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A quantum chemical study of the hydrating shell influence on the structural and vibrational properties of beryllium aqua and hydroxo complexes

Dmitri A. Rozmanov*, Olga V. Sizova, Kim A. Burkov

Division of Inorganic Chemistry, Department of Chemistry, St Petersburg State University, 198504 St Petersburg, Universitetsky Ave. 26, Petrodvorets, Russian Federation

Abstract

Clusters of beryllium aqua and hydroxo complexes surrounded by the hydrating shell of 30–50 water molecules modelled by the effective fragment potential method have been investigated by a computational approach. The results have been compared with the existing experimental and calculated data and discussed in terms of structural parameters, partial charges, Mayer's bond orders and frequencies of the total symmetric stretching vibration Be–O. It was found that the hydration changes the electron structure of the most polar complex, shortens and strengthens the Be–O bonds and increases the frequencies of the Be–O stretching vibrations by 12–16% in all the complexes in comparison with the free ones. Evidence of negative partial molar volume of the beryllium cation has been obtained.
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1. Introduction

In our recent works [1,2], we have studied the beryllium aqua and hydroxo complexes, $Be(H_2O)_4^{2+}$, $Be(OH)(H_2O)_3^+$, $Be_2(OH)(H_2O)_6^{3+}$ and $Be_3(OH)_3(H_2O)_6^{3+}$. It was shown that ab initio quantum chemical calculations that take into account the water molecules of the first hydrating shell only gave the structural parameters of the complexes in satisfactory accord with the experimental data. The calculated frequencies of the total symmetric stretching vibration Be–O in the complexes under investigation had been obtained in the proper order by magnitude, however, the absolute values of the frequencies were lower than those of the experimental ones by 19–15% and that is unusual for the RHF calculations. It was also shown that accounting for 1 and 2 water molecules in the second hydrating shell leads to the increase in the stretching frequencies and to the better agreement with the experimental values. Thus, the goal of

the present paper is to investigate the influence of the bulk solvent on the calculated structural and vibrational properties of the beryllium aqua and hydroxo complexes: $Be(H_2O)_4^{2+}$, $Be(OH)(H_2O)_3^+$, $Be_2(OH)(H_2O)_6^{3+}$ and $Be_3(OH)_3(H_2O)_6^{3+}$.

To achieve this goal the quantum chemical calculations of the enhanced model systems have been done. In those systems the mentioned beryllium species were put in the surrounding of 30–50 water molecules modelled by the effective fragment potentials approach (EFP) [3,4]. This method was successfully used for modeling the water clusters [5,6], studying the effect of hydration [7,8], modeling the inert parts of large organic molecules [9].

2. Computational details

The calculations were carried out using the general quantum chemistry package GAMESS (US) [10]. The structural parameters and the vibrational properties of the beryllium aqua hydroxo complexes in the surrounding of 30–50 model water molecules in the outer hydrating shells were calculated. The calculations were performed at the RHF level of theory using DZV basis set augmented by

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* Corresponding author.
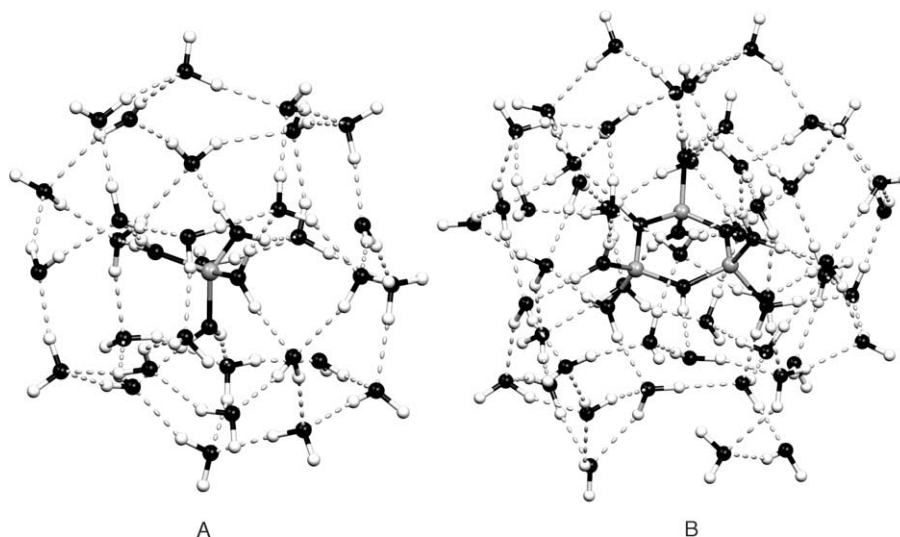*E-mail address:* rozmanov@mail.ru (D.A. Rozmanov).

