1356 *J. Phys. Chem. A* **1998,** *102,* 1356−1364

Proton Transfer in Dissociative Protonation Processes

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Received: June 5, 1997; In Final Form: September 17, 1997

Proton transfer in dissociative protonation processes involving fluoroadamantane and other smaller model compounds with different reference bases has been studied, through the use of B3LYP density functional theory calculations. All systems investigated are characterized by single-well potential energy curves. Solvent effects on proton-transfer potential energies were studied by means of a self-consistent isodensity polarized continuum model (SCIPCM) approach. It was found that also in solution the proton-transfer potential is single-well. However, the effects of the solvent on the characteristics of the complex are not negligible. The distance between the heavy atoms, and as a consequence the position of the minimum, changes, and the well becomes less deep. For fluoroadamantane the proton transfer leads to the C−F bond fission, so that the equilibrium conformation corresponds to a tightly bound complex between adamantyl cation and hydrogen fluoride, solvated by one molecule of the corresponding reference base.

Introduction

Proton-transfer processes are of paramount importance in chemistry and biochemistry,[1] and consequently they have been extensively studied.[2] While a considerable amount of literature was devoted to investigate dynamical effects[3−8] as well as hydrogen tunneling,[9,10] many other focused on the static aspects of the problem,[11−26] i.e., on the characterization of the corresponding potential energy surfaces (PES). In this respect, it seems nowadays well established that some proton-transfer processes are characterized by a symmetric single-well potentiall,[14,21,23] in which the proton locates midway between the two groups involved. Single-well potentials have been predicted[18,26] not only for symmetric but also for asymmetric neutral complexes as those between amines and hydrogen halides.[18] Some other proton-transfer reactions are associated with double wells.[12−16,20,22,24] In this case, the lack of symmetry of the complexes is not a necessary condition, and there are some examples[12,13,20] of symmetric complexes with double wells, as is the case of the complexes between ammonium ion and ammonia ($NH_4^+-NH_3$).

From the experimental point of view the presence of a double-well potential is usually associated with intense continua in the infrared spectrum,[27−32] indicating large proton polarizability of the hydrogen bonds caused by shifts of the proton within these bonds.

Particular attention was paid to the influence of solvent interactions not only on the dynamics of the process[33−38] but also on the nature of the proton-transfer potential.[39−45] Although there is not a general rule, it has been found that when the species involved in the processes are neutral, the proton-transfer complex is generally favored by more polar solvents.[39] When the complex is charged, the hydrogen-bonded intermediate is quite stable, and solvent effects are less important. Another problem related to this one is the possible influence of the solvent on the energy barriers for proton transfer when a double well is present.[21,40,41] In this respect it is important to mention that in some specific cases, as the NH_3-HCl complex,[39] it has been found that although the complex exhibits a single-well potential for the proton transfer in the gas phase, the effects of the solvent give rise to two minima corresponding to an ionic and a molecular complex.

Proton-transfer processes are also of relevance in the protonation reactions in the gas phase, where a protonated species BH^+ reacts with a reference base B' to yield $B'H^+$ as a product. In general, protonation induces important structural changes in the base which can lead to a bond fission.[47] Actually in dissociative proton attachment processes,[46] a spontaneous fragmentation of the protonated species takes place. This possibility depends on the electronegativity of the basic center and on the stability of the cation produced by the bond fission. The more electronegative the basic center and the more stable the cation formed, the more likely the dissociative protonation occurs.[47] Actually, in ref 46 it was shown from both the experimental and the theoretical points of view that the protonation of fluoro- and chloroadamantane in the gas phase leads to the formation of a halogen halide neutral molecule and an adamantyl cation as final products of the reaction.

The aim of this paper is to investigate, through the use of density functional theory (DFT) methods, the proton-transfer potential energy curve associated with these particular processes, taking as suitable model systems fluoroadamantane (FAD) and fluoromethane. For the former, proton attachment is dissociative,[46] while for the latter the stability of the methyl cation is not big enough to favor the bond fission. However, the small size of the latter will permit systematically studying the proton-transfer processes for a wider set of reference bases. It is well established that correlation effects are important when describing protonation processes, and they become crucial when the breaking of a bond takes place. Due to the large size of the FAD system, our calculations will be performed in the framework of the DFT methods. On one hand, these methods have shown to be reliable to describe both protonation processes[48−52] and hydrogen bonds,[53−55] and on the other hand, they have led to appropriate descriptions of proton-transfer mechanisms, both in the gas phase and in solution.[21−23,39,56,57]

S1089-5639(97)01849-5 CCC: $15.00

Computational Details

The calculations in the present paper were carried out using GAUSSIAN 94 series of programs.[58] Geometry optimizations for all the structures were performed within the framework of density functional theory (DFT) which constitutes a cheaper alternative to conventional ab initio methods. In this sense, the B3LYP functional was chosen since it has been largely proved to be reliable in the study of noncovalent interactions as hydrogen bonds.[53−57] The exchange functional B3 is a hybrid method proposed by Becke[59] that includes a mixture of Slater functional,[60] Becke's 1988 gradient correction,[61] and some Hartree−Fock exchange. The correlation part, LYP, is the gradient-corrected functional of Lee, Yang, and Parr.[62] The "fine grid" option was used throughout to avoid numerical inaccuracies in the energy and gradient calculations.

Since the inclusion of polarization functions is basic when describing molecule−ion interactions and it has been shown that diffuse components do not introduce significant changes on either energetics or topological features of the electronic charge densities, all the optimizations have been carried out at the 6-31G* level. Harmonic vibrational frequencies were evaluated at the same level to confirm the nature of the stationary points for all the structures given.

