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SCF MO LCGO Studies on Hydrogen Bonding: The System $(HOHOH)^-$

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The closed shell ground state of the system $(HOHOH)^-$ has been studied for different geometrical configurations within the SCF LCGO MO framework, using an extended basis set of gaussian type functions to approximate the molecular wavefunctions. The most stable structure was found to have a linear, slightly asymmetrical hydrogen bridge between the two oxygen nuclei. The OO-distance was determined to be $d(\mathrm{OO}) = 4.75$ a.u. ($= 2.51$ Å), and a binding energy, relative to the subsystems H_2O and OH^-, of $B = 24.3$ kcal/mole was obtained, in reasonable agreement with the most recent experimental measurement ($B_{\mathrm{exp}} = 22.5$ kcal/mole). The proton transfer process between the two subsystems has been studied in a range near the equilibrium OO-distance.

The systems $H^+(H_2O)_n$ and $OH^-(H_2O)_n$ play an important role as well in the chemistry of aqueous solutions as in atmospheric physics [1]. In the last years several experimental studies on the solvation effects of the ions H^+ and OH^- in the gas phase have been published [2]. From the similarity in the elastic scattering cross sections of both solvated systems it can be concluded that the two clustered species should have similar cluster sizes and similar geometrical structures. While Friedman and coworkers found experimentally nearly equal binding energies for both systems at the same stage of hydration (e.g. $B(H_5O_2^+) = 32.3$ kcal/mole; $B(H_3O_2^-) = 34.6$ kcal/mole) [2], Kebarle obtained from experiments of a different nature a considerably smaller value in the case of the monohydrated species $(H_3O_2)^- : B(H_3O_2^-) = 22.5$ kcal/mole [3]. The only theoretical study on the various H^+ and OH^- hydrated ions has been performed within the framework of the CNDO method [4]. In addition to our studies on the system $(H_2OHOH_2)^+$ [5] some preliminary results of *ab initio* SCF LCGO MO calculations on the related system $(HOHOH)^-$ will be given here.

The SCF results of these studies have been obtained within the framework of Roothaan's finite expansion procedure using gaussian type functions: $\eta = x^l y^m z^n \exp(-\alpha r^2)$ (unnormalized) as basic functions. The calculations have been carried out with a modified version (G. D.) of the program system IBMOL/IV. As described in the previous studies on hydrogen bonded systems [6] an (11.7.1/6.1) gaussian basis set was chosen to approximate the molecular wavefunctions, contracted to a [5.4.1/3.1] set to reduce the number of linear parameters [7]. The exponents of the polarization functions ($\alpha(d_{\mathrm{O}}) = 1.00$; $\alpha(p_{\mathrm{H}}) = 0.75$) were taken from SCF calculations on the single water molecule. Using this basis set the following SCF energies have been obtained for the two subsystems H_2O and OH^-: $E^{\mathrm{SCF}}(H_2O) = -76.05199$ a.u. and $E^{\mathrm{SCF}}(OH^-) = -75.40671$ a.u. (best values re-

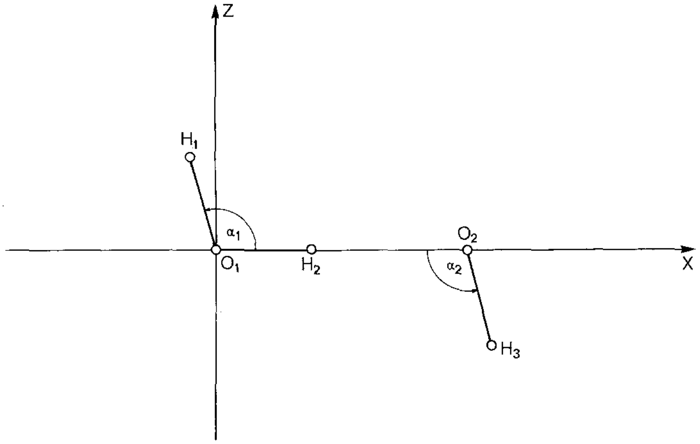

Fig. 1. Coordinate system for (HOHOH)$^-$

ported in the literature: $E^{SCF}(H_2O) = -76.05936$ a.u. [8], $E^{SCF}(OH^-) = -75.41754$ a.u. [9]). In these calculations the molecular geometries were kept fixed at their experimentally determined values ($d(OH)_{H_2O} = 0.9572$ Å $= 1.8089$ a.u.; angle (HOH) $= 104.52°$; for the d(OH)-distance in OH^- the d(OH)-value of H_2O was taken). The energy values are believed to be off from the corresponding Hartree-Fock limits by not more than about 0.015 a.u.

