Theor Chim Acta (1989) 75: 299-306

Theoretica Chimica Acta

Theoretical study of the calcium dication hydrates

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(Received April 28, revised August 3/Accepted September 5, 1988)

Ab initio SCF calculations have been carried out for calcium dication surrounded by 1-4 or 6 water molecules using several basis sets. The structure of the hydrated ions is examined and the hydration energy estimated. The changes in the structure of water within the complex are qualitatively explained in terms of charge transfer and coulombic interactions among the atoms. Finally, the influence of electron correlations is discussed.

Key words: Hydration—Charge transfer—Calcium water interactions

1. Introduction

The interaction of cations with water has always been an interesting problem in chemistry [1], and especially that of the alkaline and alkaline earth ions in view of their biological [2] and electrochemical [3] importance. During the last two decades considerable effort has been directed towards securing good quality experimental [4] and theoretical [5] data for the prediction of the structure of ion hydrates.

Doubly charged cations behave differently from singly charged ions in their interaction with water [6], mainly due to the notable charge transfer arising in the interaction which may lead to avoided crossings of the fundamental and the lowest lying triplet state [6]. This yields products such as $Me^{+}\cdot(H_2O)^{+}$ for the lighter ions (Be^{2+} and Mg^{2+}). Ca^{+2} is the first ion of its family to have a lower

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** *Present address*: SRI International, Life Sciences Division, Molecular Theory Program, Loc 205-40, 333 Ravenswood Ave, Menlo Park CA 94025, USA electron affinity than the ionization potential of water, so that the crossing of the ground state surface with a triplet state is not probable.

Most of the studies in this field were performed using frozen geometries for the water molecules since the lack of electron correlation terms was considered more important than the deformation energy of water in the field of the ion [6]; however, omission of the structural changes in the subsystems did not permit a proper analysis of other properties which were affected by the distortions. Hermansson et al. [7] studied the water molecule in the field of several ions by optimizing the geometry of the whole complex, but concluded that the procedures tested were unable to systematize the observed deformations in the structure of the water molecule.

The paper is structured as follows. In the following section the computational method will be described. In Sect. 3, the structures and energies of interaction for the polyhydrates will be discussed. A simple qualitative approach to charge transfer (CT) will be used in Sect. 4 to correlate the distortion of the H_2O structure in the field of the dication. Finally, the effect of the inclusion of correlation energy will be described in Sect. 5.

2. Computational approach

Ab initio MO LCAO-SCF calculations have been carried out for the free water molecule, the Ca^{+2} ion and $Ca^{+2}\cdot(H_2O)_n$ complexes, where the coordination number, *n*, was taken as 1, 2, 3, 4 and 6. The HONDO-5 [8] and the MONSTER-GAUSS [9] programs were employed.

Among others, the MINI-*n* (M*n*) basis sets [10] were tested, since these bases are known to yield good charge distributions and a small basis set superposition error (BSSE) [11]. M*n*** denotes that a *d* polarization function has been added to the O atom and that *p* functions have been added to the H. The polarization functions used for the cation were obtained by minimizing the total energy of the isolated ion. We will make it explicit whether the polarization function for the ion is *p* (M*np*) or *d* (M*nd*). Clementi's (C) [12] and Dunning's double zeta [13] including polarization functions on H and O (DZP) for water, and Wachter (*W*)'s basis set [14] for calcium were used to study the basis set influence on the monohydrate. Clementi's and Wachter's basis sets are close to the HF limit for the water molecule and Ca^{+2}, respectively. Symmetry constrains were used for the polyhydrates, according to the point group of the resulting supermolecule [8]. The counterpoise correction (CP) [15] and the corrected counterpoise correction (CCP) [16] were included with the BSSE to obtain the interaction energies whenever small or medium sized basis sets were used, even though the corrected energy is not known to be more reliable than the uncorrected one [17].

Finally, we studied the effect of the electronic correlation using second order Moller-Plesset theory (MP2) [18] using the DZP M1*p* basis set. At the MP2 optimized geometry we performed a frozen core configuration interaction with single and double excitations (CISD) to check the configurations that are dominant in this interaction.

