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The Influence of Solvation on the Calculated Activation Energy for the Reaction $CH_3F + F^-$

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The influence of the solvent on the activation energy of the synchronous, concerted, narcissistic reaction: $CH_3F + F^- \rightarrow |CH_3F_2|^- \rightarrow FCH_3 + F^-$, has been investigated by means of CNDO/2 method. The reaction path has been fully followed *in vacuo*, and at a suitable point only, of reaction coordinate, in solution. The geometries of H_2O, F^-, CH_3F, and $|CH_3F_2|^-$, *in vacuo* and in different hydrated cages, have been optimized.

Der Einfluß des Lösungsmittels auf die Aktivierungsenergie der synchronverlaufenden Reaktionen $CH_3F + F^- \rightarrow |CH_3F_2|^- \rightarrow FCH_3 + F^-$, wurde mit der CNDO/2 Methode geprüft. Der Reaktions-Ablauf wurde in Vakuum vollkommen und in der Lösung an einem geeigneten Punkt der Reaktionskoordinate durchgeführt. Die Geometrien von H_2O, F^-, CH_3F, und $|CH_3F_2|^-$ im Vakuum und in verschiedenen hydrierten Käfigen wurden optimalisiert.

L'influence du solvent sur l'énergie d'activation de la réaction synchronique, concertée, narcissistique: $CH_3F + F^- \rightarrow |CH_3F_2|^- \rightarrow FCH_3 + F^-$ a été examinée par la méthode CNDO/2. On a suivie l'entier chemin de réaction *in vacuo*, alors qu'on a observé un seul point convenable de la coordonée de réaction en solution. On a optimizé les géometries de H_2O, F^-, CH_3F, et $|CH_3F_2|^-$ *in vacuo* et en differentes cages hydratés.

Introduction

The electronic structure of initial and transition states for nucleophilic substitution reactions have been extensively investigated in the past few years [1–5]. The symmetrical SN 2 reaction:

$$F^- + CH_3F \rightarrow [CH_3F_2]^- \rightarrow FCH_3 + F^- \tag{1}$$

is a case in which reactants and products are identical, and is an example of synchronous, concerted narcissistic reaction [6].

The reaction path in the vacuo has been studied by Veillard *et al.* [7–8] through *ab initio* MO calculation on Gaussian basis, that is each atomic orbital is a linear combination of gaussian functions (GTO).

Particular attention has been given to the choice of the basis set. When no polarization functions were included in the basis the transition state was found to be more stable than the reactants. An activation energy of 7.9 kcal/mole has been found when *d* orbitals on carbon and fluorine atoms were introduced. On other hand it has been pointed out that the variation of solvation energy is generally competitive, and in the present case prevailing on the variation of inner energy of the system, in determining the activation energy.

The role of the solvent on the energy and electronic structure of initial and transition states for reaction (1), is here investigated by means of theoretical calculations. The complexity of the system and the amount of computational time discourage from employing *ab initio* methods; consequently the study of the reaction:

$$F^-_{aq} + CH_3F_{aq} \rightarrow [CH_3F_2]^-_{aq} \tag{2}$$

has been performed within the framework of a semiempirical MO LCAO method; namely the energy of these systems have been calculated by the CNDO/2 method [9] as a function of bond-lengths and bond-angles.

Calculations

CNDO calculations have been performed following the standard procedure with a program written by Santry [10], and using the parameters assigned by Pople and Segal [9]. The geometry and the electronic structure for H_2O, F^-, CH_3F, and $CH_3F_2^-$ systems, *in vacuo* and in different hydration cages, have been optimized through an energy minimizing process. When more complex systems are involved we have been forced to limit the number of geometrical parameters to be optimized following criteria that will be discussed at due time. In a first stage of calculations an indicative value for the hydration energy has been obtained as the difference between the energy of the hydrated cage and that of the corresponding isolated units. To study the path followed by the system in going from reactants to products and to evaluate the energy changes, several points have been calculated along the reaction path. For the hydrated system only one intermediate point has been determined for a suitable value of the reaction co-ordinate.

