A Theoretical Investigation on the Role of Solvent in Solvolytic Reactions. Part 5.[1] Fluoromethane in Methane

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The effect of an apolar solvent, *i.e.* methane, on the dissociation process of fluoromethane was investigated by MO theory at the CNDO/2 level of approximation. Unlike in polar solvents (water and hydrofluoric acid) fluoromethane is predicted to dissociate without the formation of intermediates. Through the analysis of the previous and present results the reliability of the solvent model and its limits of applicability are discussed.

In line with our interest in the effect of solvent on the course of organic reactions, in previous investigations the solvolytic reaction of fluoromethane, the simplest model system representative of alkyl halides, was studied through quantum mechanical methods, at the MO level of approximation.[2] The aim was to rationalize the large amount of experimental work following the differentiation between dissociated carbonium ions and carbonium ion pairs, in terms of the structures recognized by Winstein,[3] *i.e.* intimate and solvent-separated ion pairs. In view of this, we chose a solvent field model focused on the first solvation shell. This oversimplified model involves a heavy computational effort, so that rigid solvent molecules of small size had to be used to keep the computational time at a reasonable level. Previously, water and hydrofluoric acid, two highly polar solvents with large dielectric constants (80 and 84 for H_2O and HF, respectively) were considered.[1,4,5] In both solvents the dissociation of fluoromethane was predicted to occur through the intervention of at least two types of intermediates, whose geometries immediately recall the models proposed for intimate and solvent-separated ion pairs.[1,5]

Since many solvolytic reactions occur in organic solvents, and water and hydrofluoric acid are far from representing an organic environment, in this paper we present a theoretical investigation of the dissociation of fluoromethane in methane, the smallest model system for an apolar organic solvent, with very low dielectric constant (ε 1—2).

The model used, its reliability and the energy-minimization process adopted throughout the calculations have already been widely discussed. The details are available in the previous Parts.[1,4-7]

Calculations

The total energy of each system, isolated or surrounded by the solvent (methane) molecules, was computed by the CNDO/2 method, using standard parametrization.[8-10] The energy-minimizing process, which iteratively optimizes the geometrical parameters through a quadratic interpolating process to self-consistency, was carried out. Powell's algorithm [11] was used. The method is completely reliable only when a limited number of variables is considered.

In our study the geometry of $CH_3^+(CH_4)_n$ and $F^-(CH_4)_m$ were fully optimized. For the $CH_3F(CH_4)_{n+m}$ system the energy-minimization process was performed by taking into consideration 18 spatial variables, subdivided in two groups of ten and eight variables, respectively, which were optimized in sequence to an energy self-consistency of 2×10^{-5} a.u.

The geometry of each solvent unit was kept rigid and the energy minima at each point of the dissociation path were confirmed by both changing the starting point of the iterative process in the variable space, and varying the number of the variables. At each point of the dissociative path *ca.* 350—400 steps were necessary to reach consistency.

Results and Discussion

Molecules and Ions in vacuo.—The total energies, fully optimized geometries, and atomic charges of F^-, CH_3^+, CH_3F, and CH_4 are reported in Tables 1 and 2.

$(CH_4)_n$ ($n = 2,4,5,6$). The geometries of small clusters of methane, built up by two, four, five, and six units, respectively, were optimized. For each cluster ($n = 4$—6), the methane units were located at the apices of highly symmetric polyhedra, whose symmetry was retained during the energy-minimization process. The geometry of each methane unit was kept constant throughout the calculation.

Relevant energy and geometry parameters are shown in Figure 1, and their values are collected in Table 1; atomic charges (electrons) are reported in Table 2. The stabilization energy, defined as ΔE kcal mol^{-1} = $[E(CH_4)_n - nE(CH_4)]/n$ where n is the number of methane units in each system, is *ca.* 0.1—0.2 kcal mol^{-1}. The cluster formed by four units is the most stable. Owing to the slight interaction energy of methane molecules, the charge redistribution in the whole cluster is very small, so that the atomic charges in each methane unit of each cluster are very near to those of the isolated molecule. By recognizing that in general the CNDO/2 method overestimates bond energy, the level of interaction predicted by our model has to be assumed as a maximum.

