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SCF MO LCGO Studies on the Hydration of Ions: The Systems H^+H_2O, Li^+H_2O, and Na^+H_2O

GEERD H. F. DIERCKSEN and WOLFGANG P. KRAEMER

Max-Planck-Institut für Physik und Astrophysik, 8000 München 23, Germany

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The energy surfaces of the systems $LiOH_2^+$ and $NaOH_2^+$ are studied for a number of different geometries within the SCF MO LCAO framework, using a gaussian basis set to approximate the wavefunction. In the minimum energy geometry of both systems the positive ion is bound to the oxygen atom of the water molecule. The computed binding energies and bond distances are: $B^{SCF}(LiOH_2^+) = 36.0$ kcal/mole, $d(LiO) = 3.57$ a.u., and $B^{SCF}(NaOH_2^+) = 25.2$ kcal/mole, $d(NaO) = 4.23$ a.u., resp. The results are compared with those of H_3O^+ and discussed in view of ion-solvent interaction in aquous solutions.

Little is known about the "structure" of liquids, and in particular about ion-solvent interaction in aquous solutions [1]. The classical theory of ion-solvent interaction was developed by Debey and Hückel in 1923 and has been of enormous impact on the research in this field [2]. By assuming that each ion is surrounded by a cloud of opposite charged ions, they were able to explain qualitatively and to correlate quantitatively a great number of experimental data. A theoretical treatment of the ion-solvent interaction based on the classical electrostatic theory was given by Buckingham in 1957 [3]. The first accurate quantumchemical study was an *ab-initio* SCF-MO-LCGO computation on the monohydration of the ion F^- [4]. A quantumchemical CNDO model calculation was used to investigate the hydration of the series of ions Li^+, Na^+, F^-, and Cl^- [5]. Preliminary results of an *ab-initio* SCF MO LCGO study on the monohydrates of the positive ions H^+, Li^+, and Na^+ will be presented in the following, using a large gaussian basis set. The aim was to get more accurate information about parts of the energyhypersurface, about the minimum energy geometry, and about the hydration energy (binding energy), than available so far.

The wavefunctions and energies have been calculated using Roothaan's SCF MO LCAO method [6]. The computations have been carried out on an IBM 360/91 computer, using the program system IBMOL/VERSION IV [7], modified by one of the authors (G. D.) to avoid the explicit integral transformation [8], and by using a test release of the program system MUNICH [9]. The molecular orbitals are expanded into a set of gaussian orbitals $\eta = x^l y^m z^n \exp(-\alpha r^2)$ (unnormalized) which are contracted to reduce the number of linear parameters. The basis sets used in these calculations consist of (14.8.1)-functions (which means in the well known terminology: 14*s*-, 8*p*-, and 1*d*-type functions) centered at the

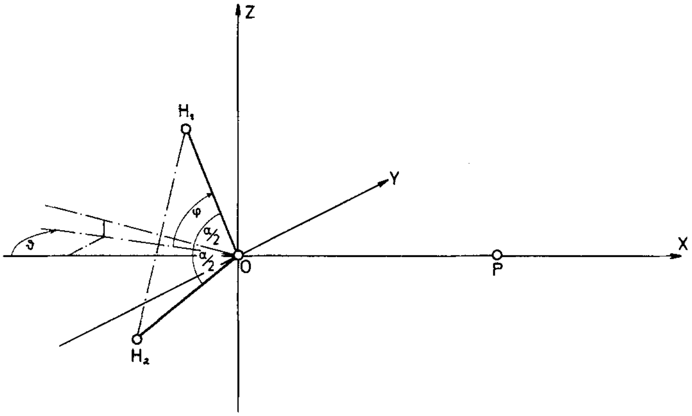

Fig. 1. Coordinate system for $Li^+ \cdot H_2O$ and $Na^+ \cdot H_2O$ (the Li^+ and Na^+ cations, resp. are in position P)

sodium atom, of (11.7.1)-functions at the oxygen, of (11.2)-functions at the lithium, and of (6.1)-functions at the hydrogens. These basis sets are contracted to [8.6.1]-functions at the sodium atom, to [5.4.1]-functions at the oxygen, to [5.2]-functions at the lithium, and to [3.1]-functions at the hydrogens. The basis sets used for the hydrogen atoms have been described previously [10]. The basis set for the sodium atom has been optimized at the atom itself, and on sodium hydroxid NaOH, resp. The *s*-type functions of the basis set for the lithium atom have been taken from the literature, and reasonable *p*-type functions have been added to account for polarization effects.

