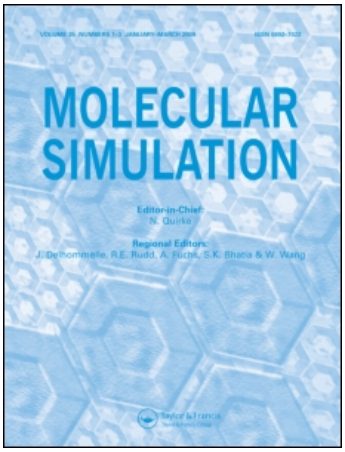

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Opposite effects of successive hydration shells on the aqua ion structure of metal cations

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Opposite effects of successive hydration shells on the aqua ion structure of metal cations

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The conformation adopted by water molecules around a metal ion in aqueous solution can be approached from a discrete representation of the solvent by studying the structure and stability of microsolvation clusters including a different number of water molecules. In this contribution, we present a quantum mechanics and *ab initio* molecular dynamics study on how the arrangement of water molecules around Mg^{2+} and Al^{3+} shows preferentially a T_h or S_6 symmetry depending on the number of hydration shells explicitly included in the calculation. The behaviour observed for both cases is the following: (1) for a cluster composed of the metal ion plus a first hydration shell, the preferred geometry shows a T_h symmetry; (2) when a second hydration shell is added, a minimum can be found with an S_6 disposition of water molecules around the metal centre; (3) however, if a third hydration shell is considered a T_h arrangement of water molecules around the central ion is strongly favoured. The structures of the different solvation complexes studied in this work are characterised. The preference for a T_h or S_6 distribution of water ligands is rationalised in terms of total energies, interaction energies and the hydrogen bond network.

Keywords: quantum mechanics; CPMD; Mg(II); Al(III); aqua ions; hydrogen bonding

1. Introduction

Aqua ions, of the general formula $[M(H_2O)_n]^{m+}$, are the most common structures adopted by metal cations, M^{m+}, in water when chemical conditions inhibit the formation of hydrolysed and polymerised derivatives [1]. The implicit net charge, $m+$, and the polar and polarisable character of water lead to such strong electrostatic effects that the perturbation exerted on the solvent goes beyond the formation of these coordination complexes or aqua ions, defining different solvation shells that surround the central metal cation. This picture of the hydration structure was first proposed by Frank and Evans [2] and is regarded as the *concentric shells model*. In a global sense, the formation of the aqua ion is not enough to describe the behaviour of an ion in solution, and the condensed medium effect has to be taken into account through different solvation shells and/or the bulk.

The structural information derived from experimental techniques for metal ions in aqueous solutions is restricted to one or two hydration shells solved by X-ray and neutron diffraction methods as well as X-ray absorption spectroscopies [1,3–6]. NMR, Raman, IR and vis-UV techniques may also help in determining particular structural and dynamic properties [1,3,5]. More recently, studies of small multivalent ion–water clusters in gas phase have been possible by a variety of techniques, which supply both thermochemical and structural information [7–12]. The characterisation of increasingly large metal–water clusters is an important source of information not only for gas-phase ion chemistry but also allows the splitting of the solvent effects into specific and long-range contributions. Key structural parameters such as coordination numbers vary from gas phase to solution, being a function of the cluster size [12].

Theoretical methods may also provide a molecular description of the environment of a metal ion in water. From a quantum-mechanical (QM) point of view, there are three ways to represent the solvation of an ion in solution. In the discrete approach, a certain number of solvent molecules are explicitly included in the calculation in order to represent the intermolecular interactions between the ion and its closest solvent environment [13]. In the continuum approach, the solvent is represented in an averaged manner by a polarisable dielectric continuum, generally characterised by macroscopic properties of the pure liquid solvent [14,15]. In the semi-continuum approach, the closest environment of the ion is represented by discrete water molecules while the rest of the solvent is described by a continuum [16,17]. The molecular description of the solvent has been tackled at two levels. On one hand, the use of force fields in order to perform computer simulations and molecular mechanics allows the inclusion of a significant number of solvent molecules, but representing the inter- and intramolecular interactions in a simplified form. On the other hand, a more refined description of the interactions can be achieved by the use of static QM calculations, although in this case the computational requirements are high and only a limited