Fig. 1. (A) $Be(H_2O)_4^{2+}$ hydroxo complex surrounded by 30 water (EFP) molecules and (B) $Be_3(OH)_3(H_2O)_6^{3+}$ hydroxo complex surrounded by 50 water (EFP) molecules. Hydrogen bonds are shown by the dashed lines.

polarizing functions at all atoms [11]. The previously obtained optimal structures of the complexes [1] were surrounded by the hydrating shell and then the geometry of the mixed cluster was optimized. During the optimization the beryllium complex was described by the quantum chemical approach while the water molecules of the outer hydrating shell were modelled by the effective fragment potentials method (EFP). In EFP the water molecules are described in the rigid structure approximation with the following parameters: the bond length $R(O–H) = 0.944$ Å and the angle $\angle (H–O–H) = 106.7°$.

The calculations can be divided into two groups by the way the starting structures were generated. In the first case the effective water molecules were placed around the complex to the vertices of several nested distorted polygons. The polygons were distorted by shifting the vertices into random directions. The displacement distances were less than the maximum allowable value. The water molecules dipoles were oriented in the beryllium–water oxygen direction. This method was used for the calculations of the $Be(H_2O)_4^{2+}$ complex with the hydrating shell of 30 effective (EFP) water molecules (Fig. 1(A)), the $Be(OH)(H_2O)_3^+$ complex with the hydrating shell of 30 water (EFP) molecules (30 water EFPs and three explicit water molecules in the cluster in total), the $Be_2(OH) \times (H_2O)_6^{3+}$ complex surrounded by 40 water (EFP) molecules ($40 + 6$ water molecules taken into account in total) and the $Be_3(OH)_3(H_2O)_6^{3+}$ complex surrounded by 43 water (EFP) molecules ($43 + 6$ water molecules in total). For the optimal clusters' structures found the second derivatives of the energy were calculated for determining the type of the point located and the vibrational spectra were obtained. At that, every effective (EFP) water molecule in the shell gave six additional vibrational degrees of freedom to the system (three rotations and three translations of the EFP molecule as a whole relatively to the rest of the system).

The spectra of 219, 216, 306 and 339 vibrations were obtained for the four clusters mentioned above, respectively.

In the second group of the calculations the initial structures of the hydrating shell for the consequent optimization were obtained by Monte–Carlo computer simulation. The complex was placed into the center of the simulation cell with the dimensions of $20 \times 20 \times 20$ Å, during the MC modeling the structure and the position of the complex remained constant. TIP4P [12] potential was used for the modeling of water. The starting configuration with the required number of the water molecules (266) was generated by the Monte–Carlo method in the grand canonical ensemble, while the further relaxation was carried out in the canonical ensemble. From the relaxed system the clusters containing the complex and about 50 adjacent water molecules were cut out. Using this technique the initial configurations of two systems for the calculation by the EFP method were prepared: $Be_2(OH)(H_2O)_6^{3+}$ complex surrounded by 49 water (EFP) molecules (55 water molecules in total) and $Be_3(OH)_3(H_2O)_6^{3+}$ complex surrounded by 50 water (EFP) molecules (56 water molecules in total Fig. 1(B)). The preliminary optimization of the cluster structural parameters was done by the RHF + EFP method using MINI basis set [13] and then, from the structures found, 11 and 10 furthest (in cases of and complexes, respectively) water molecules were removed. The structures of the clusters left were optimized at the RHF + EFP/DZVP level of theory, and then the Hessian and the vibrational spectra were calculated (360 and 381 vibrational modes, respectively).