As in the problem of $(H_5O_2)^+$, mainly two different geometrical configurations of the system (HOHOH)$^-$ have been studied in more detail at the present stage of investigations (for a definition of geometrical parameters see Fig. 1):

In structure *A*, the molecular geometry of the two subsystems H_2O and OH^- is kept fixed at the experimental values, given above, and the two subsystems are bound to each other by a linear, asymmetrical hydrogen bridge with the water molecule acting as the proton donor and the negatively charged hydroxyl-ion as the electron donor (proton acceptor). The angle between the OH^--bond axis and the axis of the linear hydrogen bridge, angle α_2, has been approximated in a first guess by the water-angle, $\alpha_2 = 104.52°$. For this configuration the mechanism of hydrogen bond formation has been studied over a wide range of internuclear separations between the oxygens. At the equilibrium d(OO)-distance an additional optimization of the angle α_2 has been performed.

The second structure under consideration, structure *B*, is an highly symmetrical one: the bridging proton has been placed midway between the two oxygen centres and the angles α_1 and α_2 were taken to be equal ($\alpha \equiv \alpha_1 = \alpha_2$). Thus structure *B* has a center of inversion. In this case a variation of the oxygen/oxygen-distance within a smaller range and of the angle α just around the equilibrium value has been carried out.

The potential curves for the d(OO)-variation in the two structures *A* and *B* are displayed in Fig. 2, the numerical values are listed in Table 1.

The energy curves (*A*) and (*B*) in Fig. 2 are quite similar in their general behavior to those found for the related system ($H_5O_2^+$) [5]. In the region of large oxygen/oxygen-separations (d(OO) greater than 5.00 a.u.) the structure *A* with an asym-

Table 1. Total SCF energies for the system $(HOHOH)^-$ in different geometrical configurations (length and energy values in a.u.)

	d(OO)	d(O1H1) = d(O2H3)	d(O1H2)	α_1	α_2	E^{SCF}
(*A*) 1	4.00	1.809	1.809	104.52	104.52	−151.46176
2	4.50					−151.49139
3	4.75					−151.49524
4	5.00					−151.49585
5	5.50					−151.49269
6	6.00					−151.48773
7	8.00					−151.47295
8	10.00					−151.46665
9	16.00					−151.46121
10	5.00	1.809	1.809	104.52	104.52	−151.49585
11					109.52	−151.49601
12					114.52	−151.49604
13					140.00	−151.49484
14					180.00	−151.49308
(*B*) 1	4.00	1.809	2.000	104.52	104.52	−151.46650
2	4.30		2.150			−151.49033
3	4.50		2.250			−151.49523
4	4.62		2.310			−151.49522
5	4.75		2.375			−151.49320
6	5.00		2.500			−151.48493
7	6.00		3.000			−151.42420
8	4.50	1.809	2.250	94.00	94.00	−151.49235
9				104.52	104.52	−151.49523
10				114.00	114.00	−151.49400

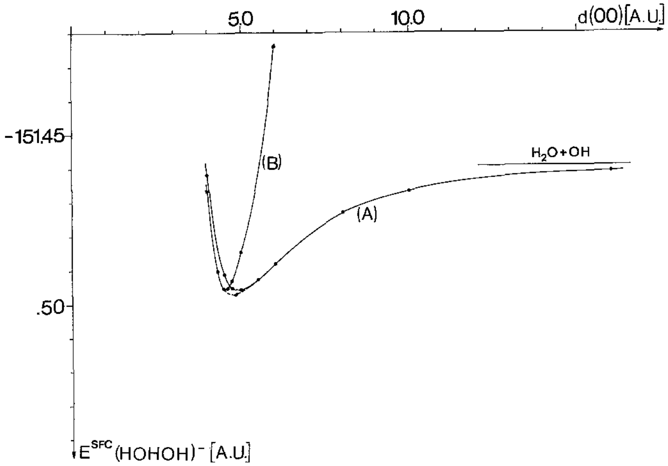

Fig. 2. Potential energy curves for the d(OO)-variation in two different structures of $(HOHOH)^-$ (A: structure *A* with a linear, asymmetrical hydrogen bond; B: structure *B* with a linear, symmetrical hydrogen bond)

metrical, linear hydrogen bond is the most stable one. As has already been pointed out in previous notes on hydrogen bond formation between a neutral molecule and a positive or negative ion [6], the bonding in those systems is of rather long range. In the case of $(HOHOH)^-$ even at an OO-distance of $d(OO) = 16.00$ a.u. a binding energy of about 1.6 kcal/mole is still left. In the region of small oxygen/oxygen-separations ($d(OO)$ smaller than 4.50 a.u.) the structure B with a symmetrical, linear hydrogen bridge becomes the more stable one. The minimum SCF energies for both structures A and B are nearly equal; the calculated energy difference is less than 0.5 kcal/mole. The corresponding equilibrium $d(OO)$-distances differ by 0.5 a.u. In the small gap between the two minima of the potential curves (A) and (B) (4.50 a.u. $\leqq d(OO) \leqq$ 5.00 a.u.), intermediate structures become more stable, in which the bridging proton is continuously shifted from the position in one of the two limiting structures to that in the other.

