

## SCF LCGO MO Studies on the Fluoronium Ion $\text{FH}_2^+$ and Its Hydrogen Bonding Interaction with Hydrogen Fluoride FH

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The stability and geometrical structure of the fluoronium ion is investigated using the one-determinant SCF LCAO MO method. The equilibrium geometry is characterized by a bond length of  $d(\text{FH}) = 0.95 \text{ \AA}$  and a bond angle of  $114.75^\circ$ . The proton binding energy is determined to be 120.1 kcal/mole. The molecules  $\text{FH}_3^{2+}$  and  $\text{FH}_3$  are found to be unstable. A binding energy of 30.7 kcal/mole is obtained for the hydrogen bond formation between the systems  $\text{FH}_2^+$  and FH. In the minimum energy structure the central proton is situated midway between the two F atoms in a symmetrical single minimum potential. The general behavior of the potential curves of the di-solvated proton involving  $\text{NH}_3$ ,  $\text{OH}_2$ , and FH as solvent molecules is discussed. In all these cases double minimum potentials are found, if the equilibrium separation between the heavy atoms is larger than approximately  $2.4 \text{ \AA}$ , and single minimum potential for separations smaller than this value.

*Key words:* SCF LCGO MO calculation – Proton solvation – Hydrogen bonding –  $\text{FH}_2^+ - \text{FH}_2^+ \cdot \text{FH}$

The present investigation deals with two topics, the solvation of a proton by a single hydrogen fluoride molecule and the hydrogen bonding interaction between the resulting fluoronium ion and another hydrogen fluoride molecule. While the ammonium and oxonium ions  $\text{NH}_4^+$  and  $\text{OH}_3^+$  are well established experimentally, this has not been possible until recently [1] for the fluoronium ion  $\text{FH}_2^+$ , although its existence has been postulated to explain in particular the electrical conductivity of acid solutions of several fluoride compounds in liquid hydrogen fluoride. Further, from the high binding energies of the proton attached to an ammonia or a water molecule, which are experimentally determined to be  $B(\text{NH}_4^+) = 207 \text{ kcal/mole}$  [2] and  $B(\text{OH}_3^+) = 168 \text{ kcal/mole}$  [3], it can be concluded that the fluoronium ion forms a relatively stable species too. The corresponding proton binding energy is expected to be somewhat smaller than  $B(\text{OH}_3^+)$  due to the higher electronegativity of the fluorine atom as compared to the oxygen atom.

In a recent publication Couzy and co-workers reported the first direct observation of the fluoronium ion [1]. By an analysis of the infrared spectra of some fluoronium salts in the solid and liquid state the geometrical structure of the  $\text{FH}_2^+$  ion was shown to be angular. But so far no accurate experimental determination of the geometrical parameters of the  $\text{FH}_2^+$  ion has been performed.

So the fluoronium ion seems to provide an ideal case for a theoretical prediction of the geometrical structure because of the small size of the electronic system. Apart from a quite simplified model calculation (FSGO model) by Frost [4] the only theoretical studies on the  $\text{FH}_2^+$  system known to the authors are LCAO MO SCF calculations by Csizmadia *and co-workers* with various size gaussian basis sets [5] and semi-empirical calculations of Schuster *et al.* using the CNDO SCF method followed by a configuration interaction expansion (CNDO CI) [6]. Only in these latter semiempirical studies the optimum geometrical structure of  $\text{FH}_2^+$  was searched, while in Csizmadia's SCF calculations a fixed geometry of the nuclear centres has been assumed ( $d(\text{FH}) = 0.917 \text{ \AA}$ ,  $\angle(\text{HFH}) = 105^\circ$  [7]). In the present work it was tried to get accurate theoretical informations about the geometrical structures of the ionic systems  $\text{FH}_2^+$  and  $\text{FH}_2^+ \cdot \text{FH}$  within the one-determinant LCAO MO SCF framework using a rather extended gaussian basis set. For the system  $\text{FH}_2^+ \cdot \text{FH}$  in particular the potentials of the central proton, involved into the hydrogen bond formation between the two FH fragments has been computed for different F-F distances. These potential curves are discussed and compared to those obtained for the systems  $\text{NH}_4^+ \cdot \text{NH}_3$ ,  $\text{OH}_3^+ \cdot \text{OH}_2$ , and  $\text{OH}_2 \cdot \text{OH}^-$ .

