Complete Active Space Self Consistent Field and Externally Contracted CI Potential Energy Curves for the CH_3F^- and CH_3Cl^- Anions

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Ab initio calculations using the Complete Active Space SCF (CAS SCF) and externally Contracted CI (CCI) methods and optimized basis sets have been performed to study the stability of the negatively charged molecular ions CH_3F^- and CH_3Cl^-. Neither of the molecules has a positive electron affinity. Both systems are essentially formed of the parent molecule with the extra electron in a very diffuse molecular orbital extending out from the methyl group. The extra electron moves over to the halogen atom when the RX bond is dissociated. The barrier for the dissociative electron attachment reaction of methyl fluoride and methyl chloride is calculated to be 230 and 130 kJ mol^{-1}, respectively. The solvent effect on the theoretical potential curves is discussed.

Electron attachment to a neutral organic molecule, initially leading either to the formation of a radical anion or direct dissociation to form a neutral radical and an anion [equations (1) and (2)], has proven to be a powerful synthetic technique with applications extending from molecular biology to industrial processes.[1] The stability and dissociation mechanisms of the radical anion formed and the possibility of dissociative electron transfer in such reactions are currently under intensive study.[2]

$$\text{R–Nu} + e^- \longrightarrow (\text{R–Nu}^{-\bullet}) \qquad (1)$$

$$\text{R–Nu} + e^- \longrightarrow \text{R}^\bullet + \text{Nu}^- \qquad (2)$$

Electrochemical dissociation of alkyl halides is an important source of alkyl radicals in various synthetic reactions.[1j,k] The same reaction type can be induced in homogeneous medium by electron transfer reductants (D), such as the solvated electron, radical anions, or metal complexes in low oxidation states. A large number of such reactions was recently[3] analysed by the Marcus treatment,[4–6] assuming that the C–X bond (X = Cl, Br, I) is virtually broken in the transition state for ET [equation (3)] and that ET is thus dissociative,[7] with no involvement or separate existence of ($RX^{-\bullet}$).[‡] With this postulate a consistent treatment was possible, and the predicted high reorganization energy (λ) for the self-exchange reaction, $RX/R^\bullet X^-$, was confirmed, in that the average values of $\lambda(RCl/R^\bullet Cl^-)$, $\lambda(RBr/R^\bullet Br^-)$, and $\lambda(RI/R^\bullet I^-)$ came out as 330, 310 and 230 kJ mol^{-1}. Data for alkyl fluorides, of which only few are available, deviated significantly from the model, and hence it was suggested that electron transfer might not be dissociative in this case and thus the radical anion of an alkyl fluoride might have a finite existence.

$$\text{C–X} + \text{D} \rightleftharpoons [\text{C}^{\bullet\cdots\cdots}\text{X D} \longleftrightarrow \text{C}^\bullet\,\text{X}^-\,\text{D}^{+\bullet}]^\ddagger \rightleftharpoons \text{C}^\bullet + \text{X}^- + \text{D}^{+\bullet} \qquad (3)$$

Against this background, it is important to elucidate further the mechanisms of these processes and understand the electron transfer properties of the various alkyl halides, in particular their dissocative potential curves. Wu[9] has studied the alkali + methyl halide reactions in terms of the electron jump model. In this way the multidimensional potential surfaces for the total process can be replaced by potential curves describing dissociation of the methyl halide anions. Potential curves, based on thermodynamic data, were presented. A more detailed analysis was presented by Shaik and Pross.[2d] The C–X bond is classified as a three-electron bond of unstable type. Introducing thermodynamic data into the qualitative valence bond model it is possible to construct potential curves that describe the dissociation of both the parent methyl halides and their anions.