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number of solvent molecules can be treated, typically up to two solvation shells. If more solvation shells are to be considered, the statistical factors become important in order to describe the solvent, and then it seems more appropriate to perform *ab initio* molecular dynamics (MD) simulations such as Born–Oppenheimer [18] or Car–Parrinello MD [19].

In the present study, we aim to analyse the effect of successively increasing the number of hydration shells around two metal ions, Mg^{2+} and Al^{3+}, whose aqua ion structure in solution has been determined experimentally [1,3,20,21]. It is well known that the first coordination shell of both Mg^{2+} and Al^{3+} is sixfold, the aqua ion exhibiting an average T_h symmetry in solution.

There are also theoretical studies on these metal ions within the discrete representation of the solvent. When the structure of the hexahydrate is quantum-mechanically optimised, i.e. only the metal ion and its first hydration shell are considered, in the absence of hydrolysis effects the resulting configurational minimum has a T_h symmetry [22,23] (Figure 1(a)). Although, at this level, we are excluding a large proportion of the solvent effects, the structure of the aqua ion is already coherent with the known T_h structure that is found in solution.

Several configurational minima have been reported when two hydration shells are included in the calculation. First of all, a minimum with T_h symmetry can be found, in which the overall shape of the system is roughly spherical [22,24] (Figure 1(b)). Pye and Rudolph [25] found another minimum in which the second-shell water molecules are distributed into three interacting clusters (Figure 12 of [25]). This structure has a lower energy than the T_h minimum. Bock et al. [26] found yet another minimum with S_6 symmetry, and lower in energy than the other two configurations (Figure 1(c,d)). In this structure, the second-shell water molecules are arranged in the form of a crown surrounding the core hexahydrate, i.e. the overall shape of the system is no longer spherical. This result is striking since it does not fit the behaviour expected for a metal hexahydrate in liquid water, as summarised by the concentric shells model of Frank and Evans. It is neither consistent with the description obtained from the MD simulations of the ions in liquid water. In the present contribution we re-examine the evolution of the stability of the T_h and S_6 aqua ion conformers by successively increasing the number of hydration shells around the metal ion, combining static QM calculations and *ab initio* MD simulations. A careful analysis of their structures, relative energies and their inter-shell interactions is needed to get and insight into this problem.

2. Methods

Gas-phase QM optimisations have been performed for the structures of Mg^{2+} and Al^{3+} aqua ions including one and two hydration shells ($[M(H_2O)_6]^{m+}$ and $[M(H_2O)_{18}]^{m+}$, respectively). For each case, the optimisation started from two configurations, one with T_h and the other one with S_6