With regard to the calculations in aqueous solution, there exist an extensive literature of quantum mechanical studies of proton transfer, treating solvent effects by means of hybrid molecular orbital/molecular mechanics (MO/MM) approaches,[63,64] the hybrid valence bond/classical empirical valence bond (EVB) method,[63,65] the recently developed frozen density functional theory (FDFT),[38,66] or by taking explicitly into account the interactions with a finite number of solvent molecules.[40,41,43,67,68] Nevertheless, the simplest way to model solvation consists of enclosing the solute in an spherical cavity of radius a_0 surrounded by the solvent, which is considered as a uniform dielectric with a given permittivity, ϵ_r. The interaction between the dipole moment of the solute with the constant electric field originated by the polarized surrounding medium will give as a result a net stabilization of the system. The main advantage of these so-called continuum models is that, whatever the complexity of the system, the solute's electronic distribution can be treated by quantum chemical methods and polarization effects evaluated at a low cost. An overview of these methods based on continuous distribution of the solvent can be found in ref 69. On the other hand, a comparison between continuum and discrete models showed[57] that the former may efficiently describe even specific effects. In particular, it has been found[70] that simple continuum models reproduce correctly solute−solvent interactions in the case of molecules bearing large dipole moments (like those treated here), whereas it fails when the dipole moment is small or higher multipole moments dominate the solute−solvent interaction. In this work we have used a more sophisticated approach than that described above, namely, the self-consistent isodensity polarized continuum model (SCIPCM). In the IPCM model the cavity is no longer spherical, but it is defined as an isodensity surface of the molecule which is a more realistic description of the shape of the cavity. Furthermore, in the SCIPCM method, the solvation effects are explicitly included in the SCF equations, and the coupling between the cavity so defined and the electron density is explicitly taken into account. As for the solvent-free calculations, the computations were done at B3LYP/6-31G* level to include electron correlation effects. The permittivity value used ($\epsilon = 74.58$) was that of water.

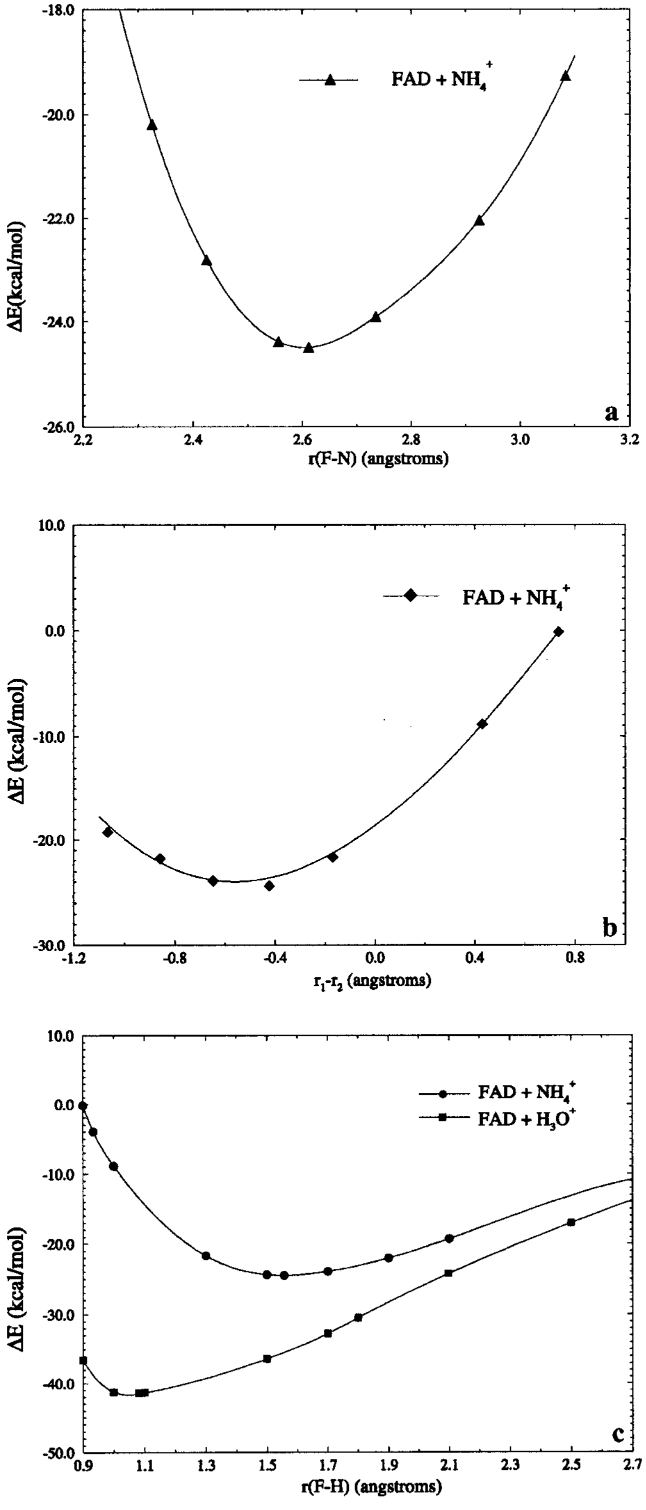


Figure 1. Potential energy curves corresponding to the proton transfer in fluoroadamantane−NH_4^+ and fluoroadamantane−H_3O^+ complexes. For the former complexes three different reaction coordinates have been used (see text). Energy values are referred to the FAD + NH_4^+ and to the FAD + H_3O^+ dissociation limits, respectively.