The SCF wavefunctions and energy expectation values have been calculated using Roothaan's SCF LCAO MO expansion method [8]. The calculations were carried out on an IBM 360/91 with the program system MUNICH [9], which is based on the use of general Gaussian functions  $\eta = x^l y^m z^n \exp(-\alpha r^2)$  as basis functions for the expansion of the molecular orbitals. A (11s7p1d/6s1p) basis set was employed for the fluorine and hydrogen centres, respectively, contracted to a [5s4p1d/1s1p] set to reduce the number of linear parameters in the SCF procedure (for a definition of the basis set notation used here, see [10]). The exponential parameters and contraction coefficients are taken from the literature [11]. The polarization functions (*d*-type functions on the F atom and *p*-type functions on the H atom) were optimized by SCF calculations on the FH molecule and their exponential parameters are obtained to be  $\alpha_d(\text{F}) = 1.23$  and  $\alpha_p(\text{H}) = 0.75$  [12]. With this basis set an SCF energy of  $E^{\text{SCF}} = -100.05638$  a.u. was calculated for FH at its experimental bond length of 1.7329 a.u. This compares with the best SCF energy value reported in the literature of  $E^{\text{SCF}} = -100.07040$  a.u. [13], which is believed to be very close to the Hartree-Fock limit. The energy value obtained with the basis set given above thus differs from this limit by about 0.015 a.u. (ca. 9.5 kcal/mole). The energy effects to be discussed here are much higher than this difference. The basis set used can consequently be regarded to yield reliable results for the geometrical structures and binding energies of the systems to be investigated within the accuracy of the Hartree-Fock method.

As mentioned previously the experimental work on the fluoronium ion  $\text{FH}_2^+$  did not permit an accurate determination of its structure. The ion was supposed to have a bond length of 1.02 Å and a bond angle somewhat larger than the angle in the water molecule (a range of 105–120° was regarded as probable) [1]. Optimization of these geometrical parameters in the present SCF study gave a significantly different bond length of  $d(\text{FH}) = 1.788$

Table 1. Total SCF energies for  $\text{FH}_2^+$  (variation of bond length  $d(\text{FH})$  and  $\text{HFH}$  angle; all values in atomic units)

	$d(\text{FH})$	$\angle \text{HFH}$	$E^{\text{SCF}}$
1	1.93755	105°	-100.23632
2	1.92755	105°	-100.23746
3	1.91755	105°	-100.23854
4	1.90755	105°	-100.23956
5	1.88755	105°	-100.24140
6	1.86755	105°	-100.24296
7	1.84755	105°	-100.24421
8	1.82755	105°	-100.24515
9	1.80755	105°	-100.24573
10	1.79755	105°	-100.24588
11	1.78755	105°	-100.24593
12	1.77755	105°	-100.24588
13	1.76755	105°	-100.24572
14	1.74755	105°	-100.24507
15	1.78755	103°	-100.24504
16	1.78755	107°	-100.24664
17	1.78755	110°	-100.24737
18	1.78755	114°	-100.24777
19	1.78755	114.75°	-100.24778
20	1.78755	115°	-100.24778
21	1.78755	116°	-100.24775
22	1.78755	120°	-100.24727
23	1.78755	140°	-100.23889
24	1.78755	180°	-100.22309
25	1.77755	114°	-100.24775
26	1.77755	115°	-100.24776
27	1.77755	116°	-100.24773
28	1.79755	114°	-100.24769
29	1.79755	115°	-100.24770
30	1.79755	116°	-100.24766