Only a few theoretical calculations of the structure or the dissociative potential curves of methyl fluoride or methyl chloride anions appear in the literature. Clark[10] has computed the structure of $CH_3F^{-\bullet}$ and $CH_3Cl^{-\bullet}$ and their silicon analogues, finding no barrier for the dissociation. Later, he observed that calculations with restricted basis sets simulate the solvent effect quite well.[11] With this method he repeated the calculations for $CH_3Cl^{-\bullet}$, finding a barrier of *ca.* 80 kJ mol^{-1}. Very recently,[12] an alkali-metal ion in $CH_3Cl^{-\bullet}\,M^+$ was found to induce a similar effect, the barrier to rotation being estimated at 7—14 kJ mol^{-1}. Canadell *et al.*[12] simulated the solvent effect in the dissociation of $CH_3Cl^{-\bullet}$ by introducing two water molecules which are allowed to accompany the departing chloride ion. Their potential curve shows a barrier of *ca.* 65 kJ mol^{-1}. Faustov *et al.*[14] reported MINDO calculations on the $CH_3Cl^{-\bullet}$ system.

According to a theoretical model,[15] the anion R^- of a non-rotating parent molecule R will be stable if and only if R possesses a permanent dipole moment >1.625 D. This prediction has been confirmed in a number of cases where the dipole moment of the parent molecule is much greater than or much smaller than the critical value.[16] If the dipole moment of the parent molecule is close to the critical value, dynamic contributions may alter the picture because the inclusion of rotational degrees of freedom in the total Hamiltonian reduces the effective binding for the negative ion.[17] On the other hand, a small electron affinity in the parent molecule, 0.1 or 0.05 times the rotational constant, is enough to counteract the corrections to the Born–Oppenheimer approximation.[18] Even when the latter is valid the neglect of core electrons on the electropositive atom reduces the applicability of the dipole model.[17a]

The dipole moment of hydrogen chloride, 1.11 D, is clearly smaller than the critical value of 1.625 D and, indeed, HCl forms complexes of hydrogen atom and chloride ion rather than true $HCl^{-\bullet}$. In electron scattering and electron transmission spectroscopic experiments[11] the main exit channel is to Cl^- ions

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[‡] A recent study[8] put the life-time of the radical anion of Ph_2CHCl at <20 ps.

although a controversial discussion of the existence of a short-lived resonant Rydberg state of HCl$^{-\bullet}$ continues.[19a] The associative reaction of H + Cl$^-$ leads to electron detachment.[20] The dipole moment of hydrogen fluoride, 1.82 D, is somewhat above the critical value but its behaviour resembles that of hydrogen chloride.[20,21] Even hydrogen cyanide with a dipole moment of 2.98 D undergoes an associative detachment reaction.[20,22]

Methyl fluoride and methyl chloride possess dipole moments of 1.81 and 1.87 D, respectively, and should therefore, according to the dipole model,[15] form stable anions. Methyl halide anions have been studied extensively, mostly using the e.s.r. technique.[23] In solid matrix the negative charge may be trapped in cavities between the molecules[23a] while in solution the anions dissociate producing a halogen anion and a planar methyl radical.[23c] Actually, a life-time of *ca.* 3×10^{-8} s has been reported for $CH_3Cl^{-\bullet}$, but the exact nature of the observed species has not been determined beyond doubt.[24] It has been suggested that it might be a complex of the parent molecule and a solvated electron.[25] The most recent e.s.r. study of the electron attachment to chloroalkanes in a rigid matrix at 77 K established the dissociative cleavage of RCl to $R^{\bullet}Cl^-$ 'collision complexes', held together by the matrix. These species are not properly described as radical anions.[8] Acetonitrile anion, $CH_3CN^{-\bullet}$, has been observed spectroscopically[26] in liquid acetonitrile. It is a short-lived species with a half-life period of 900 ns.

In this paper we report quantum chemical *ab initio* calculations with optimized basis sets for the potential energy curves of methyl fluoride, methyl chloride, and their anions. We discuss the potential curves for the dissociation of methyl fluoride, methyl chloride, and their anions and speculate on the solvent effects on the quantum chemical potential curves.

Calculations

The multiconfiguration MCSCF calculations were performed using the Complete Active Space SCF (CAS SCF) method in its 'Super-CI' implementation.[27] In the CAS approach the total molecular orbital space is divided into inactive, active, and secondary subspaces. The active subspace comprises the valence molecular orbitals which suffer strong modifications and/or changes in occupation number during the chemical reaction and the most important correlating orbitals. The electrons are distributed in all possible ways among the active orbitals giving a complete CI expansion within the active subspace. The inactive orbitals are doubly occupied in all configurations, the secondary orbitals are empty. Thus no list of configurations needs to be compiled in advance; the only choice requiring chemical intuition is the designation of active orbitals.

