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Proton Transfer in the Mono- and the Dihydrated Complexes of HF and HCl: An MP2/6-31+G** ab Initio Study in the Self-Consistent Reaction Field Model of Solvation

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A comprehensive study of the manifestation of proton transfer in the mono- and the dihydrated complexes of hydrogen fluoride and hydrogen chloride is presented. This includes a general ab initio study at the Hartree–Fock and at the second-order Møller–Plesset (MP2) levels of approximation, *in vacuo* and in simulated polar and nonpolar solvents, by means of the self-consistent reaction field approach, using the extended split-valence type 6-31+G** basis set. The potential energy surface along the hydrogen-bond coordinate, for the two monohydrated complexes, in a gas-phase or in a nonpolar solution, is generally flat, displaying a single minimum, which corresponds to a hydrogen-bonded molecular complex. Unlike the weak acid/weak base $\text{H}_2\text{O}\cdots\text{HF}$ complex, a second minimum is observed at the Hartree–Fock level when the strong acid/weak base $\text{H}_2\text{O}\cdots\text{HCl}$ complex is embedded in a highly polar environment. However, the inclusion of intramolecular electron correlation causes this minimum to vanish, therefore indicating that (i) the acidity of hydrogen chloride is not strong enough to yield proton transfer, (ii) the mechanism accounting for the protolytic dissociation should involve more than a single water molecule, and (iii) the stabilization of the $\text{H}_3\text{O}^+\cdots\text{Cl}^-$ complex, characterized by the emergence of a second minimum, is likely to be related to the general trend of the Hartree–Fock approximation to neglect dispersion. The incorporation of a second water molecule, as an attempt to increase by cooperative effect the donor character of the oxygen atom directly bound to the hydrogen halide, leads to a similar artifact when $(\text{H}_2\text{O})_2\cdots\text{HCl}$ is surrounded by a nonpolar solvent. In contrast, the presence of an energy minimum corresponding to an $(\text{H}_2\text{O})_2\text{H}^+\cdots\text{Cl}^-$ ionic complex, at both the Hartree–Fock and the MP2 levels of approximation, in a moderately polar solution, supports the view that (i) two water molecules are required in this kind of acidic dissociation and (ii) there is no explicit participation of the hydronium ion (H_3O^+) in the course of the process. Finally, whether the solvent is polar or not, there is no evidence of proton transfer in the dihydrated $(\text{H}_2\text{O})_2\cdots\text{HF}$ complex, hence suggesting that the protolytic dissociation of hydrogen fluoride might imply additional water molecules.

Introduction

That both hydrogen-bond formation and proton transfer play a key role in a wide range of chemical and biological reactions has given rise to the development of various methods for the observation of such phenomena. Since hydrogen-bond formation and proton transfer may occur either in a low-pressure gaseous state, in a polar or nonpolar solution, or at the boundary between a gas phase and the surface of a solid, the tools of investigation are very different. However, most experimental approaches preclude any detailed information concerning the molecular structure. For this reason, quantum chemical calculations on hydrogen-bonded complexes have recently received a great deal of attention.^{1–10} As soon as relatively large basis sets are employed, ab initio SCF computations on small isolated molecules have proven to be in good agreement with the corresponding experimental data. Unfortunately, such calculations are suitable for a very small number of gas-phase reactions involving both hydrogen-bond formation and proton transfer.

Modeling the environment is a difficult task, and for a few years now, several schemes have been proposed to simulate the average effects of the solvent on the properties of the solute. The widely used self-consistent reaction field (SCRF) methods^{11–18} emphasize the quantum chemical representation of the electronic structure of a solute molecule embedded in a rudimentary model of the solvent, employed at various degrees of complexity.^{19–21} A common approach consists of placing the solute in a cavity

surrounded by a *continuum* characterized by a macroscopic dielectric permittivity. Recently, a very efficient algorithm,²² allowing the optimization of equilibrium geometries, has been developed in the framework of the *continuum* model of solvation. In addition, the extension of the formalism to the Møller–Plesset level of approximation²³ has demonstrated the necessity of including electron correlation for a correct description of proton transfer in solution.⁸ Interestingly, this fact concurs with other works, using different approaches.^{24,25}

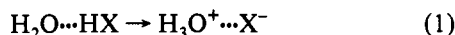
In this paper, we examine the effects of both the solvent and the intramolecular electron correlation on the proton-transfer mechanism in $(\text{H}_2\text{O})_n\cdots\text{HF}$ and $(\text{H}_2\text{O})_n\cdots\text{HCl}$ ($n = 1, 2$). In other words, we try to investigate the protolytic dissociation of a weak acid (*i.e.* hydrogen fluoride) and a strong acid (*i.e.* hydrogen chloride) and the influence of the environment on this reaction. Since the hydrogen halide HX ($\text{X} = \text{F}, \text{Cl}$) is explicitly solvated by one or two water molecules, the present approach constitutes a combined discrete-*continuum*^{26–28} description of the environment. The geometries of the mono- and the dihydrated complexes have been optimized, and the potential energy curve of $\text{H}_2\text{O}\cdots\text{HX}$ has been computed as a function of the length of the hydrogen bond, *in vacuo* and in a polar and a nonpolar solution, at the Hartree–Fock and at the second-order Møller–Plesset²⁹ (MP2) levels of approximation, using the extended split-valence type 6-31+G** basis set.^{30,31} It should be clearly understood that the data obtained at the Hartree–Fock level are an intermediate step in our calculations and have no direct physical significance. Owing to the fact that, in these complexes, most of the correlation effects are recovered at the MP2 level,³² the corresponding results should be regarded as meaningful.

