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SCF MO LCGO Studies on the Hydration of Ions: The System $Li^+ \cdot 2H_2O$

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The energy of the dihydrated lithium cation $Li^+ \cdot 2H_2O$ is studied in several different points within the SCF MO LCAO framework, using a gaussian basis set to approximate the wavefunction. The computed binding energies (hydration energies) and bond distances are compared to the values found for the monohydrate. The results are discussed in view of ion-solvent interaction, and especially of the effect of ions on adjacent hydrogen bonds, in aqueous solutions.

Recently the mono-hydrates of the series of cations H^+, Li^+, and Na^+ [1] as well as of the anion F^- [2] have been studied within the SCF MO LCAO framework. The wavefunctions have been expanded into a large gaussian basis set and a relatively high accuracy in the total SCF-energy has been achieved. The purpose of these calculations has been to get some idea about ion solvent interactions. It was well understood that these mono-hydrates can only serve as a very crude approximation to the real structure of ionic aqueous solutions. In this letter a number of preliminary results of calculations on the di-hydrates of the cation Li^+ are presented. The aim was to get an accurate information about the minimum energy structure and the associated hydration energy. In addition the mutual influence of a water molecule on the Li^+-monohydrate, and from an other point of view, of a Li^+ cation on the water dimer has been studied. Recently, a quantum chemical CNDO-model calculation has been used to investigate the di- and tetra-hydrates of a series of ions including the cation Li^+ [3].

The wavefunctions and energies have been calculated using Roothaan's SCF-MO-LCAO method [4]. The computations have been carried out on an IBM 360/91 computer, using the program IBMOL/VERSION IV [5], modified by one of the authors (G. D.) to avoid the explicit integral transformation [6], and using a test release of the program system MUNICH [7]. The molecular orbitals are expanded into a set of gaussian functions $\eta = x^l y^m z^n \exp(-\alpha r^2)$ (unnormalized) which are contracted to reduce the number of linear parameters. The basis set used in these calculations consists of (11.7.1)-functions centered at the oxygens, of (11.3)-functions at the lithium, and of (6.1)-functions at the hydrogens. These basis sets are contracted to [5.4.1]-functions at the oxygens, to [5.2]-functions at the lithium, and to [3.1]-functions at the hydrogens, as has been described more explicitly in previous notes [1, 8, 9].

The constituting systems H_2O, $(H_2O)_2$, Li^+, and $Li^+ \cdot H_2O$ have already been studied and the results are in good agreement with the experiments. In particular the following SCF-energies have been calculated for the systems above in their

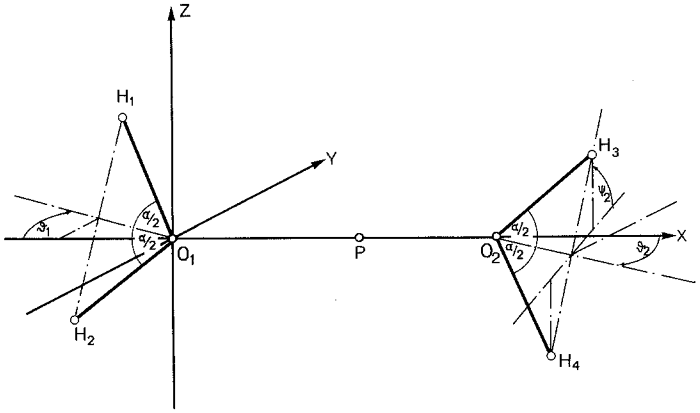

Fig. 1. Coordinate system for $Li^+ \cdot H_2O$ in the geometrical structure *D* (the Li^+ cation is in position *P*)

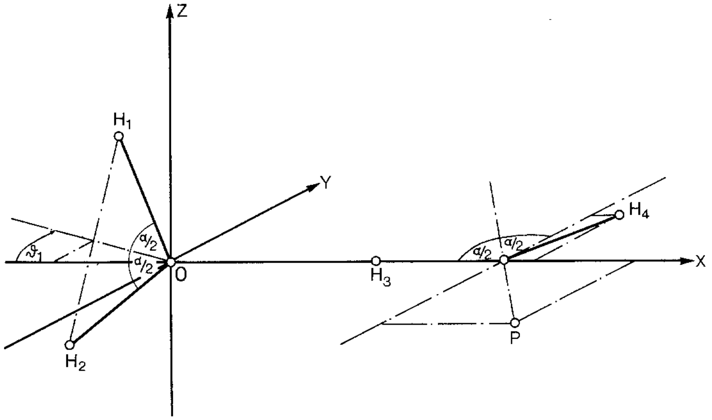

Fig. 2. Coordinate system for $Li^+ \cdot H_2O$ in the geometrical structure *A* (the Li^+ cation is in position *P*)

experimentally or computationally, resp., determined geometries: $E^{SCF}(H_2O) = -76.05199$ a.u. [9], $E^{SCF}((H_2O)_2) = -152.11167$ a.u. [9], $E^{SCF}(Li^+) = -7.23621$ a.u. [1], and $E^{SCF}(Li^+ \cdot H_2O) = -83.34558$ a.u. [1].

