ΔG_5 value for HR2 is of +9.5 kcal mol^{-1}, value of the same order of magnitude as that experimentally reported in liquid water (+10.9 kcal mol^{-1} [27]).

5. Conclusion

From the results discussed in this Letter, it appears that the first hydration shells have a strong incidence on the HR1 reaction, and a smaller one on the HR2. In particular, for HR2, its Helmholtz free energy cost is not strongly affected by the number of water molecules interacting with $BeOH^+$ and $Be(OH)_2$, and this energy value appears to be of the same order of magnitude as that experimentally reported in the bulk phase, whatever the number of water molecules considered. For HR1, even if our results exhibit that first shell molecules strongly stabilise Be^{2+}, it remains still strongly exothermic. Hence, to be able to reproduce the experimental results in the bulk phase for HR1, hydration shells of greater order than those here considered have to be accounted for.

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