

## A Theoretical Investigation of the Role of the Solvent on the Structure of the Intermediates in Solvolytic Reactions. Part 4. Methanediazonium Ion and Methyl Fluoride in Hydrofluoric Acid

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The effect of a solvent other than water, *i.e.* hydrofluoric acid, on the dissociation process of  $\text{CH}_3\text{N}_2^+$  and  $\text{CH}_3\text{F}$  was investigated by MO theory at the CNDO/2 level of approximation. As in water,  $\text{CH}_3\text{N}_2^+$  in HF dissociates without the formation of intermediates, while  $\text{CH}_3\text{F}$  forms stable ion pairs. The structure of dissolved ions and molecules is more affected by water than by HF, and water is more effective in promoting charge transfer and separation, in line with the physical properties of the solvents.

WITHIN the scope of a theoretical investigation on solvent effects on the course of organic reactions, the geometry and electronic structure of the intermediates in the solvolysis of fluoromethane,<sup>1</sup> benzenediazonium,<sup>2</sup> and methanediazonium<sup>3</sup> cations in water have been investigated and discussed.

Due to the amount of computations involved, only semiempirical calculations were feasible, and therefore the CNDO/2 method<sup>4</sup> was employed. The aim of this qualitative approach was to explore the possibility that stabilization by the surrounding water molecules favours the formation of intermediates.

The theoretical results suggested that dissociation in water of both  $\text{C}_6\text{H}_5\text{N}_2^+$  and  $\text{CH}_3\text{F}$  occurs through the intervention of at least two types of ion pairs unlike  $\text{CH}_3\text{N}_2^+$  which, in the same solvent, dissociates in a single stage. Moreover it was verified that the energy minima predicted along the reaction co-ordinate of  $\text{C}_6\text{H}_5\text{N}_2^+$  and  $\text{CH}_3\text{F}$ <sup>1,2</sup> are not artefacts dependent on the model for the solvent field. So far only water has been taken into consideration as a solvent and to check further the reliability of the proposed model<sup>1-3</sup> for describing the first solvation shell, we here report the solvolysis of both  $\text{CH}_3\text{N}_2^+$  and  $\text{CH}_3\text{F}$  in hydrofluoric acid. HF was chosen as it is a high-dipole rigid molecule with a dielectric constant of magnitude close to that of water, and it is small enough to keep the computational time at a reasonable level. So a limited number of solvent units were sufficient adequately to represent the first solvation shell of undissociated solutes and dissociated ions. Solvation cages for  $\text{N}_2$ ,  $\text{CH}_3^+$ ,  $\text{F}^-$ ,  $\text{CH}_3\text{N}_2^+$ , and  $\text{CH}_3\text{F}$  were built up by means of 4, 5, 6, 9, and 11 hydrofluoric acid molecules respectively. The total energy of the clusters was minimized through the optimization of a relevant number of geometrical parameters.

The assumptions included in the solvent model and its limitations were previously discussed and are available in refs. 1–3.

### CALCULATIONS

For each system, isolated or surrounded by the appropriate number of HF molecules, an energy-minimizing

process,<sup>5</sup> which iteratively optimizes the geometrical parameters through a quadratic interpolating process till self-consistency is obtained, was carried out.

The total energy was computed by the CNDO/2 method, using standard parametrization.<sup>4,6,7</sup> The geometry of the solvent units was kept rigid and the symmetry in the isolated solute was retained. For isolated molecules and ions all geometrical parameters were optimized. For solvated systems a reduced number of parameters was taken into consideration in the minimization procedure. However, the calculated minima were confirmed by repeating the iterative process starting from different points in the space variables and by increasing the number of variables.

### RESULTS AND DISCUSSION

**Molecules and Ions in vacuo.**—The geometries of isolated systems, ions, or molecules were fully optimized (see refs. 1–3) and the relevant data are collected in Table 1.