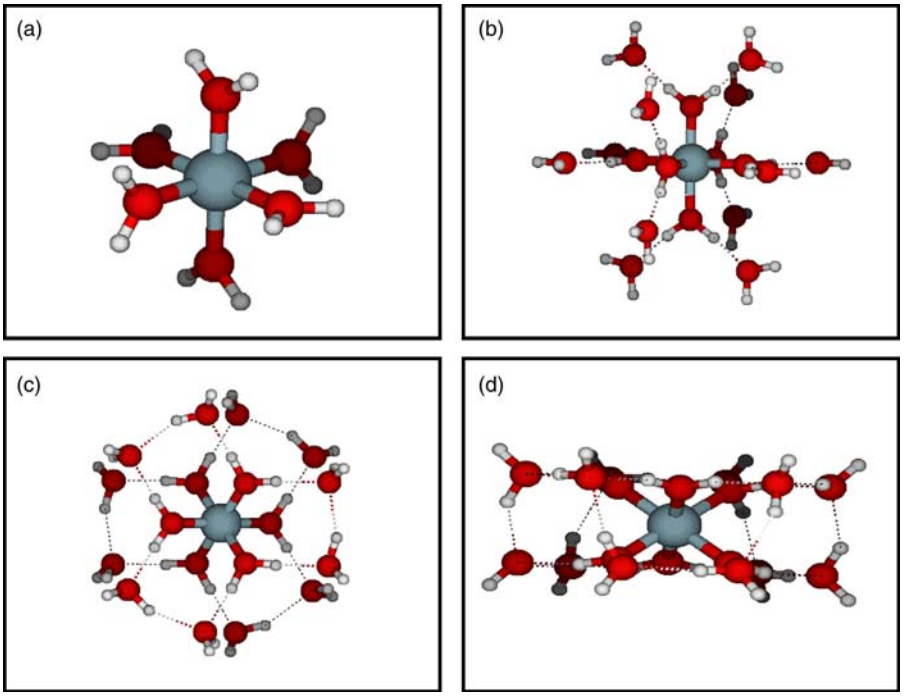

Figure 1. Representative configurations of the QM-optimised structures of: (a) $[M(H_2O)_6]^{m+}$; (b) $[M(H_2O)_{18}]^{m+}$, T_h conformer; (c) and (d) $[M(H_2O)_{18}]^{m+}$, S_6 conformer.

arrangement of ligands, and no symmetry restrictions were applied during the minimisation process. In the one-shell complexes, a single minimum was found showing T_h symmetry. Inclusion of a second hydration shell allows the finding of two minima, having T_h and S_6 symmetry, respectively.

When a third solvation shell is explicitly taken into account, the number of degrees of freedom in the system increases to make a QM optimisation of the structure hardly affordable in terms of computational costs. Furthermore, the shape of the potential energy surface (PES) includes a large number of local minima with similar energies, and it is difficult to reach a global minimum. Therefore, we have employed an alternative strategy using *ab initio* Car–Parrinello MD simulations [19] (CP–MD) to obtain a configuration that, while being only a local minimum on the PES, is representative of a T_h or S_6 arrangement of ligands in the second hydration shell of the aqua ion.

For each metal cation, Mg^{2+} and Al^{3+}, $[M(H_2O)_{42}]^{m+}$ initial configurations have been built by the addition of 24 extra water molecules around the T_h and S_6 $[M(H_2O)_{18}]^{m+}$ minima using the Packmol code [27,28]. The coordination number of 24 water molecules for the third shell was chosen in order to provide the minimum number of water molecules that may coordinate with the 12 second-shell water molecules by hydrogen bonding. An initial relaxation of the system has been performed by equilibration of the nuclei to a low temperature (50 K) and during a short period of time ($\sim$0.4 ps) in order to avoid strong deviations from the initial symmetry (T_h or S_6) within the $[M(H_2O)_{18}]^{m+}$ unit. Afterwards an annealing procedure is applied, slowly diminishing the temperature of the system by applying a reducing factor on the nuclei velocities at each MD simulation step, until the temperature is below 5 K. Due to the thermal agitation experienced by the system during this process, in the final conformation the inner $[M(H_2O)_{18}]^{m+}$ core does neither maintain the initial symmetry nor is a minimum on the PES. However, it is close enough to be qualitatively representative of the T_h or S_6 coordination modes (see Figure 2).