The optimized molecular orbitals from the CAS SCF calculations were used in the configuration interaction calculations to recover most of the dynamical correlation energy. The externally Contracted CI (CCI) method[28] was used.

The details of the active subspaces and the basis sets are discussed for each case individually.

Results and Discussion

Hydrogen Fluoride.—A set of pilot calculations was performed along the potential energy curve of hydrogen fluoride molecule and its anion in order to study the effect of diffuse basis functions upon the total energy and electron distribution in a negative ion of the type RF$^-$. The Cartesian Gaussian atom-centred basis sets were as follows. For fluorine the (11*s* 7*p*) primitive set of van Duijneveldt[29] was contracted to (6*s* 3*p*) and augmented with three diffuse uncontracted *s* functions, two diffuse *p* functions, and two *d* functions. The exponents of the diffuse *s* functions were multiplied by a factor *k* which was optimized at each point on the potential energy curve. For hydrogen the (6*s*) primitive set of Huzinaga[30] was contracted to (4*s*). One diffuse *s* function and two *p* functions were added. The final basis sets for this series of calculations are shown in Table 1.

Table 1. The basis sets used in the pilot calculations on HF and HF$^-$. The scaling factor *k* is optimized for the various bond distances

Atom	Type	α	c
F[a]	*s*	39 319.3	0.000 212
		5 882.86	0.001 644
		1 338.04	0.008 542
		379.579	0.034 537
		124.178	0.111 312
		44.7674	0.271 582
	s	17.2325	1.0
	s	6.838 30	1.0
	s	1.885 52	1.0
	s	0.773 160	1.0
	s	0.280 330	1.0
	s	0.07 × k	1.0
	s	0.023 × k	1.0
	s	0.0078 × k	1.0
	p	136.512	0.002 641
		32.0732	0.019 813
		10.0183	0.085 070
		3.600 21	0.229 995
		1.359 510	0.378 512
	p	0.505 550	1.0
	p	0.178 860	1.0
	p	0.060	1.0
	p	0.020	1.0
	d	0.83	1.0
	d	0.14	1.0
H[b]	*s*	68.1600	0.002 55
		10.2465	0.019 38
		2.346 48	0.092 80
	s	0.673 320	1.0
	s	0.224 660	1.0
	s	0.082 217	1.0
	s	0.020	1.0
	p	0.70	1.0
	p	0.20	1.0

[a] Based on ref. 29. [b] Based on ref. 30.

The active space consisted of five orbitals of σ symmetry and four orbitals of π symmetry (or actually a_1, b_1, and b_2 symmetries because the C_{2v} point group was used). Only the 1a_1 and 2a_1 (roughly the fluorine 1*s* and 2*s*) orbitals were kept inactive. In the ensuing CCI calculations the uncontracted CI space consisting of 101 600 and 166 012 configurations for HF and HF$^-$, respectively, was contracted to 971 and 1 011 configurations, respectively.

The resulting CAS SCF and CCI potential energy curves are shown in Figure 1. The total energies at selected points are given in Table 2, together with the optimal values of the scaling factor *k*. The present potential energy curve for the neutral HF molecule is quite accurate. A detailed comparison with the experimental results,[31] the recent extensive MRD-CI calculations by Bettendorff *et al.*,[32] and the CI calculations of Segal and Wolf[33] is given in Table 3. The present spectroscopic constants are obtained through numerical solution of the rovibrational Hamiltonian in the theoretical potential.[34] The potential energy curve for the HF$^-$ anion is an excellent agreement with the MRD-CI results of Bettendorff *et al.*[19a] At large interatomic distances the electron affinity is calculated to be 261.0 and 281.0 kJ mol^{-1} at the CAS SCF and CCI levels of approximation, respectively. This can be compared with the experimental electron affinity of fluorine, 332.6 kJ mol^{-1}.[35] Thus the H + F^- asymptote is computed to lie 275.8 kJ mol^{-1} above the $v = 0$ HF ground state level. The earlier theoretical estimates are 268.6[19a] and 275 kJ mol^{-1}.[33] The value deduced from experimental data is 256 kJ mol^{-1}.[35]

