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SCF LCAO MO Studies on the Hydration of Ions: The System $F^- \cdot 2H_2O$

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The energy surface of the dihydrated fluoride anion ($F \cdot 2H_2O$)⁻ is studied for a number of different geometry points near the equilibrium structure within the SCF LCAO MO framework, using an extended gaussian basis set to approximate the molecular wavefunctions. For the first and second hydration step of the fluoride anion the corresponding hydration energies are calculated to be $B_1^{SCF} = 24.1$ kcal/mole and $B_2^{SCF} = 20.8$ kcal/mole (experimental measurements: 23.3 kcal/mole and 16.6 kcal/mole, respectively). The hydration energies and equilibrium bond distances obtained for the dihydrated fluoride anion ($F \cdot 2H_2O$)⁻ are compared with those found for the monohydrate ($FHOH$)⁻ and with corresponding results of the dihydrated lithium cation ($Li \cdot 2H_2O$)⁺. The system ($F \cdot 2H_2O$)⁻ is taken as a very simple model to discuss some basic features of the hydration process of small ions and to study the influence of a negative ion on an adjacent hydrogen bond.

In a series of previous investigations the monohydrates of the cations H^+ , Li^+ , Na^+ [1] and of the anions F^- [2], OH^- [3] as well as the dihydrated lithium cation [4] have been studied, expanding the molecular wavefunction of these systems into an extended basis set of gaussian functions to achieve a good approximation to the SCF-wavefunctions and a high accuracy in the total SCF-energies. It has been possible in these studies to obtain some detailed information about the minimum energy geometries and the single hydration energies. In the dihydrated system ($Li \cdot 2H_2O$)⁺ the mutual interactions between all possible subparts have been studied: the interactions between the atomic Li^+ -ion and two single water molecules or a dimeric water system, as well as between the monohydrated lithium cation and a single water molecule. To complete these investigations some results of SCF-calculations on the dihydrated fluoride anion ($F \cdot 2H_2O$)⁻ will be presented here. The only theoretical work on this system published so far has been a quantum chemical CNDO calculation (CNDO = complete neglect of differential overlap) studying the mono-, di-, and tetrahydrates of a series of ions, including the (F^-)-anion [5].

The calculation of the wavefunctions and energies on the basis of Roothaan's SCF LCAO MO method has been carried out on an IBM 360/91 computer, using the program system IBMOL/VERSION IV [6], modified by one of the authors (G. D.) to avoid the explicit integral transformation [7], and using a test release of the program system Munich [8]. The molecular orbitals are expanded into a set of gaussian functions: $\eta = x^l y^m z^n \exp(-r^2)$ which are contracted to reduce the number of linear parameters. The basis sets used in these calculations have been described previously [2, 9] and consist of (11.7.1)-functions centred at the oxygen and fluorine nuclei, respectively, and of (6.1)-functions centred at the

hydrogens (for a definition of the basis set notation used here, see [10]). In the actual SCF-calculations two different contractions of these basis functions are used: a contraction to [5.3.1]-functions at the oxygen and the fluorine centres and to [3.1]-functions at the hydrogen centres as well as a contraction to [5.4.1]-functions at the oxygens and the fluorine together with the same contracted set at the hydrogen centres as described above. An initial search for the equilibrium geometrical structure of the system $F^- \cdot 2H_2O$ is performed using the first, more contracted basis set, according to the experience that equilibrium geometrical parameters are somewhat less sensitive to small changes in the basis set than various other expectation values. Around the minimum obtained in this preliminary search some additional calculations using the slightly less contracted [5.4.1]-basis set are then performed, leading to the SCF-energies and hydration energy values discussed in this paper. For the systems F^- , H_2O , $(H_2O)_2$, and $(FHOH)^-$, previously studied, the calculated SCF-energies, using the contractions [5.4.1] at the oxygen and the fluorine centres, are found to be $E^{SCF}(F^-) = -99.45059$ a.u. [2]; $E^{SCF}(H_2O) = -76.05199$ a.u. [9] (for the experimental geometry); $E^{SCF}((H_2O)_2) = -152.11167$ a.u. [9]; $E^{SCF}(FHOH^-) = -175.54093$ a.u. [2]. The last two energy values are obtained for the theoretically calculated geometries which are close to the experimentally determined structures.