$F^-(CH_4)_n$ ($n = 4,6$). The first solvation shell of the fluorine anion was simulated by four and six methane units, located at the apices of a regular tetrahedron or an octahedron, respectively. The optimized geometries reported in Table 1 show that the mean $F \cdots C$ distance varies from 2.58 Å in the tetrahedral cage to 2.66 Å in the octahedral one. The rotation of each methane molecule is practically free ($\Delta E < 5 \times 10^{-5}$ a.u.), so that each reported geometry represents one among the possible configurations of the system. Charge distributions are also reported in Table 2. A significant charge transfer (0.28 electrons) from fluorine anion to the solvent is predicted by the calculation. The finding reflects on the value of solvation energy, defined as ΔE kcal mol^{-1} = $\{E[F^-(CH_4)_n] - E[F^-] - E[(CH_4)_n]\}/n$. The value of 13—17 kcal mol^{-1} predicted by CNDO/2 is an overestimation, owing to the computational method, involving basis overextension.

$CH_3^+(CH_4)_5$. In line with previous calculations of the first solvation shell of this ion,[1] five methane molecules were used to build up the solvation cage. They were located at the apices of a trigonal bipyramid.

Table 1. Energy and geometry parameters optimized by CNDO/2 for $CH^+(CH_4)_n$ ($n = 0,5$), $F^-(CH_4)_n$ ($n = 0,4,6$), and $(CH_4)_n$ ($n = 1,2, 4$—6) [a]

	Symmetry [b]	$-E$/hartree	$-E$/kcal mol^{-1}	$F\cdots C$ (Å)	$C\cdots C$ (Å)	$C\cdots H$ (Å)
CH_3^+ [c]	D_{3h}	8.6718				
					1.928 ap [e]	
$CH_3^+(CH_4)_5$ [c]	D_{3h}	59.6021	44.0			
					3.525 eq	
F^-		27.4810				
$F^-(CH_4)_4$ [d]	T_d	68.0541	17.0	2.579		
				2.661 ap		
$F^-(CH_4)_6$	D_{4h}	88.3003	13.0			
				2.663 eq		
CH_4 [d]	T_d	10.1160				
$(CH_4)_2$ [d]	C_s [a]	20.2322	0.1		3.919	2.803
$(CH_4)_4$ [d]	T_d	40.4652	0.2		3.892	2.776
$(CH_4)_5$ [d]	a	50.5808	0.1		3.922	2.806
$(CH_4)_6$ [d,f]	C_s [a]	60.6967	0.1		4.005 (2) [a]	
					3.393 (3) [a]	

[a] See Figure 1 for the geometry of the clusters and numbering of the atoms. [b] That of the solvent cage in the case of solvated systems. [c] CH = 1.119 Å. [d] CH = 1.116 Å. [e] ap = Apical; eq = equatorial (Figure 1). [f] $\alpha = 56.01°$ (Figure 1).

Table 2. Atomic charges (electron) calculated by CNDO/2 for $CH_3^+(CH_4)_n$ ($n = 0,5$), $F^-(CH_4)_n$ ($n = 0,4,6$), and $(CH_4)_n$ ($n = 1,2, 4$—6)