The nature of the bonding features of the complexes was analyzed in terms of the topological characteristics[71] of the electronic charge density, ρ, and its Laplacian, $\nabla^2\rho$. For this purpose we have located the bond critical points (bcps), i.e., points where the electronic charge density is minimum along the bond path and maximum in the other two directions, because the values of ρ and $\nabla^2\rho$ at these points offer quantitative information on the strength and nature of the bonding. In

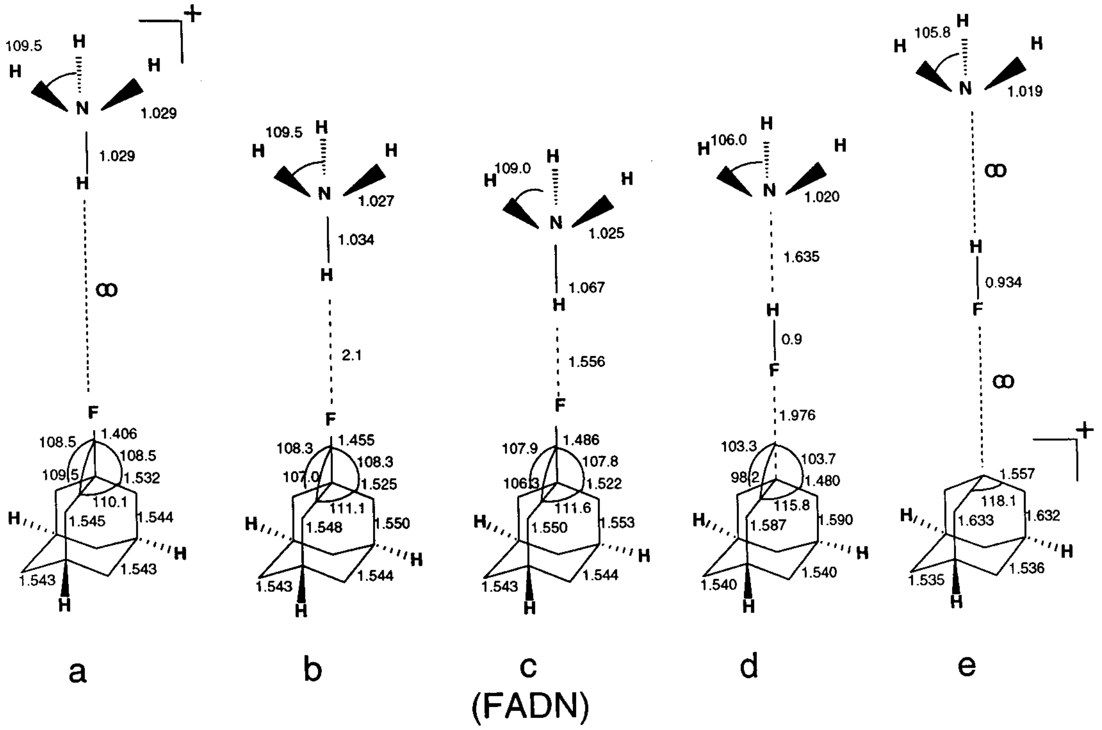


Figure 2. Schematic representation of the evolution of the structure of FAD$-$NH$_4^+$ complexes along the proton-transfer process. Bond distances in angstroms and bond angles in degrees. Structure **c** corresponds to the minimum of the potential energy curve in Figure 1.

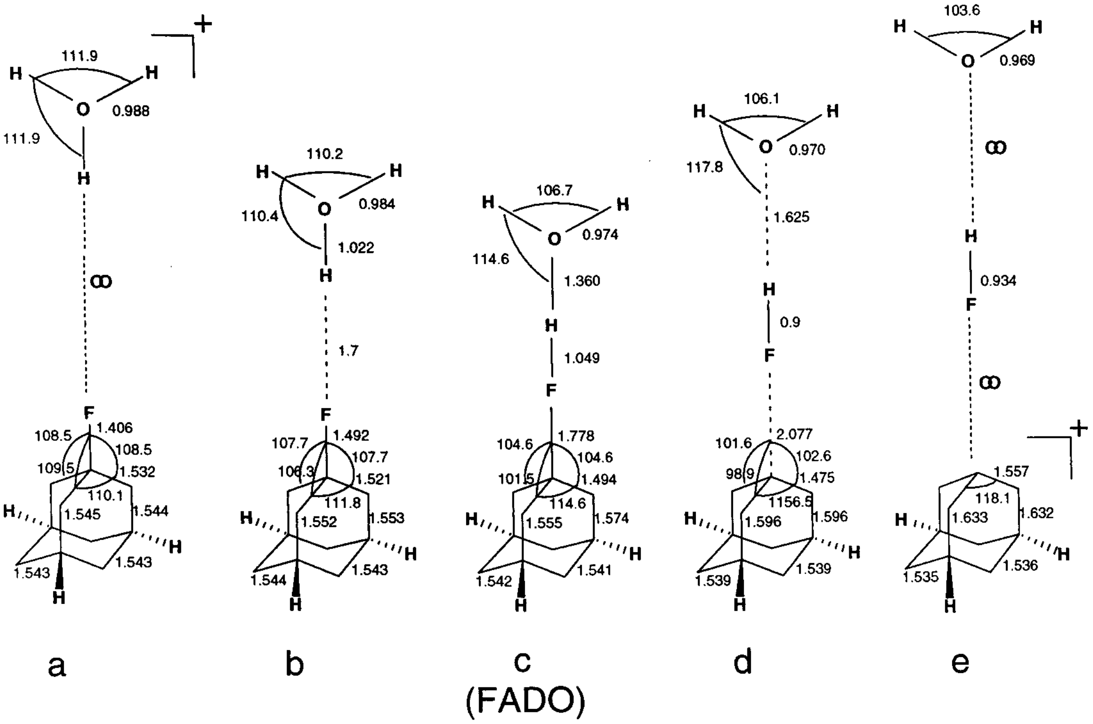


Figure 3. Schematic representation of the evolution of the structure of FAD$-$H$_3$O$^+$ complexes along the proton-transfer process. Bond distances in angstroms and bond angles in degrees. Structure **c** corresponds to the minimum of the potential energy curve in Figure 1.

general, negative values of $\nabla^2\rho$ are associated with covalent bonds while positive values of the Laplacian are typically associated with closed-shell interactions (ionic bonds, HBs, and van der Waals complexes). A more reliable information on the relative strength of the linkage can be obtained by means of the energy density,[72] $H(\mathbf{r})$, in the sense that negative values of $H(\mathbf{r})$ are associated with stabilizing charge concentration in the internuclear region. These topological calculations were done using the AIMPAC series of programs.[73]