The accuracy of the computed hydration energies and bond distances can be proved by a comparison with mass spectroscopic measurements of the corresponding gas-phase hydration reactions, recently published by Kebarle and co-workers [11]. For all the hydrated systems studied in this series of investigations [1-4] the deviation of the calculated first hydration energies from the corresponding experimental data is only about 5%, while for the second hydration energies larger deviations are obtained (about 25%). The calculated equilibrium bond distances are in good agreement with experiments within an error of about 2-4%.

The molecular structures of the system $(F \cdot 2H_2O)^-$ investigated here may be described as follows:

A fluorine anion and two water molecules are able to form essentially three different geometrical configurations under the condition that the (F^-) -ion is bonded to the oxygen centres in the water molecules by a hydrogen bond. This hydrogen bond is in the following always assumed to be a linear one, in agreement with our previous studies on the monohydrate $(FHOH)^-$ [2]. In the first structure (denoted as *S*) in Table 1), which has a highly symmetrical form, the two water molecules are attached to the fluoride anion F^- each by a linear hydrogen bond in such a way that the five centres $O \dots H \dots F \dots H \dots O$ are positioned on a straight line and that the fluorine nucleus acts as a centre of inversion for the whole molecular system (F^- in position *P* in Fig. 1). In both of the two remaining structures (denoted as *A*) and (*D*) in Table 1) the fluoride anion is attached to the dimeric water system as a whole, the geometrical configuration of which is taken from a previous study on this system [9]. In the structure (*A*), the (F^-) -anion is bonded by one of the hydrogens of the proton acceptor part of the water dimer (F^- in position P_1 in Fig. 2), while in the last possible structure (*D*) the (F^-) -anion is bonded by the outer hydrogen of the proton donor part of $(H_2O)_2$ (F^- in position P_2 in Fig. 2). For all the three

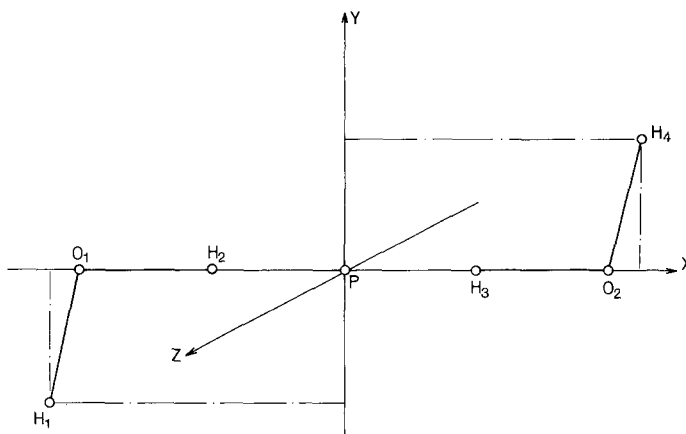


Fig. 1. Coordinate system for $F^- \cdot 2H_2O$ in the geometrical structure (S) (the fluoride anion is in position P)

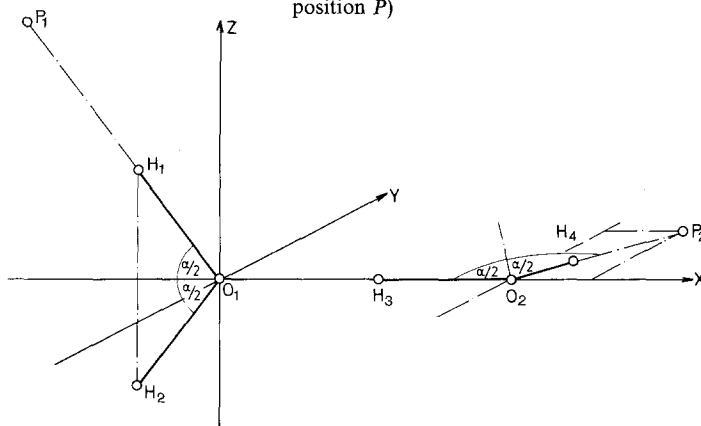


Fig. 2. Coordinate system for $F^- \cdot 2H_2O$ in the geometrical structures (A) and (D) (the fluoride anion is in position P_1 for structure (A) and in position P_2 for structure (D))

structures (S), (A), and (D) described here, the internuclear distances $d(FO)$ between the fluoride and the corresponding oxygen centres have been varied around their equilibrium values. In addition, for the structures (A) and (D) a further variation of the oxygen/oxygen internuclear distance $d(OO)$ has been performed, keeping the distance $d(FO)$ fixed at its previously determined equilibrium value. During all the calculations referred here the water molecules were taken in their experimentally determined geometry ($d(OH) = 1.80887$ a.u., $\sphericalangle(HOH) = 104.52^\circ$).