3. Results and discussion

The interatomic distances and the Mayer's bond orders [14] calculated in the present work are given in Table 1.

Table 1
Interatomic distances (Å) and the Mayer's bond orders [14] in the aqua hydroxo complexes studied

Comples	Number of outer water molecules	Interatomic distances		Bonds orders	
		Be–OH$_2$	Be–OH	Be–OH$_2$	Be–OH
Be(H$_2$O)$_4^{2+}$	exp. [15]	1.67 (solution)	–	–	–
	exp. [16]	1.61 (solid)			
	–[a]	1.648	–	0.574	–
	30[b]	1.619	–	0.618	–
Be(OH)(H$_2$O)$_3^+$	–	1.712	1.455	0.448	1.155
	30	1.669	1.512	0.526	0.964
Be$_2$(OH)(H$_2$O)$_6^{3+}$	–	1.673	1.617	0.528	0.669
	40	1.646	1.582	0.566	0.698
	49	1.642	1.584	0.576	0.692
Be$_3$(OH)$_3$(H$_2$O)$_6^{3+}$	exp. [16]	1.659	1.589	–	–
	–	1.703	1.598	0.475	0.676
	43	1.669	1.579	0.518	0.692
	50	1.673	1.581	0.512	0.693

Experimental data and values calculated by RHF method [1] and the ones calculated by RHF method when the hydration effect is modelled by the effective fragment potentials approach (this work).

[a] Calculated by RHF method [1].
[b] Calculated by RHF + EFP approach.

The frequencies of the total symmetric beryllium–water stretching vibration are shown in Table 2 along with the experimental data and the calculation results from our recent work [1]. The effective charges on the beryllium ions, water molecules and the hydroxo groups in the quantum chemical parts of the clusters are presented in Table 3. For the binuclear and the three-nuclear complexes in all the tables the results of two calculations with different number of effective water molecules are given.

The calculated optimal structures of the Be(H$_2$O)$_4^{2+}$ (A) and Be$_3$(OH)$_3$(H$_2$O)$_6^{3+}$ (B) clusters surrounded by 30 and 50 water (EFP) molecules, respectively, are shown in Fig. 1.

If one compares the interatomic distances obtained with the distances calculated earlier by RHF/DZVP method without taking into account the outer water molecules [1] then it can be seen that the average metal–hydroxo group distance decreased in the binuclear and three-nuclear complexes by 0.04 and 0.02 Å, while in the mono-hydroxide it increased by 0.05 Å.

The bond lengths in the aqua complex and in the trimeric species approached the experimental values found for the solid state. Since the kinetic energy is neglected in the optimization process, it is obvious that the results of quantum chemical calculations of condensed phase should resemble the structural parameters obtained for the solid state at 0 K. The decreasing and strengthening of the metal–water bonds can be related to the compression of the complexes by the outer-shell water molecules that are involved in the network of the hydrogen bonds (in Fig. 1 the hydrogen bonds are clearly visible, marked by dashed lines).

The bond orders analysis confirms the conclusions made from the analysis of the interatomic distances. In all the cases, excluding the Be–OH bond in the monohydroxide, the bond orders increased. At the same time, in all the compounds the difference in the bond orders in metal–water and metal–hydroxo group somewhat decreased due to the interaction with the electric field of the solvent.