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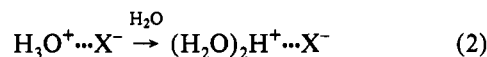
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At the present time, there is no generally accepted mechanism regarding the interaction between water molecules and acids, either in polar or nonpolar solvents. Early studies have indicated the existence of the H_3O^+ cation in aqueous solutions. From Zundel's point of view,^{33,34} the dissociation process is split into two distinct equilibrium steps: (i) the transformation of the hydrogen-bonded complex into an ion pair



and (ii) the formation of the structurally symmetrical $(\text{H}_2\text{O})_2\text{H}^+$ cation, according to the following scheme



These two steps are characterized by a very flat proton-transfer potential energy surface and, as a result, by an infrared continuous absorption. Alternatively, from Librovich's point of view,³⁵⁻³⁷ the process involved in an acidic dissociation implies the participation of two water molecules in the course of the first step. There is no formation of the H_3O^+ cation in aqueous solution, and the infrared continuous absorption is directly related to the motion of the proton between the two oxygen atoms in the $(\text{H}_2\text{O})_2\text{H}^+$ cation.

The goals of our investigation are (i) to evaluate the hydration energies and the geometrical parameters for the two $(\text{H}_2\text{O})_n\cdots\text{HF}$ and $(\text{H}_2\text{O})_n\cdots\text{HCl}$ hydrogen-bonded complexes ($n = 1, 2$), in the *continuum* model of solvation, (ii) to assess the influence of intramolecular electron correlation on the structure of these complexes, in several environments (*viz. vacuum*, polar and nonpolar solutions), and (iii) to outline a mechanism for the protolytic dissociation of strong and weak acids in polar and nonpolar environments.

Methodology—Modeling the Solvent

The influence of the liquid environment on a particular system of interest may be evaluated by means of the self-consistent reaction field (SCRf) model of solvation. In this approach, the solute polarizes the surroundings, which, in turn, creates an electric field, depending on the molecular charge distribution. This field, often referred to as reaction field, perturbs the nuclear and electronic structure of the solute. In the present study, the solvent is represented by a *continuum*^{38,39} defined by its dielectric permittivity ϵ , and the solute is placed in a cavity, the shape of which is adapted to the molecular geometry. The potential generated by the charge distribution of the solute is expanded into a multipole series. The formalism of the spherical tensors was used, so that the component m of the multipole moment operator of rank ℓ is written M_ℓ^m , where ℓ varies from 0 to ∞ and m varies from $-\ell$ to ℓ . The solute-solvent free energy of interaction takes the form

$$A = -\frac{1}{2} \sum_{\ell} \sum_m R_\ell^m \langle M_\ell^m \rangle \quad (3)$$

where $\langle M_\ell^m \rangle$ stands for the average of the total molecular multipole moment operator (including the nuclear contribution), and where each component R_ℓ^m of the reaction field results from the polarization of the solvent by the solute and can be written as

$$\langle R_\ell^m \rangle = \sum_{\ell'} \sum_{m'} f_{\ell\ell'}^{mm'} \langle M_{\ell'}^{m'} \rangle \quad (4)$$

The reaction field factors $f_{\ell\ell'}^{mm'}$ depend on both the shape of the cavity and the permittivity ϵ of the solvent. If we assume that these factors are known (*vide infra*), the $F_{\mu\nu}$ component of the Hartree-Fock matrix, in the SCRf formalism, may be simply

expressed by

$$F_{\mu\nu} = F_{\mu\nu}^0 + \sum_{\ell\ell'} \sum_{mm'} \langle M_{\ell'}^{m'} \rangle f_{\ell\ell'}^{mm'} \langle \mu | M_\ell^m | \nu \rangle \quad (5)$$

where $F_{\mu\nu}^0$ is the corresponding Hartree-Fock component for the isolated molecule.

The application of a direct Møller-Plesset perturbation approach to the intramolecular electron correlation leads to the result⁴⁰ that the second-order correction to the solute-solvent free energy of interaction can be evaluated from the usual^{29,41} MP2 expression:

$$E^{(2)} = -\frac{1}{4} \sum_{i,j,a,b} \frac{|\langle ij || ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (6)$$

where i and j are the SCRf occupied molecular orbitals and a and b are the virtual ones, having the energies ϵ_i , ϵ_j , ϵ_a , and ϵ_b , respectively.

The key feature of the method is the computation of the reaction field factors $f_{\ell\ell'}^{mm'}$. In the most general case, they may be obtained numerically, but in the favorable situation, where the shape of the cavity is approximated by an ellipsoid,^{42,43} these factors can be derived analytically,⁴⁴ giving rise to a very efficient computational procedure. In addition, if the ellipsoid is defined as the volume having the same axes of inertia as the volume defined by the constituent van der Waals spheres of the solute, the derivatives of the reaction field factors may also be computed analytically, leading to a powerful geometry optimization algorithm.²² This scheme is applied at both the Hartree-Fock and the MP2 levels of approximation.