The computational SCF-results for the two different contractions, used in this investigation, are summarized in Table 1 and are displayed in Fig. 3. Some of the most interesting results, like the hydration energies and the bond distances, based on the less contracted, second basis set mentioned above, are collected in Table 2.

The symmetrical structure (S), which may be characterized by the formula $(HOHFHOH)^-$, is found in these studies to represent the most stable geometrical configuration of the dihydrated system $(F \cdot 2H_2O)^-$. From the variation of the

Table 1. Total SCF-energies of the system $(F \cdot 2H_2O)^-$ in different geometrical configurations (structure (S): $(HOHFHOH)^-$; structure (A): $(HOHO(H)HF)^-$; structure (D): $(FHOHOH_2)^-$)

	$d(FO)$ [a.u.]	$d(OO)$ [a.u.]	$d(OH)$ [a.u.]	$\angle HOH$	$\angle (P_1 O_1 O_2)$	E^{SCF} [a.u.]	
(S):	1	4.00	8.00	1.80887	104.52°	-251.56672	
	2	4.50	9.00			-251.61542	
	3	4.725	9.45			-251.61984	
	4	4.82	9.64			-251.62013	
	5	5.00	10.00			-251.61907	
	6 ^a	4.725	9.45	1.80887	104.52°	-251.62567	
	7 ^a	4.82	9.64			-251.62614	
	8 ^a	5.00	10.00			-251.62537	
(A):	1	4.00	5.66925	1.80887	104.52°	127.74°	-251.58738
	2	4.25					-251.60007
	3	4.50					-251.60437
	4	4.83					-251.60373
	5	5.00					-251.60202
	6	5.50					-251.59508
	7	4.50	5.06925	1.80887	104.52°	127.74°	-251.60527
	8		5.20000				-251.60557
	9		5.36925				-251.60546
	10 ^a	4.62	5.12	1.80887	104.52°	127.74°	-251.61262
	11 ^a		5.26				-251.61286
	12 ^a		5.40				-251.61274
(D):	1	4.00	5.20	1.80887	104.52°	104.52°	-251.54902
	2	4.50					-251.57209
	3	5.00					-251.57438
	4	6.00					-251.56670
	5	8.00					-251.55579
	6	5.00	5.50	1.80887	104.52°	104.52°	-251.57715
	7		5.80				-251.57843
	8		6.40				-251.57908
	9		10.00				-251.57960

^a These calculations have been performed using the [5.4.1] contraction at the oxygen and the fluorine centres.

hydrogen bond lengths between the fluorine centre and the two oxygen nuclei in the attached water molecules, an equilibrium FO-distance of $d(FO) = 4.82$ a.u. was obtained for both of the two different contractions (Fig. 3). From the minimum SCF-energy value of the less contracted basis set the binding energy, corresponding to a dissociation into: $(FHOH)^- + H_2O$ is calculated to be $B_2^{SCF} = 20.8$ kcal/mole. This energy is identified as the hypothetical second hydration energy of the fluoride anion. In previous studies on the monohydrated system $(FHOH)^-$ the first hydration energy was determined to be $B_1^{SCF} = 24.07$ kcal/mole [2]. The total binding energy of the system $(HOHFHOH)^-$ with respect to a complete decomposition into: $F^- + 2H_2O$, is obtained to be 44.9 kcal/mole, leading to an average hydration energy per water molecule in the dihydrated system of 22.45 kcal/mole. The corresponding experimental values, obtained from mass spectroscopy measurements of the gas-phase hydration reactions, were recently published by Kebarle and co-workers [11]: $-H_1 = 23.3$ kcal-Mole; $-H_2 = 16.6$ kcal/mole (from these two values an ex-