Results

1. $(H_2O)_n$ $(n = 1, 2, 4, 6)$

The isolated water molecule, the dimer, tetramer and hexamer have been considered. The structures taken into consideration are drawn schematically in Fig. 1, where the point group symmetry, the variables to be optimized and the net-charges for the optimized geometry are also reported.

The minimum-energy geometry for isolated water corresponds to a bond-length (r) of 1.029 Å and a bond angle (θ) of 104° 30′ [1]. For the oligomers the O–H bond-lengths not involved in hydrogen bridges were kept constant at $r = 1.029$ Å in all our calculations.

The minimum-energies (in a.u.), stabilization energy (in kcal/mole) and the optimized geometrical parameters for the different structures are collected in Table 1.

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[1] This result agrees with the values obtained by Burton and Daly [11].

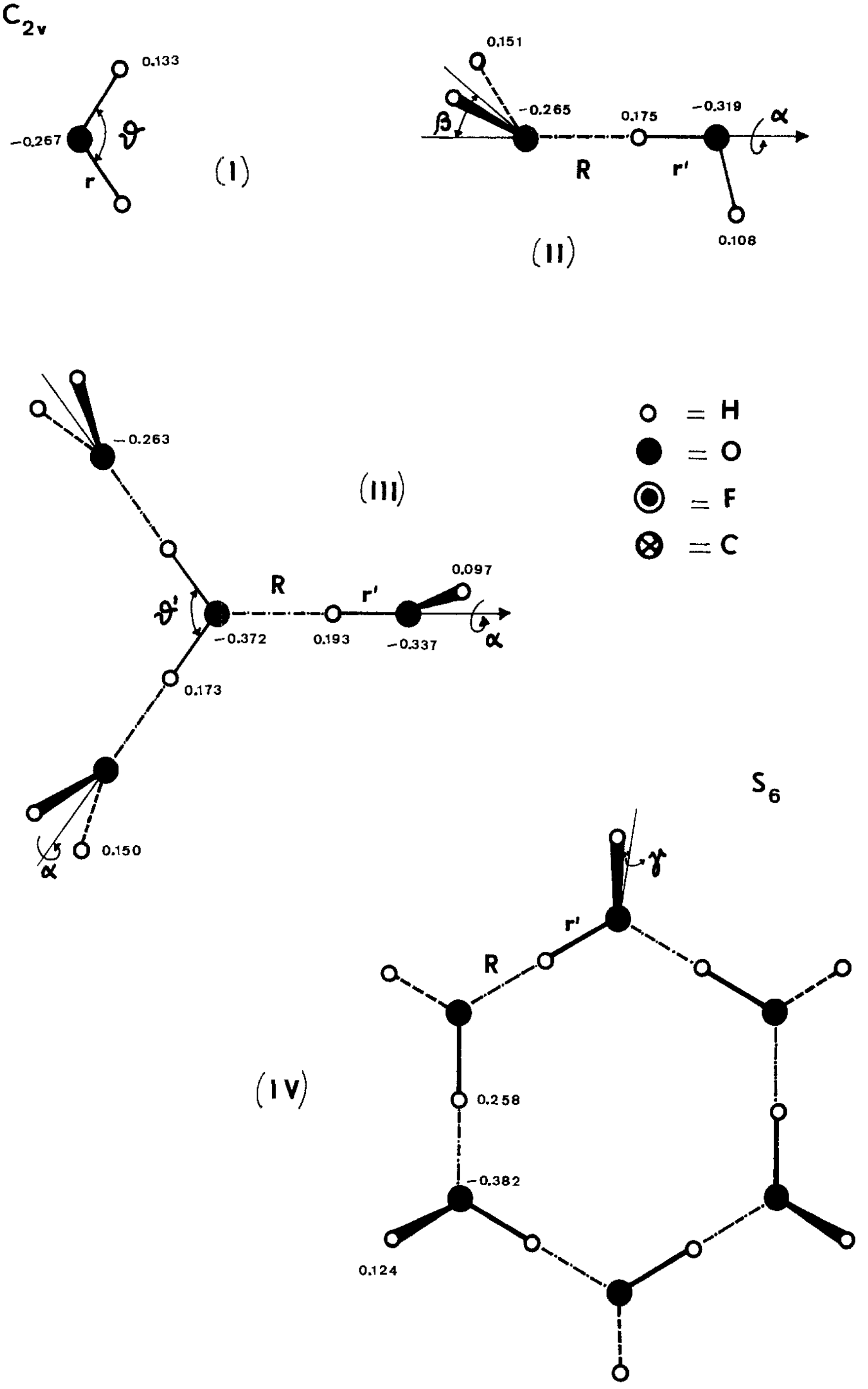


Fig. 1. Optimized geometries for water oligomers. Letters indicate the optimized variables and figures the net-charges

