# Theoretical Study of the Dissociation of Hydrogen Fluoride and the Fluoronium Ion in Water

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Semiempirical calculations have been performed on the dissociation of HF and $[H_2F]^+$ in water. New conformations of the initial species are obtained by allowing bond making as well as bond breaking to occur, showing that the appearance of new species is related to geometrical restrictions placed on the water molecules solvating the system.

In a recent paper [1] the dissociation of MeF solvated by 11 water molecules was investigated using the CNDO/2 method. A limited number of geometrical variables was considered, keeping the water molecules rigid and retaining partial local symmetries. The most important point of this calculation is a plot of the total energy of the solvate against the C–F distance, which exhibits three well established minima corresponding to three different species. The first minimum corresponds to the covalent R–X molecule in solution, the second minimum to an intimate $R^+X^-$ ion pair. Further extension of the C–F bond allows water molecules to enter into the region between the C and F atoms and thus the third minimum corresponds to a solvent-separated $R^+||X^-$ ion pair. In order to confirm these results, more extensive and sophisticated calculations would be required.

The most simple case analogous to dissociation of MeF is that of the HF molecule. We have studied its dissociation in water. Specifically, our system comprises one HF molecule and six water molecules. For each H–F distance we have optimized all the geometrical parameters of the system allowing bond making as well as bond breaking to occur. The reduced size of this system allows us to avoid the approximation of keeping the water molecules rigid.

The existence of the $[H_2F]^+$ ion is well established.[2-5] It has been studied theoretically using both semiempirical [6,7] and non-empirical [7-13] molecular-orbital (m.o.) methods. The potential surface of the $[H_2F]^+ \longrightarrow HF + H^+$ reaction does not show an energy barrier between the reactants and the products.[7,12,13] On introducing the solvation energy [7] by means of the Jano formula,[14] a potential barrier appears in the curve for protonation, increasing in importance in relation to the value of the dielectric constant. We have studied the dissociation of $[HF_2]^+$ surrounded by five water molecules. All the geometrical parameters have been optimized for each H–F distance. As in the previous study made by Leibovici,[7] the solvent is considered as a continuum without taking into account anisotropic interactions.

## METHOD OF CALCULATION

Owing to the impossibility of calculating the multidimensional potential-energy surface for the majority of chemical reactions, two types of approximations are normally used. The first attempts to reduce the dimensionality of the surface by eliminating certain degrees of freedom. In practice, however, a sufficient reduction in these degrees of freedom is impossible without imposing unrealistic conditions. The second type of approximation involves chosing one or two degrees of freedom as independent variables of the potential energy and allowing the system to relax by optimizing the remaining degrees of freedom for each set of values of the independent variables.

The second method was chosen, taking the H–F distance as an independent variable. Optimization of the remaining parameters of the system, for each value of the independent variable, was carried out by means of a variable metric minimization method using the gradient of the potential energy. This technique starts with an initial geometry $q^\circ$ in the multidimensional space of the variables to be optimized, and a series of points, $q^n$, are successively generated with the formula (1), where the constant $\alpha_n$ and the matrix

$$q^{n+1} = q^n - \alpha_n A^n g^n \qquad (1)$$

$A^n$ in each iteration depend on the method used and $g^n$ is the gradient vector calculated in $q^n$. The calculations were carried out using the GEOMO program of Rinaldi.[15] This permits the optimization of geometries through different semiempirical methods. In this work we have used the CNDO/2 method.[16] Minimization of the energy can be carried out by any one of the methods proposed by Murtagh and Sargent,[17] Fletcher,[18] or Rinaldi.[19] We used Rinaldi's method and calculated the partial derivatives through the analytical procedure proposed by Rinaldi and Rivail.[20]

## RESULTS AND DISCUSSION

It is well known that the results obtained from minimization methods that use the gradient of the potential energy depend to a large extent on the geometry of the starting point. For HF solvated with six water molecules we have adopted as starting geometry a tetrahedral co-ordination for fluorine with the hydrogen atom solvated with one water molecule so that the oxonium ion can be formed, placing the two remaining water molecules in accordance with the branched structure of $[H_9O_4]^+$.[21] Figure 1 shows the optimized geometry including the H(2)–F(1) distance to be optimized. In this Figure the different atom co-ordinates are drawn in projection on the *XY* plane, indicating as thick solid lines the bonds situated above the *XY* plane, as thin lines the bonds lying in the plane, and as broken lines those below the plane. When the projections of two atoms appear together, they have been slightly distorted for clarity. The geometry in Figure 1 corresponds to the first minimum in the potential-energy curve, and it can be seen that the three H(12)–F(1), H(15)–F(1), and H(18)–F(1) distances are equal. At **1.3** Å a new minimum appears, whose geometry is shown in Figure 2, the H(12)–F(1) distance has decreased to 1.07 Å, and a new HF molecule has been formed. The H(12)–O(13) bond has been broken forming a new water molecule, since O(13) captures a hydrogen previously bound to O(6). The latter oxygen atom captures a hydrogen atom from O(3) to form a new water molecule, while O(3) forms a water molecule from the HF hydrogen.