$\text{N}_2(\text{HF})_4$ . Four molecules of HF were used to describe

TABLE 1

Total energy and optimized geometrical parameters for  $\text{CH}_3^+(\text{HF})_5$ ,  $\text{N}_2(\text{HF})_4$ , and  $\text{F}^-(\text{HF})_n$  ( $n = 0, 4-6$ )

	$-E/\text{hartree}$	$-\Delta E$ (kcal mol <sup>-1</sup> )	$a$ (Å)	$b$ (Å)	$\alpha$ (°)	$\beta$ (°)
$\text{CH}_3^+$ <sup>a</sup>	8.6711					
$\text{CH}_3^+(\text{HF})_5$ <sup>b</sup>	151.2510	249.0	1.655	1.516	90	120
$\text{N}_2$ <sup>c</sup>	23.0905					
$\text{N}_2(\text{HF})_4$	136.9110	11.5	2.800		50	0
$\text{F}^-$	27.4841					
$\text{F}^-(\text{HF})_4$	141.5719	214.0	1.295 <sup>d</sup>			
$\text{F}^-(\text{HF})_5$	170.0395	233.0	1.330 <sup>e</sup>	1.341		
$\text{F}^-(\text{HF})_6$	198.5018	249.0	1.367 <sup>f</sup>	1.367		

<sup>a</sup> C-H 1.13 Å. <sup>b</sup> H-F 1.00 Å. <sup>c</sup> N-N 1.143 Å. <sup>d</sup>  $T_d$  symmetry. <sup>e</sup>  $T_{bp}$  symmetry. <sup>f</sup> Square bipyramid.

the first solvation shell of  $\text{N}_2$  (see Figure 1). The relevant parameters are collected in Table 1. A detailed analysis of the solvation of  $\text{N}_2$  is available in ref. 8.

$\text{CH}_3^+(\text{HF})_5$ . The first solvation shell of this cation was simulated by five HF molecules set at the apices of a trigonal bipyramid, as shown in Figure 1. According to CNDO/2 calculations each HF molecule points at the

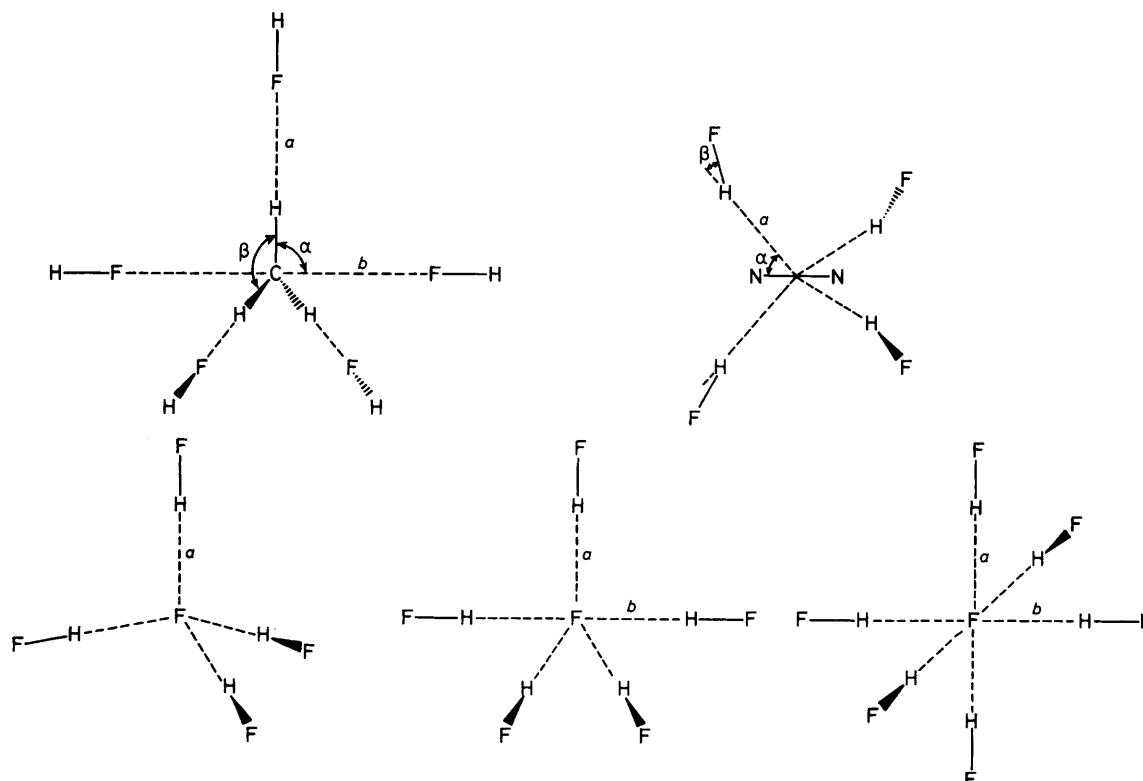


FIGURE 1 Optimized geometrical parameters for  $\text{CH}_3^+(\text{HF})_6$ ,  $\text{N}_2(\text{HF})_4$ , and  $\text{F}^-(\text{HF})_n$ ,  $n = 4-6$

central ion with the fluorine atom. The optimized  $\text{H} \cdots \text{F}$  distance is 1.655 Å in the case of the three equatorial F atoms and the  $\text{C} \cdots \text{F}$  distance is 1.515 Å in the case of the apical F atoms (see Figure 1).