a.u. = 0.95 Å and a bond angle of  $\angle(\text{HFH}) = 114.75^\circ$  yielding a total SCF energy of  $E^{\text{SCF}} = -100.24778$  a.u. The results of the corresponding calculations are listed in Table 1. Schuster *et al.* calculated a FH bond length of  $d(\text{FH}) = 1.956$  a.u. = 1.04 Å and a bond angle of  $\angle(\text{HFH}) = 120^\circ$  with the CNDO SCF method. Including CI they obtained  $d(\text{FH}) = 1.977$  a.u. = 1.05 Å and  $\angle(\text{HFH}) = 114.5^\circ$ . This latter result for the bond angle is in good agreement with the ab initio SCF results of the present study, while both CNDO values for the bond length are not quite satisfactory. The proton binding energy corresponding to the reaction  $\text{FH}_2^+ \rightleftharpoons \text{FH} + \text{H}^+$  is determined from the SCF results to be  $B(\text{FH}_2^+) = 120.1$  kcal/mole. The binding energy values obtained from both CNDO calculations [CNDO SCF:  $B(\text{FH}_2^+) = 198$  kcal/mole; CNDO CI:  $B(\text{FH}_2^+) = 166$  kcal/mole] are significantly too high. The obtained proton binding energy in the fluoronium ion of  $B(\text{FH}_2^+) = 120.1$  kcal/mole compares well with the corresponding energy values for the ammonium ion [ $B(\text{NH}_4^+) = 207$  kcal/mole] and the oxonium ion [ $B(\text{OH}_3^+)$ ]

Table 2. Total SCF energies for  $\text{FH}_3^+$  (variation of bond length  $d(\text{FH})$  and out of plane angle  $\phi$ ; all values in atomic units)

	$d(\text{FH})$	$\phi$	$E^{\text{SCF}}$
1	1.78	0°	-100.05157
2	1.80	0°	-100.05594
3	1.90	0°	-100.06957
4	1.96	0°	-100.07244
5	1.98	0°	-100.07269
6	2.00	0°	-100.07263
7	2.02	0°	-100.07228
8	2.10	0°	-100.06841
9	1.98	5°	-100.07223
10	1.98	10°	-100.07064
11	1.98	20°	-100.06126

= 168 kcal/mole], the binding energy differences being about 40 kcal/mole between  $\text{NH}_4^+$  and  $\text{OH}_3^+$  and between  $\text{OH}_3^+$  and  $\text{FH}_2^+$ .

The high stability of the ion  $\text{FH}_2^+$  and the fact that only two hydrogen centres are bound to the fluorine atom gives rise to the question whether the fluoronium ion is able to bind another proton to form  $\text{FH}_3^+$ . The results of SCF calculations connected with this question are summarized in Table 2. From these data it is seen that the  $\text{FH}_3^+$  system has a planar structure with a FH bond length of  $d(\text{FH}) = 1.98$  a.u. = 1.05 Å, which is increased by ca 11% compared to the bond length in  $\text{FH}_2^+$ . The minimum SCF energy is obtained to be  $E^{\text{SCF}} = -100.07269$  a.u. This means that the di-protonated system  $\text{FH}_3^+$  is stable against a dissociation into  $\text{FH} + 2\text{H}^+$  with a binding energy of  $B = 10.2$  kcal/mole (the average binding energy per bonded proton is thus 5.1 kcal/mole). On the other hand, the  $\text{FH}_3^+$  system is seen to be unstable with respect to a dissociation into  $\text{FH}_2^+ + \text{H}^+$  by 109.9 kcal/mole. This result may easily be understood from purely electrostatical considerations. The repulsional forces between the two protons are too strong to be compensated by the sum of the binding energies of each proton to the fluorine centre in the FH molecule.

Similar stability studies are performed for the neutral  $\text{FH}_3$  molecule. The SCF results are collected in Table 3. As in  $\text{FH}_3^+$  the neutral system is obtained to be planar with a FH bond length of  $d(\text{FH}) = 2.25$  a.u. = 1.19 Å. From the minimum SCF energy value of  $E^{\text{SCF}} = -100.85866$  a.u. it follows that the  $\text{FH}_3$  molecule is unstable with respect to a dissociation into  $\text{FH} + \text{H}_2$  by 206.8 kcal/mole. For this purpose the SCF energy of the  $\text{H}_2$  molecule was calculated to be  $E^{\text{SCF}} = -1.131644$  a.u. at a bond length of  $d(\text{HH}) = 1.4$  a.u. using the same basis set as for the H centres in the present study.