The results obtained for the systems H_2O, LiOH, Li^+, NaH, and Na^+ are in good agreement with those of other extended basis set calculations of high accuracy. The data for the H_2O molecule have already been reported [10]. For the lithiumhydroxid molecule LiOH, using the experimental bond distance $d(\text{LiO}) = 5.71$ a.u., the total SCF-energy is computed to be $E^{\text{SCF}}(\text{LiOH}) = -82.94586$ a.u. (best value $E^{\text{SCF}}(\text{LiOH}) = -82.9285$ a.u. [12]), and for the lithium cation Li^+ the total SCF-energy is calculated to be $E^{\text{SCF}}(\text{Li}^+) = -7.23621$ a.u. (best value $E^{\text{SCF}}(\text{Li}^+) = -7.23641$ a.u. [13]). The following values are computed for the sodium hydridmolecule NaH and the sodium cation Na^+: $E^{\text{SCF}}(\text{NaH}) = -162.38160$ a.u. at $d(\text{NaH}) = 3.5665$ a.u. (best value $E^{\text{SCF}}(\text{NaH}) = -162.3928$ a.u. [14]), and $E^{\text{SCF}}(\text{Na}^+) = -161.66679$ a.u. (best value $E^{\text{SCF}}(\text{Na}^+) = -161.67676$ a.u. [13]).

The investigations presented here are essentially restricted to calculations on the following three basic structures of the systems $LiOH_2^+$ and $NaOH_2^+$ (the geometrical parameters used are defined in Fig. 1): the structure (*A*), symmetrical to the AO axis (A = Li, Na), with A and O being next neighbours, the structure (*B*) with a linear hydrogen bridge between the centers A and O, and finally the structure (*C*), again symmetrical to the AO-axis, but with two hydrogen bridges between the centers A and O. In all three structures the geometry of the water molecule is kept fixed to its experimental values ($d(\text{OH}) = 1.80887$ a.u. $\alpha(\text{HOH}) = 104.52°$), if not stated otherwise.

Table 1. Total SCF energies for the system $[LiH_2O]^+$ in different geometrical configurations

	d(LiO) [a.u.]	d(OH) [a.u.]	α	φ	ϑ	E^{SCF} [a.u.]
A 1	2.00	1.80887	104.52°	52.26°	0°	−83.019833
2	2.70					−83.308046
3	3.00					−83.335744
4	3.50					−83.345583
5	4.00					−83.340019
6	5.00					−83.323975
7	7.00					−83.306211
8	10.00					−83.296868
9	16.00					−83.291533
10	3.50	1.70887	104.52°	52.26°	0°	−83.340777
11		1.90887				−83.339057
12	3.50	1.80887	99.52°	49.76°	0°	−83.344413
13			106.10°	53.05°		−83.345651
14			107.02°	53.51°		−83.345623
15			109.52°	54.76°		−83.345317
16	3.50	1.80887	104.52°	52.26°	20°	−83.344577
17					30°	−83.343240
18					40°	−83.341221
B 19	5.00	1.80887	104.52°	104.52°	180°	−83.258478
20	8.00					−83.277972
21	14.00					−83.285045
C 22	5.00	1.80887	104.52°	232.26°	0°	−83.263524
23	6.00					−83.268985
24	9.00					−83.278235
25	15.00					−83.284380

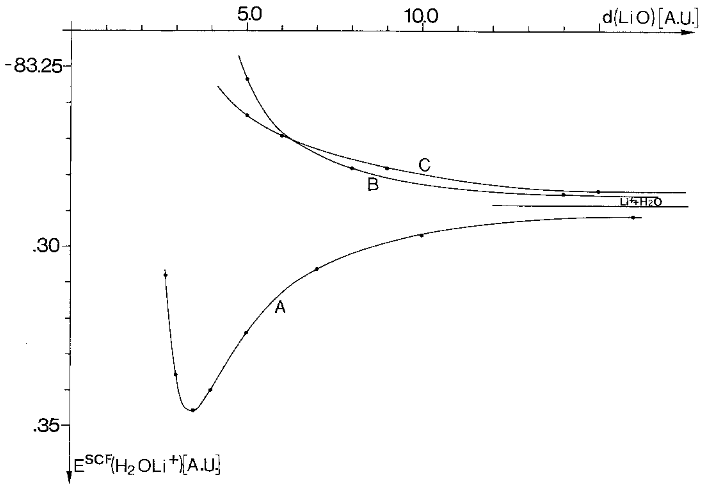

Fig. 2. Potential energy curves for the d(LiO) variation in different geometrical structures of the system $Li^+ \cdot H_2O$

The results of the various calculations are summarized in Table 1 and Fig. 2 for the system $LiOH_2^+$, and in Table 2 and Fig. 3 for the system $NaOH_2^+$.

No energy minimum is found for structures (*B*) and (*C*). Hence there is no stable configuration with a hydrogen bridge between the two centers A and O. For

Table 2. Total SCF energies for the system $[NaH_2O]^+$ in different geometrical configurations

	d(NaO) [a.u.]	d(OH) [a.u.]	α	φ	ϑ	E^{SCF} [a.u.]
A 1	3.00	1.80887	104.52°	52.26°	0°	−237.66777
2	3.50					−237.74098
3	4.00					−237.75792
4	4.25					−237.75887
5	4.50					−237.75775
6	5.00					−237.75312
7	6.00					−237.74353
8	7.00					−237.73691
9	10.00					−237.72757
10	15.00					−237.72270
11	4.25	1.80887	99.52°	49.76°	0°	−237.75798
12			109.52°	54.76°		−237.75836
B 13	5.00	1.80887	104.52°	180°	0°	−237.68217
14	8.00					−237.70876
15	10.00					−237.71250
16	14.00					−237.71573
C 17	5.00	1.80887	104.52°	232.26°	0°	−237.69223
18	8.00					−237.70659
19	10.00					−237.71061
20	14.00					−237.71451