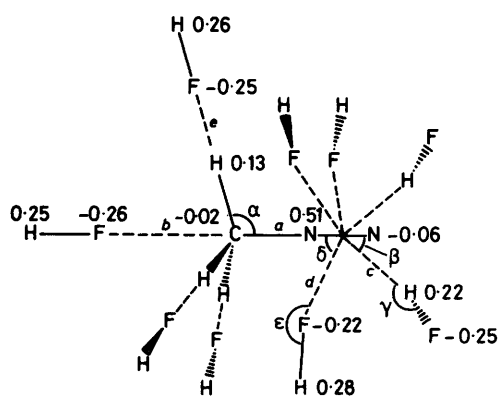


FIGURE 2 Optimized geometry and charge distribution for  $\text{CH}_3\text{N}_2^+(\text{HF})_9$

$\text{F}^-(\text{HF})_n$ ;  $n = 4-6$ . Four, five, and six molecules of HF were employed to build the first solvation shell of  $\text{F}^-$ , starting with the solvent units located at the apices of polyhedra of high symmetry. The final geometries at the end of the optimization without symmetry constraints show that the symmetry is practically retained. The optimized geometrical parameters, collected in Table 1, show the regular increase of the  $\text{F} \cdots \text{F}$  distance and the decrease of the solvation energy per molecule as the number of solvent molecules increases. By keeping in mind the previous remarks on the hydration of  $\text{F}^-$ ,<sup>1</sup> and

on the basis of the observed trend, an octahedral cage was chosen.

$\text{CH}_3\text{N}_2^+(\text{HF})_9$ . Since four and five HF units were used to describe the first solvation shell of  $\text{N}_2$  and  $\text{CH}_3^+$  respectively, nine HF molecules were taken to solvate the methanediazonium ion.

The total energy of the cluster was minimized with respect to the geometrical parameters shown in Figure 2; the optimized values are collected in Table 2.

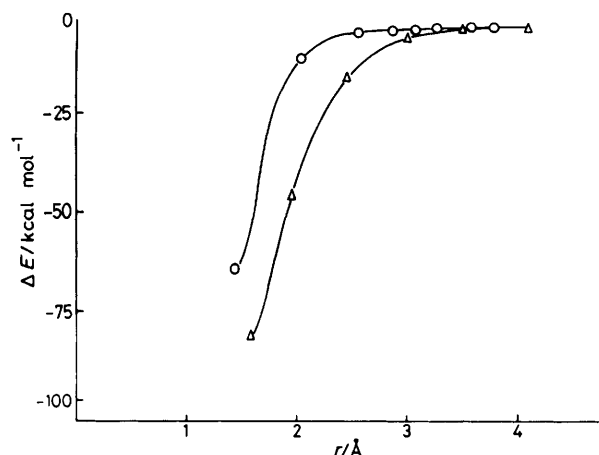


FIGURE 3 Energy curves for  $\text{CH}_3\text{N}_2^+$  in  $\text{H}_2\text{O}$  ( $\Delta$ ) and HF ( $\circ$ ):  $\Delta E = E_A - E_\infty$  in  $\text{kcal mol}^{-1}$

In the same Table the geometry of the optimized solvated system at several points along the reaction co-ordinate is shown. The three-fold symmetry axis

of isolated  $\text{CH}_3\text{N}_2^+$  was preserved. The dissociation paths in hydrofluoric acid and water are compared in Figure 3. Only one energy minimum is predicted in HF at  $a$  1.444 Å. On a qualitative ground the two curves are quite similar.  $\text{H}_2\text{O}$  has a stronger stabilization effect than HF, though the C-N bond is more

at several points of the reaction co-ordinate, were computed. The results are summarized in Table 4. In the columns A and B the total energy of solvated  $\text{CH}_3\text{N}_2^+$  and the energies of the corresponding solvent cages are reported. The solute-solvent plus solute energy ( $E_B - E_A$ ) is given in column C, and the difference between the

