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Hydration of Beryllium, Magnesium, Calcium, and Zinc Ions Using Density Functional Theory

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In order to study the coordinative behavior of doubly charged metal ions in water, a few representative metals have been chosen for theoretical studies. These are the group 2 metal ions beryllium, magnesium, and calcium and the group 12 zinc ion. The density functional method B3LYP has been used with very large basis sets. It is found that the water dipole moment and polarizabilities, which are critical for the accuracy of the binding energies, are very well reproduced provided that the basis set on the metal is included in the calculations. One of the main points of the present investigation has been to study the boundary between the first and second hydration shells. Trends of binding energies and structures are also discussed.

1. Introduction

The coordinative behavior of the magnesium, zinc, and calcium ions has attracted considerable attention lately, mainly because of their important bioinorganic roles. Systematic comparisons of crystallographic data for complexes of these cations reveal large variations in their preferred coordination geometry. For oxygen donor ligands the most common coordination numbers range from 4 to 6 for Zn^{2+},[1] and from 6 to 9 for Ca^{2+},[2,3] but for Mg^{2+} octahedral six-coordination is found to be dominating, in particular for monodentate ligands.[1−5] The present study also includes Be^{2+} hydration for comparison. The small Be^{2+} ion forms bonds to oxygen atoms with substantial covalent character and has a strong tendency to achieve its maximum coordination number of 4.[4,5] Beryllium has no biological role, and its high toxicity probably results from the ability of Be^{2+} to displace Mg^{2+} from Mg-activated enzymes due to its stronger coordination.[7]

A large number of molecular orbital (MO) calculations have been performed on hydrated ions in order to compare their structural and ligand exchange properties.[1,2,4,8−11] However, isolated clusters where all water molecules are directly coordinated to the metal ion are representative of gas-phase conditions, and it has become increasingly clear that a description relevant for aqueous solutions should include water molecules in outer shells. For example, MO calculations for a cluster consisting of a zinc ion and six water molecules have shown alternatively the $[Zn(H_2O)_4](H_2O)_2{}^{2+}$ or the $[Zn(H_2O)_6]^{2+}$ configuration to be the more stable, depending on the chosen conditions,[1,11] although experimental structure studies show the zinc ion to be hexahydrated in aqueous solution.[6,12−14] Also for simulations of ion hydration using molecular dynamics or Monte Carlo methods the problem of the nonadditivity of pairwise ion−water potentials has long been recognized.[15] For example, an early investigation resulted in a hydration number of 6 for the Be^{2+} ion instead of the experimentally determined value of 4, and various schemes have been developed for the hydrated ions in this study to include the many-body effects in the interaction potentials used.[8b,16−18]

The properties and reactions of the ions in biological systems, e.g. the possibility to replace Ca^{2+} by Mg^{2+} in proteins[3] or the flexibility of the Zn^{2+} environment in the active site of many metalloenzymes, often correspond to small energy differences.[19] Therefore, it seems necessary to develop theoretical methods and models that can satisfactorily reproduce experimental results on relatively simple systems such as aqueous solutions before attempting more than qualitative biochemical conclusions.

Continuum representations of the surrounding solvent, in particular solvent reaction field models consisting of a polarizable continuum of a dielectricum surrounding a cavity containing an $[M(H_2O)_n]^{q+}$ ion, often result in reasonable solvation energies.[8,20] However, it was found that only specific interactions give the expected *decrease* of the first sphere M−O bond length of the hydrated $[M(H_2O)_n]^{q+}$ ion because of the increasing charge separation within the hydrogen-bonded water ligands. The long-range continuum interactions had the opposite effect and caused a model-dependent *increase* of the M−O distance,[20] probably caused by the induction of multipoles in the dielectricum surrounding the charged $[M(H_2O)_n]^{q+}$ cluster, which then counteract the primary ion−multipole attraction forces. Thus, for investigating effects on geometry and energy on hydrated metal ions in solution a model should be used that properly accounts for the hydrogen bonding.

In this work we have systematically studied the effect of successive additions of water molecules around the beryllium, magnesium, calcium, and zinc ions, aiming to determine the requirements necessary for obtaining high-accuracy interaction energies, to investigate the differences in their bonding properties, and also to test the ability of the largest models we have been able to use, to explain experimental observations for aqueous solutions. The method used is a density functional theory (DFT) method termed B3LYP,[21] which is based on empirically parametrized hybrid functionals including Hartree−Fock exchange and gradient corrections of the density. Very large basis sets, much larger than those previously applied for systems of the size treated here, have been used including several

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TABLE 1: Successive (ΔE) and Total (E_{tot}) Water Binding Energies (kcal/mol) According to Eqs 2 and 3 Obtained at the B3LYP Level in $Be(H_2O)_n^{2+}$ Clusters. The Bond Distances (Å) Are Given for the First Coordination Shell (Denoted by [ ]) with the Number of Distances within Brackets When Not Equal to *n*.[a] For the Second Coordination Shell, the Average Binding Energy per Water to $[Be(H_2O)_4]^{2+}$ Is Used

complex	Be−O	ΔE	E_{tot}	q(Be)
$[Be(H_2O)]^{2+}$	1.55	146.1	146.1	+1.53
$[Be(H_2O)_2]^{2+}$	1.54	118.4	264.5	+1.06
$[Be(H_2O)_3]^{2+}$	1.59	74.2	338.7	+0.86
$[Be(H_2O)_3](H_2O)^{2+}$ [b]	1.53, 1.60(2)	37.5	376.2	+0.79
$[Be(H_2O)_3](H_2O)^{2+}$ [c]	1.57(2), 1.58	33.6	372.4	+0.81
$[Be(H_2O)_4]^{2+}$	1.65	45.7	384.4	+0.72
$[Be(H_2O)_5]^{2+}$	1.68(2), 1.70, 1.92(2)	10.8	395.2	+0.73
$[Be(H_2O)_4](H_2O)^{2+}$ [c]	1.64(2), 1.66(2)	28.2	412.5	+0.70
$[Be(H_2O)_4](H_2O)_2^{2+}$ [b,c]	1.61, 1.65(2), 1.68	26.6	437.5	+0.67
$[Be(H_2O)_4](H_2O)_2^{2+}$ [c,d]	1.64	27.2	438.8	+0.68
$[Be(H_2O)_5](H_2O)^{2+}$ [b]	1.64, 1.67, 1.68, 1.96(2)	25.2	420.4	+0.70
$[Be(H_2O)_6]^{2+}$	1.84	12.4	407.7	+0.63
$[Be(H_2O)_6](H_2O)^{2+}$ [b]	1.76, 1.84, 1.85(2), 1.87, 1.88	19.8	427.5	+0.60
$[Be(H_2O)_6](H_2O)^{2+}$ [c]	1.80, 1.81, 1.86(3), 1.89	18.2	425.9	+0.63
$[Be(H_2O)_4](H_2O)_4^{2+}$ [d]	1.63, 1.64(2), 1.66	23.9	479.8	+0.62
$[Be(H_2O)_4](H_2O)_4^{2+}$ [c,d]	1.66	22.2	473.2	+0.70
$[Be(H_2O)_4](H_2O)_5^{2+}$	1.63(2), 1.64, 1.66	22.6	497.4	+0.61
$[Be(H_2O)_4](H_2O)_6^{2+}$	1.64	21.5	513.4	+0.59
$[Be(H_2O)_4](H_2O)_7^{2+}$	1.62, 1.64(2), 1.65	20.0	524.3	+0.54
$[Be(H_2O)_4](H_2O)_8^{2+}$ [d]	1.63	19.0	536.4	+0.50

[a] The coordinates are mailed to anyone interested upon request. [b] One hydrogen bond. [c] Hydrogen bonds to two different waters. [d] Figure 1.

polarization sets and also sets of diffuse functions. The interaction energies are analyzed in terms of the charge−dipole and the charge−polarizability interactions, and high accuracy for these contributions is demonstrated. The interaction with water molecules outside the first hydration shell has also been of particular interest for the present study. Many of the results are intended to be used for future benchmark tests.