Computational Details

The choice of an adequate basis set may be particularly cumbersome, depending on the nature of the molecules to be studied. Quantum chemical computations on negative ion complexes require particular care since conventional basis sets do not properly describe molecular systems in which electrons occupy diffuse lone pairs or diffuse antibonding orbitals. The inclusion of diffuse functions has proven to give better results than standard basis sets because charges are spread out farther from the nuclei.³⁰ As mentioned by Del Bene,³² the extended split-valence type 6-31+G** basis set appears to be fairly well adapted to a great variety of charged complexes. In this work, the geometry optimization of the individual subunits, as well as the mono- and dihydrated complexes, has been carried out using this basis set. As may be seen in the following sections, the results obtained at this level are generally in agreement with the available experimental data.

Related to the choice of an adequate basis set is the treatment of the basis set superposition error (BSSE). This is, in the most general case, achieved by computing counterpoise corrections.⁴⁵ However, the frequently observed overestimation of the BSSE has made this approach questionable, so that several authors have proposed to increase the basis set to the maximum size affordable rather than carrying out counterpoise correction calculations.^{46,3} Due to the nature of the computations described in the present contribution, these corrections will not be introduced.

The proton transfer in the two monohydrated complexes $\text{H}_2\text{O}\cdots\text{HF}$ and $\text{H}_2\text{O}\cdots\text{HCl}$ has been studied in the C_s geometry (see Figure 1a). As previously pointed out by Latajka and Scheiner,⁵ the ab initio optimized structures slightly depart from those observed experimentally, which belong to the C_{2v} point group. In order to construct the corresponding potential energy surfaces, the hydrogen-bond length $d(\text{O}_2\text{--H}_4)$ has been used as the reaction coordinate and increased step by step from 0.9 to 3.0 Å, or more, depending on the nature of the environment. At each step, this distance was kept fixed, whereas all other parameters were optimized. Furthermore, the energy minimum *minimorum*

TABLE 1: Optimized Parameters of the Individual Subunits in a Vacuum and in Polar and Nonpolar Solvents, at the HF and MP2 Levels of Approximation, Using the Extended Split-Valence 6-31+G Basis Set**

molecule ^a	in vacuo		in solution			
	HF	MP2	$\epsilon = 2.0$		$\epsilon = 78.3$	
			HF	MP2	HF	MP2
H₂O						
<i>d</i> (OH) (Å)	0.943	0.962	0.944	0.963	0.946	0.965
\angle HOH (deg)	107.1	105.4	106.9	105.2	106.5	105.0
μ (D)	2.23	2.28	2.34	2.39	2.51	2.57
<i>E</i> (au)	-76.031 23	-76.235 89	-76.035 15	-76.239 85	-76.041 57	-76.246 44
<i>E</i> _{solv} (kcal/mol)			-2.5	-2.5	-6.5	-6.6
HF						
<i>d</i> (HF) (Å)	0.902	0.926	0.904	0.928	0.907	0.931
μ (D)	2.04	2.09	2.11	2.17	2.22	2.28
<i>E</i> (au)	-100.024 30	-100.218 11	-100.227 10	-100.220 85	-100.031 27	-100.224 97
<i>E</i> _{solv} (kcal/mol)			-1.8	-1.7	-4.4	-4.3
HCl						
<i>d</i> (HCl) (Å)	1.266	1.269	1.267	1.270	1.270	1.272
μ (D)	1.49	1.50	1.61	1.61	1.79	1.79
<i>E</i> (au)	-460.067 36	-460.218 36	-460.068 99	-460.219 90	-460.071 66	-460.222 44
<i>E</i> _{solv} (kcal/mol)			-1.0	-1.0	-2.7	-2.6
H₃O⁺						
<i>d</i> (OH) (Å)	0.961	0.979	0.961	0.980	0.961	0.982
\angle HOH (deg)	114.7	112.7	113.7	111.7	112.1	110.2
<i>E</i> (au)	-76.311 04	-76.511 17	-76.374 05	-76.574 15	-76.436 66	-76.636 81
<i>E</i> _{solv} (kcal/mol)			-39.4	-39.5	-78.8	-78.8
F⁻						
<i>E</i> (au)	-99.418 59	-99.623 84	-99.489 65	-99.697 14	-99.558 91	-99.766 40
<i>E</i> _{solv} (kcal/mol)			-44.6	-46.9	-88.0	-88.1
Cl⁻						
<i>E</i> (au)	-459.539 66	-459.599 49	-459.657 78	-459.671 14	-459.741 29	-459.799 58
<i>E</i> _{solv} (kcal/mol)			-37.5	-44.0	-74.1	-80.6

^a Full geometry optimization in *vacuo* and in solution, using the split valence 6-31+G** basis set; indices given in Figure 1.

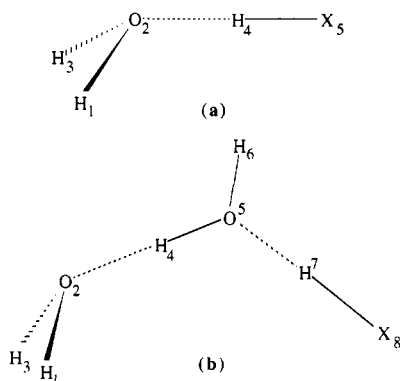


Figure 1. (a) Mono- and (b) dihydrated complexes of two hydrogen halogenides (X = F and Cl).

of the two monohydrated complexes has been located by relaxing all the variables. As an alternative to the use of *d*(O₂H₄) as a reaction coordinate, we have also checked that varying *d*(H₄X₅) leads to analogous results.