Table 1. Minimum and stabilization energies, and optimized geometry for water (distances in Å; angles in degree)

	E (a.u.)	ΔE (kcal/mole)	r	θ	R	r'	θ'	α	β	γ
I	− 19.8912		1.029[a]	104° 30′						
II	− 39.7960	4.30			1.498	1.043		0°	0°	
III	− 79.6074	6.68			1.487	1.036	105° 12′	0°		
IV	−119.4593	11.72			1.357[b]	1.068				52°

[a] Experimental values: $r = 0.9571$ Å, $\theta = 104° 32'$ [13a].

[b] The calculated distance O–O for IV is intermediate between the experimental values found for ice (2.76 Å) [14] and polywater (2.3 Å) [15].

It seems interesting that in the case of structure (IV), the planar model (C_6 symmetry) is less stable than the no planar one (S_6 symmetry) [12]. By inspection of energy data reported in Table 1, a value of about 10–12 kcal/mole may be assigned to the stabilization energy for a mole of solvated water. This value can be favourably compared with the evaporation-heat of water (10.5 kcal/mole [16]).

2. $F^- \cdot nH_2O$ ($n = 0, 2, 4, 6, 8, 12$)

The calculated energy for fluoride ion is −27.4841 a.u. The hydration of the fluoride ion has been studied considering several complexes in which F^- is bound with two, four (tetrahedral cage), six (octahedral cage), eight (cubic cage), and twelve (dodecahedral cage) molecules of water respectively.

The total energy was minimized with respect to the distances r_0 and R_0, shown in Fig. 2, where the complex with $n = 4$ is schematically drawn. The bond-angle and the O–H distance of water not interested in hydrogen-bonds were kept constant, that is equal to the values obtained for water molecule.

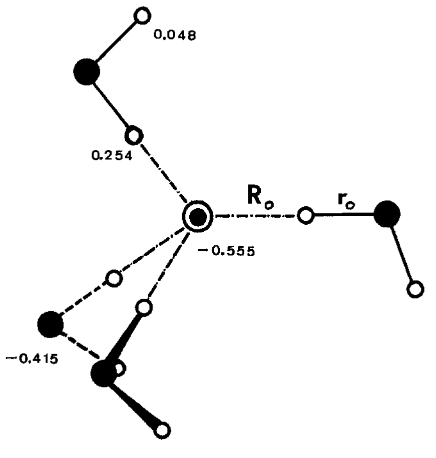


Fig. 2. Geometry for tetrahedral cage of fluoride ion

Table 2. Minimum and stabilization energies, optimized geometries and net-charge on fluorine for $F^- \cdot nH_2O$ systems

$F^- \cdot nH_2O$	E(a.u.)	ΔE(kcal/mole)	r_0(Å)[a]	R_0(Å)[a]	q_F
$n=0$	− 27.4841				−1.00
2	− 67.4559	118.85	1.101	1.221	−0.601
4	−107.3101	163.98	1.067	1.315	−0.555
6	−147.1334	189.57	1.054	1.389	−0.547
8	−186.9248	195.22	1.047	1.481	−0.577
12	−266.4755	186.37	1.042	1.680	−0.660

[a] r_0 and R_0 are defined in Fig. 2.

The more significant calculated data, that is, minimum-energy, stabilization-energy, optimized geometrical parameters, and net-charge on the fluorine atom for the different systems are collected in Table 2.