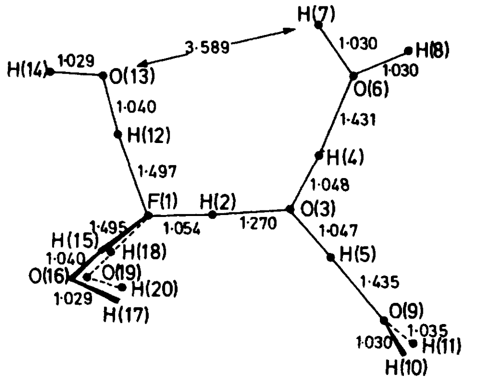

FIGURE 1 Optimized geometry of $HF\cdot6H_2O$

So, the initial species $HF\cdot6H_2O$ is obtained again in a new conformation. Therefore, by allowing the water molecules to dissociate, the ion pair $H^+F^-$ cannot be formed. To interpret the present results we must keep in mind that the CNDO/2 method systematically overestimates bonding properties, and overemphasizes solvation energies. Although our results come from calculations made with a limited number of water molecules, it can be concluded that in a study of the dissociation of HF surrounded by a limited number of water molecules it is not completely necessary to maintain a fixed structure for the water molecules, therefore allowing bond making as well as bond breaking to occur. The obtained results seem to agree with the observed weak acid behaviour of HF in aqueous solution.

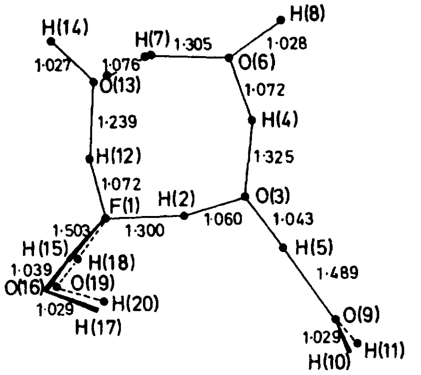

FIGURE 2 Optimized geometry of the second minimum appearing in the potential-energy curve at $D[H(2)-F(1)] = 1.30$ Å for $HF\cdot6H_2O$

In order to compare the present work with the previously mentioned dissociation of MeF, we have calculated the potential-energy curve for HF dissociation, while maintaining rigid structures for the water molecules. Starting from a cyclic structure in which hydrogen bonds occur between two water molecules from the fluorine solvation shell on one side and two water molecules from the hydrogen solvation shell on the other side, the potential-energy curve has been evaluated as a function of the H(2)–F(1) distance by using a partial optimization of the geometrical parameters, the angle of the water molecules being fixed at 104.52° and the OH bond lengths at 1.040 or 1.029 Å depending on whether or not hydrogen bonding occurs. The curve is shown in Figure 3. The first minimum, A, at an H(2)–F(1) distance of 1.087 Å corresponds to the ' covalent ' HF molecule in solution. At an H(2)–F(1) distance of 3.05 Å a decrease in the total energy of the system occurs which accords with a drastic change in the position of the water molecules, the hydrogen-bonded pair filling the gap between the F(1) and H(2) atoms. From this point, the energy decreases smoothly up to an H(2)–F(1) distance of 4.55 Å, at which a second minimum, B, is obtained. In this interval (3.05—4.55 Å) of H(2)–F(1) distances, the water molecules, which form the above mentioned hydrogen bonds, are gradually filling the gap between the F(1) and H(2) atoms. The structure corresponding to the second minimum B can be classified as a solvent-separated ion pair. The total energy of the system increases for H(2)–F(1) distances greater than 4.55 Å, since we are now separating two charged species and working against coulombic attraction. From these results for HF dissociation in water, the three minima appearing in the curve of potential energy against the C–F distance obtained in the previous work [1] may be due to maintaining rigid structures for the water molecules; thus we are able to question the theoretical basis of some of the proposed intermediates in solvolytic reactions.

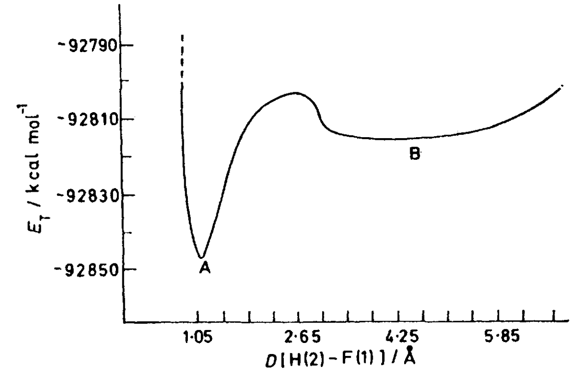

FIGURE 3 Curve of potential energy of $HF\cdot6H_2O$ species against H(2)–F(1) distance. The minimum A corresponds to the ' covalent ' HF molecule in solution; minimum B corresponds to a solvent-separated ion pair

In optimizing the $[H_2F]^+$ species by the CNDO/2 method, we obtain a H–F length of 1.03 Å and a H–F–H angle of 121°, while the optimized H–F bond length in HF is 1.00 Å. This increase of 0.03 Å in bond length agrees with the results of *ab initio* calculations and with the experimental decrease in the force constant.[5,22] The angle H–F–H = 121° is between the minimum [8] and maximum[9] values obtained from non-empirical calculations.