3. Geometries and interaction energies

In Table 1, the geometrical parameters for the $Ca^{+2}\cdot(H_2O)$ complexes are shown for the various basis sets. All the M*n* basis sets tend to systematically overestimate the OH distance and underestimate the HOH angle, while the distances between the cation and the molecule are only slightly underestimated in comparison to the CW basis. The DZP, M1*p* basis yields satisfactory results when compared with those of the CW. This is in agreement with other similar studies that point out that the quality of the basis set for water is much more important than that for the metal-ion [19].

In contrast, the changes observed in the molecular parameters for the isolated water molecule compared with the same molecule in the field of the ion follow the same qualitative trends for all basis sets. For all of them, the OH distance and the HOH angle are bigger in the field of the ion than they are in the isolated molecule for the same basis set. This confirms the good qualitative behavior of the smaller basis sets in describing intermolecular interactions, as has already been pointed out [11].

It is worth noticing that the symmetry of the water molecules around the Ca^{+2} is identical with that of water molecules around Be^{+2} [20]. The planarity of the

Table 1. Total energies (in atomic units) and geometrical parameters (distances in Å and angles in degrees) for polyhydrates using different basis sets

Basis		-TE (a.u.)	R_{O-Ca}	R_{O-H}	HÔH
Monohydrates, C_{2v}					
M1	M1	720.077437	2.166	1.046	100.8
M3	M3	750.695713	2.272	1.043	101.1
M3**	M3*p*	750.829350	2.280	1.017	99.4
M3**	M3*pd*	750.856047	2.245	1.018	99.6
M1*p*	DZP	749.355787	2.342	0.957	103.4
C	W	752.278880	2.395	0.945	106.5
M1*p*	DZP (MP2)	749.577334	2.349	0.973	102.2
Dihydrates, D_{2d}					
M3	M3	826.519882	2.289	1.042	101.2
M3**	M3*p*	826.696883	2.313	1.017	99.4
Trihydrates, D_3					
M3	M3	902.340384	2.291	1.043	101.3
M3**	M3*p*	902.560880	2.321	1.016	99.6
Tetrahydrates, S_4					
M3	M3	978.155245	2.306	1.042	101.4
M3**	M3*p*	978.420265	2.325	1.015	99.8
Hexahydrates, T_h					
M3	M3	1129.764606	2.331	1.042	102.3

Table 2. Hydration energies (E in Kcal/mol) for different basis sets, using the CP and CCP corrections to compensate the BSSE

Basis		E	E+CP	E+CCP
Monohydrates, C_{2v}				
M1	M1	54.5	51.1	52.0
M3	M3	49.9	44.4	45.8
M3**	M3*p*	44.6		
M3**	M3*pd*	47.0		
DZP	M1*p*	50.6	50.9	50.7
C	W	51.0		
DZP	M1*p*(MP2)	51.6	49.5	49.8

monomer suggests the formation of a π bond between the p_π orbital of the calcium and the lone pair of the molecule that is orthogonal to the molecular plane. For the dimer, the accumulation of two consecutive π bonds leads to a D_{2d} structure that is comparable with that of allene. Also, the D_3 structure for the trimer indicates an important π interaction as a factor defining the structure of these complexes [20]. The HOMO is the π orbital, and it defines the donation from the water lone pairs to the calcium p orbitals.

A comparison with experimental data is possible for the hexacoordinated system. The $Ca^{+2}\cdots OH_2$ distance in the solid state is 2.33 Å which is remarkably similar to the values shown in Table 1.

Table 2 displays the interaction energies between the Ca^{+2} and water for the different basis sets. The values are corrected for BSSE by using CP and CCP for the smallest basis; the correction is small for these bases, in accord with the results by Hobza and Sauer [11]. Figure 1 gives the total energy as a function of the ion oxygen distance for the M3,M3 and M3*p*,M3** basis.