For both $(HOHOH)^-$-structures A and B a variation of the angles α_2 and α, respectively, has been considered keeping the OO-distances at their corresponding equilibrium values. From the numerical results, given in Table 1 (A10–A14; B8–B10), it follows that in the symmetrical structure B even very small deviations of α from the water-angle cause a strong increase in the potential energy. In the case of structure A the optimum value for the angle α_2 at $d(OO) = 5.00$ a.u. turnes out to be somewhat larger than 104.52°, the angle in the water molecule. But the appropriate potential curve is rather flat.

The position of the central proton, involved in hydrogen bond formation, is determined by a potential which has the well known double-minimum shape for the asymmetrical structure A, while in the region, where structure B is the more stable one, the two potential minima coincide thus giving a single-minimum potential curve governing the motions of the bridging proton. The probability of exchanging the central proton between the two subsystems according to the equation: $HOH + OH^- = HO^- + HOH$ depends to some extend on the height of the energy barrier separating the two potential minima. In the case of the single-minimum potential curve this probability is apparently one half. But even for larger distances between the two subsystems the probability for a proton exchange is still fairly good. From the potential curves (A) and (B) in Fig. 2 and from additional calculations on the proton transfer process in the range of medium $d(OO)$-values (see Fig. 3, numerical values are listed in Table 2) it can be seen that the energy barrier decreases very rapidly with decreasing OO-separations in this region. This fact provides a reasonable explanation for the high mobility of hydroxyl-ions in aqueous solutions.

From these preliminary results, presented here, it follows that contrary to the related problem of $(H_5O_2)^+$ a slightly asymmetrical structure of the system $(HOHOH)^-$ is obtained to give the minimum SCF energy. This structure is characterized by the following geometrical parameters: $d(OO) = 4.75$ a.u., $d(O1H2) = 2.19$ a.u. (structure A: $d(O1H2) = 1.81$ a.u., structure B: $d(O1H2) = 2.38$ a.u. for $d(OO) = 4.75$ a.u.). Thus the deviation of the position of the central proton from the symmetrical position is 0.19 a.u. The minimum SCF energy is found to be $E^{SCF}(HOHOH^-) = -151.49744$ a.u. for this structure. This corresponds to a binding energy of $B = 24.3$ kcal/mole, relative to the separated systems H_2O and OH^-. This value is in reasonable agreement with the experi-

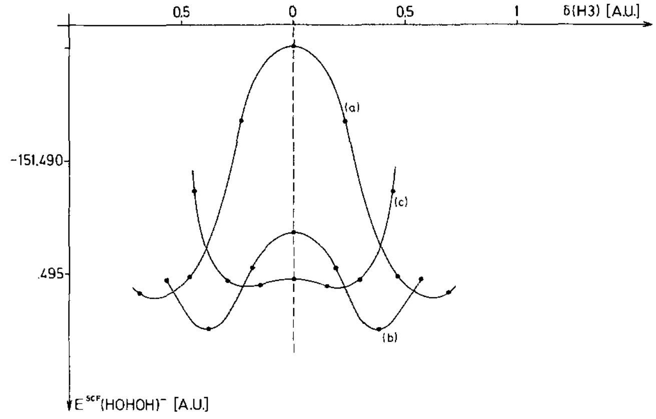

Fig. 3. Potential energy curves for the proton transfer in $(HOHOH)^-$ at three different d(OO)-separations (a: $d(OO) = 5.00$ a.u.; b: $d(OO) = 4.75$ a.u.; c: $d(OO) = 4.50$ a.u.)

Table 2. Proton transfer process in $(HOHOH)^-$ (ΔH2-deviation of the central proton from the position midway between the two oxygen centres) (length and energy values in a.u.)

	d(OO)	d(O1H1) $= d$(O2H3)	ΔH2	$\alpha_1 = \alpha_2$	E^{SCF}
(AB) 1	4.50	1.809	0.	104.52	−151.49523
2			0.147		−151.49551
3			0.294		−151.49525
4			0.441		−151.49139
5	4.75	1.809	0.	104.52	−151.49320
6			0.189		−151.49474
7			0.378		−151.49744
8			0.567		−151.49524
9	5.00	1.809	0.	104.52	−151.48493
10			0.230		−151.48825
11			0.460		−151.49512
12			0.690		−151.49585

mental measurement obtained by Kebarle: $B_{exp} = 22.5$ kcal/mole [3]. It has already been mentioned that in the present calculations a variation of the positions of the outer hydrogen centres has not been taken into account. This lack of complete optimization of the geometrical configuration may cause the small deviation of the calculated structure from the symmetrical one, which was expected to minimize the SCF energy.

Some further studies on this point together with a discussion of various one-electron properties will be published elsewhere.

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