In the following paragraphs the interaction between the fluoronium ion and another hydrogen fluoride molecule is studied in some more detail. The geometrical configuration where the two FH fragments are linked together via a linear hydrogen bond can be considered to be the most stable structure for the ionic system:  $(\text{HFHFH})^+$ . Optimization of the geometrical parameters

Table 3. Total SCF energies for  $\text{FH}_3$  (variation of bond length  $d(\text{FH})$  and out of plane angle  $\phi$ ; all values in atomic units)

	$d(\text{FH})$	$\phi$	$E^{\text{SCF}}$
1	1.78	0°	-100.77664
2	1.80	0°	-100.78488
3	1.90	0°	-100.81779
4	2.10	0°	-100.85216
5	2.22	0°	-100.85839
6	2.24	0°	-100.85862
7	2.25	0°	-100.85866
8	2.26	0°	-100.85864
9	2.30	0°	-100.85813
10	2.25	5°	-100.85799
11	2.25	10°	-100.85614
12	2.25	20°	-100.85061

in this configuration gives a minimum SCF energy of  $E^{\text{SCF}} = -200.35304$  a.u. The geometrical parameters are determined to be  $d(\text{FH}^{\text{centr.}}) = 2.14$  a.u. = 1.13 Å ( $\text{H}^{\text{centr.}}$  is the central hydrogen atom involved in hydrogen bond formation),  $d(\text{FH}^{\text{end}}) = 1.75$  a.u. = 0.93 Å ( $\text{H}^{\text{end}}$  are the two hydrogen atoms at the ends of the ion) and  $\angle(\text{H}^{\text{end}}\text{F}\text{H}^{\text{centr.}}) = 120.96^\circ$ . The corresponding SCF results are listed in Table 4. A brief survey of the course of independent optimizations of the various geometrical parameters is presented in Table 5. The italic parameter values have been optimized to the given value with the remaining parameters kept fixed to the values listed in the same line. The minimum SCF energy obtained for the actual optimization is given in the last column.

Table 4. Total SCF energies for  $(\text{HFHFH})^+$  (variation of geometrical parameters  $d(\text{H}^{\text{centr.}}\text{F})$  ( $\text{H}^{\text{centr.}}$  is the H atom in the hydrogen bond),  $d(\text{H}^{\text{end}}\text{F})$  ( $\text{H}^{\text{end}}$  are the outer H atoms), and HFH bond angle; all values in atomic units)

	$d(\text{H}^{\text{centr.}}\text{F})$	$d(\text{H}^{\text{end}}\text{F})$	$\angle(\text{HFH})$	$E^{\text{SCF}}$
1	1.78755	1.78755	114.75°	-200.29102
2	1.82755	1.78755	114.75°	-200.30660
3	2.00755	1.78755	114.75°	-200.34499
4	2.12755	1.78755	114.75°	-200.35131
5	2.14755	1.78755	114.75°	-200.35137
6	2.20755	1.78755	114.75°	-200.35025
7	2.14755	1.90	114.75°	-200.34107
8	2.14755	1.85	114.75°	-200.34690
9	2.14755	1.75	114.75°	-200.35224
10	2.14755	1.70	114.75°	-200.35083
11	2.14755	1.75	119.75°	-200.35299
12	2.14755	1.75	124.75°	-200.35273
13	2.14755	1.75	120.96°	-200.35301
14	2.12755	1.75	120.96°	-200.35299
15	2.16755	1.75	120.96°	-200.35281
16	2.13942	1.749	120.96°	-200.35304

Table 5. Course of optimization of geometrical parameters in (HFHFH)<sup>+</sup> (all values in atomic units)

$d(\text{H}^{\text{centr.}}\text{F})$	$d(\text{H}^{\text{end}}\text{F})$	$\alpha(\text{HFH})$	$E^{\text{SCF}}$
2.14755	1.78755	114.75°	-200.35137
2.14755	1.749	114.75°	-200.35224
2.14755	1.75	120.96°	-200.35301
2.13942	1.749	120.96°	-200.35304

Table 6. Theoretical and experimental binding energies for the systems  $\text{H}^+ \cdot \text{XH}_n$  and  $\text{H}^+ \cdot 2\text{XH}_n$  ( $\text{XH}_n = \text{NH}_3, \text{OH}_2, \text{FH}$ ). (All values in atomic units)