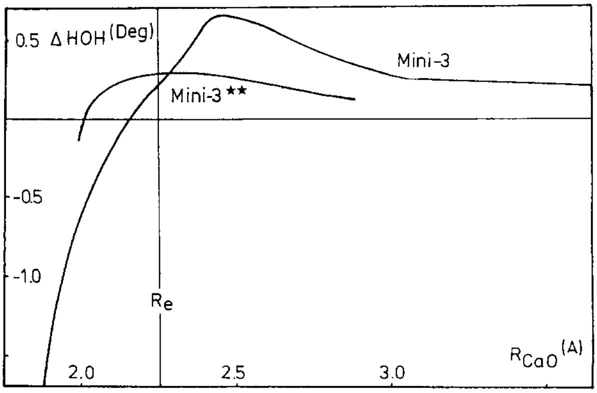

Fig. 1. The charge transfer between Ca^{+2} and H_2O (in e) vs. the Ca-O distance (in Å)

4. Charge transfer and the structure of water in the ion field

Mulliken's classical treatment [21] of CT may provide a useful tool to depict qualitatively the changes in the structure of water in the field of the metal ion. Under this theory, the wavefunction of the complex is written as a linear combination of the wavefunction of two systems:

$$\Phi_{\overline{DA}} \simeq c_1\Phi_{DA} + c_2\Phi_{D^+A^-}$$

where D stands for a donor subsystem and A for an acceptor. Φ_{DA} describes the wavefunction of the system without interaction while $\Phi_{D^+A^-}$ denotes the interaction after an electron has been transferred from D to A (charge transfer state). In this scheme c_2/c_1 can be considered as a measure of the CT between the two interacting subsystems. It is possible to rewrite this model in terms of Mulliken's populational analysis. The net atomic charges (Q) for the atoms in the complex can be written in this context as:

$$Q_{i\overline{DA}} \simeq Q_{iDA} - \lambda_i Q_{iD^+A^-}$$

where i represents an atom in the system and λ is a functional form related to c_2/c_1 [21], and in this way to the charge transfer.

The use of this theory is relatively straightforward in this case as one subsystem (the acceptor) is a single atom: the CT is given by the charge excess of the dication,

$$\lambda_{Ca} = Q_{Ca}(Ca^{+2}; H_2P) - Q_{Ca}(Ca^{+2}\cdots OH_2),$$

since the net atomic charge of Ca^{+2} in the ionic state (D^+A^-) is 1. λ_{Ca} gives a parameter that allows a parametrization of the CT in the complex; the validity of this parameter has been discussed by del Re et al. [22].

Figure 2 shows the CT parameter λ_{Ca} as a function of the ion oxygen distance. As the equilibrium position is approached (see Fig. 1) from the situation in which D and A are infinitely separated, λ increases its value; this is related to an increase in the overlap among the oxygen lone pairs and the $4s$ orbital of the

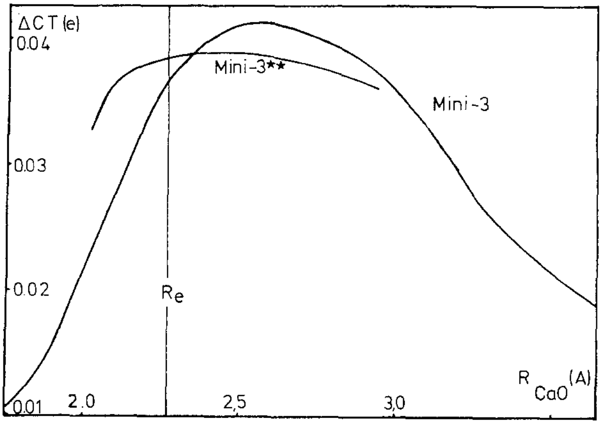

Fig. 2. The angle HOH (in Deg.) vs. the Ca-O distance (in Å)

cation. It then reaches a maximum and, finally decreases as the overlap between the orbital also starts to decrease. The functional dependence of the HOH angle with the $\mathrm{Ca}\cdots\mathrm{O}$ distance can be described in a similar way (Fig. 2): the water angle increases, reaches a maximum and decreases as water approaches the metal ion. The position of the maxima (for both λ and the angle) is coincident for all basis sets, even though the values of the position of the maxima among different basis sets may differ considerably.