Regarding the computations within the framework of the SCRF model of solvation, three different macroscopic dielectric permittivities were chosen, representing a polar (*viz.* $\epsilon = 78.3$), a slightly polar (*viz.* $\epsilon = 10.0$), and a nonpolar (*viz.* $\epsilon = 2.0$) solvent, which roughly correspond to water, 1-octanol, and cyclohexane, respectively, at *ca.* 293 K. All the calculations have been carried out within the ellipsoidal approximation for the cavity introduced in the previous section. This formalism has been implemented in the Gaussian 92⁴⁷ ab initio package, as a set of independent links.⁴⁸ The computations presented here were performed with a multipole expansion up to the order $\ell = 6$.

Results and Discussion

Prior to the study of the hydrogen-bonded complexes (H₂O)_{*n*}...HF and (H₂O)_{*n*}...HCl (*n* = 1, 2), preliminary calculations on the individual subunits (*i.e.* H₂O, HF, HCl, H₃O⁺, F⁻, and

Cl⁻) have been carried out at both the Hartree-Fock and the MP2 levels of approximation, in a vacuum and in solution. Our results are reported in Table 1. Both the geometry and the energy parameters of these species have been discussed extensively in the literature. However, it is worth noting that the MP2/6-31+G** values are in good agreement with the experiment,⁴⁹⁻⁵³ which gives, for H₂O, *d*(OH) = 0.957 Å, \angle HOH = 104.5°, and $\mu = 1.85$ D⁵⁴ (it should be mentioned that our quantum mechanically evaluated dipole moment slightly departs from this experimental value, obtained *in vacuo*). In contrast, the results corresponding to a condensed phase are in much better agreement with the commonly accepted value of 2.6 D, determined in ice⁵⁰) and *E*_{solv} = -6.3 kcal/mol. Similarly, the reference values for HF, *d*(HF) = 0.917 Å, $\mu = 1.83$ D, for HCl, *d*(HCl) = 1.274 Å, $\mu = 1.09$ D, for H₃O⁺, *d*(OH) = 1.01 Å, \angle HOH = 118.5°, *E*_{solv} = -93.9 kcal/mol, for F⁻, *E*_{solv} = -107.0 kcal/mol, and for Cl⁻, *E*_{solv} = -77.0 kcal/mol, compare well to our results. In addition, it may be observed that the proton affinities of the basic subunits, evaluated at the MP2 level of approximation, are very close to the corresponding experimental quantities (*viz.* for H₂O, F⁻, and Cl⁻, respectively, $\Delta A_{\text{MP2}} = -172.7$, -372.9, and -343.4 kcal/mol, whereas $\Delta A_{\text{exp}} = -172.9$, -371.3, and -333.4 kcal/mol).

Consideration of the surroundings generally does not reveal any major modification of the geometry for most subunits. As may be observed in the case of the water molecule, the main effect of the solvent consists of slightly increasing the bond lengths and decreasing the valence angle. Put together with the polarization of the solute by the reaction field, the molecular dipole moment is increased accordingly. This kind of alteration also occurs for the hydronium ion,¹⁰ as well as the hydrogen fluoride and the hydrogen chloride molecules.²¹ It should be mentioned that the ellipsoidal cavity model of solvation is fairly well adapted to this kind of calculation, as demonstrated by the good agreement of our results with experimental data.

H₂O...HX Complexes in *Vacuo*. With such complexes, one may *a priori* expect to obtain two minima in the potential energy surface, corresponding to an ion pair H₃O⁺...X⁻ and a molecular

TABLE 2: Optimized Parameters of the Monohydrated H₂O–HF and H₂O–HCl Complexes in a Vacuum and in Polar and Nonpolar Solvents, at the HF and MP2 Levels of Approximation, Using the Extended Split-Valence 6-31+G Basis Set**

complex ^a	in vacuo		in solution			
			$\epsilon = 2.0$		$\epsilon = 78.3$	
	HF	MP2	HF	MP2	HF	MP2
H₂O–HF						
<i>d</i> (O ₂ H ₄) (Å)	1.802	1.713	1.753	1.657	1.700	1.584
<i>d</i> (H ₄ F ₅) (Å)	0.913	0.943	0.918	0.951	0.926	0.966
∠H ₁ O ₂ H ₄ (deg)	149.1	133.8	137.5	130.4	125.6	122.6
μ (D)	4.68	4.38	4.79	4.95	4.98	5.32
<i>E</i> (au)	–176.069 34	–176.470 31	–176.076 14	–176.477 62	–176.087 03	–176.489 51
Δ <i>E</i> _{O...H} ^b (kcal/mol)	–8.7	–10.1	–8.7	–10.6	–8.9	–11.4
H₂O–HCl						
<i>d</i> (O ₂ H ₄) (Å)	2.011	1.903	1.961	1.847	1.915 ^c 0.995 ^d	1.760
<i>d</i> (H ₄ Cl ₅) (Å)	1.275	1.282	1.280	1.289	1.288 ^c 2.011 ^d	1.304
∠H ₁ O ₂ H ₄ (deg)	180.2	145.7	141.7	134.5	123.9 ^c 129.3 ^d	123.8
μ (D)	4.34	4.38	4.41	4.57	4.53 ^c 12.87 ^d	4.91
<i>E</i> (au)	–536.067 36	–536.465 32	–536.112 64	–536.471 01	–536.121 80 ^c –536.120 11 ^d	–536.480 72
Δ <i>E</i> _{O...H} ^b (kcal/mol)	–5.5	–7.0	–3.4	–9.0	–3.6 ^c –35.2 ^d	–9.7

^a Full geometry optimization in *vacuo* and in solution, using the split valence 6-31+G** basis set; indices given in Figure 1. ^b Water–halogenide interaction energy. ^c Molecular complex. ^d Ion pair.