Molecule	$B_1(\text{theor})^a$	$B_1(\text{exp})^a$	$B_{2(\text{av})}(\text{theor})^b$	$B_2(\text{theor})^c$	$B_2(\text{exp})^c$
$\text{H}^+ \text{NH}_3$	215.84 [11]	207.0 [2]	—	—	—
$\text{H}^+ \text{OH}_2$	173.05 [12]	$168.2 \pm 3.4$ [3]	—	—	—
$\text{H}^+ \text{FH}$	120.14	—	—	—	—
$\text{H}^+ \cdot 2\text{NH}_3$	—	—	125.0 [13]	32.0 [13]	—
$\text{H}^+ \cdot 2\text{OH}_2$	—	—	102.7 [12]	32.36 [12]	36.0 [15]
$\text{H}^+ \cdot 2\text{FH}$	—	—	75.35	30.68	—

$$^a B_1 = E(\text{H}^+ \cdot \text{XH}_n) - E(\text{XH}_n).$$

$$^b B_{2(\text{av})} = (E(\text{H}^+ \cdot 2\text{XH}_n) - 2E(\text{XH}_n))/2.$$

$$^c B_2 = E(\text{H}^+ \cdot 2\text{XH}_n) - E(\text{H}^+ \cdot \text{XH}_n) - E(\text{XH}_n).$$

The bond energy of the molecule (HFHFH)<sup>+</sup> with respect to the total dissociation into 2 FH molecules and a proton follows to be  $B_{\text{total}} = 150.8$  kcal/mole. Subtracting from this  $B_{\text{total}}$ -value the first solvation energy of the proton  $B_1 = B(\text{FH}_2^+) = 120.1$  kcal/mole a hypothetical second solvation energy of  $B_2 = 30.7$  kcal/mole is obtained which corresponds to the reaction:  $\text{H}^+ \cdot 2\text{FH} \rightleftharpoons \text{H}^+ \cdot \text{FH} + \text{FH}$ . On the other hand an average di-solvation energy of  $B_{2(\text{av.})} = 75.4$  kcal/mole can be defined from the  $B_{\text{total}}$ -value, corresponding to the di-solvation reaction  $\text{H}^+ \cdot 2\text{FH} \rightleftharpoons \text{H}^+ + 2\text{FH}$ . These energy results may be compared to the first and second solvation energies and to the average di-solvation energies of the proton with respect to ammonia and water as solvent systems. The corresponding values are collected in Table 6 together with experimental data if available. From this comparison it follows that the first solvation energies  $B_1$  decrease with increasing nuclear charge of the central atom in the solvent molecule; i.e. with increasing acid character of the solvent molecule. The same behavior is observed in the series of the average di-solvation energies. It is somewhat surprising that the second solvation energies remain approximately constant within the accuracy of the present SCF calculations. The enormous difference between the first and second solvation energies makes it highly improbable for a third solvent molecule to be directly bonded to the central proton. From experimental data on crystal structures it is known that non-bonded oxygen atoms cannot come closer to each other than about 3.5 Å [19]. Similar results are expected to hold for nitrogen and fluorine atoms. Keeping non-bonded X-atoms (X = N, O, F) at a distance of 3.5 Å apart from each other the distance to the central proton would be  $d(\text{XH}) = 2.02$  Å for an

equilateral triangular arrangement of the X-centres and  $d(\text{XH}) = 2.13 \text{ \AA}$  for a tetrahedral configuration of the X-centres. Thus the triangular and tetrahedral arrangements of the solvent molecules lead to a remarkable increase in the XH-bond length compared to the  $d(\text{XH})$  values obtained for the monosolvate systems  $\text{H}^+ \cdot \text{XH}_n$ . From the resulting loss in XH-bond stability it can be concluded that chain structures are more likely to be formed than solvate clusters with a central proton. In these chains the bond energy per additional hydrogen bond to be formed is expected to approach rapidly the energy value calculated for the H-bond energy between the neutral solvent molecules [i.e. 2.7 kcal/mole for  $(\text{NH}_3)_2$ , 4.9 kcal/mole for  $(\text{OH}_2)_2$ , and 4.5 kcal/mole for  $(\text{FH}_2)_2$ ].