The most stable packing corresponds to a cage of eight water molecules; the calculated stabilization-energy (187 kcal/mole) overextimates, as expected, the experimental hydration energy (120 kcal/mole) [17]. On other hand, a more realistic value of solvation-energy should be calculated as the difference between the energy of the n-hydrated complex and the energy of n suitably packed molecules of water. Assuming (see the preceeding section) a value of 12 kcal/mole for the stabilization energy of a molecule of solvated water, the complexes with four and six water units show the maximum stabilization, and the corresponding hydration-energy are 128 and 117 kcal/mole respectively, in nice agreement with the experimental value (120 kcal/mole) and a theoretical value previously evaluated (126.7 kcal/mole) [18], considering the difference between the systems

$$F^- + (H_2O)_5 \text{ and } H_2O + [F(H_2O)_4]^- .$$

By inspection of the last column of Table 2 it appears that the charge-transfer from fluorine to the solvent for the different structures, shows a regular trend, with the strongest delocalization for the octahedral cage.

3. $CH_3F \cdot nH_2O$ ($n = 0, 3, 4, 7$)

The geometry of the isolated system has been optimized minimizing the total energy with respect to the bond-distances r_{C-F} and r_{C-H} and the bond-angles θ (see Fig. 3–I).

Afterwards the system in which fluorine atom is bound to three water molecules has been considered.

The calculated geometry shows that one further molecule can be placed around the fluorine atom. Keeping fixed the geometry of methyl group, as found for isolated molecule, the variables indicated in Fig. 4 have been optimized.

Two conformations (oxigen atoms staggered or eclypsed in respect with methyl protons) have been considered and the total-energy of the staggered conformation is lower by 5.15 kcal/mole than that of the eclypsed one. The system in which in addition the methyl group is hydrated have been also considered. The optimized parameters are reported in Fig. 5 where the more stable eclypsed conformation is shown.

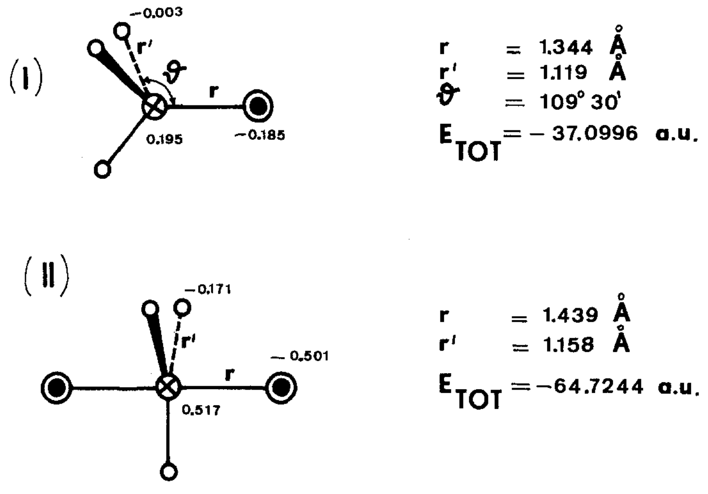


Fig. 3. Optimized geometry, energy, and net-charges for CH_3F (I) and $CH_3F_2^-$ (II)

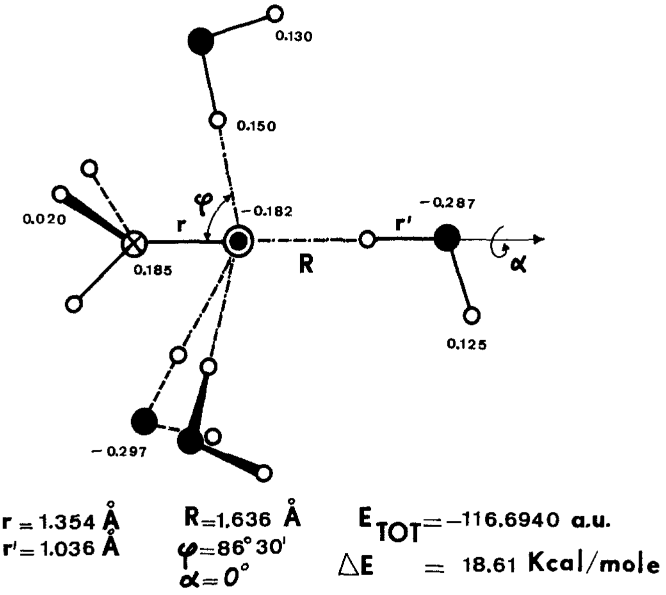


Fig. 4. Optimized geometry, energy, and net-charges for $CH_3F \cdot 4\,H_2O$. After the optimization of the variables r, R, r', and θ it has been verified that the total energy is in a minimum when $\alpha = 0$, that is the external proton of water molecule lying along the C–F bond, is in the symmetry plane of the system

Net-charges for all atoms in CH_3F, $CH_3F \cdot 4\,H_2O$, and $CH_3F \cdot 7\,H_2O$ systems are shown in the proper figures (3–I; 4 and 5).