Results and Discussion

Fluoroadamantane Protonation. To describe the proton-transfer process in the reactions between FAD and ammonium ion, we have used three different reaction coordinates, namely, the distance between the heavy atoms (r(F···N)), the proton coordinate defined as the F···H distance, and the ($r_1 - r_2$) coordinate, where r_1 is the distance from the proton to the nitrogen atom of the ammonia molecule, while r_2 is the distance

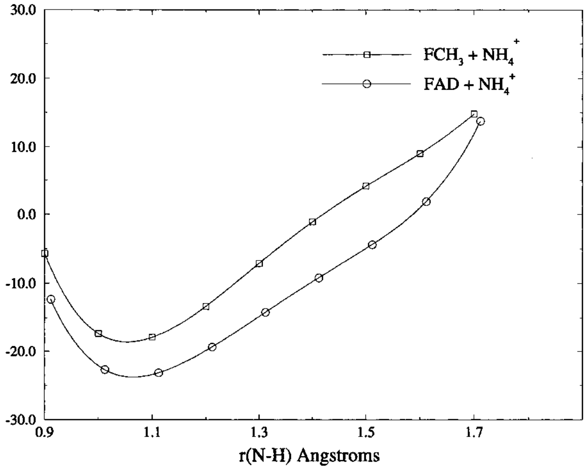


Figure 4. Potential energy curve corresponding to the proton transfer in FADN and fluoromethane$-$NH$_4^+$ complexes in the equilibrium conformation. The N$\cdots$F distance was kept equal to its value in the equilibrium conformation of the complex.

from the proton to the fluorine atom of the FAD molecule. As illustrated in Figure 1, the three plots correspond to single-well potentials.

In the first case (see Figure la) the minimum of the potential can be envisaged as an ion$-$dipole complex between NH$_4^+$ and FAD, where the F$\cdots$N distance is 2.6 Å. This description is consistent with that obtained when the $r_1 - r_2$ coordinate is used, in the sense that, in this case, the minimum appears for a value of the coordinate equal to -0.5 Å, which corresponds to an ion$-$dipole complex with the proton attached to the NH$_3$ moiety rather than to the FAD one. Also, either for positive or negative values of the coordinate the energy steadily increases. Taking into account that positive values would correspond to species where the proton is attached to the FAD subunit, these results indicate that the proton transfer is energetically unfavorable.

This is also consistent with the potential energy curve of Figure lc. The use of the F$\cdots$H coordinate has the advantage, with respect to the F$\cdots$N coordinate, that we can explore the situations where the proton has been transferred from the NH$_4^+$ subunit to the FAD molecule. As shown in this figure, when this happens, the energy of the system rapidly increases, showing that the proton transfer is unfavorable. The situation is completely different when the reference base is water rather than ammonia. As shown in Figure lc, the minimum of the potential appears at much shorter F$\cdots$H distances, indicating that the proton transfer is, in this case, energetically favorable. However, this process is barrierless since all structures with the proton constrained to be attached to the H$_2$O moiety lie systematically higher in energy than the minimum that can be viewed as a protonated FAD species solvated by a water molecule. This different behavior of the FAD$-$NH$_4^+$ (FADN) and FAD$-$H$_3$O$^+$ (FADO) complexes along the energetic profile of Figure 1c has been illustrated in Figures 2 and 3.

To confirm that the interaction FAD$-$NH$_4^+$ implies an asymmetric single-well potential, i.e., that the only minimum corresponds to the conformation in which the proton is attached to the most basic molecule, we have carried out two additional studies. In the first one we have specifically investigated the proton transfer within the FAD$-$NH$_4^+$ complex in its equilibrium conformation. For this purpose the F$\cdots$N distance was fixed equal to that in the FAD$-$NH$_4^+$ complex in its equilibrium conformation, and the N$\cdots$H distance was used as a reaction coordinate. The results obtained show again (see Figure 4) the proton-transfer potential to be of asymmetric single-well type.

TABLE 1: Calculated B3LYP/6-31G* Total Energies (hartrees) and Experimental[a] Proton Affinities (kcal/mol)

species[b]	B3LYP/6-31G*	PA$_{exp}$
FAD	−489.966 15	199.3[d]
AD$^+$	−389.838 23	
FCH$_3$	−139.733 92	145.0
HFCH$_3^+$	−139.972 52	
NH$_3$	−56.547 95	204.0
NH$_4^+$	−56.893 89	
H$_2$O	−76.408 96	166.5
H$_3$O$^+$	−76.689 08	
CO	−113.309 45	142.0
HCO$^+$	−113.545 23	
NO$_2$	−205.023 78	140.0
HNO$_2^+$	−205.248 39	
HCl	−460.795 70	128.6
H$_2$Cl$^+$	−461.008 73	
HF	−100.420 17	117.0
H$_2$F$^+$	−100.623 08	
FADN (FAD, NH$_4^+$)[c]	−546.899 07	
FADO (FAD, H$_3$O$^+$)	−566.721 30	
1a (FCH$_3$, NH$_4^+$)	−196.657 33	
1b	−196.769 06	
2a (FCH$_3$, H$_3$O$^+$)	−216.469 71	
2b	−216.588 01	
3a (FCH$_3$, HCO$^+$)	−253.326 63	
4a (FCH$_3$, HNO$_2^+$)	−345.056 63	
5a (FCH$_3$, H$_2$FCl$^+$)	−600.800 54	
6a (FCH$_3$, H$_2$F$^+$)	−240.442 46	
6b	−240.555 56	
7a (FCH$_3$, HFCH$_3^+$)	−279.767 04	

[a] Values taken from ref 42, unless otherwise stated. [b] Letter **a** designates complexes in the gas phase while letter **b** designates complexes in aqueous solution. [c] The reactants which yield the different complexes are given within parentheses. [d] Value taken from ref 21.