Finally the potentials of the central hydrogen atom have been calculated for the equilibrium configuration of the  $(\text{HFHFH})^+$  ion with a FF-distance of  $d(\text{FF}) = 4.279$  a.u. as well as for a slightly enlarged FF-distance of  $d(\text{FF}) = 4.599$  a.u. The results are listed in Table 7 and displayed in Fig. 1. For the equilibrium configuration the potential curve has a symmetrical single minimum; i.e. the optimum position of the central hydrogen atom is midway between the two F atoms. At the larger FF-distance of  $d(\text{FF}) = 4.599$  a.u. a symmetrical double minimum potential results. The height of the barrier is only 0.7 kcal/mole. At the two minima of the potential curve the central H atom is off from the midway position by about 0.3 a.u. Similar calculations have been performed for the systems  $(\text{H}_2\text{OHOH}_2)^+$  [15],  $(\text{HOHOH})^-$  [20], and  $(\text{H}_3\text{NHNH}_3)^+$  [16, 17]. The potential curves for the oxonium hydrate ion and the hydroxyl hydrate ion are displayed for comparison in Fig. 2 and 3. The equilibrium configurations of the systems involve a double minimum potential curve for  $(\text{HOHOH})^-$  and  $(\text{H}_3\text{NHNH}_3)^+$ , an indication of a double minimum for  $(\text{H}_2\text{OHOH}_2)^+$  where the barrier is beyond the numerical interpretability, and a single minimum curve for  $(\text{HFHFH})^+$ . Comparing the potential curves for the various distances  $d(\text{XX})$  between the two heavy atoms of the systems  $(\text{H}_n\text{XHXH}_n)^\pm$  one can draw

Table 7. Total SCF energies for the proton transfer in  $(\text{HFHFH})^+$  at two different FF separations. (All values in atomic units)

1	$d(\text{FF})$	$\Delta(\text{H}^{\text{centr.}})^a$	$E^{\text{SCF}}$
1	4.27884	0.0	-200.35304
2	4.27884	0.1	-200.35271
3	4.27884	0.2	-200.35152
4	4.27884	0.4	-200.34299
5	4.59884	0.0	-200.34695
6	4.59884	0.1	-200.34717
7	4.59884	0.2	-200.34769
8	4.59884	0.3	-200.34808
9	4.59884	0.4	-200.34756
10	4.59884	0.5	-200.34495
11	4.59884	0.6	-200.33855

<sup>a</sup>  $\Delta(\text{H}^{\text{centr.}})$  gives the displacement of the proton from the midway position between the two F atoms.

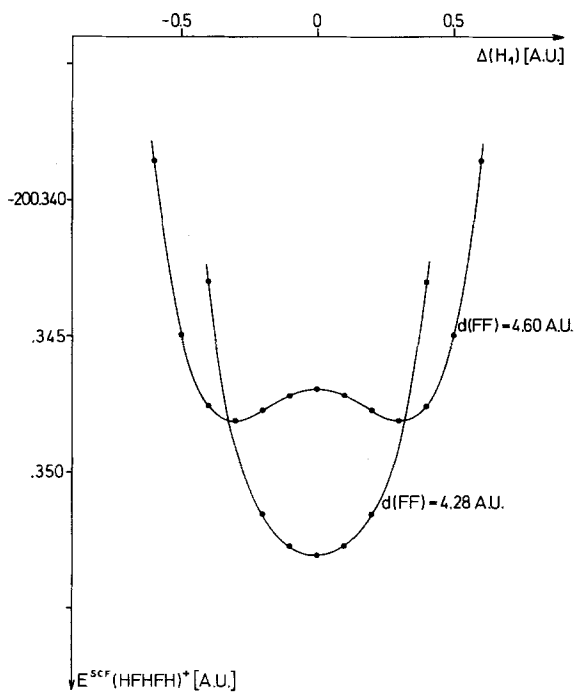


Fig. 1. Potential energy curves for the proton transfer in  $(\text{HFHFH})^+$  at two different F–F separations [ $d(\text{FF}) = 4.28$  a.u. and  $d(\text{FF}) = 4.60$  a.u.]. (The abscissa gives the displacement of the proton from the midway position between the two F atoms)