2. Computational Details

The calculations on the present metal complexes were performed in two steps. First, an optimization of the geometry was performed using the B3LYP method with hybrid functionals and double-ζ basis sets. In the second step the energy was evaluated in the optimized geometry using very large basis sets including diffuse functions and with two polarization functions on each atom. The final energy evaluation was also performed at the B3LYP level. All these calculations were performed using the GAUSSIAN-94 program.[22]

The present DFT calculations were made using the empirically parametrized B3LYP method.[21,23] The B3LYP functional can be written as

$$F^{B3LYP} = (1 - A)F_x^{Slater} + AF_x^{HF} + BF_x^{Becke} + CF_c^{LYP} + (1 - C)F_c^{VWN} \quad (1)$$

where F_x^{Slater} is the Slater exchange, F_x^{HF} is the Hartree−Fock exchange, F_x^{Becke} is the gradient part of the exchange functional of Becke,[21] F_x^{LYP} is the correlation functional of Lee, Yang, and Parr,[24] and F_x^{VWN} is the correlation functional of Vosko, Wilk, and Nusair.[25] *A*, *B*, and *C* are the coefficients determined by Becke,[21] using a fit to experimental heats of formation, although instead of using F_x^{VWN} and F_x^{LYP} in the expression above the correlation functionals of Perdew and Wang were applied when the coefficients were determined.[26]

TABLE 2: Successive (ΔE) and Total (E_{tot}) Water Binding Energies (kcal/mol) According to Eqs 2 and 3 Obtained at the B3LYP Level in $Mg(H_2O)_n^{2+}$ Clusters. The Bond Distances (Å) Are Given for the First Coordination Shell (Denoted by [ ]) with the Number of Distances within Brackets When Not Equal to *n*[a]

complex	Mg−O	ΔE	E_{tot}	q(Mg)
$[Mg(H_2O)]^{2+}$	1.94	81.5	81.5	+1.82
$[Mg(H_2O)_2]^{2+}$	1.95	70.9	152.4	+1.64
$[Mg(H_2O)_3]^{2+}$	1.97	55.1	207.5	+1.54
$[Mg(H_2O)_4]^{2+}$	1.99	43.9	251.4	+1.44
$[Mg(H_2O)_4](H_2O)^{2+}$ [b]	1.94(1), 2.00(3)	23.7	275.1	+1.41
$[Mg(H_2O)_4](H_2O)^{2+}$ [c]	1.97(2), 2.00(2)	24.4	275.8	+1.42
$[Mg(H_2O)_4](H_2O)_2^{2+}$ [c]	1.98	23.7	299.5	+1.41
$[Mg(H_2O)_5]^{2+}$	2.03(3), 2.07(2)	28.0	279.4	+1.37
$[Mg(H_2O)_5](H_2O)^{2+}$ [b]	1.99(1), 2.03(2), 2.08(2)	20.8	300.2	+1.35
$[Mg(H_2O)_5](H_2O)^{2+}$ [c]	2.01(1), 2.03(2), 2.07(2)	19.6	299.0	+1.35
$[Mg(H_2O)_6]^{2+}$	2.08	24.5	303.9	+1.29
$[Mg(H_2O)_6](H_2O)^{2+}$ [b]	2.04(1), 2.08(4), 2.10(1)	18.0	321.9	+1.27
$[Mg(H_2O)_6](H_2O)^{2+}$ [c]	2.07(2), 2.09(4)	19.0	322.9	+1.28
$[Mg(H_2O)_6](H_2O)_2^{2+}$ [d]	2.01(1), 2.08(2), 2.09(3)	15.3	337.2	+1.24
$[Mg(H_2O)_6](H_2O)_{12}^{2+}$ [f]	2.07	13.1[e]	460.8	+1.13
$[Mg(H_2O)_7]^{2+}$	2.09(2), 2.15(1), 2.22(2), 2.27(2)	3.9	307.8	+1.34

[a] The coordinates are mailed to anyone interested upon request. [b] One hydrogen bond. [c] Hydrogen bonds to two different waters. [d] Two hydrogen bonds to the same water. [e] Average binding energy per water to $[Mg(H_2O)_6]^{2+}$. [f] Figure 2.

TABLE 3: Successive (ΔE) and Total (E_{tot}) Water Binding Energies (kcal/mol) According to Eqs 2 and 3 Obtained at the B3LYP Level in $Ca(H_2O)_n^{2+}$ Clusters. The Bond Distances (Å) Are Given for the First Coordination Shell (Denoted by [ ]) with the Number of Distances within Brackets When Not Equal to *n*[a]

complex	Ca−O[b]	ΔE	E_{tot}	q(Ca)
$[Ca(H_2O)]^{2+}$	2.26	56.9	56.9	+1.93
$[Ca(H_2O)_2]^{2+}$	2.28	47.5	104.4	+1.84
$[Ca(H_2O)_3]^{2+}$	2.30	42.0	146.4	+1.78
$[Ca(H_2O)_4]^{2+}$	2.32	35.6	182.0	+1.71
$[Ca(H_2O)_4](H_2O)^{2+}$ [c]	2.25(1), 2.32(3)	20.7	202.7	+1.69
$[Ca(H_2O)_4](H_2O)^{2+}$ [d]	2.28(2), 2.32(2)	22.1	204.1	+1.70
$[Ca(H_2O)_4](H_2O)_2^{2+}$ [d]	2.29	21.6	225.7	+1.69
$[Ca(H_2O)_5]^{2+}$	2.33(2), 2.34(1), 2.36(2)	27.7	209.7	+1.64
$[Ca(H_2O)_5](H_2O)^{2+}$ [c]	2.28(1), 2.33(2), 2.36(2)	18.5	228.2	+1.63
$[Ca(H_2O)_5](H_2O)^{2+}$ [d]	2.31(2), 2.33(1), 2.36(4)	18.8	228.5	+1.63
$[Ca(H_2O)_6]^{2+}$	2.37	24.7	234.4	+1.56
$[Ca(H_2O)_6](H_2O)^{2+}$ [c]	2.32(1), 2.37(5)	16.3	250.7	+1.55
$[Ca(H_2O)_6](H_2O)^{2+}$ [d]	2.34(2), 2.37(3), 2.38(1)	17.6	252.0	+1.55
$[Ca(H_2O)_6](H_2O)_{12}^{2+}$ [e]	2.35	12.9[f]	389.2	+1.43
$[Ca(H_2O)_7]^{2+}$ [e]	2.38(2), 2.41(1), 2.42(2), 2.44(2)	13.8	248.2	+1.54
$[Ca(H_2O)_8]^{2+}$ [e]	2.39(2), 2.43(2), 2.45(2), 2.64(2)	8.8	257.0	+1.49

[a] The coordinates are mailed to anyone interested upon request. [b] A basis set correction of −0.05 Å has been added; see text. [c] One hydrogen bond. [d] Hydrogen bonds to two different waters. [e] Figure 3. [f] Average binding energy per water to $[Ca(H_2O)_6]^{2+}$.