The analysis of the frequencies of the Be–H$_2$O stretching vibrations (Table 2) shows that the calculated frequencies

Table 2
The experimental and calculated frequencies of the total symmetric stretching vibration metal–water in the beryllium aqua hydroxo complexes

Complex	Experiment (cm^{-1})	RHF [1] (cm^{-1})	RHF + EFP (cm^{-1})	Number of outer water molecules
Be(H$_2$O)$_4^{2+}$	527 [17] (100%)	484.3 (100%)	561.0 (100%)	30
	534 [18] (100%)			
	533 [19]			
Be(OH)(H$_2$O)$_3^+$	–	435.1 (90%)	534.5 (95%)	30
Be$_2$(OH)(H$_2$O)$_6^{3+}$	497 [17] (94%)	442.3 (91%)	507.2 (90%)	40
			505.3 (90%)	49
Be$_3$(OH)$_3$(H$_2$O)$_6^{3+}$	408 [17] (77%)	367.0 (76%)	439.4 (78%)	43
	415 [18] (78%)		426.2 (76%)	50

The calculated results for the free complexes (RHF) [1] and for the complexes surrounded by the outer hydrating shells (RHF + EFP) modelled by effective fragment potentials approach (this work) are given. The absolute and the relative values (in parentheses) values are shown. In the last column the numbers of water (EFP) molecules in the outer hydrating shells in the systems studies are reported.

Table 3
The effective charges of the atoms, the charge transfers to the berylluim cation from the water molecules and hydroxo-groups in the complexes studied

Complex	Number of outer water molecules	Effective charges			Charge transfer	
		Be^{2+}	H_2O	OH^-	c H_2O	c OH^-
$Be(H_2O)_4^{2+}$	$-^a$	0.624	0.344	–	−0.344	–
	30^b	0.508	0.373	–	−0.373	–
$Be(OH)(H_2O)_3^+$	–	0.477	0.265	−0.271	−0.265	−0.729
	30	0.467	0.315	−0.411	−0.315	−0.589
$Be_2(OH)(H_2O)_6^{3+}$	–	0.639	0.315	−0.167	−0.315	−0.417
	40	0.528	0.347	−0.138	−0.347	−0.431
	49	0.543	0.340	−0.124	−0.340	−0.438
$Be_3(OH)_3(H_2O)_6^{3+}$	–	0.596	0.281	−0.158	−0.281	−0.421
	43	0.515	0.310	−0.135	−0.310	−0.433
	50	0.522	0.305	−0.133	−0.305	−0.434

The results obtained by RHF method [1] and by RHF method when the hydration effect is modelled by effective fragment potentials approach (this work).
  [a] Calculated by RHF method [1].
  [b] Calculated by RHF+EFP approach.

increased in their absolute magnitude in all the compounds when the outer-shell water molecules are taken into account as they are compared with the data calculated for the free complexes [1]. This is in agreement with the structural changes discussed earlier. However, the relative values of the frequencies (as the percent of the frequency in the aqua cation) remained practically the same in the aqua cation and two polynuclear complexes. In the mono-hydroxide the relative frequency of the stretching vibration metal–water increased substantially as compared with other complexes, this effect is caused by the stabilization of the metal–water bonding in presence of the outer water molecules (vide infra). In addition, the Be–O stretching vibrations couple with the intermolecular vibrations of the water molecules in the outer shells. This coupling effectively increases the frequencies of the mixed Be–O vibrations in all the complexes.

In contrast with the results for the free complexes [1], in the present work the absolute values of the calculated frequencies were found to be greater than the experimental values. However, the experimental vs. calculated frequencies ratios are still higher then the usual one (0.89) when the restricted Hartree–Fock method is used [20]. If one calculates the frequencies that would correspond to the factor of 0.89 for the complexes where the experimental data is available ($Be(H_2O)_4^{2+}$, $Be_2(OH)(H_2O)_6^{3+}$ and $Be_3(OH)_3(H_2O)_6^{3+}$), then one can speculate that those frequencies approximate the theoretical values that should be obtained at RHF level if the hydration is fully taken into account. It appears that the values of the calculated frequencies for these free complexes [1] are in range of 0.79–0.81 of those theoretical limits and that the calculated values from this work are in range of 0.92–0.94. Hence, we can estimate that the hydration should be responsible for 19–21% of the total values of frequencies of the stretching Be–O vibrations and that our approach to the hydration modeling allows us to retrieve additional 11–14% of

the limiting frequencies. This is about 58–68% of the total effect of the hydration influence on the vibrational frequencies.