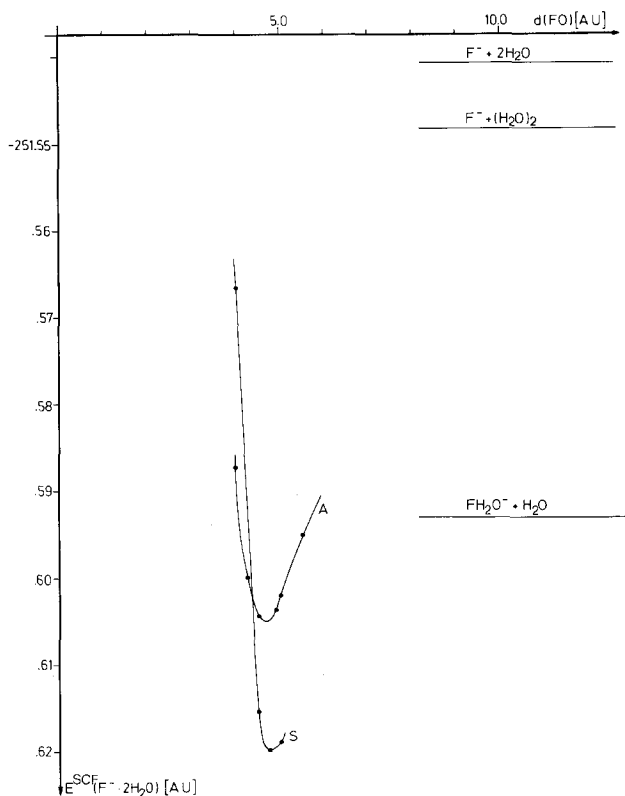


Fig. 3. Potential energy curves for the $d(FO)$ -variation in the two different geometrical structures (S) and (A) of the system $F^- \cdot 2H_2O$

perimental average hydration energy for the dihydrate may be derived: 19.95 kcal/mole).

A comparison of these results for the dihydrated fluoride anion with previous studies on the hydration of the lithium cation [4] shows a general similarity of the hydration process for both types of ions. In both cases the bond lengths between the ionic centres and the oxygen nuclei of the water molecules are nearly unchanged if a second water molecule is added to the monohydrated system. The very small enlargements of the bond lengths of 0.05 a.u. for the two dihydrated systems, $(HOHFHOH)^-$ and $(H_2OLiOH_2)^+$, are beyond the accuracy of our calculations. As might be expected from chemical experience, there is further in both cases a remarkable change in bond strength comparing the mono- and the dihydrates. The differences between the single hydration energies of the monohydrates and the average hydration energies of the dihydrates are $\Delta B = 1.62$ kcal/mole for $(HOHFHOH)^-$ and $\Delta B = 2.05$ kcal/mole for $(H_2OLiOH_2)^+$ (in both cases the experimental measurements give a stronger decrease in the hydration energies: $\Delta B(HOHFHOH)^- = 3.35$ kcal/mole and $\Delta B(H_2OLiOH_2)^+ = 4.1$ kcal/mole).

Apart from these general similarities the absolute values of the hydration energies of the lithium – and the fluorine-ion are quite different. As would be

Table 2. Calculated binding energies and geometrical parameters for different structures of the systems $(F \cdot nH_2O)^-$, $n = 1, 2$ ^a

System	B^{SCF} [kcal/mole]	Dissociation products	$d(FO)$ [a.u.]	$d(FH)$ [a.u.]	$d(OO)$ [a.u.]	$d(OH)$ [a.u.]	$\angle(HOH)$
$(FHOH)^-$	24.1	$F^- + H_2O$	4.77	2.96	—	1.80887 (not varied)	104.52° (not varied)
$(HOHFHOH)^-$	44.9 40.1 20.8	$F^- + 2H_2O$ $F^- + (H_2O)_2$ $(FHOH)^- + H_2O$	4.82	3.01	9.66	1.80887 (not varied)	104.52° (not varied)
$(HOHO(H)HF)^-$	36.6 31.8 12.5	$F^- + 2H_2O$ $F^- + (H_2O)_2$ $(FHOH)^- + H_2O$	4.62	2.83	5.26	1.80887 (not varied)	104.52° (not varied)
$(FHOHOH_2)^-$	22.9 18.2 0	$F^- + 2H_2O$ $F^- + (H_2O)_2$ $(FHOH)^- + H_2O$	4.77	2.96	∞	1.80887 (not varied)	104.52° (not varied)

^a All values, except those of the structure $(FHOHOH_2)^-$, are obtained from calculations using the [5.4.1] contraction at the oxygen and fluorine centres.

expected from the smaller size of the lithium cation its polarisation effect on the attached water molecules should be much stronger than that of any other ion discussed here, as it is the smallest known cation (except the proton). This explains the high bond energies calculated for the lithium hydrates [1, 4]. Our calculations show however that provided the ions are of comparable size, the sign of the ionic charge does not affect the hydration energies very much:

$$B^{SCF}(Na^+ \cdot H_2O) = 25.2 \text{ kcal/mole [1]},$$

$$B^{SCF}(F^- \cdot HOH) = 24.1 \text{ kcal/mole [2]},$$

$$B^{SCF}(HO^- \cdot HOH) = 24.3 \text{ kcal/mole [3]}.$$

These results are in close agreement with experimental measurements performed by Kebarle and co-workers [11].