The B3LYP energy calculations were made using the large 6-311+G(2d,2p) basis sets in the GAUSSIAN-94 program. This basis set has two sets of polarization functions on all atoms and also diffuse functions which are found to be important when interactions with oxygen-containing systems such as water are studied. In the B3LYP geometry optimizations a much smaller basis set, the LANL2DZ set of the GAUSSIAN-94 program was used. For the magnesium, calcium, and zinc atoms this

TABLE 4: Successive (ΔE) and Total (E_{tot}) Water Binding Energies (kcal/mol) According to Eqs 2 and 3 Obtained at the B3LYP Level in $Zn(H_2O)_n{}^{2+}$ Clusters. The Bond Distances (Å) Are Given for the First Coordination Shell (Denoted by [ ]) with the Number of Distances within Brackets When Not Equal to *n*[a]

complex	Zn−O	ΔE	E_{tot}	q(Zn)
$[Zn(H_2O)]^{2+}$	1.90	101.9	101.9	+1.74
$[Zn(H_2O)_2]^{2+}$	1.91	86.6	188.5	+1.56
$[Zn(H_2O)_3]^{2+}$	1.96	53.6	242.1	+1.42
$[Zn(H_2O)_4]^{2+}$	2.01	41.2	283.3	+1.33
$[Zn(H_2O)_4](H_2O)^{2+}$ [c]	1.99(2), 2.02(2)	25.0	308.3	+1.32
$[Zn(H_2O)_4](H_2O)_2^{2+}$ [c]	2.00	24.2	332.5	+1.31
$[Zn(H_2O)_4](H_2O)_8^{2+}$ [d]	1.98	17.5[e]	423.1	+1.18
$[Zn(H_2O)_5]^{2+}$	2.04(2), 2.06(1), 2.11(2)	24.0	307.3	+1.29
$[Zn(H_2O)_5](H_2O)^{2+}$ [b]	2.00(1), 2.05(2), 2.13(2)	21.5	328.8	+1.27
$[Zn(H_2O)_5](H_2O)^{2+}$ [c]	2.04(2), 2.05(1), 2.11(2)	20.3	327.6	+1.27
$[Zn(H_2O)_6]^{2+}$	2.12	21.8	329.1	+1.25
$[Zn(H_2O)_6](H_2O)^{2+}$ [b]	2.06(1), 2.12(4), 2.14(1)	18.1	347.2	+1.23
$[Zn(H_2O)_6](H_2O)^{2+}$ [c]	2.10(2), 2.12(1), 2.13(3)	18.3	347.4	+1.24
$[Zn(H_2O)_6](H_2O)_6^{2+}$ [d]	2.11	14.7 [f]	417.5	+1.19
$[Zn(H_2O)_6](H_2O)_{12}^{2+}$ [g]	2.11	12.4 [f]	477.4	+1.14

[a] The coordinates are mailed to anyone interested upon request. [b] One hydrogen bond. [c] Hydrogen bonds to two different waters. [d] Figure 4. [e] Average binding energy per water to $[Zn(H_2O)_4]^{2+}$. [f] Average binding energy per water to $[Zn(H_2O)_6]^{2+}$. [g] Figure 2.

means that a nonrelativistic ECP according to Hay and Wadt was used.[27] The metal valence basis set used in connection with this ECP is essentially of double-ζ quality. The remaining atoms are described by standard double-ζ basis sets.

At the final geometries, zero-point vibrational effects were obtained by calculating Hessians at the Hartree−Fock level. As usual, the frequencies were scaled by 0.90. This procedure was tested against caclulated B3LYP Hessians in some representative cases and was found to work very well with one exception, namely the isolated water molecule, for which the zero-point energy becomes too small. Instead, the zero-point energy for water, 13.42 kcal/mol, was taken from a B3LYP calculation using the large 6-311+G(2d,2p) basis at a geometry optimized using the same large basis set.

3. Results and Discussion

There are two objectives of the present paper. The first one concerns the energetics, and the second one the structures. These two aspects will be discussed in two different subsections below. The main information of the water binding energies and M−O bond distances within the first hydration shell for clusters of type $[M(H_2O)_n](H_2O)_m{}^{2+}$ are gathered in Tables 1−4 for the Be^{2+}, Mg^{2+}, Zn^{2+}, and Ca^{2+} ions, respectively. The total, E_{tot}, and successive, ΔE, water binding energies in Tables 1−4 are obtained according to

$$E_{tot} = E(M^{2+}) + nE(H_2O) - E\{M(H_2O)_n{}^{2+}\} \tag{2}$$

$$\Delta E = E\{M(H_2O)_{n-1}{}^{2+}\} + E(H_2O) - E\{M(H_2O)_n{}^{2+}\} \tag{3}$$

Details of the different types of optimized geometries obtained can be seen in Figures 1−4. All these results are obtained at the B3LYP level as described in section 2.

3.1. Water Binding Energies in $[M(H_2O)_n](H_2O)_m{}^{2+}$ Clusters. One main purpose of the present study was to investigate the computational requirements for obtaining accurate water binding energies in metal complexes.

3.1.1. Basis Set Effects. The interaction between water and a charged metal complex is mainly electrostatic, and it is therefore important to describe the multipole moments and polarizability of water correctly. This is a very difficult problem requiring very large basis sets. The leading terms of the interaction energy can be written

$$\Delta E = \mu_z q R^{-2} + {}^1\!/_2 \alpha_{zz} q^2 R^{-4} \tag{4}$$

where μ_z is the dipole moment, α_{zz} the polarizability component, and z the axis between the metal ion and oxygen. The experimental values for a free water molecule are 1.85 D and 9.62 $a_0{}^3$.[28,29] In a recent study of the interaction between a lithium ion and water,[30] the first term was found to contribute about 80% and the second term about 20% of the interaction energy at the equilibrium geometry. Higher order terms, like those arising from the interaction of the water quadrupole moment, contribute a few percent each, mostly canceling each other. In that study, exactly the same methods were used as in the present one. The dipole moment and polarizability are known to be hard to calculate, and the values obtained at the B3LYP level using a standard double-ζ basis set of 2.44 D and 5.14 $a_0{}^3$ are not surprising. These values correspond to errors of 32% and 47%, and errors of the same relative size can therefore be expected for the metal ion−water interaction energies. Using the large basis set 6-311+G(2d,2p), the values are substantially improved to 1.96 D and 7.96 $a_0{}^3$, respectively. However, the relative errors of 6% and 17% are still surprisingly large.

If the relative errors given above for the 6-311+G(2d,2p) basis are translated to errors in interaction energies, it is clear that results of quantitative accuracy would not be obtained even with these very large basis sets. Fortunately, the situation is not as severe as it may appear. In the recent study on lithium ions mentioned above,[30] a rather surprising finding was noted. A basis set at a distance of 1.83 Å from oxygen (that is at the position a lithium ion would have taken in a lithium complex) was included *without* the actual lithium atom when calculating the water dipole moment and polarizability of water. This ghost basis set resulted in much improved values of 1.88 D and 9.27 $a_0{}^3$ with relative errors of only 2% and 4%, respectively. In this context it is also of interest that the actual B3LYP interaction energy obtained for the Li^+−H_2O system using the large basis set is in perfect agreement with experiment, differing by only 1%. The accuracy obtained for the interaction energy is thus much better in line with the values for the dipole moment and polarizability calculated with the ghost basis than without this basis. The effect of a ghost basis on another atom is normally termed a basis set superposition error (BSSE). However, in this case the dominating effect is not on the total energy but on properties such as the dipole moment and the polarizability. Only when the water molecule interacts with a system with a charge distribution such as an ion will these effects give rise to changes in the total energy. These effects of the ghost basis can therefore not be removed by a counterpoise correction, as is normally done with the total energy BSSE. The present experience on this type of *ghost basis effect* is quite definitely that it *improves the results considerably*, and from a pragmatic point of view it should therefore not be removed. Only further experience will tell if this is true in general. Even from a fundamental viewpoint the removal of the ghost basis set effect on the properties of water is questionable, since these basis functions describe both charge-transfer effects and a region of the water molecule of such a diffuse nature that a purely electrostatic picture is hardly valid anyway for normal equilibrium distances.