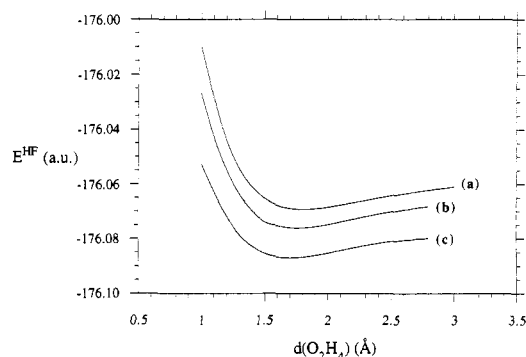


Figure 2. Hartree-Fock/6-31+G** energy versus intermolecular distance $d(\text{O}_2\text{H}_4)$ for the H₂O–HF complex: (a) in *vacuo*, (b) in a nonpolar solvent ($\epsilon = 2.0$), and (c) in a polar solvent ($\epsilon = 78.3$).

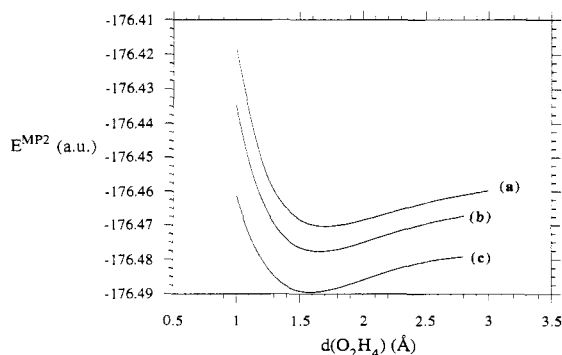


Figure 3. MP2/6-31+G** energy versus intermolecular distance $d(\text{O}_2\text{H}_4)$ for the H₂O–HF complex: (a) in *vacuo*, (b) in a nonpolar solvent ($\epsilon = 2.0$), and (c) in a polar solvent ($\epsilon = 78.3$).

complex H₂O...HX. However, as indicated in Figures 2–5, this is not exactly the case. Only the molecular complex is stabilized in a low-pressure gaseous state. For H₂O...HF and H₂O...HCl, respectively, the minimum of the energy is located at $d(\text{O}_2\text{H}_4) = 1.802$ and 2.011 Å, at the Hartree–Fock level, and 1.713 and 1.903 Å, at the MP2 level (see Table 2). These results concur with prior observations concerning the overestimation of the hydrogen-bond length at the Hartree–Fock level and the general trend of the MP2 correction to shift the minimum energy state toward a lower value of the intermolecular distance.^{32,8} The

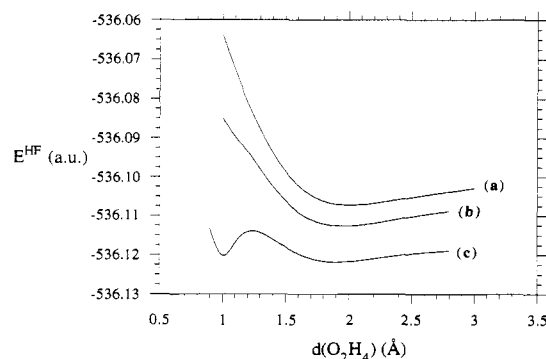


Figure 4. Hartree-Fock/6-31+G** energy versus intermolecular distance $d(\text{O}_2\text{H}_4)$ for the H₂O–HCl complex: (a) in *vacuo*, (b) in a nonpolar solvent ($\epsilon = 2.0$), and (c) in a polar solvent ($\epsilon = 78.3$).

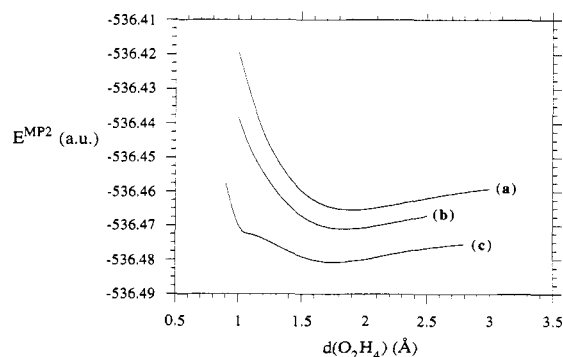


Figure 5. MP2/6-31+G** energy versus intermolecular distance $d(\text{O}_2\text{H}_4)$ for the H₂O–HCl complex: (a) in *vacuo*, (b) in a nonpolar solvent ($\epsilon = 2.0$), and (c) in a polar solvent ($\epsilon = 78.3$).