This similarity in the behavior of λ and the angle may be explained by simple electrostatic considerations. As water donates part of its electron density to the calcium ion it increases the repulsion between the charge deficient H atoms; this leads to an increase in the water angle, due to the electrostatic repulsion between the hydrogen atoms, until an extreme configuration is reached in which the structure of the ionized water has a much larger HOH angle than the neutral system. There is a second factor that should be taken into account: the repulsion between the Ca ion and the H atoms in the water molecule. This interaction tends to reduce the HOH angle, and becomes dominant as the $\mathrm{Ca}^{+2}\cdots\mathrm{OH}_2$ distance decreases ($R < R_{\mathrm{eq}}$). This effect explains the radically different slope of both curves for distances that are shorter than the equilibrium position.

The OH distance along this coordinate behaves as described by Gutman [23]; this means the OH distance increases as the distance between the cation and the molecular system decreases due to polarization of the molecule by the ion. On the contrary, this rule is not able to describe the proper qualitative changes of the water angle in the field of the ion, since it is based on mere electrostatic considerations, and would lead to the conclusion that the repulsive interaction of Ca and H atoms will cause the angle to decrease.

For the polyhydrates, the coordination radius increases with the coordination number. There is also an increase in the charge transfer from the water to the molecule that leads to an increase in the molecular angle as explained above.

5. The effect of electronic correlation

The inclusion of the electronic correlation did not lead to any significant changes in the geometry or hydration energy of the water molecule, as can be seen from Table 1; these results are in accord with similar studies on Be^{2+} [20], where the relatively small influence of the basis set and the electronic correlation on the hydration energy for that system was noted.

The changes induced in the water molecule structure by electronic correlation are similar to those observed in a MP2 calculation of isolated water, that is, a reduction in the HOH angle and an increase in the OH distance [24] when compared with the Hartree–Fock values. A CISD was carried out at the geometry optimized using MP2. Even using the frozen core approximation, the number active configurations included was 5131. The ground state configuration:

$$\mathrm{core} \times 5a_1^2 6a_1^2 2b_2^2 2b_1^2 7a_1^2 3b_2^2 8a_1^2 3b_1^2$$

is the dominant one (weight = 0.9470), pointing out that the description at the Hartree–Fock level is quite accurate for this system.

The next most important configuration is a double excitation from the $3b_1$ to the $4b_1$ (weight = 0.0025):

$$\text{core} \times 5a_1^2 6a_1^2 2b_2^2 2b_1^2 7a_1^2 3b_2^2 8a_1^2 3b_1^0 4b_1^2.$$

This configuration describes the in–out correlation in the intermolecular space. The left–right correlation is included through a double excitation from the in plane water lone pair to the $4s$ orbital of calcium:

$$\text{core} \times 5a_1^2 6a_1^2 2b_2^2 2b_1^2 7a_1^2 3b_2^2 8a_1^0 3b_1^2 9a_1^2.$$

The weight of this configuration is 0.0017. Another important configuration is the following:

$$\text{core} \times 5a_1^2 6a_1^2 2b_2^2 2b_1^2 7a_1^2 3b_2^2 8a_1^1 3b_1^1 9a_1^1 4b_1^1$$

with a weight similar to the previous (0.0016).

The interactions are so strong for the dications that the correlation energy does not affect the values of the hydration energies; nor does it produce significant qualitative changes in the structure of the complex. At the MP2 level, the structural changes observed in water because of the presence of the ion are the same as those observed at the Hartree–Fock level.

5.1. Final remarks

In this paper we have reported the predicted structure of calcium hydrates using several different basis sets. Huzinaga's MINI-*n* bases show only a small BSSE, evaluated using the CP and CCP methods. They also seem reliable when evaluating the hydration energy and the metal-ion molecule distance. In general, the large interaction energies between the cation and the molecule make the BSSE correction modest. It is partially for this reason that almost any basis set is able to estimate the interaction energy quite accurately (about 50 Kcal/mol).

The structures of the complexes were analyzed in terms of the formation of a π bond between the $4p$ orbital of the ion and the water lone pair and orthogonal to the plane of the water molecule. The structural changes of water in the field of the ion were interpreted in terms of coulombic repulsive effects and CT as defined within Mulliken's theory. Treatment beyond the Hartree–Fock level does not seem to yield any extra information.

Work is in progress to extend the ideas developed in this paper to other ions and CT systems.

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