Figure 4 shows the optimized geometry of the $[H_2F]^+\cdot 5H_2O$ species. There are remarkable differences between the $[H_2F]^+$ and $[H_2F]^+\cdot 5H_2O$ species. Thus in $[H_2F]^+\cdot 5H_2O$ the H(1)–F(2) and H(3)–F(2) bonds are not equivalent, the difference being *ca.* 0.3 Å. Also, in $[H_2F]^+\cdot 5H_2O$ species, the H–F–H angle has increased to 142°. The shortest HF bond length in $[H_2F]^+\cdot 5H_2O$ is close to the HF bond length in $HF\cdot 6H_2O$, so that the former species can be considered as a solvated HF molecule interacting with a solvated proton. Thus the $[H_2F]^+$ ion does not really exist in aqueous solution.

The curves of potential energy against the H(1)–F(2) and H(3)–F(2) distances have been evaluated for the $[H_2F]^+\cdot 5H_2O$ species. A second minimum appears in the curve for the H(3)–F(2) distance, at $D = 1.65$ Å at which the H(4)–F(2) distance is 1.31 Å and a restructuring of the water molecules occurs similar to that observed with HF. Thus we obtain the initial $[H_2F]^+\cdot 5H_2O$ structure in a new conformation. New stable conformations of the $[H_2F]^+\cdot 5H_2O$ species are obtained on increasing the H(3)–F(2) distance. For instance, when the H(2)–F(2) distance is 3.55 Å the H(4)–F(2) distance becomes 1.22 Å, and this structure is 10.5 kcal $mol^{-1}$ more stable than the initial one,* showing the great dependence of the energy on the considered conformation when a species is solvated with a small number of water molecules.

On evaluating the curve of potential energy against the H(1)–F(2) distance a second minimum appears at 2.20 Å. Figure 5 shows the geometry corresponding to this second minimum. A conformation similar to the initial one is obtained when the fluorine atom has captured a hydrogen atom from a water molecule that originally solvated H(1), which in turn forms with the O(7)–H(9) bond a new water molecule.

The dissociation of the initial species cannot occur if bond making and bond breaking is not allowed.

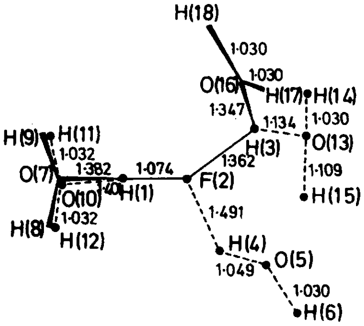

FIGURE 4 Optimized geometry of $[H_2F]^+\cdot 5H_2O$

We have made a study of the dissociation of $[H_2F]^+\cdot 5H_2O$, keeping the O(7)–H(8) and O(7)–H(9) distances fixed at the values they have when H(1)–F(2) = 2.10 Å and the breaking of water molecule H(8)–O(7)–H(9) has not yet occurred. By thus preventing the formation of a new H–F bond we obtain a minimum at 2.90 Å corresponding to a structure in which molecule H(8)–O(7)–H(9) solvates the H(1) and F(2) atoms simultaneously. This structure can be regarded as a solvent-separated ion pair.

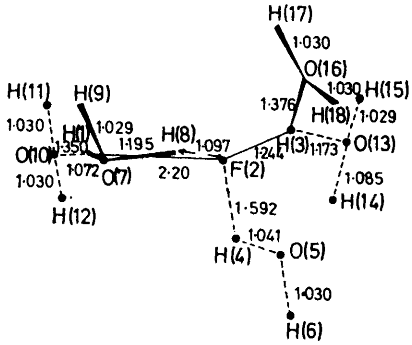

FIGURE 5 Optimized geometry of the second minimum appearing in the potential-energy curve at $D$[H(1)–F(2)] = 2.20 Å for $[H_2F]^+\cdot 5H_2O$

In conclusion, in studying the dissociation of HF and $[H_2F]^+$ solvated with a limited number of water molecules, using the CNDO/2 method, it is found that a conformation different from the initial species is obtained, and the dependence of energy on conformations is described. The formation in the dissociation processes of intimate ion pairs and solvated ion pairs seems to be related to the restrictions which arise from the requirement to keep the water molecules fixed so they cannot form new bonds.

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* Throughout this paper: 1 cal = 4.184 J.

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