[a]	q_F	$q_{C(X)}$ [b]	$q_{H(X)}$ [b]	$q_{C(CH_4)}$	$q_{H(CH_4)}$	$q_{C'(CH_4)}$	$q_{H'(CH_4)}$
CH_3^+		0.418	0.193				
			0.189 (1)		-0.011 eq (1)		$+0.083$ ap (1)
$CH_3^+(CH_4)_5$		0.183		-0.046 eq		-0.063 ap	
			0.072 (2)		$+0.036$ eq (2)		$+0.090$ ap (2)
F^-	-1.0						
					$+0.157$ (1)		
$F^-(CH_4)_4$	-0.728			-0.137			
					-0.029 (2)		
					$+0.121$ (1)		
$F^-(CH_4)_6$	-0.722			-0.115			
					-0.021 (2)		
CH_4		-0.040	$+0.011$				
					$+0.013$ (1)		$+0.011$ (1)
$(CH_4)_2$				-0.046		-0.044	
					$+0.011$ (2)		$+0.011$ (2)
					$+0.013$		
$(CH_4)_4$				-0.047			
					$+0.011$		
					$+0.011$		
$(CH_4)_5$		-0.052	$+0.012$	-0.044			
					$+0.012$		
			$+0.011$ (1)				
$(CH_4)_6$		-0.051			$+0.011$ (2)		$+0.012$ (2)
			$+0.012$ (2)	-0.045 (2)		-0.045 (3)	$+0.011$ (3)
					$+0.011$ (3)		

[a] For symmetry and numbering of atoms see Figure 1 and Table 1. [b] X = CH_3^+ or central CH_4.

The optimized geometrical parameters, shown in Figure 1, are collected in Table 1. It appears that the apical methanes approach the ion [C(CH_3^+) $\cdots$ C(CH_4) 1.935 Å] markedly more than the equatorial ones [(C(CH_3^+) $\cdots$ C(CH_4) 3.525 Å]. As in the case of solvated fluorine anion the rotation of methane units is practically free. The charge transfer from the solvent to the ion is overestimated in this case also (see Table 2), and so is the solvation energy (ΔE ca. 44 kcal mol^{-1}).

$CH_3F(CH_4)_n$ ($n = 8,9$). The first solvation shell of fluoro-methane was described by nine molecules of methane, which correspond to the overall number of solvent units used for solvating the dissociated ions, i.e. five for CH_3^+ and four for F^-, respectively. In the minimum of the dissociation path a calculation was also performed with eight solvent units (see later).

Owing to the lack of any symmetry constraint a very large number of geometry variables, described in Figure 2, had to be used, so that the energy-minimization process required both particular care and a lot of computational time.