There are essentially two geometrical structures that can be formed by two water molecules and a lithium cation assuming that the lithium is bonded directly to oxygen: In one of these structures (*D*), the lithium is positioned midway between the oxygen atoms of the two water molecules, which are arranged symmetrically to the OLiO-axis with their molecular planes perpendicular to each other (Fig. 1). In the second structure (*A*) the lithium is bonded to the oxygen centre of that water molecule which is acting as the proton donor in the water dimer (Fig. 2). For both structures the potential curves due to a variation of the d(LiO)-distance around the energy minimum has been studied. In all these calculations the geometry of the water molecules is kept fixed to its experimental values (d(OH) = 1.80887 a.u., α(HOH) = 104.52°).

The results of the various calculations are summarized in Table 1 and Fig. 3.

Table 1. Total SCF energies for the system $[Li(H_2O)_2]^+$ in different geometrical configurations (*A*) and (*D*)

	d(LiO) [a.u.]	d(OO) [a.u.]	α	ϑ_1	ϑ_2	ψ_2	E^{SCF} [a.u.]
Configuration D, Fig. 1:							
1	3.00	6.00	104.52°	0°	0°	0°	−159.42388
2	3.50	7.00					−159.44778
3	4.00	8.00					−159.43924
4	3.50	7.00	104.52°	20°	20°	90°	−159.44583
5				30°	30°		−159.44352
Configuration A, Fig. 2:							
6	3.00	5.669	104.52°	0°	—	—	−159.41332
7	3.50						−159.42132
8	4.00						—159.41402
9	5.00						−159.39459
10	3.50	4.469	104.52°	0°	—	—	—159.41448
11		4.769					−159.42131
12		5.069					−159.42327
13		5.369					−159.42284
14		5.969					−159.41940

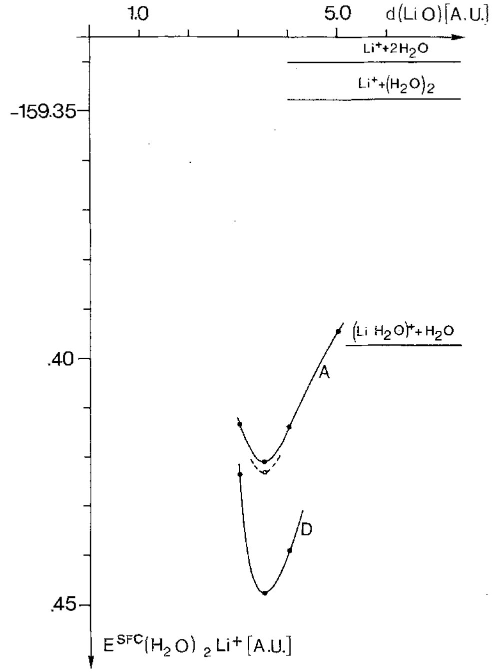

Fig. 3. Potential energy curves for the d(LiO)-variation in two different geometrical structures of the system $Li^+ \cdot 2H_2O$ (the dotted line indicates the estimated curve *A* near the equilibrium LiO-distance after an additional d(OO)-variation)

Table 2. Calculated binding energies and geometry parameters for the most stable structures of the systems $(AOH_2)^+$, and $(H_2OAOH_2)^+$, with A = H, and Li

	B^{SCF} [kcal/mole] A = H, Li	d(AO) [a.u.] A = H, Li	d(OO) [a.u.]	$\vartheta_1 = \vartheta_2$	ψ_2	Remarks
	$A^+ + H_2O$					
HOH_2^+	173.24	1.82	—	—	—	
$LiOH_2^+$	36.02	3.57	—	—	—	
	$A^+ + 2H_2O$ $AOH_2^+ + H_2O$					
$H_2OHOH_2^+$ (exp)	205.98	2.26	4.52	30°	0°	
	32.98		(4.60)			
$H_2OLiOH_2^+$	67.54	3.62	7.24	0°	Fig. 1	
	31.52			(not varied)		
$HLiOHOH_2^+$	52.15	3.51	5.12	0°	—	Fig. 2
	16.13			(not varied)		

It is easily seen from Fig. 3, that both structures *A* and *D* are stable with respect to all possible subsystems: $Li^+ + 2H_2O$, $Li^+ + (H_2O)_2$, and $LiOH_2^+ + H_2O$. The more interesting results for these systems, such as some bond distances and various binding energies, are summarized in Table 2. From there it follows, that structure *D* is more stable than structure *A* by about 15.4 kcal/mole.