The comparison of the effective atomic charges obtained in this work with the results for the free complexes [1] (Table 3) allows one to establish correlations between the regularities noted with the distribution of the electron density and with the influence of the solvent molecules on the electron structure of the complexes. It should be noted, however, that in the EFP method the interaction of the outer hydrating shell with the complex is described in terms of polarization caused by the distributed electric charge of the shell, therefore, the charge transfer between the complex and the effective water molecules is impossible.

As a result of the interaction of the induced dipoles on the first and the second coordination shells the charge transfer from the water molecules of the first shell to the beryllium atoms increased in all the complexes studied that lead to the decrease of positive charges on the metal atoms.

In the $Be_2(OH)(H_2O)_6^{3+}$ and $Be_3(OH)_3(H_2O)_6^{3+}$ complexes the charge on the hydroxo group became less negative, while in the $Be(OH)(H_2O)_3^+$ complex it became more negative. In the complexes, $Be(H_2O)_4^{2+}$, $Be_2(OH) \times (H_2O)_6^{3+}$ and $Be_3(OH)_3(H_2O)_6^{3+}$ the account for hydration effect changes the absolute values of the charges, but despite the somewhat lower polarity of the Be–O bonds the qualitative picture of the distribution of the electron density did not change. In the $Be(OH)(H_2O)_3^+$ complex the positive charge on the beryllium atom decreased as well, however, much less (by 0.01 electrons) than in all other less polar complexes (by 0.08–0.12 electrons). At the same time the positive charges on the water molecules increased and the negative charge on the OH-group became even more negative. Hence, the polarity of the Be–O bonds in $Be(OH)(H_2O)_3^+$ increases substantially when the complex is surrounded by the hydrating shell. The stabilizing polarization of the water molecules in the first shell in this complex

Table 4
Average numbers of neighboring oxygen atoms (N), average distances to the neighboring oxygen atoms (R, Å), average numbers of neighboring oxygen atoms in the second hydrating shell (N_{1-2}), average distances to the neighboring oxygen atoms in the second shell (R_{1-2}, Å) within 3.1 Å radius for the oxygen atoms of the water molecules and the hydroxo-groups of the complexes in the clusters studied

Complex	Number of outer water molecules	H_2O				OH^-			
		N	R	N_{1-2}	R_{1-2}	N	R	N_{1-2}	R_{1-2}
$Be(H_2O)_4^{2+}$	30	5	2.652	2	2.666	–	–	–	–
$Be(OH)(H_2O)_3^+$	30	5	2.669	2	2.704	6	2.774	3	2.879
$Be_2(OH)(H_2O)_6^{3+}$	40	5.5	2.704	2.17	2.734	7	2.719	1	3.011
	49	5.17	2.697	2.17	2.746	7	2.690	1	2.866
$Be_3(OH)_3(H_2O)_6^{3+}$	43	5	2.681	2	2.726	7	2.676	1	2.846
	50	5	2.695	2	2.756	7	2.684	1	2.863

occurs by the same scheme as in all the other complexes studied. At the same time the mutual polarization of the water molecules in the second shell and the terminal hydroxo group results in some transfer of the electron density from the Be–O bond to the OH-group itself and leads to weakening of the Be–OH bond and to strengthening of the Be–OH$_2$ bonds. The polarization interactions can be expressed by the following scheme:

$$(Be^{\delta^+} -^{\delta^-}OH_2^{\delta^-}) - (^{\delta^-}OH_2^{\delta^+}),$$

$$(Be^{\delta^+} -^{\delta^-}OH^{\delta^-}) - (^{\delta^+}H_2O^{\delta^-}),$$
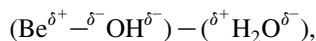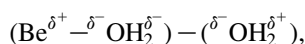
where δ^+ and δ^- are the partial charges. Thus, the outer hydrating shells (second and more distant) can be considered as a polarizing buffer that assists in strengthening of bonding between the metal cation with weak donors (H_2O) and weakens the bonding when the cation is bound to strong donors (OH^-). In the $Be_2(OH)(H_2O)_6^{3+}$ and $Be_3(OH)_3(H_2O)_6^{3+}$ complexes this weakening of the Be–OH bonds by the outer hydrating shells did not occur due to the bridging position of the OH-groups. In this case the negative charge on the hydroxo group is lower in the absolute value, and the group itself is less available for interaction with solvent molecules due to the steric masking by the neighboring water molecules in the first shell.