The total energy and geometrical parameters, optimized at each point of the dissociation co-ordinate r according to the technique previously described in the Calculations section, are
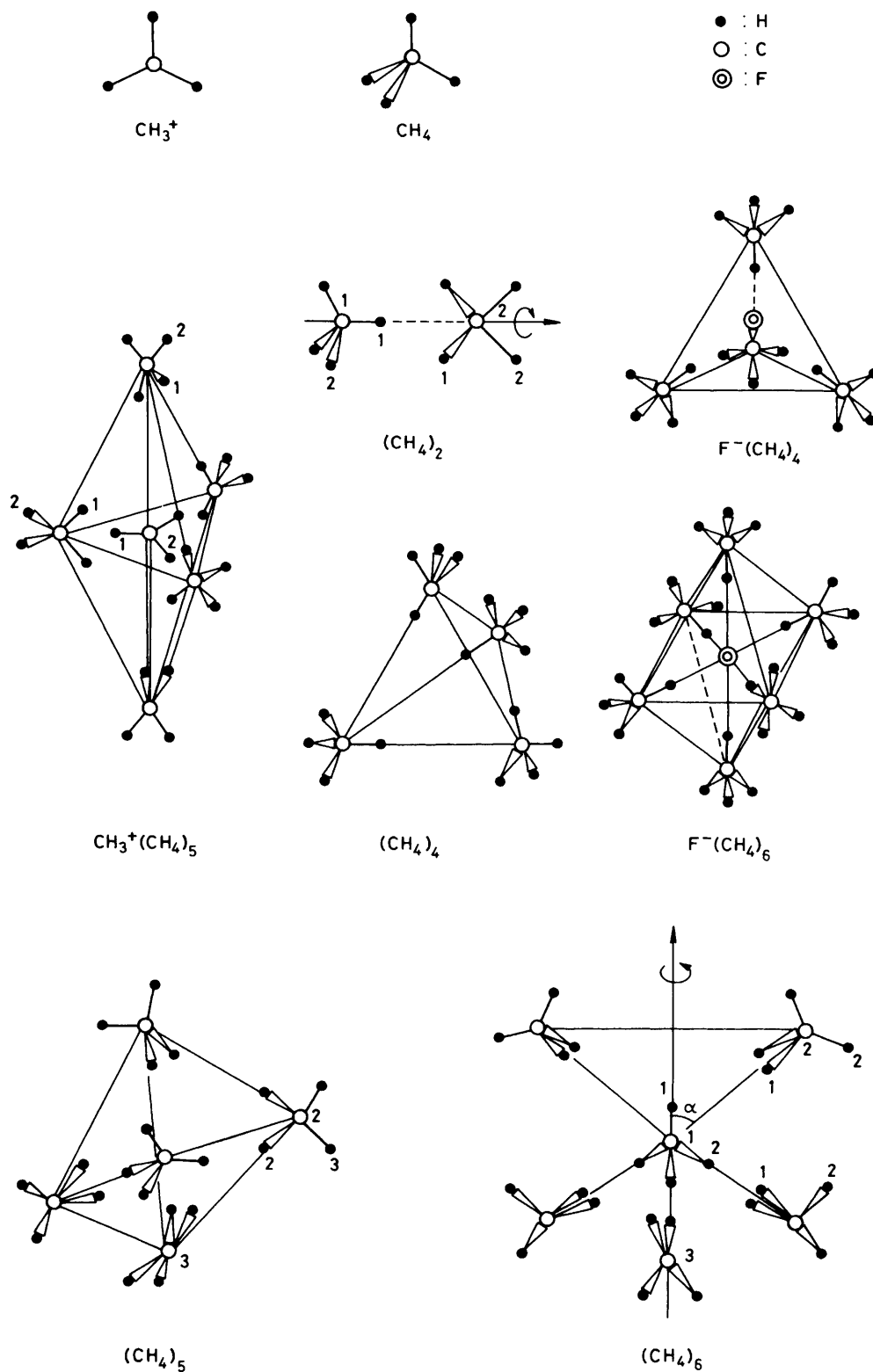
Figure 1. Geometries for isolated and solvated (CH_4) systems. Symmetries of the solvent clusters: $CH_3^+(CH_4)_5$, D_{3h}; $F^-(CH_4)_4$, T_d; $F^-(CH_4)_6$, D_{4h}; $(CH_4)_2$, C_s; $(CH_4)_4$, T_d; $(CH_4)_5$, T_d; $(CH_4)_6$, C_s, like the most stable form of CH_5^+

shown in Table 3, where atomic charges are also included. The results deserve some comments. First, it appears that the geometry of fluoromethane dissolved in methane differs only slightly from that predicted *in vacuo*, at variance with the

geometries in more polar solvents, *e.g.* $r(C-F) = 1.344$ *in vacuo*; 1.345 in CH_4; 1.366 in HF; 1.388 Å in H_2O; $H\hat{C}F = 109.3$ *in vacuo*; 109.4 in CH_4; 106.2 in H_2O; 100.7° in HF. Moreover, the dissociation path shows a regular trend and no

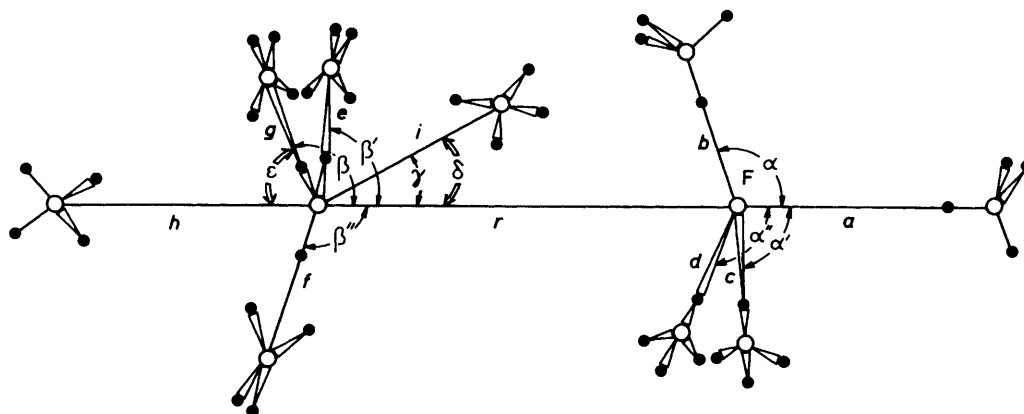**Figure 2.** Geometry and optimized parameters for $CH_3F(CH_4)_9$; ε and δ represent dihedral angles