Gas-phase QM calculations and CP–MD simulations were performed using the CPMD program package [29]. Norm-conserving Gaussian pseudopotentials of the Troullier–Martins type [30] and a plane waves (pw)

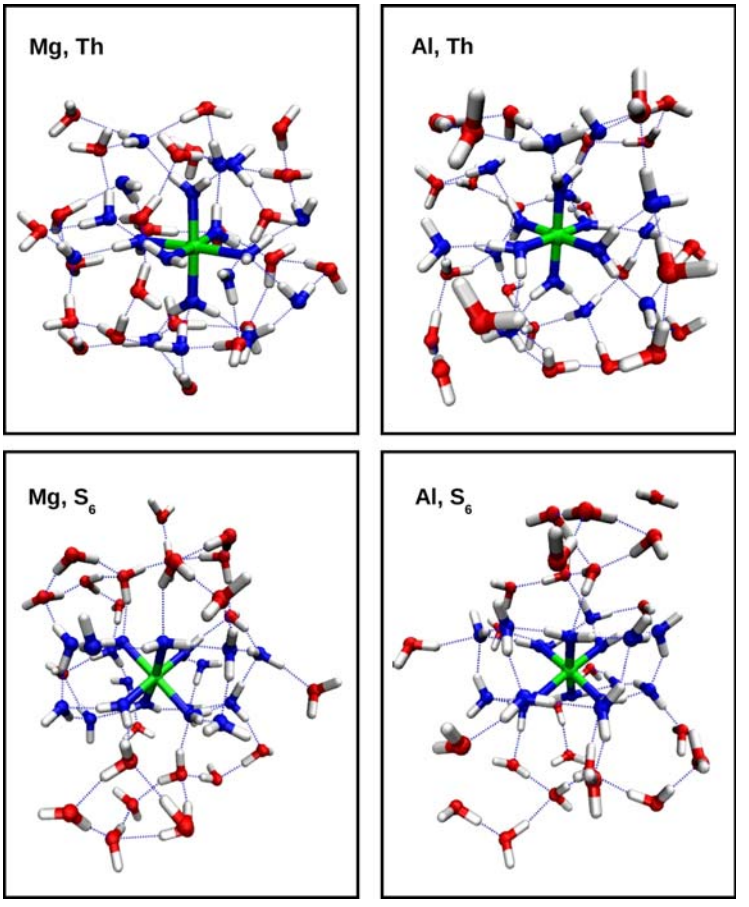

Figure 2. Final structures resulting from the annealing process for the $[Mg(H_2O)_{42}]^{2+}$ and $[Al(H_2O)_{42}]^{3+}$ clusters.

cut-off of 80 Ry were employed, applying cluster boundary conditions [31] to avoid spurious electrostatic coupling of periodic images of the charged clusters. During the simulations, the equations of motion were integrated using a time step of 4 au together with a fictitious electron mass parameter of 400 au and the hydrogen mass for H. All calculations were carried out with the Perdew–Burke–Ernzerhof (PBE) exchange and correlation generalised gradient approximation (GGA) functional [32,33].

3. Results and discussion

3.1 Comparison between plane waves and Gaussian functions

Previous QM calculations cited in the literature used Gaussian functions (gf) as basis sets [22–26]. In order to check the influence of pw or gf as a basis set, the gas-phase QM optimisations of the structures containing one or two hydration shells were also performed using the 6–311++G(2d2p) basis sets [34,35] with the Gaussian03 code [36] using the same PBE exchange and correlation GGA functional [32,33] as for the pw calculations. The interatomic distances using pw are larger than those obtained with gf (see supporting information). The maximum differences are of circa 0.1 Å within the first hydration shell, and somewhat larger in the second shell for the T_h structures. At least some hundredths of Angstrom within this difference can be ascribed to the fact that gf are intrinsically affected by basis set superposition error while pw is not [31]. However, the inner description of H_2O in the first and second shells is not affected by the use of pw or gf. Furthermore, the energy difference between the T_h and S_6 structures including the metal ion plus two solvation shells is the same, within 0.3 kcal/mol, if computed with pw or gf for both Mg^{2+} and Al^{3+}. Therefore, pw provide a description equivalent to that obtained with gf, at least concerning the issues studied in this contribution, and only results obtained with pw will be discussed in the rest of the paper.