6-31+G**/MP2 geometrical parameters are in reasonable agreement with the available experimental data,^{55–57} e.g. $d(\text{O}_2\text{F}_4) = 2.655$ and 2.664 Å and $d(\text{O}_2\text{Cl}_4) = 3.185$ and 3.215 Å, theoretical and experimental values, respectively.

Computations at higher levels of accuracy^{58,5} do not yield smaller discrepancies with the experimental data. It is worth pointing out the relatively reduced influence of intramolecular electron correlation on the optimized geometry of both complexes, except for the $\angle \text{H}_1\text{O}_2\text{H}_4$ valence angle in H₂O...HCl, where the SCF, MP2, and experimental values are 180.2 , 145.7 , and 180° .

Nevertheless, such a difference is not critical for our study and, as pointed out by Scheiner and Latajka,⁵ there is a practically free motion of the water molecule around HCl.

H₂O...HX Complexes in Solution. As may be seen in Table 2, the effects of both polar and nonpolar solvents did not cause any major modification in the geometry of the two hydrogen-bonded complexes. As expected, the intermolecular distance $d(\text{O}_2\text{H}_4)$ is slightly decreased, at the expense of $d(\text{H}_4\text{X}_5)$. The dependence of the dipole moment and the solvation energy on the polarity of the surroundings is clearly demonstrated throughout our calculations.

The most remarkable fact emerging from this study is the presence of two minima for the H₂O...HCl complex and a single minimum for the H₂O...HF complex (see Figures 2 and 4), at the Hartree–Fock level of approximation. These observations are in accordance with *chemical intuition*, which suggests that proton transfer preferentially occurs in the monohydrated complex of hydrogen chloride, which coarsely corresponds to a strong acid–weak base interaction. It should be noted that only a polar solvent, *i.e.* water ($\epsilon = 78.3$), allows the ion pair H₃O⁺...Cl[−], characterized by a second minimum, to be stabilized. The weak acid–weak base interaction represented by the H₂O...HF complex does not lead to the same result, in polar as well as nonpolar solvents. Experimental evidences, such as the continuous absorption or the significant broadening of the H...X stretching band witnessed by infrared spectroscopy,^{59–62,7} confirm that strong acids and bases in polar solutions are likely to yield proton transfer.

The inclusion of intra- and intermolecular (*i.e.* dispersion) electron correlation corrects the deficiencies of the restricted Hartree–Fock theory and, in the case of the H₂O...HCl complex, contributes to the cancellation of the second minimum (see Figure 5). This supports the view that the ion pair H₃O⁺...Cl[−] is unstable and that the basicity of a single water molecule is not strong enough to yield proton transfer. As shown in Figure 5, the presence of a point of inflexion around $d(\text{O}_2\text{H}_4) \approx 1.0 \text{ \AA}$ may be interpreted as a reminiscence of the ion pair. The smoothing effect of the potential energy surface at the MP2 level has already been observed in the case of the ammonia–hydrogen chloride complex. However, in this particular case, the acid/base properties of the two individual subunits are strong enough, so that, even in a nonpolar solvent (*viz.* typically cyclohexane), the energy minimum corresponding to the ion pair NH₄⁺...Cl[−] does not vanish as a consequence of the incorporation of intramolecular electron correlation. Due to the presence of a single minimum at the Hartree–Fock level, the shape of the potential energy surface for the water–hydrogen fluoride complex remains obviously unchanged at the MP2 level (see Figure 3).

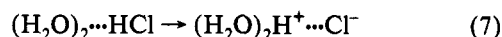
So far, we have seen that the two monohydrated complexes are characterized by a flat single minimum potential energy surface, except for H₂O...HCl, which displays a second minimum at the Hartree–Fock level and in an aqueous solution (*i.e.* $\epsilon = 78.3$). This minimum, corresponding to an ion pair, is suppressed when intramolecular electron correlation is involved, hence indicating that either the basicity of H₂O or the acidity of HCl, and *a fortiori* of HF, is not strong enough to yield protolytic dissociation. The inclusion of a second water molecule in order to reinforce the donor character of H₂O directly bound to HX is likely to favor the ionic form. That this is not completely true may be seen in the following section.

(H₂O)₂...HX Complexes in Vacuo and in Solution. According to Librovich's mechanism, two water molecules are expected to participate to the process of acidic dissociation. In this scheme, the oxygens of both water molecules are supposed to be bound to the hydrogen of the hydrogen halide, leading to the formation of the (H₂O)₂H⁺. Unfortunately, in the framework of the approach used in the present study, such a structure is not stable and a rearrangement of the water molecules occurs (see Figure 1b). This does not, however, contradict Librovich's point of view,

since only two water molecules have been taken into account in the course of our computations, hence neglecting the specific hydrogen-bonding due to the neighboring solvation shells.