The second study consisted in optimizing, without imposing any restrictions, the structure **d** of the FADN complex (see Figure 2), i.e., the structure where the proton was transferred to the FAD subunit. This structure was found to collapse, without activation barrier, to the minimum **c**, which, as mentioned above, is a NH$_4^+$$-$FAD ion$-$dipole complex. For the case of FADO complexes we took as the initial structure that where the proton remains attached to the water molecule (structure **b** in Figure 3). When this initial geometry was optimized without imposing any restrictions, it collapsed to the minimum (structure **c** in Figure 3), where the proton has been transferred to the FAD moiety.

Hence, we may conclude that when the reference base is more basic than FAD, the potential energy curve has a single minimum which corresponds to an ion$-$dipole complex between the FAD moiety and the protonated reference base. However, when the reference base has a smaller proton affinity than FAD, the proton transfer is a barrierless process, and the only minimum of the potential is the protonated FAD species solvated by the reference base.

It is interesting to mention that these results were somewhat anticipated by Scheiner and Yi[26] when studying the interactions between NH$_4^+$ and imidazole (Im). These authors found a global minimum corresponding to an ion$-$dipole complex between NH$_3$ and protonated Im, because ammonia is significantly less basic than Im. Higher in energy they found another minimum corresponding to a complex between NH$_4^+$ and Im. Nevertheless, as stated by the same authors, this is an artifact of the HF method which likely disappears when electron correlation effects are included, so they finally conclude[26] that

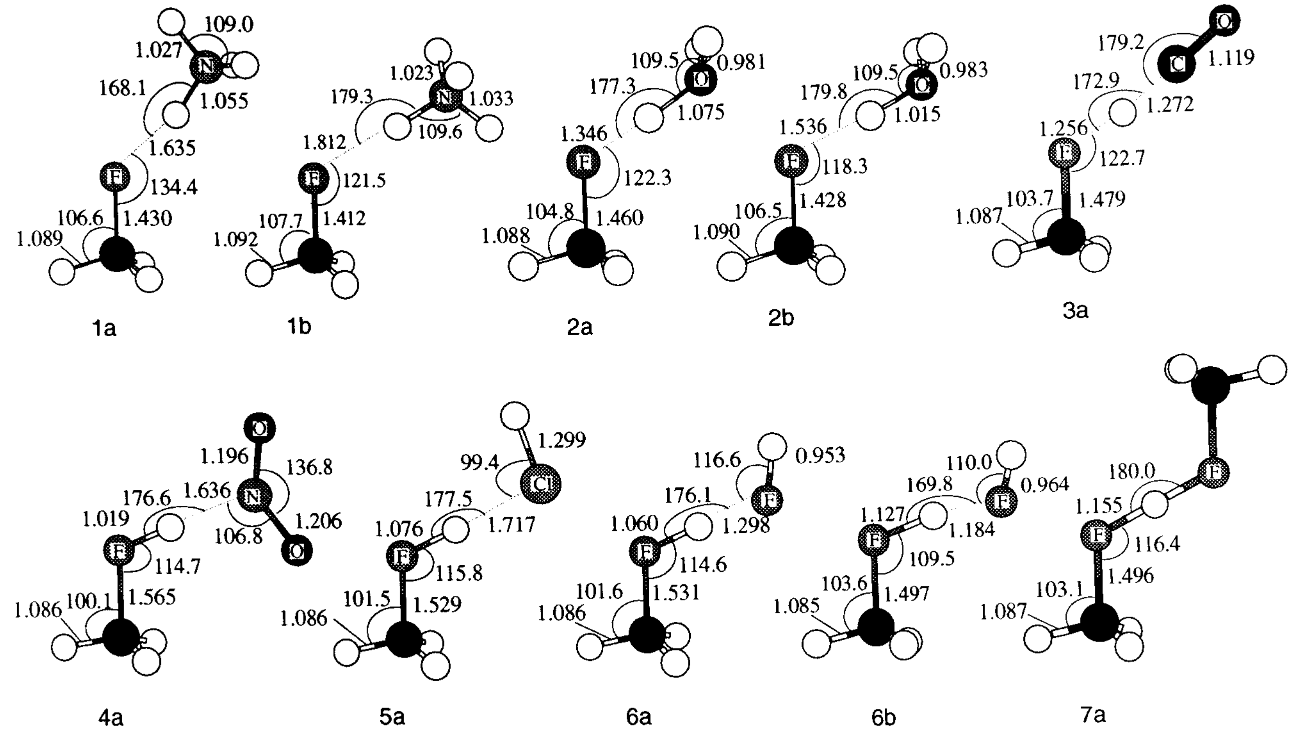


Figure 5. B3LYP/6-31G* optimized geometries for the different complexes between fluoromethane and the protonated forms of (**1**) NH_3, (**2**) H_2O, (**3**) CO, (**4**) NO_2, (**5**) HCl, (**6**) HF, and (**7**) CH_3F. The letter **a** designates gas-phase geometries and the letter **b** optimized geometries in aqueous solution. Bond distances in angstroms and bond angles in degrees.

the proton-transfer potential is of an asymmetric single-well type for all intents and purposes.