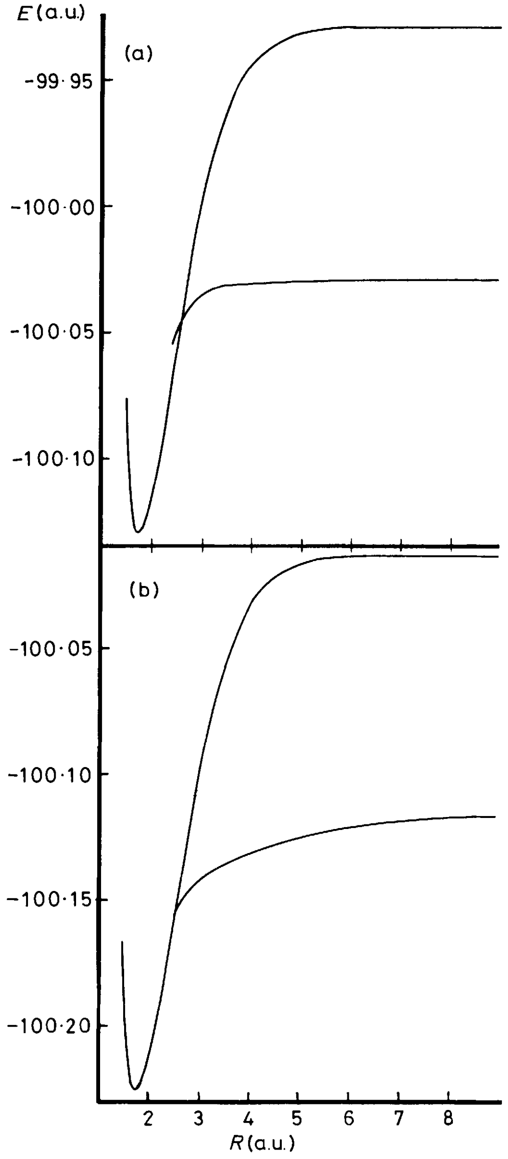

Figure 1. The potential energy curves for hydrogen fluoride and its anion: (a) the CAS SCF results; (b) the CCI results

The present calculations show that the potential energy curve for the anionic system remains attractive from the separated atoms limit to *ca.* 135 pm where it crosses the potential curve for the neutral system. The scaling factor *k* for the diffuse orbitals remains constant in this range. At smaller internuclear separations the potential energy curve for the anionic system is essentially parallel with that for the neutral system and slightly above it. At the same time the extra electron escapes *via* a very diffuse *s*-type orbital centered on hydrogen. The distance between the HF and HF^- curves diminishes as the orbital for the escaping electron is made more diffuse.

The central conclusions from the pilot calculations are as follows. (a) The present basis set is adequate for describing both the neutral and the negatively charged system. Sufficiently diffuse functions must be present in the basis set but there is no need to optimize the exponents along the reaction co-ordinate since no appreciable improvement of the form of the potential energy curve is achieved. The essentially free electron is only made more diffuse. The form of the electron cloud and thereby the related properties, *e.g.* the multipole moments, are obviously affected. (b) The present potential curve for the anionic system shows that there is no barrier to the associative detachment reaction of hydrogen and fluoride ion. The escape route of the departing electron is *via* a diffuse orbital on hydrogen. (c) The present results are in good agreement with the previous theoretical study by Bettendorff *et al.*[19a] and the experimental data. (d) The system is adequately described at the CAS SCF level of approximation.

Methyl Radical.—The basis sets used for the methyl radical are of the same quality as those used for hydrogen fluoride: For carbon the (11*s* 7*p*) set of primitive Gaussians[29] was contracted to (6*s* 3*p*) and augmented with three *s*, two *p*, and two *d* functions. The final carbon basis set is shown in Table 4. The hydrogen basis set is the same as previously.