The geometry optimization of the two complexes (H₂O)₂...HF and (H₂O)₂...HCl, at both the Hartree–Fock and the MP2 levels of approximation, *in vacuo*, does not lead to a second minimum. However, the transition from a vacuum to a nonpolar solution (*viz.* $\epsilon = 2.0$) stabilizes the ion pair in the case of the dihydrated complex of HCl, hence indicating that, in comparison with the monohydrated complex, the lowering of the solvent polarity is partially compensated by the cooperative effects in the water dimer,⁹ which increase the donor character of the water molecule directly bound to the hydrogen chloride (see Table 3). Unfortunately, the magnitude of this effect is not sufficient to maintain the second minimum when electron correlation is incorporated. These observations strongly suggest that the basicity of the water bound to the hydrogen halide is significantly increased in the presence of additional water molecules. Consequently, proton transfer may be witnessed in solutions of lesser polarity. As an attempt to stabilize the ion pair at the MP2 level of approximation, additional computations were carried out with a solvent of higher permittivity. Embedding the solute in a very polar solution, *viz.* water ($\epsilon = 78.3$), leads to an excessive lengthening of the ellipsoidal cavity, hence causing the SCF procedure to diverge and the geometry optimization of (H₂O)₂...HX to be aborted. In this critical situation, the individual subunits drift away because of too great a charge separation, that increases the total dipole moment as well as the perturbation term due to the surroundings significantly.

For these reasons, a solvent of smaller dielectric constant, *i.e.* $\epsilon = 10.0$, was employed, which coarsely corresponds to 1-octanol. As a result, both the ionic and the molecular complexes of (H₂O)₂...HCl are stabilized. In contrast with the unrealistic solvated ion pairs observed in the case of H₂O...HCl (using $\epsilon = 78.3$), or (H₂O)₂...HCl (using $\epsilon = 2.0$), at the Hartree–Fock level of approximation, the MP2 energy minimum of the ionic complex is now lower than that of the molecular complex (see Table 3). Seemingly, this deepest minimum corresponds to an (H₂O)₂...H⁺...Cl[−] ion pair, therefore supporting the view that the protolytic dissociation of hydrogen chloride involves two explicit water molecules, as proposed by Librovich:^{35–37}



The geometrical parameters (see Table 3) of the cation (H₂O)₂H⁺ concur with the data reported earlier in the literature: *viz.* $d(\text{O}_2\text{O}_5) = 2.468 \text{ \AA}$ in the present work and 2.417 \AA in a vacuum, at the MP2/6-31+G(d) level of approximation.³ Interestingly, (i) the short distance $d(\text{O}_2\text{O}_5)$ is in agreement with prior spectroscopic measurements in condensed phase^{63,64} and (ii) the position of the central proton with respect to the two neighboring water molecules is not fully symmetrical, which is not unexpected, due to the presence of the chloride ion.⁶⁵

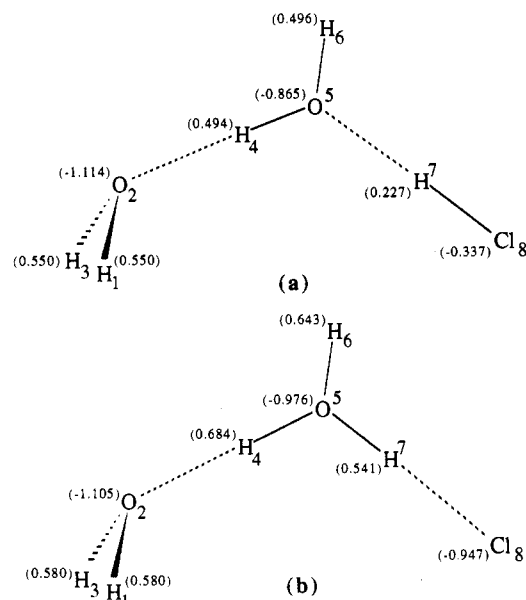
These facts clearly suggest that the hydronium ion (H₃O⁺) does not participate in the dissociation of HCl, as confirmed by experimental evidence.⁶⁶ As an illustration of the proton-transfer mechanism, the net atomic charges of the two complexes of hydrogen chloride have been fitted to their respective molecular electrostatic potentials,^{67–69} using the corresponding MP2/6-31+G** wave functions. The potential-derived point charge models for both structures are reported in Figure 6.

One of the most problematic remaining issues of the present survey is the absence of proton transfer for hydrogen fluoride, whether the hydrogen halide is bound to one or two explicit water molecules. In principle, and following Librovich's point of view, an ionic complex (H₂O)₂H⁺...F[−] should be observed if one considers that, due to its small size, the solvation of F[−] is more favorable than that of Cl[−] (see Table 1). On the other hand, it is worth noting that the intermolecular distance in HF⁵² (*viz.*

TABLE 3: Optimized Parameters of the Dihydrated $(\text{H}_2\text{O})_2\text{-HF}$ and $(\text{H}_2\text{O})_2\text{-HCl}$ Complexes in a Vacuum and in Nonpolar and Moderately Polar Solvents, at the HF and MP2 Levels of Approximation, Using the Extended Split-Valence 6-31+G Basis Set**