It must be noted that the proton-transfer process involving FAD leads finally to a C−F bond fission. As the proton of the reference base approaches the fluorine atom, the C−F distance steadily increases, and the adamantyl moiety also evolves to approach the equilibrium structure of the adamantyl cation (see Figures 2 and 3). Actually, as illustrated in Figure 3, the FADO complex in its equilibrium conformation can be viewed as an ion−dipole complex between adamantyl cation and hydrogen fluoride solvated by a water molecule. However, as mentioned above, NH_4^+ does not lead to a dissociative proton attachment reaction, because the proton transfer does not take place, while for H_3O^+ the proton transfer occurs without activation barrier. Consistently, according to our estimations (see Table l), the energy required to dissociate the FADN complex into FAD + NH_4^+ is only 24.4 kcal/mol, while the energy required to dissociate it to adamantyl cation + HF + NH_3 is significantly higher (58.2 kcal/mol). In contrast, the dissociation of the FADO complex into adamantyl cation + HF + H_2O is more favorable from the energetic point of view (33.8 kcal/mol) than its dissociation into FAD + H_3O^+ (41.5 kcal/mol). These results also indicate that even in this latter case the formation of adamantyl cation + HF as reaction products requires a significant amount of energy, since the minimum of the potential energy curve corresponds to a tightly bound complex.

There remain, however, some questions that need to be addressed. Is the proton-transfer potential always a single-well curve in these kinds of processes? In other words, provided that the reference base has an intrinsic basicity close to that of the FAD molecule, would the proton transfer occur also without a barrier? And, have the solvent effects some relevance in this case, ie., as has been found for other systems,[39] can the single-well potential found for the process in the gas-phase become a double-well potential in solution?

Since FAD is a very large system which would render all these calculations very time-consuming, we have chosen as a suitable model compound fluoromethane. The set of reference bases employed includes the two already mentioned, NH_3 and H_2O, as well as CO, NO_2, ClH, FH, and FCH_3, so that we assure that all possibilities are taken into account, in the sense that such a set includes bases that are significantly more basic than fluoromethane, significantly less basic, slightly more basic, slightly less basic, and with exactly the same intrinsic basicity.

Fluoromethane Protonation. The total energies of the different bases under consideration and their protonated forms have been summarized in Table 1. This table contains also the corresponding experimental proton affinities[74] and the total energies of the complexes between fluoromethane and the different protonated reference bases. The optimized geometries for these complexes are given in Figure 5.

The potential energy curves corresponding to the proton-transfer processes between NH_4^+, HCO^+, FH_2^+, and fluoromethane have been plotted in Figure 6. In all cases we have superimposed the optimized geometries of the complexes for some selected values of the F−H distance, which as before was taken as the reaction coordinate. It can be observed that in all cases the potential energy curves present a single-well shape. As for FAD, the equilibrium conformation for the FCH_3−NH_4^+ system corresponds to an ion−dipole complex between fluoromethane and ammonium ion, where no proton transfer took place. A similar behavior is observed for the complexes with H_3O^+, in contrast to what has been found above for the case of FAD, due to the fact that fluoromethane is significantly less basic than FAD (see Table 1). This represents a quite interesting case where the reference base is the same and the proton-transfer potential curve presents a single minimum, both when the proton transfer occurs and when it does not take place.

According to the values given in Table 1, carbon monoxide has a proton affinity only slightly smaller (3 kcal/mol) than that

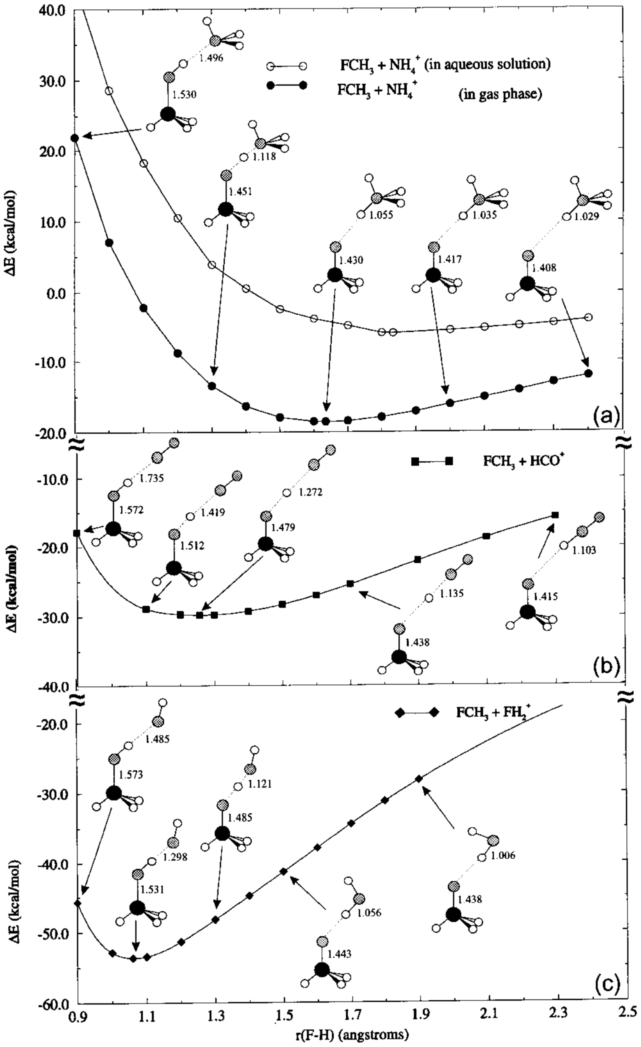


Figure 6. Potential energy curve corresponding to the proton transfer in (a) fluoromethane$-$NH$_4^+$, (b) fluoromethane$-$HCO$^+$, and (c) fluoromethane$-$FH$_2^+$ complexes. For each reaction values are referred to the corresponding fluoromethane + X$^+$ dissociation limit. Bond distances are given in angstroms.

of fluoromethane; however, the corresponding potential energy curve for the proton transfer is again single-well. As illustrated in Figure 6b, due to the similar basicities of both partners, the proton is approximately midway between the two heavy atoms involved in the corresponding hydrogen bond. A topological analysis of the corresponding charge densities reveals, however, that no proton transfer took place strictly speaking, in the sense that, as illustrated in Figure 7, in complex **3a** the proton remains attached to the CO moiety, and no covalent interaction seems to exists between the proton and the fluorine atom of the fluoromethane subunit.