TABLE 2  
Geometry and charge distribution optimized by CNDO/2 for  $\text{CH}_3\text{N}_2^+(\text{HF})_9$ <sup>a</sup>

$a$ (Å)	1.441	2.000	2.500	2.800	3.000	3.200	3.500	3.700	4.000
$b$ (Å)	2.07	1.45	1.40	1.39	1.39	1.39	1.39	1.39	1.39
$c$ (Å)	2.73	2.65	2.65	2.65	2.74	2.74	2.74	2.74	2.74
$d$ (Å)	1.75	1.74	1.75	1.75	1.78	1.78	1.78	1.78	1.78
$\alpha$ (°)	108.1	84.0	76.3	74.9	74.5	74.4	74.4	74.4	74.4
$\beta$ (°)	57.9	61.7	60.7	60.7	57.2	57.2	57.2	57.2	57.2
$\gamma$ (°)	25.7	22.0	19.8	19.8	20.9	20.9	20.9	20.9	20.9
$\delta$ (°)	64.4	57.6	52.9	50.8	52.2	50.2	50.2	50.2	50.3
$\epsilon$ (°)	206.0	217.2	215.9	212.4	211.6	211.2	210.8	210.6	210.4

<sup>a</sup> The distance  $\epsilon$  (see Figure 2) was kept fixed at 1.655 Å.

relaxed (see Figure 3). The C-N bond distance at the energy minimum is 1.39 *in vacuo*, 1.444 in HF, and 1.526 Å in  $\text{H}_2\text{O}$ . The  $\widehat{\text{HCN}}$  bond angle is more affected by  $\text{H}_2\text{O}$  than HF. Indeed  $\widehat{\text{HCN}}$  is 108.5 *in vacuo*, 108.2

TABLE 3

Atomic charges<sup>a</sup> for  $\text{CH}_3\text{N}_2^+$  calculated in different media

	$q_C$	$q_H$	$q_N$	$q_{N'}$	$q_{\text{tot}}$
<i>in vacuo</i>	0.020	0.320	0.255	0.135	+1.000
HF	0.020	0.504	-0.061	0.127	+0.844
$\text{H}_2\text{O}$	0.096	0.386	-0.192	0.100	+0.600

<sup>a</sup> In electrons, computed in the CNDO/2 minimum.

in HF, and 90° in water. The stronger influence of water on the geometry of methanediazonium ion is due both to strain factors and a more effective charge transfer. The charge distributions at the minimum show the behaviour evidenced in Table 3.

Well aware of the poor quantitative significance of

energy of solvent cages and that of a corresponding number of isolated solvent units is given in column D. By subtracting the energy of the system calculated *in vacuo* at the same reaction co-ordinate, reported in column E, from  $E_C$ , a measure of the solute-solvent interaction energy at each point of the reaction path is obtained (column F).

The mean value of the binding energies of the solvent units of the first solvation shell (column D) is *ca.* 0.2 kcal mol<sup>-1</sup> per HF unit, slightly larger than the corresponding value for water molecules, but markedly smaller than the value predicted for solvation of  $\text{CH}_3\text{F}$  in the same solvent (see Table 7). Moreover the trends of solute-solvent interaction energy alone [column F of Table 4 for  $\text{CH}_3\text{N}_2^+(\text{HF})_9$  and of Table 8 in ref. 3 for  $\text{CH}_3\text{N}_2^+(\text{H}_2\text{O})_9$ ] are very similar and become practically the same starting from  $a$  2.5 Å.

$\text{CH}_3\text{F}(\text{HF})_{11}$ . The eleven solvent units used to

TABLE 4

Total energy, solvent cage energy, and different contributions to solvation energy for  $\text{CH}_3\text{N}_2^+(\text{HF})_9$ <sup>a</sup>