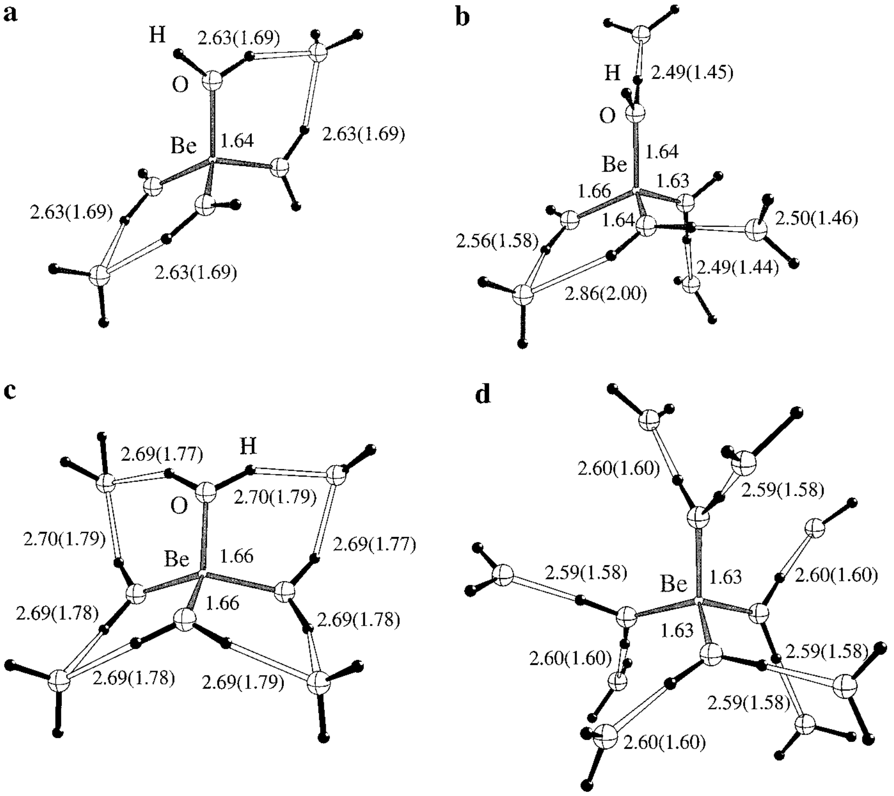

Figure 1. Be^{2+}−water clusters. Open bonds denote O···H hydrogen bonds with O···O(O···H) bond lengths in angstroms. (a) $[Be(H_2O)_4](H_2O)_2^{2+}$, (b) $[Be(H_2O)_4](H_2O)_4^{2+}$, (c) $[Be(H_2O)_4](H_2O)_4^{2+}$ (all water with 2 hydrogen bonds), (d) $[Be(H_2O)_4](H_2O)_8^{2+}$.

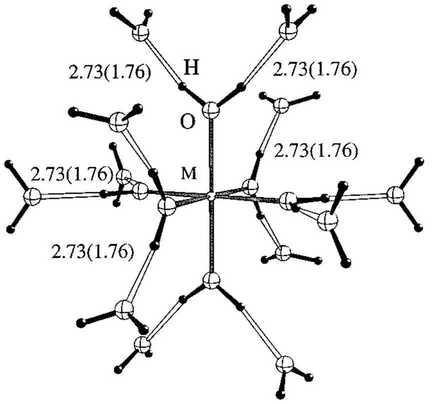

Figure 2. Molecular geometry of $[M(H_2O)_6](H_2O)_{12}^{2+}$, M = Mg and Zn, from the DFT calculation. Open bonds denote O···H hydrogen bonds with O···O(O···H) bond lengths in angstroms.

For the largest systems discussed here the 6-311+G(2d,2p) basis was too extensive to be used, and smaller basis sets were therefore tested. These results are presented here before the discussion of the binding energies in the tables, mainly to get an idea of the sensitivity and accuracy of the results. The first test case was $Mg(H_2O)^{2+}$ where a 6-311+G(1d,1p) basis was used on Mg throughout the tests. The water binding energy is then 81.8 kcal/mol (without zero-point correction) using the 6-311+G(2d,2p) basis on water. Removing the most diffuse functions of the 6-311+G(2d,2p) basis increases the binding energy significantly by 5.7 kcal/mol to 87.5 kcal/mol. It is in fact better to remove the second polarization set and use the 6-311+G(1d,1p) basis, which increases the binding energy only by 1.5 kcal/mol to 83.3 kcal/mol. These trends are obviously enlarged for the next test case, $Mg(H_2O)_6^{2+}$, where the total binding energy is increased by as much as 30.4 kcal/mol, from 318.4 kcal/mol to 348.8 kcal/mol, by removing the diffuse functions from the largest water basis. In contrast, removing the second polarization set changes the total interaction energy only by 2.8 kcal/mol down to 315.6 kcal/mol. This latter effect furthermore shows that the basis set effects are not just additive compared to $Mg(H_2O)^{2+}$.

The conclusions from these studies is that *the diffuse set of functions on water is definitely needed for obtaining water binding energies of quantitative accuracy*, but not the second set of polarization functions. To remove further polarization functions is clearly not possible without significant loss of accuracy. As an example, the binding energy for $Mg(H_2O)_6^{2+}$ using the double-ζ type basis LANL2DZ is 59.6 kcal/mol too large. Still, this basis set is good enough in most cases to be used for obtaining accurate geometries, as discussed below in the next subsection.

Two further results of basis set effects on interaction energies are also of general interest. As discussed below, the bond distances for the calcium complexes are generally found to be about 0.05 Å longer than experimental values when using the double-ζ type LANL2DZ basis. Two tests on $Ca(H_2O)_6^{2+}$ were made to investigate the cause of this effect. First, the ECP for calcium was replaced by an all-electron basis set, but this gave a very small effect on the bond distance of +0.01 Å and on the binding energy of 0.26 kcal/mol (0.04 kcal/mol per water). Second, d functions were added. This was found to have the desired effect on the bond distances shortening them by 0.05 Å, but again the effect on the energy was small, 0.97 kcal/mol (0.16 kcal/mol per water). The most important conclusion that can be drawn from these results is that the coupling between the geometry and the interaction energy is very weak. Practically no gain in accuracy (0.97 kcal/mol for $Ca(H_2O)_6^{2+}$) for the interaction energy is obtained by improving the Ca−O distance by as much as 0.05 Å. In contrast, the inclusion of diffuse functions has very large effects on the interaction energy

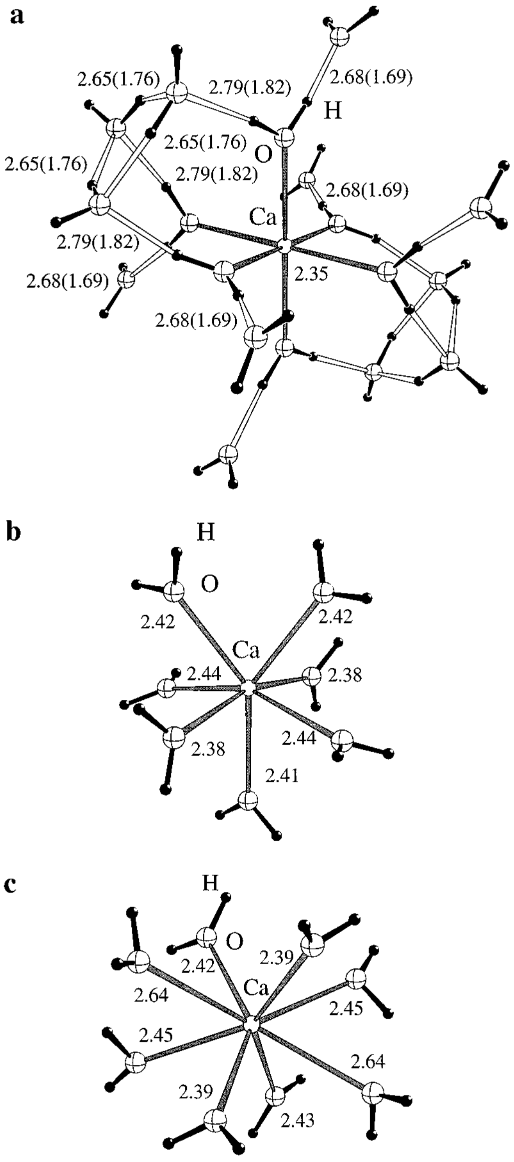

Figure 3. Ca^{2+}−water clusters. Molecular geometry of (a) $[Ca(H_2O)_6](H_2O)_{12}{}^{2+}$ (b) $[Ca(H_2O)_7]^{2+}$, (c) $[Ca(H_2O)_8]^{2+}$. Bond lengths in angstroms.