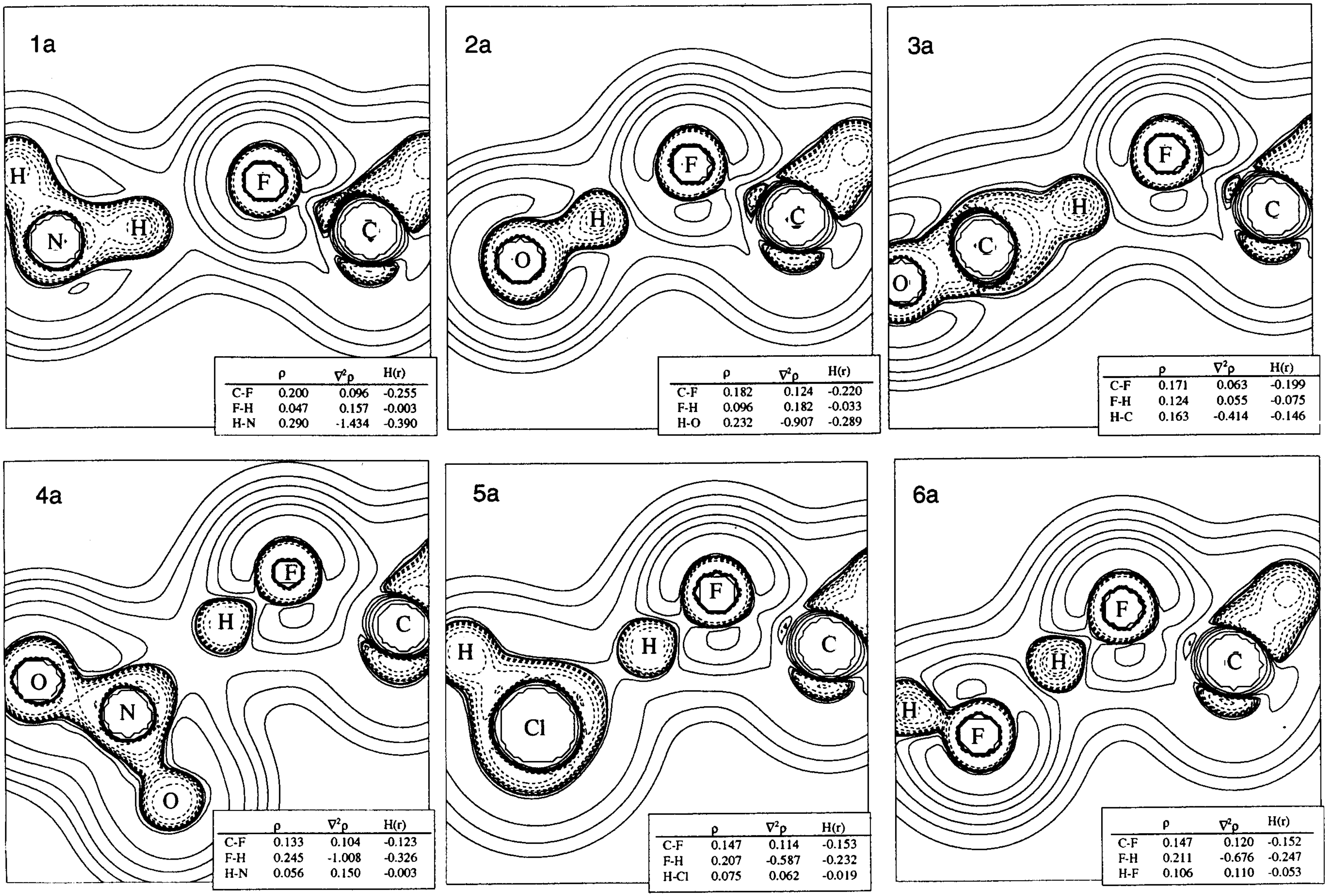
Quite interestingly, a further increase of only 2 kcal/mol in the difference between the proton affinities of fluoromethane and the reference base (NO$_2$) changes completely the situation, and the proton transfer takes place. As shown in Figures 5 and 7, in complex **4a**, the proton is covalently bound to the fluoromethane molecule and forms a hydrogen bond with the NO$_2$ subunit. Obviously, when the intrinsic basicity of the reference base is significantly lower than that of fluoromethane, as is the case for hydrogen chloride and hydrogen fluoride, the proton-transfer process also takes place without activation barrier, and therefore the potential energy curve is once more single-well (see Figure 6). Finally, for the particular case of the CH$_3$FH$^+$$-FCH_3$ complex **7a**, we have found also a symmetric single-well potential in which the proton is midway between the two CH$_3$F subunits (see Figure 5).

The evolution of the charge density distribution in the protonation processes of fluoromethane as a function of the strength of the reference base is clearly illustrated in Figure 7, where we have plotted the Laplacians of the charge densities of the different complexes investigated. As illustrated by the values of the energy density, it is apparent that there are essentially only two kinds of situations: either the proton is covalently bound to the reference base and forms a hydrogen bond with the fluoromethane molecule (**1a**, **2a**, **3a**) or it is covalently attached to the latter and forms a hydrogen bond with the reference base (**4a**, **5a**, **6a**). It is important to emphasize, as we have mentioned above, that this is indeed the case even when the difference between the intrinsic basicities of the interacting bases is as small as 3.0 kcal/mol. As we have mentioned above, in complex **7a** the proton is midway between both fluorine atoms and the energy densities at the corresponding F$-$H bonds are about half the normal value in typical F$-$H covalent linkages. This clearly shows that both CH$_3$F subunits are bound to the proton by strong ionic hydrogen bonds.

It is also worth noting that as the intrinsic basicity of the reference base approaches that of the fluoromethane molecule, the C$-$F bond of the latter becomes sizably activated; i.e., the charge density within the C$-$F bonding region decreases, its energy density becomes less negative and the linkage becomes weaker and longer. This finding is consistent with the fact that in systems as FAD this eventually leads to the C$-$F bond fission, favored by the great stability of the adamantyl cation.