complex ^a	in vacuo		in solution		
	HF	MP2	$\epsilon = 2.0$		$\epsilon = 10.0$
			HF	MP2	MP2 ^c
(H ₂ O) ₂ -HF					
<i>d</i> (O ₅ H ₇) (Å)	1.744	1.643	1.721	1.604	1.519
<i>d</i> (O ₂ H ₄) (Å)	1.949	1.837	1.965	1.837	1.815
<i>d</i> (H ₇ F ₈) (Å)	0.918	0.923	0.952	0.960	0.976
∠H ₁ O ₂ H ₄ (deg)	120.0	118.2	119.5	118.8	123.9
∠H ₄ O ₅ H ₇ (deg)	119.3	114.2	116.1	114.8	120.1
μ (D)	5.72	5.72	6.11	6.01	7.19
<i>E</i> (au)	-252.112 05	-252.720 97	-252.125 38	-252.734 65	-252.752 29
Δ <i>E</i> _{O...H} ^b (kcal/mol)			8.4	8.6	20.04
(H ₂ O) ₂ -HCl					
<i>d</i> (O ₅ H ₇) (Å)	1.938	1.809	1.952 ^d	1.792	1.758 ^d
<i>d</i> (O ₂ H ₄) (Å)	1.973	1.860	1.082 ^e		0.994 ^e
<i>d</i> (H ₇ Cl ₈) (Å)	1.280	1.291	2.023 ^d	1.877	1.950 ^d
∠H ₁ O ₂ H ₄ (deg)	119.9	118.2	1.710 ^e		1.408 ^e
∠H ₄ O ₅ H ₇ (deg)	123.1	116.4	1.284 ^d	1.298	1.305 ^d
μ (D)	5.50	5.46	1.694 ^e		2.085 ^e
<i>E</i> (au)	-612.149 06	-612.714 91	120.1 ^d	120.1	125.0 ^d
Δ <i>E</i> _{O...H} ^b (kcal/mol)			123.7 ^e		123.1 ^e
			110.9 ^d	112.0	116.2 ^d
			113.3 ^e		118.9 ^e
			5.62 ^d	5.91	6.42 ^d
			10.70 ^e		15.52 ^e
			-612.161 53 ^d	-612.727 43	-612.744 99 ^d
			-612.148 30 ^e		-612.746 85 ^e
			7.8 ^d	7.8	18.9 ^d

^a Full geometry optimization in *vacuo* and in solution, using the split valence 6-31+G** basis set; indices given in Figure 1. ^b Water–water interaction energy. ^c Inclusion of a cavitation correction.⁷¹ ^d Molecular complex. ^e Ion pair.

**Figure 6.** Molecular electrostatic potential derived net atomic charges of the (a) molecular and the (b) ionic complex of $(\text{H}_2\text{O})_2\text{-HCl}$.

0.917 Å) is appreciably smaller than in HCl ⁵² (*viz.* 1.274 Å), therefore explaining the unfavorable dissociation of hydrogen fluoride. Furthermore, Legon and Millen⁵⁷ have reported that the stretching force constant in $\text{H}_2\text{O}\cdots\text{HCl}$ and $\text{H}_2\text{O}\cdots\text{HBr}$ is about twice as important in $\text{H}_2\text{O}\cdots\text{HF}$.

Thus, it seems that hydrogen fluoride is too weak an acid to yield proton transfer,⁷⁰ at least in the conditions described here. Test computations using a more polar solvent, *viz.* water ($\epsilon = 78.3$), did not allow the emergence of the ion pair $(\text{H}_2\text{O})_2\text{H}^+\cdots\text{F}^-$. The mechanism accounting for the protolytic dissociation may consequently involve additional water molecules in order to increase the donor character of the oxygen bound to the hydrogen halide more significantly.

Conclusions

In this paper, we have studied the manifestations of proton transfer in the mono- and dihydrated complexes of HF and HCl, at the Hartree–Fock and the MP2 levels, *in vacuo* and in solution, using the 6-31+G** basis set.

The results obtained in a vacuum, at the MP2 level of approximation, are in satisfactory agreement with both the literature and the experimental data. The two complexes are characterized by a flat potential energy surface, *in vacuo* and in solution. The monohydrated complex of HF, in both polar and nonpolar environments, does not exhibit any proton transfer, hence confirming that such a phenomenon is very unlikely to occur in the case of a weak acid–weak base interaction. In contrast, a second minimum, corresponding to the stabilization of the ion pair, is observed with $\text{H}_2\text{O}\cdots\text{HCl}$ in a polar solution. This minimum, however, vanishes if intramolecular electron correlation is involved, thus indicating that the protolytic dissociation of HCl may imply a different mechanism, including additional water molecules.

In order to increase the basicity of the donor by cooperative effect, a second water molecule has been included in each complex. The presence of a second minimum for $(\text{H}_2\text{O})_2\cdots\text{HCl}$, in a nonpolar solution (*viz.* $\epsilon = 2.0$), emerging at the Hartree–Fock level and cancelled at the MP2 level, suggests that the addition of successive water molecules compensates the decrease of the solvent polarity and participates in proton-transfer reactions. This fact is confirmed by the stabilization of both the ionic and the molecular complexes of $(\text{H}_2\text{O})_2\cdots\text{HCl}$ in a moderately polar solvent (*viz.* $\epsilon = 10.0$), when intramolecular electron correlation is included. Seemingly, the mechanism accounting for the dissociation of hydrogen chloride implies the participation of two explicit water molecules and the formation of a nonsymmetrical cation $(\text{H}_2\text{O})_2\text{H}^+$ rather than H_3O^+ , as related to Librovich's proposal.

Regarding hydrogen fluoride, only the molecular complex of $(\text{H}_2\text{O})_2\cdots\text{HF}$ is observed, which is likely to be rooted in the nature of HF, and supports the view that additional water molecules

should be incorporated into our computations in order to yield protolytic dissociation.

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