The methyl radical was assumed to have D_{3h} symmetry. The calculated bond distance is 108 pm, to be compared with the previous theoretical values of 107.7[36] and 107.9 pm[37] and with the experimental result of 107.9 pm.[38] In the methyl anion the C–H bond distance was found to be slightly longer than in the

Table 3. Comparison of the spectroscopical constants for the X $^1\Sigma^+$ ground state of the neutral hydrogen fluoride molecule

Ref.	r_e/pm	D_e/kJ mol^{-1}	ω_e/cm^{-1}	$x_e\omega_e$/ cm^{-1}	B_e/cm^{-1}
32	92.3	577	4 148.64		20.32
33	91.7	581			
31	91.680	591.1	4 138.32	89.88	20.9557
This work	93.3	527	3 850		20.1
CCI	93.7	557	3 850		20.1

Table 2. Total energies at selected points along the dissociation curves for HF and HF^-. The scaling factor *k* (see Table 1) is optimized for HF^-

	HF		HF^-		
R(a.u.)	E_{CASSCF}(a.u.)	E_{CCI}(a.u.)	E_{CASSCF}(a.u.)	E_{CCI}(a.u.)	k
20	−99.928 895	−100.012 857	−100.028 309	−100.119 858	0.8
10	−99.928 893		−100.028 488		0.8
6	−99.929 275		−100.029 672		0.8
3.5	−99.964 921	−100.056 388	−100.031 259	−100.136 881	0.8
2.75	−100.028 047	−100.123 394	−100.041 062	−100.146 408	0.6
2.50	−100.057 613	−100.153 526	−100.051 385	−100.157 091	0.6
1.763[a]	−100.129 669				
1.771[b]		−100.224 912			

[a] R_e according to the CASSCF calculations, 93.3 pm. [b] R_e according to the CCI calculations, 93.7 pm.

Table 4. The basis set used for carbon in the pilot calculations on the methyl radical and methyl anion

Atom	Type	α	c
C	*s*	15 469.4	0.000 242
		2 316.47	0.001 879
		527.099	0.009 743
		149.438	0.039 167
		48.8562	0.123 636
		17.6209	0.288 316
	s	6.810 82	1.0
	s	2.727 60	1.0
	s	0.756 740	1.0
	s	0.300 730	1.0
	s	0.114 090	1.0
	s	0.0228	1.0
	s	0.0076	1.0
	s	0.0025	1.0
	p	51.7233	0.002 734
		12.3397	0.018 979
		3.772 24	0.080 806
		1.324 87	0.227 779
		0.505 460	0.388 443
	p	0.198 270	1.0
	p	0.077 310	1.0
	p	0.0258	1.0
	p	0.0086	1.0
	d	0.34	1.0
	d	0.057	1.0

methyl radical, namely 111 pm. The anion has C_{3v} symmetry and the bond angle was found to be 111°. These values are in good agreement with previous theoretical results.[39]

It has turned out to be a very difficult task to reproduce theoretically the electron affinity of the methyl radical. Most of the calculations, including the present ones, predict the methyl radical to be more stable than the methyl anion at their respective equilibrium geometries. According to the present CCI (CAS SCF) calculations the $^{\bullet}CH_3 + e^-$ system has 24.9 kJ mol^{-1} (73.1 kJ mol^{-1}) lower energy than the methyl anion. Driessler *et al.*[40] concluded, after having considered all the possible sources of error in their calculations, that the electron affinity of the methyl radical cannot exceed 30 kJ mol^{-1}. The experimental value was later revised from 77 to 8 kJ mol^{-1}.[41]

Methyl Fluoride and Methyl Chloride Anions.—The basis sets. The basis sets in Table 1 and 4 are prohibitively large for calculations on methyl fluoride, methyl chloride, and their anions. Various slightly smaller basis sets for fluorine, carbon, and hydrogen were tested against the calibration calculations described previously, resulting in the following choice: For fluorine and carbon the (11*s* 7*p*) sets of primitive Gaussians[29] were contracted to (5*s* 3*p*) and augmented with two diffuse *s* and *p* functions and one *d* function [α_d(F) 0.80 and α_d(C) 0.40]. For hydrogen the (4*s*) set of primitive Gaussians[30] was contracted to (3*s*) as suggested by Dunning[42] and augmented with one additional *s* function (α 0.04) and one *p* function (α 0.2). The electron affinity thus obtained for fluorine was 260 kJ mol^{-1} at the CAS SCF level of approximation. Similarly, the 'electron affinity' of the methyl radical was found to be −74.8 kJ mol^{-1}. The chlorine basis set consisting of (10*s* 6*p*) primitive functions was taken from Roos and Siegbahn[43] and contracted to (7*s* 5*p*). It was augmented with two diffuse *s* functions (α_s 0.06 and 0.01), two *p* functions (α_p 0.05 and 0.015), and two *d* functions (α_d 0.8 and 0.2).