As for the case of the FADN complexes, we have considered it of interest to study specifically the proton-transfer processes within the complex in its equilibrium conformation. For this purpose we have chosen, as a suitable benchmark case, the complex **1a** between fluoromethane and ammonium ion because it presents the longest distance between the two heavy atoms involved. The corresponding potential energy curve has been plotted in Figure 4. The F···N distance was fixed equal to that in the fluoromethane$-$ammonium complex, and the reaction coordinate corresponds to the N$-$H distance. It is evident that, as was found for the FADN complexes, the potential is again of an asymmetric single-well type.

Solvent Effects. The possible solvent effects on the characteristics of the proton-transfer potential energy curve have been investigated for three different cases, including two in which proton transfer does not occur (reactions with NH$_4^+$ and H$_3$O$^+$) and one in which it takes place (reaction with FH$_2^+$). The optimized geometries of the corresponding complexes in solution have been also included in Figure 5. In the three cases investigated the interaction with the solvent does not change significantly the shape of the potential energy curve, in the sense that it is still single well. For the sake of conciseness we shall discuss in detail only the fluoromethane$-$NH$_4^+$ system. As illustrated in Figure 6a, the effects of the surroundings is to displace the minimum to larger F···H distances and to decrease the depth of the well, with respect to the dissociation products. This latter effect indicates that, although solvent effects stabilize the complex, the stabilization of the reactants is more effective. The origin of the first effect is less evident, mainly if one takes into account that for complexes fluoromethane$-$FH$_2^+$, the effect is just the opposite: the proton appears closer to the FH moiety, while the F···F distance contracts slightly when solvent effects are present (see Figure 5). These findings could be explained as follows: solute$-$solvent interactions with charged species



1a

	ρ	$\nabla^2\rho$	H(r)
C-F	0.200	0.096	-0.255
F-H	0.047	0.157	-0.003
H-N	0.290	-1.434	-0.390

2a

	ρ	$\nabla^2\rho$	H(r)
C-F	0.182	0.124	-0.220
F-H	0.096	0.182	-0.033
H-O	0.232	-0.907	-0.289

3a

	ρ	$\nabla^2\rho$	H(r)
C-F	0.171	0.063	-0.199
F-H	0.124	0.055	-0.075
H-C	0.163	-0.414	-0.146

4a

	ρ	$\nabla^2\rho$	H(r)
C-F	0.133	0.104	-0.123
F-H	0.245	-1.008	-0.326
H-N	0.056	0.150	-0.003

5a

	ρ	$\nabla^2\rho$	H(r)
C-F	0.147	0.114	-0.153
F-H	0.207	-0.587	-0.232
H-Cl	0.075	0.062	-0.019

6a

	ρ	$\nabla^2\rho$	H(r)
C-F	0.147	0.120	-0.152
F-H	0.211	-0.676	-0.247
H-F	0.106	0.110	-0.053

Figure 7. Contour maps of the Laplacian of the charge density of complexes **1a**, **2a**, **3a**, **4a**, **5a**, and **6a** in their equilibrium conformations. Positive values of the Laplacian are denoted by solid lines and negative values by dashed lines. The values of the charge density, ρ, its Laplacian $\nabla 2\rho$, and the energy density $H(\mathbf{r})$ at the bond critical points are also given. All values in au.

are stronger than with neutral species, so in the complexes these interactions should be stronger with the moiety that supports the positive charge. Keeping this in mind, let us consider the complexes fluoromethane−ammonium ion. The two extreme situations would correspond to a $CH_3F-NH_4^+$ complex and to a $CH_3FH^+-NH_3$ complex, the former being the most stable in the gas phase. Upon solvation one should expect also the former to interact better with the solvent than the latter. In the $CH_3F-NH_4^+$ complex, the positive charge is associated with the NH_4 moiety where the N−H polarity is large, while in the $CH_3FH^+-NH_3$ complex the positive charge is quite dispersed within the CH_3FH^+ moiety, due to the presence of the methyl group. Hence, as predicted by our calculations, the former species is stabilized in solution and the proton transfer disfavored. Let us consider the complexes between fluoromethane and hydrogen fluoride. The two extreme situations would correspond to a $CH_3F-FH_2^+$ complex and to a CH_3FH^+-FH complex, the latter being now the more stable in the gas phase. However, using arguments similar to those employed above, solvation effects would be more effective for the former than for the latter. As a consequence, in solution the proton transfer is less favorable than in the gas phase and the distance between the proton and the FH (or the CH_3F) moiety smaller (or larger).

Conclusions

We have found through the use of DFT theoretical calculations that proton transfers involved in typical dissociative protonation processes are characterized by single-well potential energy curves. Hence, the proton transfer occurs without barrier if the process is thermodynamically favorable. Solvation effects do not give rise to two minima as has been found for other systems,[39] and the potential continues to be single-well. However, the effects of the solvent on the characteristics of the complex are not negligible. The distance between the heavy atoms, and as a consequence the position of the minimum change, and the well becomes less deep.

For fluoroadamantane the proton transfer, when favorable, leads to a C−F bond fission. However, the equilibrium conformation corresponds to a tightly bound complex between adamantyl cation and hydrogen fluoride, solvated by one molecule of the corresponding reference base. This implies that the formation of adamantyl cation and HF as products of the reaction requires a significant amount of energy, necessary to dissociate the aforementioned tightly bound complex in their components.

Acknowledgment. This work has been partially supported by the D.G.E.S. Project PB96-0067. L.G. also acknowledges a predoctoral grant from the Ministerio de Educación y Cultura. A generous allocation of computational time at the Centro de Computación Científica de la Facultad de Ciencias de la Universidad Autónoma de Madrid and at the Cray-J90 computer of CIEMAT is also acknowledged.

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