(30.4 kcal/mol for $Mg(H_2O)_6{}^{2+}$, see above) and probably very small effects on the geometry, in light of the very good agreement with experimental structures obtained without these functions (see below).

Finally, basis set effects were tested on interaction energies for hydrogen bonds which are present in many of the current systems. Since these bonds are much weaker than the charge-induced interaction energies discussed mostly in this paper, more care is needed to obtain the same relative accuracy. However, there is no general problem of obtaining accurate results using the B3LYP method. The water dimer binding energy is obtained as 2.8 kcal/mol (including zero-point vibrational effects) using the 6-311+G(2d,2p) basis set both for the geometry and for the interaction energy, which must be considered a highly satisfactory result when compared to the experimental value of 3.6 ± 0.5 kcal/mol.[31] The very sensitive O−O distance (experimental value 2.98 Å)[32] is found to be 2.92 Å at the same level. Using the small LANL2DZ basis, a much shorter distance of 2.74 Å is obtained, but again, this should have only a very small effect on the total interaction energies.

3.1.2. Metal Ion First-Shell Water Binding Energies. In previous studies done by others on similar systems, the Hartree−Fock or MP2 methods have usually been employed.[1,2,4,9] The values obtained for the water binding energies (Tables 1−4) in the present study using the B3LYP method are found to be somewhat different from those obtained previously. For example, our studies of the beryllium ion generally yield larger water binding energies than those obtained by Bock et al.[4a] using the MP2 method. To find the reason for the difference, some test calculations were set up in which the MP2 method was used together with the same basis set (6-311+G(2d,2p)) and geometry as in our B3LYP calculation. For $[Be(H_2O)_2]^{2+}$ we obtained a total binding energy of 264.5 kcal/mol at the B3LYP level, but only 255.5 kcal/mol when using the MP2 method. Our MP2 value is, however, in good agreement with the largest basis set value 255.3 kcal/mol (adjusted to 0 K) obtained by Bock et al.[4a] Thus, the conclusion is that the difference in the results arises from the different methods used, and not from the basis sets or geometries. A likely origin of this is a difference in the description of the electrostatic moment and polarizabilities. As shown above, the B3LYP method gives excellent values for these quantities provided that a ghost basis set on the metal position is included. With the above background it seems clear that the interaction energies given in Tables 1−4 should be quite accurate since the large 6-311+G(2d,2p) basis set was used in almost all cases (except for the cases with a full second hydration shell included, with an almost equally large basis set). The general features of the interaction energies within the first hydration shell for the different ions are displayed in Figure 5.

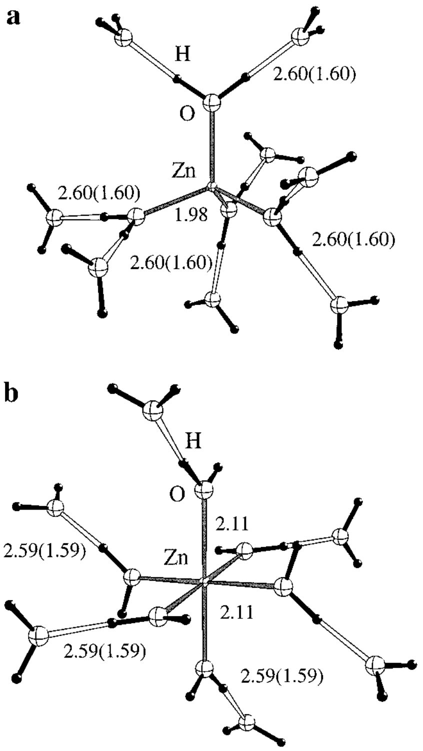

Figure 4. Molecular geometry of (a) $[Zn(H_2O)_4](H_2O)_8{}^{2+}$ and (b) $[Zn(H_2O)_6](H_2O)_6{}^{2+}$ clusters with bond lengths in angstroms.

Most of the trends seen in Figure 5 have quite obvious origins, and many of these have been noted in previous work. There is, for example, a strongly decreasing trend for the water binding energies, originating from an increasingly saturated charge transfer as more water molecules are added to the first hydration shell. This is a clear manifestation of the nonpairwise additivity of the cation−water interaction terms.[15,16,33] This leads to very similar binding energies, 24.5, 24.7, and 21.8 kcal/mol, for the

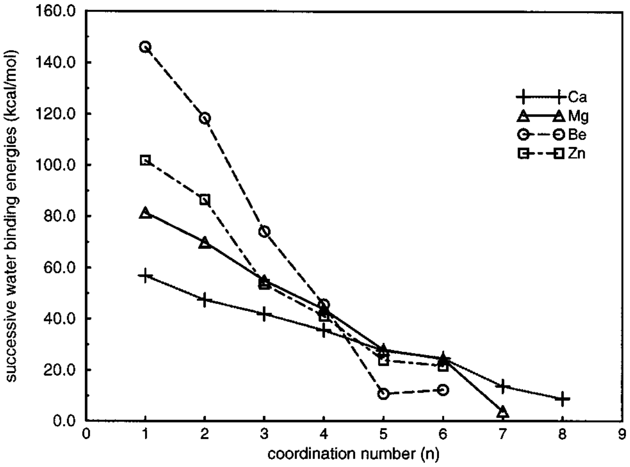

Figure 5. Water binding energies for stable $[M(H_2O)_n]^{2+}$ clusters (M = Be, Mg, Ca, Zn).

sixth water of the first shells of the Mg^{2+}, Ca^{2+}, and Zn^{2+} ions, respectively. Also for Be^{2+} the fourth water binding energy is quite similar to the corresponding energies of Mg^{2+} and Zn^{2+}. These values are 45.7, 43.9, and 41.2 kcal/mol, respectively. In contrast, the first water binding energy varies very much between the ions and follows the size of the ion in line with eq 4. It is very large with 146.1 kcal/mol for the small Be^{2+} ion and much smaller with only 56.9 kcal/mol for the large Ca^{2+} ion. The corresponding M−O distances are 1.55 and 2.26 Å, respectively. It is clear from these numbers that a description of the interaction energies solely by the electrostatic expression in eq 4 is not valid for most cases in the tables. Charge-transfer effects are definitely needed to explain most trends.[34] For singly charged ions, increasing Pauli repulsion between the water ligands and core polarization effects have sometimes been used to explain the decreasing water binding energy trend.[29,35] This is not possible for doubly charged ions where charge transfer from water over to the s,p orbitals of the metal ion is a dominating effect.

One of the main points of the present study on isolated ion−water clusters was to study the interface between the first and second hydration shells. Starting with beryllium, it is clear that four-coordination is strongly preferred. There is an abrupt energy decrease going from the fourth to the fifth water in the first shell, from 45.7 kcal/mol to 10.8 kcal/mol. Also, if beryllium is kept three-coordinated, the binding energy of the fourth ligand in the second shell of 37.5 kcal/mol is not competitive with the 45.7 kcal/mol obtained when the fourth ligand is in the first shell.

The optimal coordination for magnesium is also rather clear but not as obvious as for beryllium. The sixth water in the first coordination shell is bound by 24.5 kcal/mol, while the binding energy is 20.8 kcal/mol if it is placed in the second shell. On the other hand, increasing the coordination to seven is very unfavorable, with the seventh water being bound by only 3.9 kcal/mol. If this water is placed in the second shell, the binding energy is 19.0 kcal/mol.