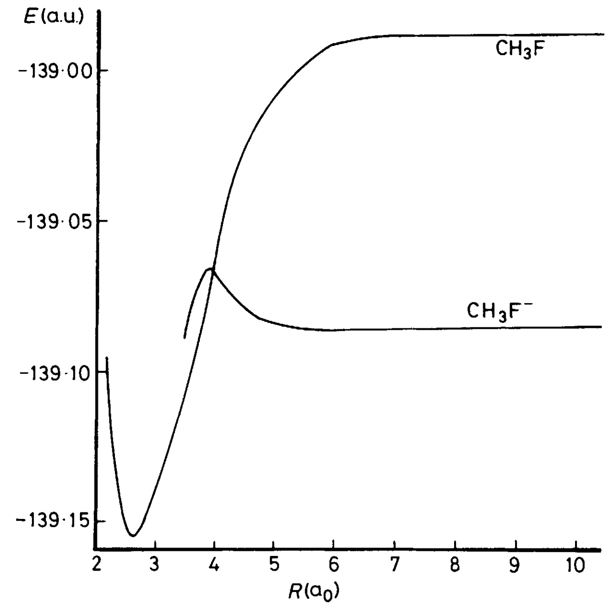

Figure 2. The potential energy curves for dissociation of the C–F bond in methyl fluoride and its anion at the CAS SCF level of approximation

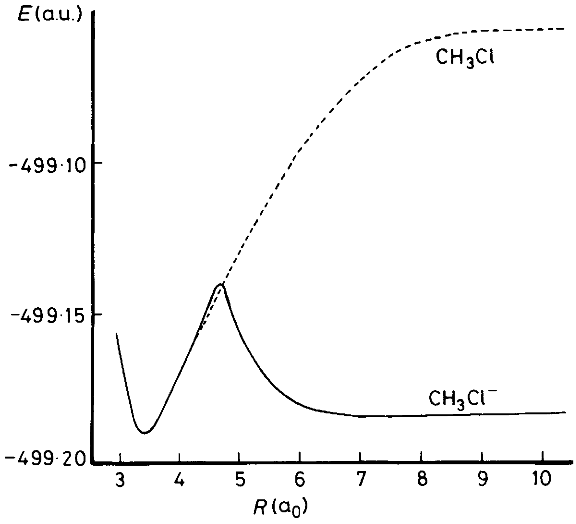

Figure 3. The potential energy curve for the dissociation of the C–Cl bond in methyl chloride anion at the CCI level of approximation. The corresponding potential energy curve for methyl chloride has not been calculated. The dotted line is merely a sketch indicating the calculated dissociation limit

The potential energy curves for CH_3F, CH_3F^-, *and* CH_3Cl^-. The calibration calculations indicate that the CAS SCF model describes the radical anions RF$^-$ adequately as well as the corresponding neutral molecules. Therefore the ensuing CCI calculations were omitted for the methyl fluoride molecule and its anion. In the CAS SCF calculations the active space consisted of four a_1 and two *e* orbitals (*i.e.* the carbon $2p_z$ and $3p_z$ orbitals, the *z* axis being the symmetry axis, and the fluorine 2*p* and 3*p* shells using the nomenclature for the separated fragments). In the case of methyl chloride, only the potential curve for the anion was computed. Here it turned out to be more economical to use the CCI method for obtaining an adequate description of the system.