Considering the two unsymmetrical structures (*A*) and (*D*) of the system $(F \cdot 2H_2O)^-$, which appear to be less stable than the symmetrical one, the effect of a negative fluorine ion approaching the hydrogen bonded dimeric water system may be studied.

The potential curve, displayed in Fig. 3, indicates that the structure (*A*), characterized by the formula $(HOHO(H)HF)^-$, should be stable with respect to the three possible dissociations into: $(FHOH)^- + H_2O$, or into: $F^- + (H_2O)_2$, or into $F^- + 2H_2O$. Using the [5.3.1] contraction at the oxygen and the fluorine centres as basis set, the equilibrium bond length between the F^- -ion and the oxygen nucleus of the water molecule acting as the proton acceptor part in the water dimer is calculated to be $d(FO) = 4.62$ a.u.; i.e. it is only very slightly different from the $d(FO)$ -value found for the monohydrate (the change being about 2.7%). The effect of the fluoride anion on the length of the adjacent hydrogen bond between the two water molecules is more distinct: for the $d(FO)$ -value given above a decrease of the oxygen/oxygen-bond length in the water dimer by approximately 8.3% (compared to the isolated dimer) is obtained. This remarkable change in the $d(OO)$ -bond length due to the F^- -ion was calculated with both of the two contracted basis sets. In accordance with these results the binding energy relative to the subsystems F^- and $2H_2O$ is larger than the sum of the binding energies of the subsystems $FHOH^-$ and $(H_2O)_2$ by about 7.7 kcal/mole. This indicates a stabilisation of the hydrogen bond in the dimer perturbed by the F^- -ion by about 7.7 kcal/mole compared to the isolated dimer. The value is estimated under the assumption that the (FHO) -hydrogen bond energy in the dihydrated fluorine anion $(HOHO(H)FH)^-$ is equal to the corresponding energy in the fluorine monohydrate $FHOH^-$, which is believed to be reasonable because of the nearly equal bond distances $d(FO)$ in both systems [4].

These results are in qualitative agreement with the stronger effects obtained for the dihydrated lithium cation, where the (Li^+) -ion is bonded to the proton donor part of the dimeric water molecule. In both cases the ions produce a charge shift in the region of the adjacent hydrogen bond in the dimeric water in such a way that the H-bond strength is increased compared to the isolated dimer [1]. The structure (*A*) of the dihydrated fluoride anion as well as the corresponding structure of the lithium dihydrate may therefore be considered as very simplified models to discuss the formation and the stabilisation of a

second hydration shell for these ions in aqueous solutions. The stabilisation of the hydrogen bond between the two water molecules due to the (F^-)-ion was determined to be 7.7 kcal/mole. Similar values should be found for other ions of comparable size (like Na^+ , OH^-). In our previous calculations on the corresponding model system in the case of the lithium cation, which may be characterized by the formula $(LiO(H)HOH_2)^+$, a stabilisation of the hydrogen bond between the two oxygen centres by about 11 kcal/mole was obtained [4]. While the hydration energies of the water molecules attached directly to the Li^+ - or the F^- -ion have been calculated to be quite different, there seems to be not such a strong difference in the influences of these two ions on an adjacent hydrogen bond, according to the fact that the polarisation effect of the lithium cation decreases rapidly with increasing distance from the ion. One has to expect that the absolute values of the stabilisation energies, which have been obtained for the very simplified models described above, become considerably smaller, if a complete first hydration shell around the ions is taken into account. Thus it might be concluded from these results, that in the case of the singly charged ions discussed in this series of investigations [1-4] a second hydration shell should be only weakly bonded and easily perturbed by other effects.

Considering finally the geometrical structure (*D*), in which the fluoride anion is attached to the proton donor part of the dimeric water system, and which may therefore be characterized by the formula $(FHOHOH_2)^-$, the computational results collected in Tables 1 and 2 (obtained with the [5.3.1]-contraction) indicate that this structure is unstable and leads to a dissociation into: $(FHOH)^- + H_2O$. The strong influence of the (F^-)-ion in the position P2 (Fig. 2) causes a stabilisation of the chemical bond between O2 and H3 (Fig. 2) and destroys the hydrogen bond between the two water molecules.

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