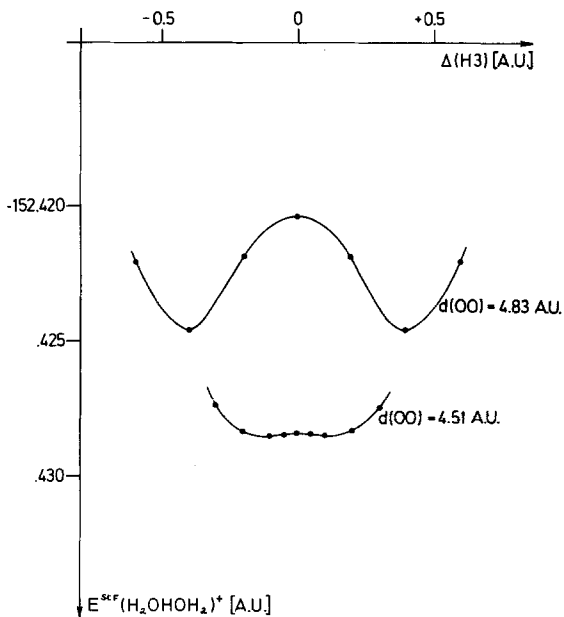


Fig. 2. Potential energy curves for the proton transfer in  $(\text{H}_2\text{OH}_2)^+$  at two different O–O separations [ $d(\text{OO}) = 4.51$  a.u. and  $d(\text{OO}) = 4.83$  a.u.]. (The abscissa gives the displacement of the proton from the midway position between the two O atoms)



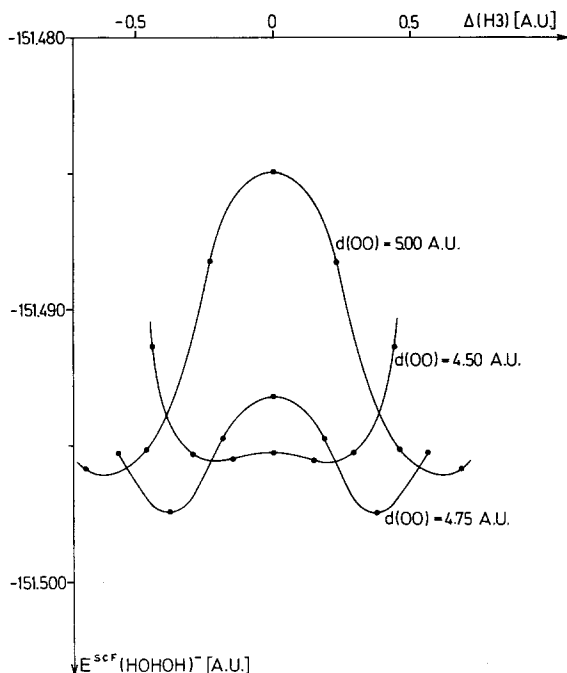


Fig. 3. Potential energy curves for the proton transfer in  $(\text{HOHOH})^-$  at three different O—O' separations [ $d(\text{OO}) = 4.50$  a.u.,  $d(\text{OO}) = 4.75$  a.u., and  $d(\text{OO}) = 5.00$  a.u.]. (The abscissa gives the displacement of the proton from the midway position between the two O atoms)

the following conclusions. If  $d(\text{XX})$  is smaller than approximately  $4.5 \text{ a.u.} = 2.4 \text{ \AA}$  a single minimum potential curve results for the central hydrogen atom, whereas for  $d(\text{XX})$ -values larger than  $4.5 \text{ a.u.}$  a double minimum potential is found. For  $d(\text{XX})$ -values in the neighbourhood of  $4.5 \text{ a.u.}$  the barrier begins to develop. In the series of ionic systems studied here this  $d(\text{XX})$ -value seems to be relatively insensitive to the nature of the heavy atoms in the solvent molecules and to whether the molecular systems is a positive or a negative ion. Although it is not possible to make general conclusions from the limited number of cases considered, this result seems to be quite remarkable for hydrogen bond formation in ionic molecules.

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