For calcium the situation is rather similar to the one for magnesium, but with an increased possibility for higher coordination. The sixth water in the first shell is bound by 24.7 kcal/mol, while if it is placed in the second shell, it is only 18.8 kcal/mol. If a seventh water is placed in the first shell, the binding energy is 13.8 kcal/mol, which is smaller than the binding energy of 17.6 kcal/mol obtained if it is placed in the second shell. This energy difference is small enough that seven-coordination might occur in solution; see the discussion below.

For a water cluster around a zinc ion the boundary between the first and the second shell is very diffuse. With six water molecules, four-coordination is actually preferred, with a total binding energy of 332.5 kcal/mol. The total binding energy for five-coordination is 328.8 kcal/mol, and for six-coordination it is 329.1 kcal/mol. The fifth water molecule is bound by 24.0 kcal/mol if placed in the first shell and by 25.0 kcal/mol in the second shell. The sixth water is bound by 21.8 kcal/mol in the first shell, by 21.5 kcal/mol if placed outside a first shell with five waters, and by 24.2 kcal/mol if placed outside four waters in a 4+2 configuration (Table 4). It is clear that a doubly charged zinc ion must be very flexibly coordinated in an actual water solution.

3.1.3. Second-Shell Water Coordination. The coordination geometry of the first ligand in the second shell has also been investigated to some extent. Two cases were tried. In the first one, this water is bound to one water molecule in the first shell through one hydrogen bond. In the second one, this water is bound to two water molecules in the first shell through two hydrogen bonds. The choice between these different types of bonding varies depending on coordination and metal ion. For beryllium, one hydrogen bond is preferred for three-, five-, and six-coordination, while two hydrogen bonds are preferred for four-coordination.

For magnesium, the situation is different, and two hydrogen bonds are instead preferred for four- and six-coordination, while for five-coordination one hydrogen bond is better. For calcium two hydrogen bonds are preferred in all cases studied, that is for four-, five-, and six-coordination. For zinc finally two hydrogen bonds are preferred for four- and six-coordination, while one hydrogen bond is preferred for five-coordination. The trends of these choices are thus rather unclear, although there is a slight tendency for preferring one hydrogen bond when the ionic radius is small, as noted from the difference between beryllium, which is small, and calcium, which is large. However, the energy differences between these modes of coordination are in general so small that in an aqueous solution both structures will be populated for all these metal ions.

The final comments on the water binding energies will be made for the cases where an entire second shell is treated. For magnesium, calcium, and zinc this means 12 water molecules outside a first shell with 6 water molecules. As indicated above, these calculations are so large that a slightly smaller basis without the second polarization set had to be used, but this does not affect the binding energies very much. The ion−oxygen distances for the first shells are in these cases 2.07 Å for magnesium, 2.35 Å for calcium, and 2.11 Å for zinc. These differences do not lead to significant differences in the average water binding energy for the second-shell water molecules, which are 13.1, 12.9, and 12.4 kcal/mol for magnesium, calcium, and zinc, respectively, although the structure of the second shell around calcium is different; cf. Figures 2 and 3a. It is interesting to note that these values are significantly smaller than the binding energies for the first water molecules placed outside the first shell, which are 19.0 kcal/mol for magnesium, 17.6 kcal/mol for calcium, and 18.3 kcal/mol for zinc. This is not surprising since for a single water the charge polarization of the first shell can be organized much more favorably than if this shell simultaneously has to adjust for all waters in the second shell. It can also be noted that even if the average binding energy is much smaller than the one for the first shell, it is still more than 3 times as large as the interaction energy between two isolated water molecules of 3.6 kcal/mol. Definite struc-

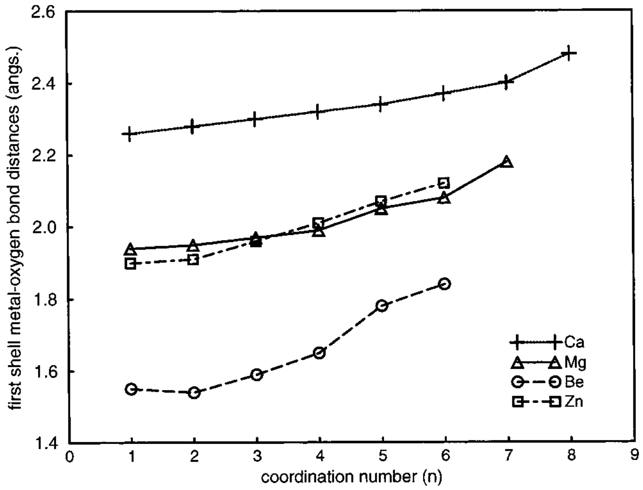

Figure 6. Mean metal−oxygen bond lengths for $[M(H_2O)_n]^{2+}$ clusters (M = Be, Mg, Ca, Zn).

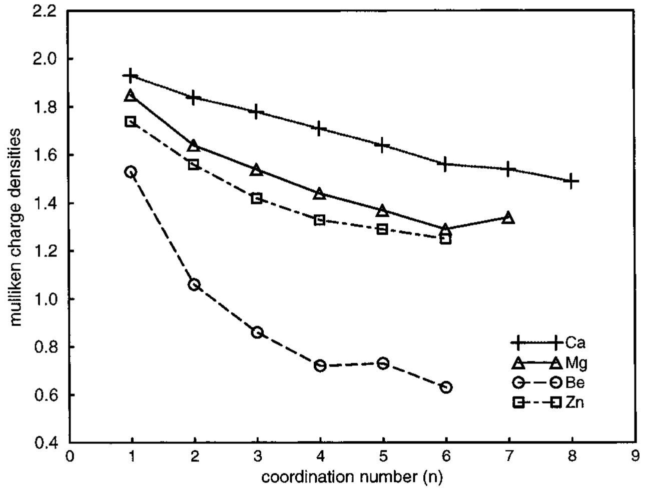

Figure 7. Mulliken population analyses of metal atom charges for $M(H_2O)_n]^{2+}$ clusters (M = Be, Mg, Ca, Zn).

tures including two solvation shells are also reported from structural studies of these ions in aqueous solution.[14]

For beryllium, eight water molecules are placed outside a first shell with only four waters. This leads to a large average binding energy of 19.0 kcal/mol for a second shell water.

For the zinc ion the effect of the second shell on the coordination geometry was investigated by calculating the energies of a cluster with 12 waters in 4+8 and 6+6 configuration in the first and second shell, respectively (Figure 4). However, the four-coordinated zinc ion with a fully hydrogen-bonded second shell showed an even greater stability versus six-coordination with an energy difference of 5.6 kcal/mol. Evidently, an even larger cluster of water molecules is needed to represent the conditions in a dilute solution. An important factor for the stabilization of six-coordination could be the different entropy contributions from the modified water structure around the four- and six-coordinated ions. The stability of the four-coordinated zinc ion is also observed in other studies.[1,11] Interestingly, it has been proposed that zinc ions are four coordinated in concentrated solutions when the mole fraction of water is decreased.[6]

3.2. The Structures of $[M(H_2O)_n](H_2O)_m{}^{2+}$ Clusters. *3.2.1. $[Mg(H_2O)_n]^{2+}$ (n = 1−7).* Stable structures were found for hydrated magnesium ions with $n = 1-7$, as shown in Figure 5. The mean Mg−O bond lengths increased monotonically from 1.94 to 2.08 Å (Figure 6), while the net charge on the magnesium atom decreases, as n increases from 1 to 6 (Table 2 and Figure 7). Addition of the seventh water, however, gives only a small increase in the binding energy ($\Delta E = 3.9$ kcal/mol) but increases the mean Mg−O distance to 2.19 Å and decreases the charge transfer to the magnesium ion with +0.05 (Figures 4−6). The fifth complex, $[Mg(H_2O)_5]^{2+}$, has an almost regular trigonal bipyramidal Mg−O geometry (equatorial bonds 2.03 Å, axial 2.07 Å), while the optimized structure of the hexahydrated $[Mg(H_2O)_6]^{2+}$ cluster has T_h symmetry, with six equal Mg−O bonds at 2.08 Å.