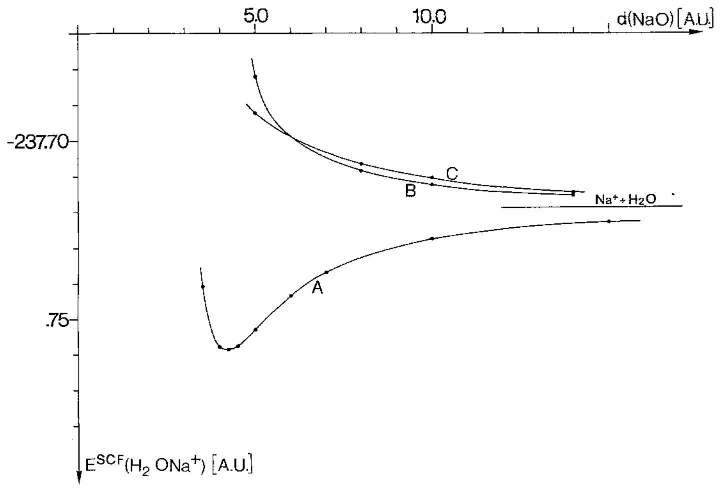

Fig. 3. Potential energy curves for the d(NaO) variation in different geometrical structures of the system $Na^+ \cdot H_2O$

Table 3. Theoretical binding energies and geometry parameters for the lowest energy structures of the systems $(AOH_2)^+$, with A = H, Li, and Na

	B^{SCF} [kcal/mole]	$d(AO)$ [a.u.]	$d(HO)$ [a.u.]	$\alpha(HOH)$	φ	ϑ
OH_2 (exp)			1.78	105.3°	—	—
			(1.81)	(104.52°)	—	—
HOH_2^+ (exp)	173.24	1.82	(1.82)	120.0°	—	—
$LiOH_2^+$	36.02	3.57	1.80	106.1°	53.05°	0°
$NaOH_2^+$ (exp)	25.16	4.23	(1.81)	(104.52°)	(52.26°)	0° (not varied)

large internuclear separations $d(AO)$ the structure (B) is lower in energy than structure (C), while for distances smaller than $d(AO) \sim 6$ a.u. the order is reversed. This is reasonable because the repulsion energy between the centers A and H increases less with decreasing separation $d(AO)$ for the bifurcated structure (C) than for the linear hydrogen bridge structure (B).

For both systems investigated an energy minimum is found only for structure (A) in which the positive ions are bound to the oxygen atom, the more electronegative part of the water molecule. This is in agreement with theoretical predictions based on classical ion-dipole interactions. For large distances $d(AO)$ the energy is increasing slowly, as it has been found already for the hydration of the negative fluoride ion F^- [4]. The bond distances $d(AO)$ and the binding energies $B(AOH_2^+)$ relative to the subsystems A^+ and H_2O for the systems HOH_2^+, $LiOH_2^+$, and $NaOH_2^+$ have been collected in Table 3. From these data it can be concluded that there is a big gap in the bond distances $d(AO)$ and the binding energies $B(AOH_2^+)$ between the hydronium ion and the other monohydrates. The hydronium cation HOH_2^+ is completely symmetric with an OH-bond distance near to that in the water molecule and has a very high binding energy. In the other two systems the AO-distance is about double as large as the OH-distance in the attached water molecule and the binding energy is much smaller. With increasing ion size the bond distance is increasing while the binding energy is decreasing. In the system $LiOH_2^+$ the influence of the lithium cation Li^+ on the structure of the attached water molecule has been studied in greater detail. As can be seen from Table 3 as well, there is no striking effect on the geometrical parameters of the attached water molecule. By a comparison of the systems $(FHOH)^-$ and $(NaOH_2)^+$ it is found that the mono-hydration of negative and positive ions of about equal ionic radii [15] leads to about equal bond distances $d(XO)$ ($X = F^-, Na^+$) and to about equal hydration energies B^{SCF}.

As has been pointed out already [4] the hydration energy of ions is much higher than the hydrogen binding energy between water molecules. This leads to the conclusion that a strong ordering effect of ions on the water molecules is to be expected in aqueous solutions. This in no way means that there has to be a "static geometrical arrangement" of water molecules around the ion, but there may as well be a "dynamic shell" of oriented water molecules directly bound to the ion. The number of water molecules making up this shell is determined by the ion size and by the mutual steric hindrance of the water molecules. Whether there is an ordering effect even on a "second shell" around the ions will be subject of another study. A number of properties of the systems under discussion have been computed and will be published elsewhere together with a more extended discussion of the energy hypersurface.

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G. Diercksen
Max-Planck-Institut für Physik und Astrophysik
D-8000 München 23, Föhringer Ring 6
Germany