The dissociation energy obtained for CH$_3$F by the CAS SCF method is 435 kJ mol^{-1} while the experimental value is 452 kJ mol^{-1}.[44] The equilibrium C–F bond distance and HCH bond angle are calculated to be 140 pm and 110°, the experimental values being 138.3 pm and 110.6°.[45] Similarly, an electron

Table 5. The CASSCF energies of the systems CH_3F and CH_3F^-. The angle α indicates how far the hydrogen atoms of the methyl group have been bent from the planar geometry. Positive value indicates umbrella motion away from the in-coming fluorine atom

	CH_3F		CH_3F^-	
R(a.u.)	α(°)	E_{CASSCF}(a.u.)	α(°)	E_{CASSF}(a.u.)
20	0	−138.988 700	0	−139.085 143
10	0	−138.988 700	−5	−139.085 328
7	0	−138.989 549	−10	−139.086 368
6	0	−138.992 127	−10	−139.086 468
5	0	−139.008 610	−10	−139.084 160
4	5	−139.063 200	−5	−139.067 296
3.5	10	−139.102 102	10	−139.090 638
3		−139.140 257		
2.8	20	−139.151 067		
2.7	20	−139.154 198		
2.6	20	−139.154 072		
2.5	20	−139.149 519		
2.65	19	−139.154 497		

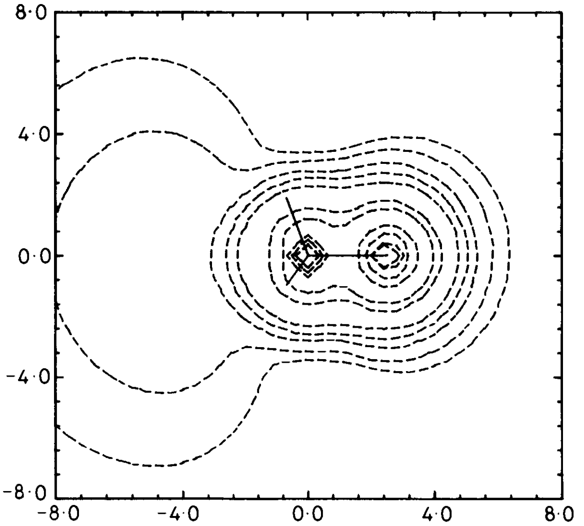

Figure 4. Total electron density of the methyl fluoride anion in the σ_v plane. The outermost contour lines correspond to 0.0005, 0.001, 0.0025, and 0.005 e^-/a_0^3. The co-ordinates are in atomic units

Table 6. The CCI energies of the system CH_3Cl^-. The angle indicates how far the hydrogen atoms have been bent from the planar geometry. Positive values indicate umbrella motion away from the approaching chlorine ion

	CH_3Cl^-	
R(a.u.)	α(°)	E_{CCI}(a.u.)
10	0	−499.170 055
6	−10	−499.179 977
5	10	−499.154 404
4.75	10	−499.140 842
4.50	10	−499.147 221
4.00	20	−499.166 180
3.50	20	−499.188 282
3.00	20	−499.160 461

affinity of 304 kJ mol^{-1} is obtained for the chlorine atom while the experimental value is 349 kJ mol^{-1}.[35] The dissociation energy of the neutral CH_3Cl is estimated to be 330 kJ mol^{-1} assuming that the potential curve for the neutral species lies *ca.* 10 kJ mol^{-1} below that for the anion at the equilibrium geometry. The experimental value is 349 kJ mol^{-1}.[46] The optimal C–Cl bond distance is 179 pm to be compared with the experimental value of 178.4 pm.[47] These characteristics of the investigated system indicate that the present calculations are fairly reliable. The calculated potential energy curves are shown in Figures 2 and 3. The total energies at selected points are given in Tables 5 and 6.

Analogously to the hydrogen fluoride anion, the potential energy curves describing the methyl halide anions are seen to have a deep minimum corresponding to a rather unperturbed CH_3X and an essentially free, or possibly solvated,[48] electron. The character of the diffuse orbital in which the free electron resides is clearly seen in Figure 4. As in hydrogen fluoride, the escape route of the departing electron is *via* the alkyl group. The barrier for the dissociative attachment reaction is 230 and 130 kJ mol^{-1} in methyl fluoride and methyl chloride anions, respectively. In contrast to the hydrogen fluoride case, there also is a barrier of 50 and 112 kJ mol^{-1} for the associative detachment reaction of methyl fluoride and methyl chloride, respectively.

Potential curves for the Rydberg states analogous to those in HF^- and HCl^- [19a] were not probed. Although such states may correspond to short-lived CH_3X^- anions, the electron impact energies required to reach them are likely to be appreciable.