3.2 Structural analysis

The $[M(H_2O)_6]^{m+}$ and $[M(H_2O)_{18}]^{m+}$ optimised structures for Mg^{2+} and Al^{3+} aqua ions (Figure 1) and the final $[M(H_2O)_{42}]^{m+}$ structures obtained from the annealing process (Figure 2) are described in Table 1 by means of selected structural data. Overall, the resulting structures are in good agreement with the data available in the bibliography for these hydration complexes [1,3,22–26]. In order to facilitate the visualisation of the different T_h and S_6 structures, the Cartesian coordinates of the $[M(H_2O)_{18}]^{m+}$ and $[M(H_2O)_{42}]^{m+}$ clusters described in Table 1 have been included as supporting information.

The QM optimisation of the $[M(H_2O)_6]^{m+}$ structure yields a T_h arrangement of water molecules around the metal ion for both Mg^{2+} and Al^{3+}. However, when a second hydration shell of water molecules is considered in the calculation, two minima can be found, with T_h and S_6 symmetries, respectively. These two conformations are remarkably distinct from the geometrical point of view: in the T_h case, the water molecules in the first and second shells have a strong ion-dipole orientation towards the central cation (Figure 1(b)) while for the S_6 conformer, the H atoms in the first shell are tilted from their ion-dipole orientation, allowing second-shell water molecules to arrange in the shape of a crown around the metal ion (Figure 1(c,d)). Due to such an arrangement of water molecules, the distance from the metal to H atoms in the first shell is slightly shorter in the S_6 conformer. This variation in the M—H_I distance translates into a more important difference concerning oxygen atoms in the second shell of the S_6 arrangement: their distance to the central ion is circa 0.4 Å shorter in the case of Mg^{2+} and 0.2 Å for Al^{3+}. Accordingly, the M—H_{II} distances are also shorter in the S_6 than in the T_h conformers. The rest of the structural parameters reported in the supporting

Table 1. Selected interatomic distances (Å) for the solvation complexes of Mg^{2+} and Al^{3+} including a different number of hydration shells. (Average distances are given in the case of the $[M(H_2O)_{42}]^{n+}$ clusters. Reference data from the literature [1,3,22–26] are given in parenthesis.)

System	Symmetry	$d_{(M-O)_I}$	$d_{(M-H)_I}$	$d_{(M-O)_{II}}$	$d_{(M-H)_{II}}$
$[Mg(H_2O)_6]^{2+}$	T_h	2.21 (2.00–2.15)	2.90	–	–
$[Mg(H_2O)_{18}]^{2+}$	T_h	2.19 (2.07–2.10)	2.89	4.50	4.78, 5.39
	S_6	2.19 (2.10)	2.87 (2.78)	4.13 (4.13)	4.07, 5.04 (5.02)
$[Mg(H_2O)_{42}]^{2+}$	T_h	2.20	2.85	4.39	4.61
	S_6	2.22	2.83	4.29	4.40
$[A1(H_2O)_6]^{3+}$	T_h	2.00 (1.87–1.95)	2.71	–	–
$[A1(H_2O)_{18}]^{3+}$	T_h	1.98	2.69	4.22	4.61, 5.07
	S_6	1.98 (1.92)	2.68	4.01 (3.99)	4.10, 4.87
$[A1(H_2O)_{42}]^{3+}$	T_h	1.98	2.68	4.28	4.78
	S_6	1.99	2.64	3.93	4.36

information are not influenced by one or the other symmetry type.

The distance between the metal centre and the oxygen atoms in the first hydration shell (M—O_I) is shortened in the $[M(H_2O)_{18}]^{m+}$ clusters with respect to the $[M(H_2O)_6]^{m+}$ structures, since the interaction between water molecules in the first shell with the outer water molecules enhances the transfer of electron density towards the metal centre [22,37]. However, further inclusion of a third solvation shell translates into a slight elongation of the M—O_I distances, showing that the water–water interactions between the first and second shells are hampered by the presence of a third shell of water molecules.