The previous molecular orbital study gave similar results,[4b,5] although no stable 7-hydrate could be found, and the distances obtained from optimizations using RHF and MP2 calculations and 6-31G* basis sets generally are 0.02−3 Å longer.

3.2.2. $[Zn(H_2O)_n]^{2+}$ (n = 1−6). All hydrated zinc ions with up to six directly coordinated water molecules form stable structures, as verified by frequency analyses. The average Zn−O distance is shorter in the two first complexes, 1.90 and 1.91 Å, respectively, than for magnesium, but then increases almost uniformly with 0.05 Å for every step as n increases from 2 to 6 (Figure 6). At the fourth complex the Zn−O distances are nearly equal to those for $[Mg(H_2O)_4]^{2+}$ and become 0.05 Å longer for the hexahydrated clusters, with Zn−O 2.12 Å in $[Zn(H_2O)_6]^{2+}$.

The smaller increase in the Zn−O bond length as well as the smaller relative decrease in the water binding energy as compared to magnesium at the formation of the second complex (Figures 5 and 6) shows a stabilization of the $[Zn(H_2O)_2]^{2+}$ cluster. This is certainly connected to the higher covalency of the zinc−oxygen bonds, probably with some involvement of the 3d orbitals giving rise to a preference for linear coordination, similar to but weaker than that frequently found for mercury(II) ions. The zinc ion clearly forms more covalent M−O bonds than magnesium, with the largest amount of charge transfer in all of the hydrated clusters; cf. Figure 7.

3.2.3. $[Ca(H_2O)_n]^{2+}$ (n = 1−8). The calcium ion is found to form stable hydrates with up to eight water molecules. The Ca−O bond length increases steadily for increasing n values, with its largest step at the formation of $[Ca(H_2O)_8]^{2+}$, and the water binding energies show a monotonic decrease (Figures 5, 6). The charges transferred to the calcium ion are also decreasing monotonically up to $n = 8$, but are much smaller than for the corresponding hydrates of the magnesium and zinc ions (Figure 7).

3.2.4. $[M(H_2O)_n](H_2O)_m{}^{2+}$ (m = 1, 2). A number of hydrates with four, five, or six (=n) water molecules in the inner sphere and one or two (=m) water molecules in the second sphere were examined and found to be stable with hydrogen bonds to one or two of the first-shell water molecules.

For the $[M(H_2O)_4](H_2O)^{2+}$ hydrates with M = Be, Mg, Ca, and Zn, the energies are generally similar for one or two hydrogen bonds from the first-shell to the second-shell water molecule, with slightly lower energy when a symmetrical hydrogen bond is formed from two water molecules (Mg, Ca). In all cases the polarizing effect of the hydrogen bond is evident from the shortening of the M−O bonds of the hydrogen-bonded first shell water ligand, 0.06−7 Å with one bond formed and 0.03−4 Å for two bonds.

With two water molecules in the second shell of the $[M(H_2O)_4](H_2O)_2{}^{2+}$ cluster, each hydrogen bonded from two inner shell water molecules, two symmetrical six-membered rings (C_{2v} symmetry, cf. Figure 1a for Be) are formed in which the O−M−O angle is reduced to 99.7°, 90.8°, 90.6°, and 82.7°

for Be, Mg, Zn, and Ca, respectively. The shortening of the M−O bonds is only 0.01 Å for Mg and Zn, but 0.03 Å for Ca.

For the isolated $[M(H_2O)_5](H_2O)^{2+}$ clusters with M = Mg, Ca, and Zn, the almost trigonal pyramidal arrangement of the M−O bonds found in all cases is expected from electrostatic reasons and agrees with previous results from SCF calculations.[4,5,9] The energy difference from a square pyramidal (SQP) $M-O_5$ conformation is small, however,[9] and when a hydrogen bond is formed, the shortened M−O bond makes the SQP structure the more stable. Also with two hydrogen bonds formed to the second-sphere water a SQP structure is stable, but the less favorable orientation of the hydrogen atoms imposed by the hydrogen bonding makes this structure higher in energy than the ones with a single hydrogen bond for the small zinc and magnesium ions, while for the calcium ion the energies are equal.

For $[M(H_2O)_6](H_2O)^{2+}$ the octahedral $M-O_6$ structure is only slightly distorted with the previously noted shortenings of the M−O bonds occurring for the hydrogen-bonded water molecule, and except for the large calcium ion a slight trans-effect is noticeable on the opposite M−O bond length (+0.02 Å). If two first-shell water molecules form hydrogen bonds to the second-shell water, the energy is slightly lower in all cases despite a more unfavorable hydrogen atom configuration, because of the larger distances than for the pentahydrated ions.

Several conformations with one or two additional outer shell water molecules have been investigated for the hexahydrated magnesium ion, $[Mg(H_2O)_6](H_2O)_m{}^{2+}$ ($m = 2, 3$). A substantial shortening (Mg−O 0.07 Å shorter than for $[Mg(H_2O)_6]^{2+}$ in T_h symmetry) occurs for the symmetrically bonded (with two hydrogen bonds to different water molecules) first-shell water, which is lower in energy than if a water chain is formed of the two second-shell water molecules (Table 2). Adding another water to the chain does not have any noticeable effect on the first-shell structure. As for a single second-shell water, the lowest energy is obtained when two hydrogen bonds are formed from two first-shell water molecules, even if the hydrogen atom configuration of the $Mg(H_2O)_6{}^{2+}$ cluster then is less favorable than in T_h symmetry.

A complete hydrogen-bonded second sphere was introduced with full geometry optimization for $[M(H_2O)_6](H_2O)_{12}{}^{2+}$, M = Mg, Zn; cf. Figure 2. When all protons of the first-shell water molecules are hydrogen bonded to the second shell, only a small influence on the M−O bonds can be seen, which for all ions are shortened by 0.01−0.02 Å; cf. Tables 1−4. The large effects previously encountered with asymmetrical hydrogen bonds in the clusters are evidently caused by the polarized water ligand giving rise to an induced polarization of the metal ion.

4. Comparisons with Experimental Results

Statistical analyses of metal ion−oxygen atom bond distributions from crystal structures show that the M−O distances increase as expected with increasing coordination number and that the flexibility of the calcium coordination is much higher than that of magnesium.[3] Special attention has been given to the importance of the influence of the second sphere on the coordination number of the hydrated magnesium and calcium ions. All the crystallographically determined magnesium(II) aqua ions are six-coordinated, with a mean Mg−O bond length of 2.066(2) Å and a mean hydrogen-bonded O···O distance to second-sphere oxygen atoms of 2.784(6) Å,[3] in satisfactory agreement with our corresponding calculated values for $[Mg(H_2O)_6](H_2O)_{12}{}^{2+}$, 2.07 and 2.74 Å (Table 2).

The average Zn−O distance for $[Zn(H_2O)_6]^{2+}$ ions in crystal structures is approximately 2.09 Å, and a diffraction study on concentrated aqueous perchlorate solutions show the zinc ion to be hexahydrated, with a Zn−O distance of 2.10(1) Å.[12] This is again in good agreement with the calculated value, 2.11 Å (Table 4), for $[Zn(H_2O)_6](H_2O)_{12}{}^{2+}$. Even though the binding energies of the $[Zn(H_2O)_4](H_2O)_m{}^{2+}$ clusters are found to be slightly larger than for the corresponding $[Zn(H_2O)_6](H_2O)_{m-2}{}^{2+}$ clusters despite the large water basis sets used in the present study, the experimental Zn−O distances show that the zinc ions are predominantly six-coordinated in aqueous solution.[6]

Our optimized Ca−O distances using the double-ζ type LANL2DZ basis set are, as already mentioned above, generally longer than the experimental for the same hydration number. The reason for this is that d functions on calcium are of some importance and these functions are missing in the LANL2DZ basis set. Previously, it was also shown for the $[Ca(H_2O)_2]^{2+}$ complex with the use of medium-sized basis sets that the addition of d functions caused a deviation from linear geometry, and a small decrease in the Ca−O distance was also noted.[36] The O−Ca−O angle was optimized to 130° but with an extremely shallow potential. Inclusion of electron correlation reduces the O−Ca−O angle even further.[2]

When d functions are added in the present computations, there is a general reduction of the Ca−O bond distances by 0.05 Å. Rather than performing a very costly reoptimization of all geometries, this correction was instead introduced for all bond distances in Table 3. The corrected Ca−O distance is then 2.37 Å for the six-coordinated Ca^{2+} ion. This is admittedly a rather uncertain procedure, and ideally a reoptimization should be done.