Table 3. Total energy,[a] geometry,[b] and atomic charges [c] optimized by CNDO/2 method for $CH_3F(CH_4)_9$ [d] along the dissociation path [e]

r	a	b	c	d	α	α'	α''	e	f	g	h	i
1.345	3.05	3.33	3.33	3.27	100.0	98.0	100.0	3.88	3.85	3.82	3.46	5.811
(1.345)	(3.06)	(3.24)	(3.24)	(3.24)	(98.5)	(98.5)	98.5	(3.85)	(3.85)	(3.85)	(3.47)	—
2.00	2.75	2.75	2.76	2.75	85.8	88.0	82.0	3.96	4.02	3.74	1.73	6.70
2.50	2.67	2.60	2.60	2.60	102.0	103.0	103.0	4.20	4.12	4.21	1.65	6.52
3.00	2.66	2.56	2.56	2.58	114.7	115.7	115.0	4.46	4.50	4.44	1.65	6.71
3.50	2.64	2.57	2.56	2.56	63.9	69.5	63.5	4.77	4.78	4.79	1.64	6.46
4.00	2.63	2.57	2.57	2.57	125.4	125.5	125.8	5.00	5.01	4.78	1.64	6.19
4.50	2.62	2.59	2.59	2.58	127.8	129.3	128.7	4.98	4.80	5.08	1.64	6.20
5.00	2.59	2.59	2.59	2.59	112.0	145.0	114.0	4.90	5.00	4.78	1.64	6.16
5.50	2.60	2.58	2.59	2.59	121.5	128.7	126.9	4.49	4.48	3.54	1.65	7.05
6.00	2.61	2.57	2.57	2.57	111.0	116.0	117.0	3.97	3.97	3.48	1.66	2.94
7.00	2.60	2.57	2.57	2.57	115.2	115.5	117.1	3.55	3.46	3.55	1.65	3.04
∞	2.58	2.58	2.58	2.58	109.7	109.7	109.7	3.52	3.52	3.52	1.93	1.93

β	β'	β''	γ	δ	ε	E (a.u.)	q(C)	q(F)	q(H)	q(H')	q(H'')
109.3	109.4	109.6	43.7	−1.00	30.00	−128.1495	0.188	−0.187	−0.001	−0.001	−0.001
(109.4)	(109.4)	(109.4)				(−128.1492) [f]	0.180	−0.187	−0.001	−0.001	−0.001
72.5	78.0	72.1	42.1	27.6	26.6	−127.8867	0.105	−0.684	0.077	0.089	0.082
64.0	70.7	64.0	38.0	−2.0	30.0	−127.8576	0.028	−0.752	0.108	0.129	0.107
63.9	63.7	70.4	38.0	29.0	30.0	−127.8476	0.020	−0.734	0.107	0.132	0.107
63.5	69.5	63.5	35.1	−2.5	30.0	−127.8382	0.029	−0.726	0.104	0.132	0.104
64.4	63.0	70.0	32.0	4.0	31.0	−127.8288	0.026	−0.725	0.100	0.129	0.101
64.0	70.1	64.1	29.0	12.0	30.0	−127.8198	0.037	−0.728	0.096	0.127	0.096
64.0	71.0	64.0	30.0	0.0	30.0	−127.8103	0.040	−0.716	0.097	0.126	0.087
65.5	69.6	65.5	24.3	5.0	29.8	−127.8032	0.041	−0.728	0.086	0.121	0.097
66.0	67.0	71.0	0.1	0.0	26.0	−127.7974	0.040	−0.726	0.089	0.129	0.092
65.8	69.0	65.4	0.0	0.0	32.0	−127.7904	0.024	−0.728	0.089	0.128	0.090
60.0	60.0	60.0	0.0	0.0	0.0	−127.6562	0.183	−0.728	0.072	0.089	0.072