The M—O and M—H interatomic distances in an $[M(H_2O)_n]^{m+}$ structure are always shorter for Al^{3+} than for Mg^{2+}, since the higher net charge on the metal centre in the case of Al makes the metal–water interactions stronger. However, the difference between the M—O distances in the first and second solvation shells ($d_{(M-O)_{II}} - d_{(M-O)_I}$)is very similar for the T_h or S_6 $[M(H_2O)_{18}]^{m+}$ clusters of both Mg^{2+} and Al^{3+}. The polarisation experienced by water molecules in the first shell of Al^{3+} is of greater magnitude than for water molecules in the first shell of Mg^{2+}, but this difference does not affect to a great extent the interactions between water molecules in the first and second hydration shells of the ion. Once the first hydration shell of a metal ion is defined, its interaction with the water molecules in the second shell and in the bulk is unspecific with respect to the chemical identity of the ion, but is dominated by the conformation adopted by the first shell.

3.3 Energy analysis

In order to assess the relative stabilities of the microsolvated clusters considered in this study, we have computed the energy differences between the T_h and S_6 conformers including two and three hydration shells, which are reported in Table 2. For the case of the two-shell structures, the S_6 conformer is energetically more stable than the T_h one, for both Mg^{2+} and Al^{3+}. The resulting energy differences are in agreement with the values previously reported by Markham et al. [24] for Mg^{2+} (34–41 kcal/mol). However, when a third solvation shell is included in the calculation, the tendency is reversed and the T_h arrangement is clearly favoured, recovering the behaviour observed for these metal ions in aqueous solution. The energy difference is so large that one would not expect to observe the S_6 conformer even at room temperature.

Table 2. Energy difference (kcal/mol) between the T_h and S_6 conformers with two and three hydration shells, including the metal hexahydrate (ΔE) or excluding it in the calculation of the total energy (ΔE^W).

	$\Delta E(T_h - S_6)$	$\Delta E^W(T_h - S_6)$
$[Mg(H_2O)_{18}]^{2+}$	+44.6	+88.4
$[Mg(H_2O)_{42}]^{2+}$	−64.8	−63.2
$[A1(H_2O)_{18}]^{3+}$	+25.4	+74.3
$[A1(H_2O)_{42}]^{3+}$	−63.6	−39.5

This behaviour can be understood in terms of different interaction energy contributions. When the metal is surrounded by only the first hydration shell, the orientation of water molecules is driven by electrostatic interactions with the cation. The most stable arrangement is the one that maximises the metal–water electrostatic interaction, but minimises the water–water repulsion. Therefore, the T_h conformer is preferred.

When a second shell of water molecules is considered, the S_6 arrangement favours attractive water–water interactions within the second shell, yielding the crown-shaped structure shown in Figure 1(c,d). The energetic gain in terms of water–water interaction is enough to modify the geometrical arrangement of the inner hexahydrate by tilting the water molecules in the first hydration shell. If a third solvation shell is added, the T_h configuration is recovered since this conformation allows a maximum interaction of the $[M(H_2O)_{18}]^{m+}$ unit with the remaining solvent molecules.

In order to illustrate these ideas, we have computed the total energy for the $(H_2O)_{12}$ and $(H_2O)_{36}$ arrangements of water molecules corresponding to the second or second- and third-solvation shells in the $[M(H_2O)_{18}]^{m+}$ and $[M(H_2O)_{42}]^{m+}$ clusters obtained from QM-optimisation and annealing, respectively. To this aim, the structures and spatial distribution of water molecules in the $(H_2O)_{12}$ and $(H_2O)_{36}$ systems are kept frozen with respect to the structures of the clusters including the metal hexahydrate. The energy differences between the T_h and S_6 arrangements of second-shell $(H_2O)_{12}$ or second- and third-solvation shell $(H_2O)_{36}$ water molecules, $\Delta E^W(T_h - S_6)$, are included in Table 2. In the clusters containing a cation surrounded by two solvation shells, $[M(H_2O)_{18}]^{m+}$, the water–water interactions are enough to stabilise the S_6 versus the T_h conformers. When a third hydration shell is included, the water–water interactions favour the T_h arrangement of water molecules around the metal ion. This result is in agreement with our picture of a S_6-crown-shaped second hydration shell in which water molecules interact with each other rather than with water molecules in some outer shell. The presence of a third solvation shell favours the maximisation of the water–water interaction through adoption of a T_h-like distribution of water molecules around the metal ion.