The geometry of the CH_3F molecule ($r_{C\text{–}F} = 1.344$ Å; $r_{C\text{–}H} = 1.119$ Å; and $\theta = 109°\,30'$) as obtained by CNDO calculations accords well both with exper-

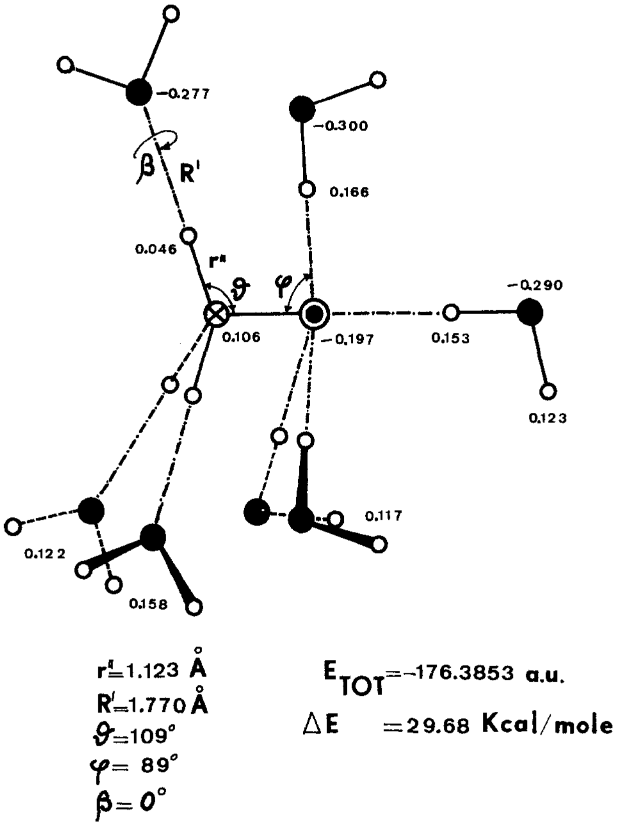


Fig. 5. Optimized geometry, energy, and net-charges for $CH_3F \cdot 7H_2O \cdot \beta$ is equal to 0° when the water molecule lies in the symmetry plane of the system

imental data ($r_{C\text{-}F} = 1.385$ Å; $r_{C\text{-}H} = 1.109$; $\theta = 110°$) [13b], and with the geometry obtained by an *ab initio* calculation ($r_{C\text{-}F} = 1.42$ Å, $r_{C\text{-}H} = 1.08$ Å, $\theta = 107° 30'$) [8].

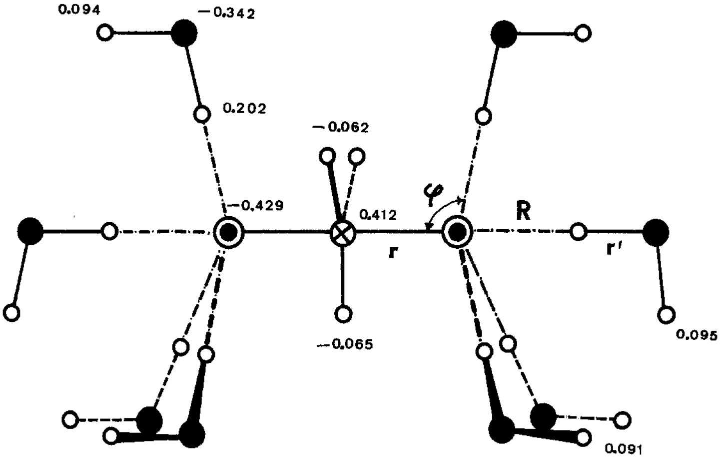
Calculated stabilization energies for $CH_3F \cdot 4\,H_2O$ and $CH_3F \cdot 7\,H_2O$ systems are 18.6 and 29.7 kcal/mole respectively and may be related to the experimental value of the hydration value: $\Delta H_S = 14.94$ kcal/mole [19].