The empirical valence bond theory often used to compare the metal−ligand bond character in crystal structures has been used in conjunction with statistical analyses of a large number of crystal structures to estimate an expected difference between a single calcium(II)−water and magnesium(II)−water bond of 0.295(5) Å.[3] Our calculated difference is reduced to about 0.32 Å (Tables 2, 3), after the correction for the d function basis set effect described above.

For calcium(II) aqua ions in crystal structures corresponding n, Ca−O, and hydrogen-bonded O···O values are 6, 2.334(9), 2.816(29); 7, 2.403(5), 3.046(7); 8, 2.481(6), 2.852(4); 9, 2.521(4).[3] Preliminary results from a recent EXAFS study on an 1 M aqueous $CaCl_2$ solution showed an asymmetric distribution of the Ca−O distances with the mean at about 2.45 ± 0.03 Å, which would indicate a coordination number in solution between 7 and 8.[37] For the interpretations of the IR measurements discussed below, a hydration number of 9 was assumed.[38] It seems clear that the actual first-shell hydration number in solution is greater than the value 6 obtained for the isolated clusters in this study, but that the energy differences must be small with a very flexible coordination geometry in solution. An indication of this gives the geometry optimization of a cluster of 18 water molecules (6 O_I and 12 O_{II}) around the Ca^{2+} ion where six of the second-shell water molecules actually form two lone-pair hydrogen bonds each (Figure 3a) and form two three-membered rings with strong internal hydrogen bonding. The hydrogen bond O···O length from a coordinated water molecule to a trigonally oriented single water molecule is typically 0.1 Å shorter than the bonds to the lone-pairs of the three-rings and indicates the importance of a relevant description of the water structure in the outer shells around the ions in aqueous solution.

Refinements of corresponding clusters $[M(H_2O)_6](H_2O)_{12}{}^{2+}$ for M = Mg and Zn give trigonal hydrogen bond geometry in nearly T_h symmetry; cf. Figure 2. The calculated oxygen−

oxygen distances of the hydrogen bonds between the first and second shell for the magnesium and zinc ions, 2.73 Å in both cases, are only slightly shorter than the experimentally based value 2.76 Å estimated from infrared spectroscopic measurements of O−D vibrational frequencies in aqueous solutions.[39−41]

Calcium, however, belongs to a group of ions with much weaker hydrogen bonding (including e.g. K^+, Na^+, Li^+, Ca^{2+}, Ba^{2+}) for which the mean value of the O···O hydrogen bond length is estimated experimentally to be centered about 2.88 Å.[38] It was found that the O−D stretching vibration bands originating from the hydrogen bonds around the Ca^{2+} (and Li^+) ions are considerably broader than the one for Na^+ and of different shape on the low-frequency side. By theoretical simulations on the hydrated Li^+ ion two groups of OH or OD oscillators around the ions were found necessary to explain the experimental results. Besides the hydrogen bonds formed from the first-shell water molecules, donation of a hydrogen bond *from* a water molecule in the second shell to a four-coordinated first-shell oxygen atom was proposed to occur to a significant extent for the Ca^{2+} and Li^+ ions.[38]

For the group of ions with stronger hydrogen bonding to which Mg^{2+} and Zn^{2+} belong, only one type of O−H (or O−D) oscillators is needed to explain the experimental data, although it can be noted that the bandwidth of the O−D band is larger for Zn^{2+} than for Mg^{2+}.[40,41] It is proposed that the single band for this group of ions corresponds to an essentially trigonal coordination around the first-shell oxygen atoms, which is supported by the relatively small difference, 0.03 Å, between calculated and estimated experimental values; see above.[38]

To summarize, it is evident that these model calculations are not able to fully represent the actual geometry and coordination around the Zn^{2+} and Ca^{2+} ions in aqueous solution, not even with a very good theoretical description of the water molecule and a complete second hydration shell. For clusters with a limited number of water molecules the dipole interactions leading to trigonal coordination around the water oxygen atoms will be emphasized in the field from the central ion and may affect its coordination geometry and numbers. The possibility for a weakly bonded water molecule to accept hydrogen bonds in a tetrahedral coordination geometry makes the description of the second shell complicated with very flexible hydrogen bonding especially for the weakly hydrated ions.

5. Conclusions

Several aspects have been considered in the present study of metal ion coordination in water. First, the requirements for obtaining accurate metal−water binding energies have been investigated. To reach high accuracy, the dipole moment and polarizability of the water molecules has to be well described. The B3LYP values for these properties using double-ζ basis sets have errors of 33% and 47%, respectively, which are improved to errors of 6% and 17%, using the very large 6-311+G(2d,2p) basis sets. These basis sets have two sets of polarization functions on each atom and also include additional diffuse functions, which is in the limit of what can be handled presently for systems with up to 10 water molecules. Errors of a similar relative magnitude as above should be expected for the interaction energies. However, it is found that if the dipole moment and polarizabilities of water molecules are calculated in a basis which also includes the basis functions of the metal atom (as ghost basis), the errors on these properties drop to only 2% and 4%, respectively, These errors should be more representative of the actual errors in the computed binding energies.

An important practical point when studying ion coordination is the geometry requirement for obtaining an accurate interaction energy. If a low-level geometry optimization is sufficient, a large part of the computational effort can be saved, which will allow the study of much larger systems. It is found that this is indeed the case. There are two aspects of the present findings in this context. First, in most cases even a low-level double-ζ geometry agrees quite well with experimental geometries, so it should be sufficient for the determination of the interaction energy. Second, even when substantial deviations from experimental geometries occur, this has little influence on the interaction energy. For $Ca(H_2O)_n{}^{2+}$ complexes it is thus found that the double-ζ geometries have errors in the Ca−O bond distances of 0.05 Å, due to the lack of d functions on calcium. When this deficiency in the geometry is corrected, the effect on the $Ca-H_2O$ interaction energy is only 0.16 kcal/mol.

Most of the trends found in the computed interaction energies have simple origins. For example, the small size of the beryllium ion leads to a strong electrostatic attraction of the first water molecules, while the larger size of the calcium ion leads to much smaller interaction energies for these water molecules. However, as more water molecules are added, the difference in $M-H_2O$ interaction energies levels out. This is due to substantial charge-transfer effects for the first water molecules, leading to a saturation of these effects as the final water molecules of the first hydration shell are added.

The energetic boundary between the first and second hydration shell varies in size between the metals. For beryllium, which is always found to be four-coordinated experimentally, the binding energy of the first water is 45.7 kcal/mol, while the fifth water (in the second shell) is bound by 28.2 kcal/mol. For magnesium, found to be six-coordinated, the corresponding energy difference is much smaller. The sixth water ligand is bound by 24.5 kcal/mol, while the first water in the second shell is bound by 24.7 kcal/mol. The situation is found to be similar for calcium, the experimental coordination varies much more in this case. The sixth water is bound by 24.7 kcal/mol and the first water in the second shell by 17.6 kcal/mol. For zinc the difference is even smaller, with values of 21.8 and 18.3 kcal/mol, respectively, for six-coordination. A rather surprising result occurred for zinc, which is experimentally found to be six-coordinated in aqueous solution. The calculations with up to 12 water molecules around the zinc ion still give a preference for four-coordination. Evidently, larger clusters of water molecules are needed to obtain the preference for six-coordination.

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