[a] Energy in hartrees. [b] Distances in Å and angles in degrees. [c] Charges in electrons. [d] See Figure 2 for the labelling of geometrical parameters. [e] Data reported in brackets refer to the cluster formed by eight methane molecules. [f] Energy of one methane molecule added (see text).

relative minima are found before dissociation, unlike the prediction for the dissociation of fluoromethane both in water [5] and in hydrofluoric acid.[1] As for the arrangements of the methane molecules around the solute, predicted by the calculations at each point of the dissociation path, we point out that the parameters reported in Table 3 correspond to energy minima. However, several other arrangements with markedly different geometries lie very close in energy, the differences not exceeding 2×10^{-3} a.u. (1—2 kcal mol^{-1}). In view of this fact each arrangement reported in Table 3 has to be considered as merely representative, being one of the many which actually occur. The irregular trend shown by some variables (e.g. δ in Table 3) is not important, since it corresponds to very slight energy variation.

It appears from Table 3 that one methane molecule, whose position is defined by parameters i, δ, and γ, is markedly more distant from fluoromethane than the other solvent units. In view of this the solvation cage of fluoromethane can be adequately described by eight methane molecules. In this case the number of geometrical variables implied in the energy-minimization process is strongly reduced (seven) owing to the higher symmetry that can be assumed for the solvent cage formed by eight methane molecules. Optimized values, enclosed within parentheses in Table 3, appear very similar to those of the solvent cage built up by nine solvent units. The total energies are also closely comparable (Table 3), provided that one methane molecule is added to the smaller cluster, and its position optimized.

Table 4. Total energy, solvent cage energy, and different contribution [a] to solvation energy for $CH_3F(CH_4)_9$

r (Å)	A	B	C	D	E	F
1.345	−128.1495	−91.0453	−37.1042	−0.0017	−37.0996	−0.0076
2.0	−127.8867	−91.0443	−36.8424	−0.0007	−36.6621	−0.1803
2.5	−127.8576	−91.0457	−36.8119	−0.0021	−36.4710	−0.3409
3.0	−127.8476	−91.0456	−36.8020	−0.0020	−36.3981	−0.4039
3.5	−127.8382	−91.0457	−36.7925	−0.0021	−36.3632	−0.4293
4.0	−127.8288	−91.0438	−36.7850	−0.0002	−36.3482	−0.4368
4.5	−127.8198	−91.0426	−36.7772	+0.0010	−36.3397	−0.4375
5.0	−127.8103	−91.0431	−36.7672	+0.0005	−36.3322	−0.4350
5.5	−127.8032	−91.0424	−36.7608	+0.0012	−36.3297	−0.4311
6.0	−127.7974	−91.0442	−36.7532	−0.0006	−36.3295	−0.4247
7.0	−127.7904	−91.0452	−36.7452	−0.0016	−36.3255	−0.4197