4. $CH_3F_2^- \cdot nH_2O$ ($n = 0, 8, 11$)

The geometry of the isolated system has been optimized minimizing the total energy with respect to the bond-distances $r_{C\text{-}F}$ and $r_{C\text{-}H}$ (see Fig. 3–II).

The same criteria followed for the energy-minimization of $CH_3F \cdot nH_2O$ systems, have been adopted for the transition state. The systems hydrated by eight and eleven water molecules respectively, are schematically drawn in Figs. 6 and 7, where the optimizing variables and the most relevant calculated results are collected.

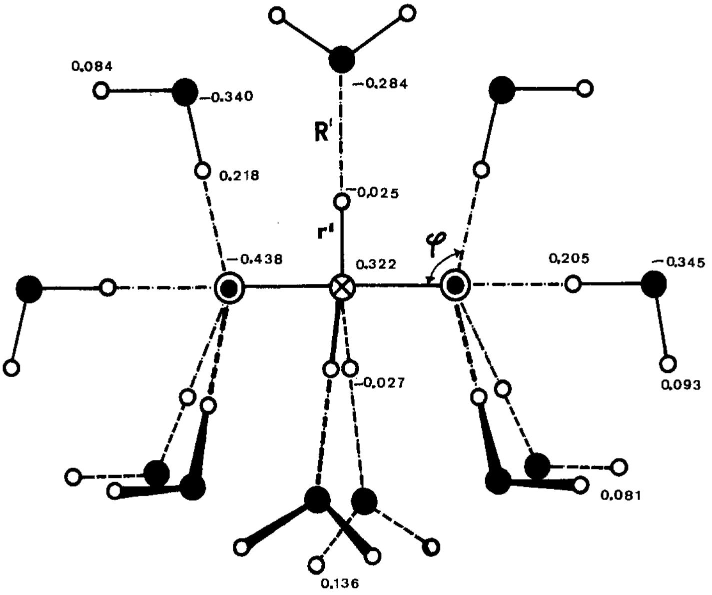
In the case in which the fluorine atom only is hydrated, the staggered conformation is favoured of 3.45 kcal/mole. However the eclypsed conformation is more



$r = 1.466$ Å
$R = 1.482$ Å
$r' = 1.047$ Å
$\varphi = 104°$

$E_{TOT} = -224.0341$ a.u.
$\Delta E = 113.01$ Kcal/mole

Fig. 6. Optimized geometry, energy, and net-charges for $CH_3F_2^- \cdot 8\,H_2O$



$r'' = 1.157$ Å
$R' = 1.732$ Å
$\varphi = 106°$

$E_{TOT} = -283.7342$ a.u.
$\Delta E = 131.53$ Kcal/mole

Fig. 7. Optimized geometry, energy, and net-charges for $CH_3F_2^- \cdot 11\,H_2O$

stable (18.72 kcal/mole) when three water molecules hydrate also the methyl group. It is interesting to observe how the stabilization energy for transition state falls between fluoride ion and CH_3F's stabilization energies; this finding is in accord with expectation as the transition state is charged, unlike CH_3F, but the charge is more spread than in the case of fluoride ion (see net-charges in Figs. 2, 4, 6, 7).

Reaction Path

Activation energies have been evaluated for the system *in vacuo* and for different degrees of solvated systems; numerical values are collected in Table 3.

The reaction path *in vacuo* has been calculated for several values of reaction coordinate. Activation energy, net-charge on the nucleophilic fluorine atom, and geometrical parameters are shown in Table 4.