An alternative way to consider the solvation effects is through the use of a continuum model instead of explicit water molecules to represent the solvent. In such an approximation, one really deals with a cation in solution,

whereas in the case of the cluster including three hydration shells, the system consists of a multiple-hydrated cation in gas phase or a drop. We have used the polarizable continuum model within the integral equation formalism (IEFPCM) [38] to optimise the structures of the $[M(H_2O)_{18}]^{m+}$ clusters in the T_h and S_6 arrangements. Contrary to the results obtained using three explicit hydration shells, the preference for the T_h arrangement is not recovered using the continuum model. A detailed comparative analysis of the importance of using a molecular description of the solvent instead of a continuum representation in order to study the relative stabilities of different conformers is currently being developed in our group for a series of metal cations, and will be the topic of another publication.

3.4 Analysis of hydrogen bonds

An additional way to quantify the water–water interactions within the different hydration complexes consists of taking into account the number of hydrogen bonds (HB) established between adjacent hydration shells. We have adopted the following criteria used by Chandra [39] to define a HB between water molecules: the distance between the two oxygen atoms is shorter than 3.5 Å, the distance between the accepting oxygen atom O^* and the hydrogen atom is less than 2.45 Å, and the $\widehat{OO^*H}$ angle is less that 30°. Then we define three indexes: W_1 is the number of HB per water molecule in which a first-shell water molecule takes part. W_{21} is the number of HB per water molecule established between water molecules in the second shell and water molecules in the first shell. W_{22} is the number of HB per water molecule formed between second-shell water molecules. Table 3 shows the values of these indexes obtained for the optimised $[M(H_2O)_{18}]^{m+}$ structures and for the final $[M(H_2O)_{42}]^{m+}$ structures obtained from the annealing process. In this sense, the two-shell structures serve as a reference in order to quantify the distortion from the original T_h or S_6 symmetry in the disordered $[M(H_2O)_{42}]^{m+}$ structures.

The W_1 index equals 2.00 for the two-shell structures, since in the symmetric clusters each water molecule in the first shell forms two HBs with accepting water molecules in the second-shell. When the water molecules form the crown-shaped S_6 structure, they are distributed within a restricted volume around the metal centre, and void regions are defined above and below such crown allowing the water molecules in the second shell to donate HB to first-shell water molecules, W_1 becoming greater than 2.00. This can also happen in the T_h conformer if the M—O distance is long enough, as in the case of Mg^{2+}. However, in the present case there is a fortuitous cancellation: the second shell of Mg^{2+} is not so strongly structured as in Al^{3+}, not all first-shell water molecules give two HB towards the second shell, and there are also first-shell water molecules accepting HB from the second shell, resulting in $W_1 = 2.00$.

W_{21} equals 1.00 for the four two-shells optimised structures, since each second-shell water molecule accepts a HB from a water molecule in the first shell. In the case of the three-shell structures for Mg^{2+}, the second shell is more diffuse, less defined, there are more than 12 water molecules in the second shell and not all of them form HB with first-shell water molecules, resulting in a W_{21} value of less than 1.00. For Al^{3+}, the second shell is much better defined and we do not observe a value smaller than 1.00.