[a] A, total energy; B, energy of the solvent cage; C, $E_C = E_A - E_B$, solute–solvent plus solute energy; D, $E_B - nE_{CH_4}$, energy difference between methane solvation shell and a corresponding number of isolated methane units; E, energy of fluoromethane *in vacuo*; F, $E_F = E_C - E_E$, solute–solvent interaction. Energies in hartrees.
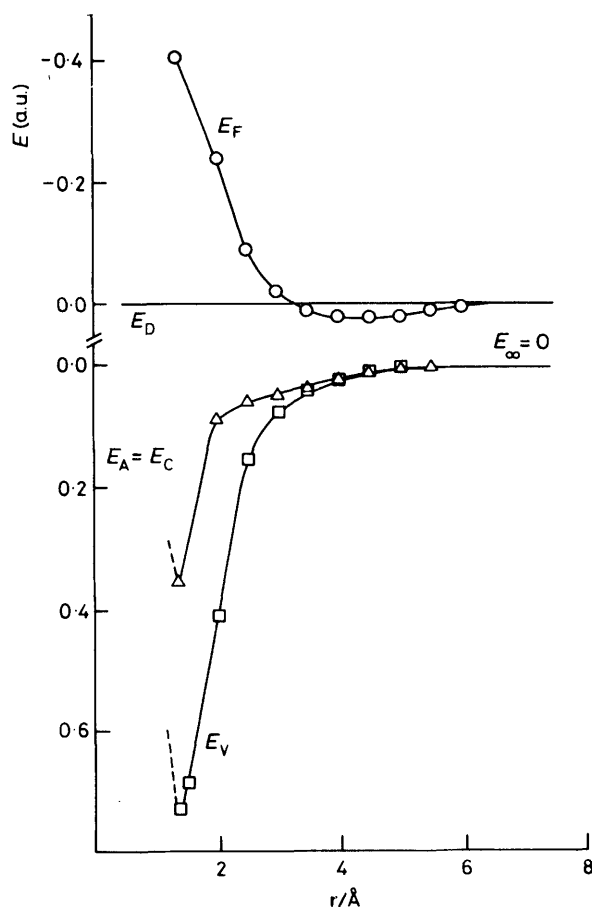
Figure 3. Different energy contributions of the solvated system $CH_3F(CH_4)_n$ ($n = 0,9$). E_V = Energy of CH_3F in vacuum; E_A = total energy of $CH_3F(CH_4)_9$; E_C = solute–solvent plus solute energy: $E_D = E_B - nE(CH_4)$, energy difference between methane solvation shell (E_B) and the energy of a corresponding number of isolated methane molecules; $E_F = E_C - E_V$, solute–solvent interactions. $E_\infty = 0$. Energies in hartrees

We think that the present calculation represents a limit for a reliable description of the solvent cage in the framework of a static model. Further and more sophisticated information can be obtained only by dynamic models (*e.g.* Monte Carlo, molecular dynamics).

The partitioning of the total energy of the cluster in terms of particular interactions of the solvent is reported in Table 4. The meaning of the different terms A—F is given in the footnotes of Table 4. The main results are outlined in Figure 3. From the Table and the Figure it appears that (*a*) the trend of total energy (E_A) of the cluster is equal to that of the solute–solvent plus solute energies (E_C), (*b*) the energy of the solvent cage (E_B) is practically independent of dissociation, and (*c*) the interaction among methane molecules (E_D) is extremely small, and in some cases repulsive. The trend of fluoromethane-methane interaction energy (E_F) is qualitatively similar to that describing the corresponding interaction with hydrofluoric acid (see Figure 8 in ref. 1), but more regular. A very flat minimum is found in the region r 3.5—5 Å, where the solute–solvent interactions are stronger. However, in methane no defined structures recalling an ion pair is predicted, even if the solvent molecules experience a moderate reorganization due to the combined action of the separated counterions.

In conclusion, it is worth noting the differences predicted by our solvent model for dissociation processes. They depend both on the nature of the solvent and solute. In the case of fluoromethane, dissociation occurs after formation of different kinds of ion pairs in polar solvents (water and hydrofluoric acid),[1,5] unlike in apolar solvents (methane), where the counterions dissociate without previous association, as shown in the present work. In the diazonium series,[1,6,7] benzene- and ethylene-diazonium cations are predicted to form ion pairs in water before dissociation,[6,7] different from the case of methanediazonium cation.[12] The difference in behaviour is so clearcut that it can be accepted with confidence in spite of the limited number of molecules used to describe the solvent medium, the approximate method of calculation, and the exclusion of any entropy effect.

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