$a$ (Å)	A	B	C	D	E	F
1.441	-288.3245	-255.9274	-32.3971	0.0029	-32.2200	-0.1771
2.0	-288.2377	-255.9277	-32.3100	0.0026	-31.9517	-0.3583
2.5	-288.2251	-255.9275	-32.2976	0.0028	-31.8090	-0.4886
2.8	-288.2229	-255.9264	-32.2965	0.0039	-31.7880	-0.5085
3.0	-288.2225	-255.9265	-32.2960	0.0038	-31.7725	-0.5235
3.2	-288.2221	-255.9269	-32.2952	0.0034	-31.7662	-0.5290
3.5	-288.2218	-255.9272	-32.2946	0.0031	-31.7635	-0.5311
3.7	-288.2217	-255.9275	-32.2942	0.0028	-31.7625	-0.5317
4.0	-288.2218	-255.9277	-32.2941	0.0026	-31.7623	-0.5318

<sup>a</sup> A, total energy; B, energy of the solvent cluster; C,  $E_C = E_A - E_B$ : solute-solvent plus ion-molecule energy; D,  $E_D = nE_{\text{HF}}$ : energy difference between HF solvation shell and a corresponding number of isolated HF units; E, energy of isolated  $\text{CH}_3\text{N}_2^+$ ; F,  $E_F = E_C - E_E$ : this term represents the solute-solvent interaction. Energies in hartrees.

CNDO atomic charges, we can on a comparative ground observe that water removes a larger part of the positive charge of  $\text{CH}_3\text{N}_2^+$  than HF does. The two solvents polarize nitrogen to an equivalent extent. In fact the difference between atomic charges on N and N' is 0.565 and 0.582 in HF and  $\text{H}_2\text{O}$ , respectively.

To investigate the role of different contributions to the total energy of the solvated system, the energy of the molecules of HF alone, fixed at the positions optimized

describe the first solvation shell of  $\text{CH}_3\text{F}$  in HF correspond to the sum of those of the first solvation shell of the separated ions, namely five and six for  $\text{CH}_3^+$  and  $\text{F}^-$ , respectively, and agree with the value predicted on the basis of structural considerations and thermodynamic data.<sup>9</sup>

The geometrical parameters shown in Figure 4 were optimized at several points of the reaction co-ordinate  $a$  in the range 1–10 Å. The curve of stabilization energy

$\{\Delta E = E[\text{CH}_3\text{F}(\text{HF})_{11}] - E(\text{CH}_3\text{F}) - 11E(\text{HF})$  in a.u. $\}$  versus the reaction co-ordinate  $a$  is shown in Figure 5, where the corresponding curve for the solvolysis of  $\text{CH}_3\text{F}$  in  $\text{H}_2\text{O}$  is reported for comparison.

It is evident that the qualitative trend of the two curves is similar. In both cases three minima well separated by barriers of comparable heights are evident. Three

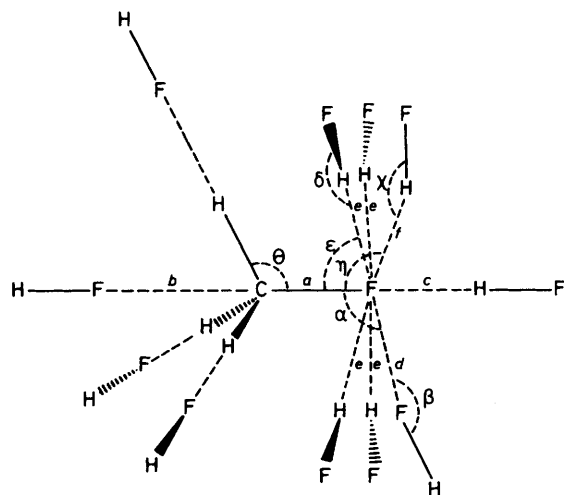


FIGURE 4 Optimized geometrical parameters for  $\text{CH}_3\text{F}(\text{HF})_{11}$

minima in HF are predicted at  $a$  1.363, 3.495, and 5.665 Å, respectively. The location of solvent molecules at each minimum is shown in Figures 4, 6, and 7, respectively. The optimized geometrical parameters are collected in Table 5. In the absolute minimum (Table 5) the HF units are regularly located around the solute in such a way as to build up a cage surrounding the solute. The fluorine atoms of HF molecules point towards the