In order to achieve better understanding of the cause of the different polarization of the Be–OH bonds in the terminal and bridging positions we analyzed the oxygen surrounding of all the oxygen atoms in the hydroxo complexes. Only the neighboring oxygen atoms within 3.1 Å distance from the oxygen atom of interest were considered. Table 4 shows the average numbers of the neighboring oxygen atoms for the oxygen atoms of the complexes in the optimized clusters and the average distances to them. The results are given separately for the oxygen atoms of the water molecules and for those of the hydroxo groups. Also, in addition, the same values are given in the table but for the case when the neighboring oxygen atoms from the second hydrating shell only are counted. The shortest average distance to the water molecules in second shell has been obtained in the beryllium aqua

complex, that does not have any hydroxo group at all, and the longest ones—in the binuclear and three-nuclear complexes, those with the bridging hydroxo groups. The distances from the oxygen atoms of the hydroxo groups of the complexes to the water molecules in the second hydrating shell are roughly the same in all the hydroxo complexes.

In the $Be(OH)(H_2O)_3^+$ complex surrounded by 30 EFP water molecules the average number of the neighboring oxygen atoms by the oxygen atoms of the water molecules in the first hydrating shell (i.e. the water molecules belonging to the complex itself) equals 5 and, on average, two of those neighboring oxygen atoms are located in the second hydrating shell. The oxygen atom of the hydroxo group of complex has a total of six neighboring oxygen atoms within 3.1 Å distance, and three of those are from the second shell. Analysis of the clusters' structure has shown that the bridging hydroxo groups form an H-bond with only one electron-donor water molecule from the second shell, while the terminal OH-group forms three H-bonds: one bond with an electron-donor and two bonds with electron-acceptor 'outer' water molecules from the second shell. Hence, in the $Be(OH)(H_2O)_3^+$ complex the outer hydrating shell polarizes the Be–OH bond stronger than in the other hydroxo complexes, and shifts the electron density from the bond to itself. One can see from the data in Table 4 that the distances between the oxygen atoms inside the complexes are shorter than those to the 'outer' shell oxygen atoms. Thus, the higher density of the oxygen in the complexes in comparison with the bulk 'outer' water suggests negative value for the partial molar volume of the beryllium cation in aqueous solution.

4. Conclusion

The results of the calculations using the effective fragment potentials methods allows us to conclude that surrounding the $Be(OH)(H_2O)_3^+$ complex, the most polar one from the complexes studied, by a hydrating shell consisting of 30–50 water molecules causes significant

changes in its electron structure, while the electron structures of less polar complexes change much less under these conditions. The shortening of the Be–O distances in the less polar complexes is probably caused by the steric compression of the complexes due to involving the complexes into the network of the hydrogen bonds and by the strengthening of the bonds in the complexes due to mutual polarization of the water molecules in the first and the second hydrating shells.

When the hydration of the system studied is enhanced, the Be–OH_2 distances become close to the experimental values in the crystal hydrate (1.61 Å), the absolute values of the calculated frequencies of the stretching Be–O vibrations in the complexes increase by 12–16%, however, the ordered sequence of the frequencies of the total symmetric stretching Be–O vibrations of the complexes studied remains the same. The increase in the frequencies of the stretching vibrations Be–OH_2 is explained by the strengthening of the metal–water bonding caused by the influence of the hydrating surrounding and by the mixing of the internal vibrations of the complexes with the intermolecular vibrations of the water molecules of the surrounding. We estimate that the hydration is responsible for about 20% of the total frequency of the stretching vibrations in the fully hydrated complexes.

The higher density of the oxygen in the complexes suggests a negative partial molar volume value for the beryllium cation in aqueous solutions.

Acknowledgements

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