The W_{22} index provides a useful and simple way to distinguish between the T_h and S_6 coordination modes. In a strictly defined, highly symmetrical T_h arrangement of water molecules, the water molecules in the second shell cannot form HB with other second-shell water molecules (Figure 1(b)) and W_{22} is zero. Likewise, in a highly symmetrical S_6 arrangement, each second-shell water molecule forms a HB with another second shell water molecule, and W_{22} is 1.00 (Figure 1(c,d)). According to this definition, we can observe that in the final structures from annealing, the symmetry of the starting configuration has remained quite unaffected in spite of the thermal fluctuations. However, the crown-like arrangement of second-shell water molecules in the S_6 conformers at the end of annealing is slightly distorted towards the much more stable T_h conformation. The distortions from the initial symmetry are higher for Mg^{2+}, given its less defined second hydration shell. The value of W_{22} greater than zero in the T_h Mg^{2+} conformer responds to the fact that there are more than 12 water molecules in the second solvation shell of the metal, and thus there is a certain degree of hydrogen bonding within the second shell.

In the absence of thermal agitation, in an ideal hydrogen-bonded structured water, each water molecule in the second shell would ideally form four HB in total, one of each would bind to a water molecule in the first shell, the remaining three being available for interaction with other water molecules. In a two-shell structure, the second-shell water molecules achieve a higher saturation of their interaction sites by establishing HB with other second-shell water molecules, and the S_6 conformer is more stable. When a third solvation shell is considered, the more stable

Table 3. Number of hydrogen bonds per water molecule in the microsolvated complexes of Mg and Al including two and three hydration shells.

	T_h			S_6		
	W_1	W_{21}	W_{22}	W_1	W_{21}	W_{22}
$[Mg(H_2O)_{18}]^{2+}$	2.00	1.00	0.00	2.00	1.00	1.00
$[Mg(H_2O)_{42}]^{2+}$	2.00	0.92	0.23	2.17	0.93	0.57
$[A1(H_2O)_{18}]^{3+}$	2.00	1.00	0.00	2.00	1.00	1.00
$[A1(H_2O)_{42}]^{3+}$	2.00	1.00	0.00	2.33	1.00	0.71

arrangement is the one that allows maximum occupation of space through maximum interaction of the second-shell water molecules with other solvent water molecules. That is achieved by adopting a T_h arrangement.

4. Concluding remarks

When an aqua ion composed of a hexahydrated metal cation plus a certain number of additional water molecules distributed within different hydration shells is considered, the energetic enhancement of a T_h versus an S_6 structure, and vice-versa, is intrinsic to the arrangement of water molecules within the second shell and is a function of the degree of hydration, i.e. the number of hydration shells surrounding the metal cation determines the preferred arrangement. There are two contributions taking part: metal cation–water and water–water interactions, the water–water contribution becoming determinant when there are two or more hydration shells included to describe the system. In a structure containing two hydration shells, the key point for the appearance of the S_6 arrangement is joined to the ability of second-shell water molecules to combine their coordination with water molecules in the first shell and the water–water interactions within the second shell. This can be achieved if the octahedral disposition of the hexahydrated aqua ion is distorted leading to the S_6 conformer. When a third hydration shell is added, the water molecules in the second shell form new HBs with water molecules in the third shell, and the second-shell network is partially lost. Then the T_h configuration is recovered as the preferred conformer. The use of a molecular description of the solvent in the third solvation shell is mandatory in order to recover the T_h arrangement of water molecules, given that a continuum representation of the solvent is not sufficient to provide the solvent–solvent interactions that reverse the relative stabilities between the S_6 and T_h conformers including only two hydration shells. Furthermore, the present results show that the use of only two hydration shells are useful to characterise gas-phase microsolvated clusters, but does not warrant a proper description of metal aqua ions in solution. The results presented in this contribution concern isolated molecular aggregates at temperatures close to 0 K. The inclusion of temperature effects and outer solvation shells to achieve the description of a condensed medium will be undertaken in the future.

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