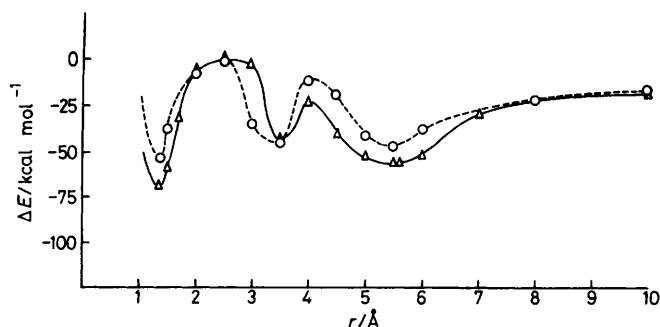


FIGURE 5 Energy curves for  $\text{CH}_3\text{F}$  in  $\text{H}_2\text{O}$  ( $\Delta$ ) and HF ( $\circ$ ):  $\Delta E = E_A - E_\infty$

hydrogens of the methyl moiety and the solvent protons point towards the fluorine atom of  $\text{CH}_3\text{F}$ . Only one solvent unit, whose position is defined by the parameters  $d$ ,  $\alpha$ , and  $\beta$  in Figure 4, shows an opposite behaviour with the fluorine pointing towards the parent atom of  $\text{CH}_3\text{F}$ .

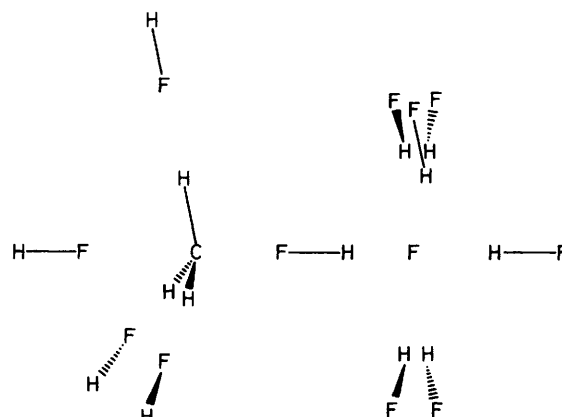


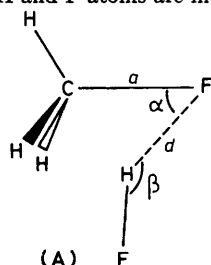
FIGURE 6 Geometry of the solvated ion-molecule pair predicted at  $a$  3.495 Å

TABLE 5

CNDO/2 optimized geometries for  $\text{CH}_3\text{F}(\text{HF})_{11}$  along the reaction path

$a^{a,b}$	1.363	1.5	1.7	2.0	2.5	3.0	3.495	4.0	4.5	5.0	5.665	6.0	7.0	10.0
$b$	2.11	1.81	1.58	1.45	1.40	1.40	1.85	1.52	1.59	1.60	1.67	1.56	1.55	1.53
$c$	1.50	1.48	1.41	1.35	1.35	1.34	1.85	1.31	1.37	1.41	1.40	1.39	1.38	1.37
$d^c$	1.63	1.62	1.55	1.36	1.28	1.23	1.11	1.42	2.12	2.62	3.38	3.59	4.58	7.60
$e$	2.23	2.25	2.31	2.38	2.33	2.41	2.45	2.22	1.44	1.43	1.37	1.37	1.37	1.37
$f$	1.43	1.40	1.32	1.25	1.25	1.33	1.34	1.25	1.23	1.21	1.26	1.41	1.37	1.36
$\alpha^{b,c}$	106.6	105.6	103.8	88.9	69.8	27.4	0.0	0.2	-0.7	-6.0	-0.5	-5.7	-3.4	-2.0
$\beta^c$	175.0	175.0	176.0	180.2	182.0	178.0	180.0	180.0	166.0	153.0	155.0	155.0	155.0	154.0
$\delta$	177.5	177.5	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
$\epsilon$	86.5	88.5	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0
$\theta$	106.2	101.7	93.3	84.7	75.9	73.0	102.6	87.5	92.0	92.0	95.8	91.7	91.4	91.2
$\eta$	109.8	108.4	102.1	97.8	96.0	90.3	98.7	85.0	40.5	37.8	8.7	12.0	2.3	0.3
$\chi$	200.5	198.9	191.1	187.9	186.2	183.6	201.1	193.0	191.5	190.0	179.2	181.0	179.2	180.0

<sup>a</sup> Distances in angstroms and angles in degrees. <sup>b</sup> The geometrical parameters are shown in Figure 4. <sup>c</sup> When  $a > 3.495$  Å the variables  $d$ ,  $\alpha$ ,  $\beta$  are defined as in structure (A), i.e. H and F atoms are interchanged.