Table 3. Activation energies for the system *in vacuo* and in different hydrated cages

	Reactions	ΔE(kcal/mole)
a	$CH_3F + F^- \rightarrow [CH_3F_2]^-$	−88.29
b	$CH_3F(H_2O)_4 + [F(H_2O)_4]^- \rightarrow [CH_3F_2(H_2O)_8]^-$	−18.82
c	$CH_3F(H_2O)_4 + [F(H_2O)_6]^- \rightarrow [CH_3F_2(H_2O)_8]^- + 2\,H_2O$	+ 6.34
d	$CH_3F(H_2O)_4 + [F(H_2O)_8]^- \rightarrow [CH_3F_2(H_2O)_8]^- + 4\,H_2O$	+12.49
e	$CH_3F(H_2O)_7 + [F(H_2O)_4]^- \rightarrow [CH_3F_2(H_2O)_{11}]^-$	−24.35
f	$CH_3F(H_2O)_7 + [F(H_2O)_6]^- \rightarrow [CH_3F_2(H_2O)_{11}] + 2\,H_2O$	+ 1.32
g	$CH_3F(H_2O)_7 + [F(H_2O)_8]^- \rightarrow [CH_3F_2(H_2O)_{11}] + 4\,H_2O$	+ 6.96

Table 4. Energy and geometrical data for the reaction path in the vacuo at different values of reaction coordinate (ϱ)[a]

ϱ(Å)[b]	∞	3	2	1.8	1.6	1.439
r (Å)	1.344	1.349	1.374	1.391	1.418	1.439
r'(Å)	1.119	1.119	1.120	1.131	1.144	1.158
θ	109° 30′	109° 12′	102° 42′	98° 6′	93° 24′	90°
q_F	− 1	− 0.998	− 0.886	− 0.768	− 0.621	− 0.501
E(a.u.)	− 64.5837	− 64.5955	− 64.6277	− 64.6584	− 64.7025	− 64.7244

[a] ϱ is the distance between the carbon atom and the incoming fluoride ion.

[b] The geometrical parameters are defined in Fig. 3.

Discussion

To evaluate the influence of the solvent on the activation energy the reaction (2) has been studied by the CNDO method. The calculated geometry of CH_3F, as reported in a previous section is in agreement with experiment. In the case of the transition state, where no comparison with experiment is possible, we can only observe that C–F bond-length (1.439 Å), obtained by CNDO calculations is remarkably shorter than the corresponding *ab initio* value (1.80 Å).

Table 5. Energy and geometry parameters for the reaction in the solvent (case b) at different values of reaction-coordinate (ϱ)

ϱ [a]	∞ $[F(H_2O)_4]^-$	∞ $CH_3F \cdot (H_2O)_4$	2.00 (Å)	Equilibrium $[CH_3F_2(H_2O)_8]^-$
r		1.354	1.378	1.466
R		1.636	1.574	1.482
R_0	1.315		1.348	
θ		109° 30′	105° 36′	90°
Φ		86° 30′	104°	104°
Φ'	109° 30′		90° 24′	
E(a.u.)	−224.0041		−224.0155	−224.0341

[a] The geometrical parameters are defined in Figs. 2, 4 and 6.
θ = FCH in $CH_3F \cdot 4\,H_2O$.
Φ' = OFO in $F^- \cdot 4\,H_2O$.

In the absence of solvent, our calculations, as *ab initio* ones [8, 20], when no polarization functions are included in the basis set predict the reactants to be less stable than the transition state. The activation energies for the series of models in which different number of water molecules have been introduced, are collected in Table 3. Solvation stabilizes the transition state much more than the reactants and if a sufficient number of water molecules is included in the system a reasonably value for the activation energy of reaction in solution is obtained.

The calculated values may be compared with a value of 20 kcal/mole extimated by Bertier *et al.* [8].

Among the data reported in Table 3, the difference of 70 kcal/mole between activation energies for the system *in vacuo* (*a*) and a system with a minimum number of molecules of water (*b*) is the most significant result. It is evident that solvation energy plays an important role on the determination of activation energy.

The reaction path has been fully followed for the reaction *in vacuo* (the relevant data are shown in Table 4). It is evident that the departure of the leaving fluorine atom is rather late: when the incoming F^- ion is at 2.0 Å from the carbon atom, the leaving F atom has moved by only 0.03 Å. An analogous result has been obtained by *ab initio* calculations where for $\varrho = 2.1$ Å, the leaving fluorine atom is moved by 0.08 Å. The presence of the solvent does not modify this situation as reported in Table 5 for the single point calculated on the reaction path ($\varrho = 2.0$ Å) for the hydrated system.

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