In the structure *D*, to be considered first in some more detail, the LiO-distance is larger by about 0.05 a.u. than in the monohydrate, and in accordance with this result the total hydration energy is smaller by appr. 4.5 kcal/mole compared to twice the hydration energy of the monohydrate. Thus the average hydration energy per LiO bond in the dihydrated system is 2.25 kcal/mole smaller than in the monohydrate. This is equivalent to the statement that a water molecule is bonded to the $Li^+ \cdot H_2O$ by only 31.52 kcal/mole (compared to the value in $Li^+ \cdot H_2O$ of 36.02 kcal/mole). A decrease of the average binding energy in this order of magnitude or even larger has to be expected for the higher hydrates. As a matter of course no extrapolation is possible from these two values available so far. It may be reasonable to assume that not the decrease in binding energy on the formation of higher hydrates is determining the highest hydration number possible, but rather the space available around the lithium cation. This is in agreement with the usual experience in the chemistry of complexes.

In structure *A* the effect of the lithium cation on an adjacent hydrogen bond can be studied. In this structure an additional optimization of the d(OO)-separation has been performed keeping the d(LiO)-distance fixed at its variationally predetermined equilibrium value. As a result of these calculations both distances, the d(LiO)- as well as the d(OO)-values, turned out to be smaller than in the isolated subsystems $LiOH_2^+$, and $(H_2O)_2$, resp. While the change in the bond distance d(LiO) is rather small (about 0.05 a.u.), the change in the equilibrium d(OO)-separation was obtained to be 10% of the value found for the isolated $(H_2O)_2$-system, which is unexpectedly large. In accordance with these results the binding energy relative to the subsystems Li^+, and $2H_2O$ is larger than the sum of the binding energies of the subsystems $LiOH_2^+$, and $(H_2O)_2$ by about 11.3 kcal/mole. This indicates that a second water molecule is bonded to the hydrogen atom of the preformed monohydrate with a binding energy of 16.13 kcal/mole, assuming that the bond strength in the monohydrate is not changed. Thus the binding energy of the dimer perturbed by a (bonded) lithium cation is about 11.3 kcal/mole larger than the binding energy of the isolated dimer of 4.83 kcal/mole. Such effects on the relatively weak hydrogen bond in the water dimer due to the neighbouring systems have already been expected. They can be explained by an induced charge shift, strongly influencing the hydrogen bond formation. The direction of this charge shift in the hydrogen bridge of the water dimer caused by the lithium cation is in full agreement with the result derived from an analyses of the electron density difference maps in the dimeric water system [9]. Equivalent effects have recently been observed in a theoretical study of the water trimer [10] and are strongly related to the "non additivity of hydrogen bond energies".

To our knowledge such a drastic effect as described above has never been observed experimentally in ionic solutions. But in comparing these results to experimental observations one has always to keep in mind, that the calculated results apply more or less only to the isolated systems. Actually, in ionic solutions there are not only positively charged ions, but negative ions as well. These negatively charged ions may be hydrogen bonded to the $Li(OH_2)_2^+$ complex such that the calculated effect is canceled to some extent.

If one is willing to conclude from these results that a second hydration shell exists at all, this layer will be very softly bonded and will be perturbed rather easily by neighbouring effects.

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References

1. Diercksen, G. H. F., Kraemer, W. P.: Theoret. chim. Acta (Berl.), **23**, 387 (1972).
2. — — Chem. Physics Letters **5**, 570 (1970).
3. Lischka, H., Plesser, Th., Schuster, P.: Chem. Physics Letters **6**, 263 (1970).
4. Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
5. Veillard, A.: IBMOL/VERSION IV, Special IBM Technical Rept., San José, California (1968).
6. Preuß, H., Diercksen, G.: Int. J. quant. Chemistry **1**, 605 (1967).
7. Diercksen, G. H. F., Kraemer, W. P.: MUNICH, Molecular Program System, Reference Manual, Special Technical Report, Max-Planck-Institut für Physik und Astrophysik (to be published).
8. — Chem. Physics Letters **4**, 373 (1969).
9. — Theoret. chim. Acta (Berl.) **21**, 335 (1971).
10. Hankins, D., Moskowitz, J. W., Stillinger, F. H.: Chem. Physics Letters **4**, 527, (1970).
    — — — J. chem. Physics **53**, 4544 (1970).

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