(A)



In the second minimum at  $a$  3.495 Å one HF molecule enters the region between the two counterions and lies along the direction of the relaxed C-F bond, as shown in Figure 6, where the location of the other HF units is also depicted. The structure of a typical solvent-separated

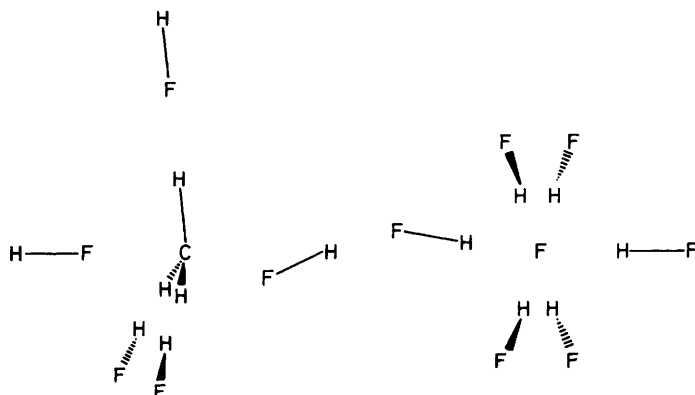
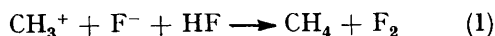


FIGURE 7 Geometry of the solvated ion-molecule pair predicted at  $a$  5.665 Å

(or loose) ion pair is evident, with the two ions lying in two distinct cages, sharing a solvent unit.

In the course of the optimization process, another energy minimum at  $a$  ca. 3.5 Å was found, with the molecule of HF lying between the counterions being reversed. The values of the energy in the two minima are quite similar. Starting from the latter minimum,



reaction (1) could take place. As we were interested in ion pair formation, we did not consider this possible reaction path further.

of  $\text{CH}_3\text{F}$ , at variance with  $\text{CH}_3\text{N}_2^+$ , water reduces the interaction energy between  $\text{CH}_3^+$  and  $\text{F}^-$  more than HF does, but in the present case the energy difference is very small. The variations of C...F bond distance and of HCF bond angle predicted at the three minima of the reaction co-ordinate are collected, together with the atomic charge distribution, in Table 6.

In the first minimum, whose geometry represents the structure of the dissolved but not dissociated  $\text{CH}_3\text{F}$ , both the C-F bond length and the HCF bond angle are modified more by  $\text{H}_2\text{O}$  than by HF.

It emerges from the comparison of the charge distributions that  $\text{H}_2\text{O}$  is more effective in promoting charge

TABLE 6  
Geometries and atomic charges of  $\text{CH}_3\text{F}$ , calculated in different media

Medium	Minimum	C-F (Å)	HCF (°)	$q_C^a$	$q_H$	$q_F^b$
<i>in vacuo</i>		1.344	109.3	0.195	-0.003	-0.185
HF	First	1.368	100.7	0.120	+0.055	-0.207
$\text{H}_2\text{O}$		1.388	106.2			-0.255
HF	Second	3.495	112.7	0.164	+0.074	-0.460
$\text{H}_2\text{O}$		3.480	102.6			-0.516
HF	Third	5.665	100.8	0.184	+0.091	-0.501
$\text{H}_2\text{O}$		5.460	95.8			-0.568

<sup>a</sup> In electrons. <sup>b</sup> The charges on separated fragments are: HF:  $q_C = 0.211$ ;  $q_H = 0.107$ ;  $q_F = -0.526$ ;  $\text{H}_2\text{O}$ :  $q_C = 0.151$ ;  $q_H = 0.247$ ;  $q_F = -0.547$ . Calculated from the clusters  $\text{CH}_3^+(\text{sol})_8$  and  $\text{F}^-(\text{sol})_8$ , respectively.

separation. The difference is quite small but significant and is in line with the physical properties of the two solvents (dielectric constants 84 and 80 for  $\text{H}_2\text{O}$  and HF, respectively). The analysis of the solvent effect performed according to the prescriptions previously given (see Table 4) gives the results collected in Table 7, and

TABLE 7  
Total energy, solvent cage energy, and different contribution <sup>a</sup> to solvation energy of  $\text{CH}_3\text{F}(\text{HF})_{11}$

$a$ (Å)	A	B	C	D	E	F
1.363	-349.9721	-312.8289	-37.1432	-0.0252	-37.0996	0.0436
1.5	-349.9387	-312.8297	-37.1090	-0.0260	-37.0497	0.0593
1.7	-349.8512	-312.8323	-37.0189	-0.0286	-36.7172	0.2218
2.0	-349.7708	-312.8314	-36.9394	-0.0277	-36.7172	0.2218
2.5	-349.7540	-312.8318	-36.9222	-0.0281	-36.5221	0.4001
3.0	-349.7580	-312.8267	-36.9313	-0.0230	-36.4422	0.4891
3.495	-349.9097	-312.7932	-37.1165	+0.0105	-36.4088	0.7077
4.0	-349.8243	-312.7875	-37.0368	+0.0162	-36.3923	0.6445
4.5	-349.8788	-312.7474	-37.1314	+0.0563	-36.3824	0.7490
5.0	-349.9182	-312.7588	-37.1594	+0.0449	-36.3753	0.7841
5.665	-349.9328	-312.7751	-37.1577	+0.0286	-36.3703	0.7874
6.0	-349.9163	-312.7769	-37.1394	+0.0268	-36.3652	0.7720
7.0	-349.8436 6	-312.7864	-37.0572	+0.0173	-36.3652	0.6920
10.0	-349.8105	-312.7845	-37.0260	+0.0192	-36.3784	0.6618

<sup>a</sup> A, total energy; B, energy of the solvent cluster; C,  $E_C = E_A - E_B$ : solute-solvent plus ion-molecule energy; D,  $E_D = n \cdot E_{\text{HF}}$ : energy difference between HF solvation shell and that of a corresponding number of isolated HF units; E, energy of isolated  $\text{CH}_3\text{N}_2^+$ ; F,  $E_F = E_C - E_E$ : this term represents the solute-solvent interaction. Energies in hartrees.

In the third minimum, which is found at  $a$  5.665 Å, two HF molecules are present between the two counterions, which are now in two separated but adjacent solvent cages. A  $\text{H} \cdots \text{F}-\text{H}$  hydrogen bond connects the two cages. This situation corresponds to a looser ion pair. The difference from dissociated ions is evident through the distortion of the clusters. In the case

illustrated in Figure 8. It appears that the curves of  $E_A$  and  $E_C$  are parallel, *i.e.* the energy of the solvated system is predicted to be independent of the interaction among the HF units. On the other hand the magnitude of the solvent interaction energy ( $E_E$ ) is about one order of magnitude larger than that of the corresponding term calculated for  $\text{CH}_3\text{N}_2^+(\text{HF})_9$ . Moreover the curve of  $E_F$

versus  $a$  (Å), shows clearly that the solute-solvent interaction energy is the main term responsible for the existence of ion-molecule pairs in solution.

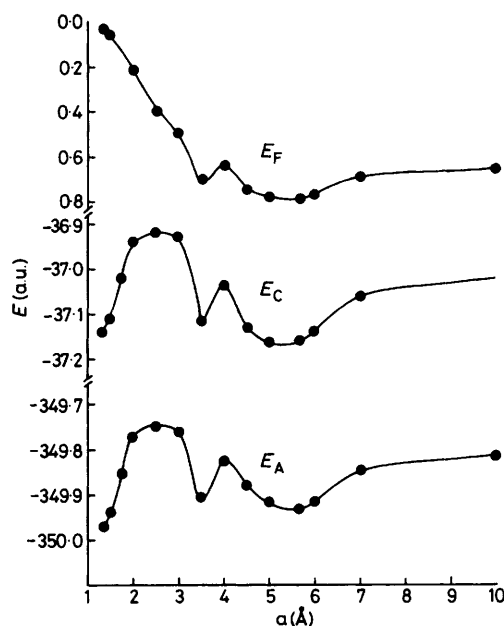


FIGURE 8 Curves of  $E_A$ ,  $E_C$ , and  $E_F$  versus  $a$  for  $\text{CH}_3\text{F}$  in HF

The curve calculated for  $\text{CH}_3\text{F}$  in HF is very similar to that predicted by CNDO/2 for the benzenediazonium ion in water (Figure 4 of ref. 2) and this finding suggests the common origin of the forces that set out the stability of different ion pairs in different solvents. In this view the main result from the present work is the conclusion that our method describes correctly the behaviour of solutes in strongly polar media, independently from the model chosen for the solvent.

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