The free methyl radical is planar. When it starts interacting with a halogen atom to form methyl halogenide the hydrogen atoms are seen to perform a smooth umbrella motion along the reaction path. However, in the case of CH_3X^- there is a weak electrostatic attraction between the negatively charged ion and the hydrogen atoms with a small positive net charge. Therefore the hydrogens are bent *towards* the halide ion at intermediate C–X distances, to be subsequently flipped over to the equilibrium geometry of CH_3X^-.

Conclusions.—Potential curves for the associative detachment reactions of hydrogen fluoride, methyl fluoride, and methyl chloride molecules have been calculated using the CAS SCF[27] and CCI[28] methods and large basis sets. Also, the equilibrium structure of methyl radical and methyl anion have been determined in a similar fashion. The calculated electron affinities, dissociation energies, and equilibrium geometries are in good agreement with experimental values. The potential curve for the hydrogen fluoride anion is found to be attractive. At large interatomic distances the hydrogen and fluoride anion have lower energy than hydrogen and fluorine atom. At shorter distances one electron escapes into a very diffuse hydrogen-centred orbital and the potential energy curves for the anionic and neutral systems unite at an interatomic distance of *ca.* 135 pm.

Potential curves for the associative detachment reaction of methyl fluoride and methyl chloride anions are both qualitatively different from the hydrogen fluoride case. At large and intermediate distances the curves are repulsive. An avoided crossing with the curve for a neutral molecule and a free electron occurs at a C–X bond distance of *ca.* 200 pm (250 pm) in methyl fluoride (methyl chloride) anion. Thereby one electron escapes from the halide ion *via* the methyl group into a very diffuse orbital mainly formed of hydrogen basis functions. The barriers for the associative detachment reaction are found to be 50 and 112 kJ mol^{-1} in methyl fluoride and methyl chloride anions, respectively. For the reverse reaction, dissociative attachment, the barriers are 230 and 130 kJ mol^{-1}, respectively. The previous theoretical estimates for the barrier height for dissociative attachment to methyl chloride, 105[13] and 80 kJ mol^{-1} [25] are somewhat lower than the present one. Canadell *et al.*[13] with a barrier height closer to the present value, report the transition state to lie at a C–Cl bond distance of 265 pm while the value obtained by Clark[25] is 228 pm. No previous calculations of the barrier in methyl fluoride anion have been found in the literature.

The quantum chemical calculations refer to gas-phase reactions. To extrapolate to the experimental environment, an aqueous solution, the energy lowering due to hydration of the species must be estimated along the reaction path. Clark[25] employed restricted basis sets without any diffuse functions for the methyl chloride ion in order to describe a caged electron. In this way he obtained for the condensed phase a potential energy curve which is purely repulsive. On this curve he found a range, *ca.* 50 kJ mol^{-1} above the energy for the separated methyl radical and chloride ion, which produces the experimental spin distribution data and corresponds to an experimental cavity size. Canadell *et al.*[13] formed a crude solvation shell by placing two water molecules around the methyl chloride anion. The water molecules were allowed to accompany the departing chloride ion during the bond cleavage. This procedure lowered the barrier for dissociative attachment to 65 kJ mol^{-1} and shifted the transition state to a slightly shorter C–Cl bond distance.

A crude estimate of the solvation energy of an ion can be obtained from the Born model.[35] In this simple model the ion is regarded as a charged sphere of radius R and the solvent as a dielectric continuum. Only the electrostatic interaction is included; the dipole and quadrupole interactions which are particularly important in molecular ions are ignored. Therefore it is not surprising that discrepances of a factor of 2 or 3 between prediction and experiment are common even in electrolyte solutions. Furthermore, the radius of the sphere is not a well defined quantity, making the model somewhat arbitrary. Bearing these reservations in mind one can estimate the solvation energies of the various species in a similar fashion to Canadell *et al.*[13] The Gibbs free energy of hydration for the methyl radical is zero in the Born model and is in reality small compared with the other quantities. For fluoride and chloride ions ΔG^{0}_{hyd} is -463 and -341 kJ mol^{-1}, respectively, and the radii are 133 and 181 pm.[35] The radius of a solvated electron, 280 pm, is deduced from the data for glassy materials.[48] This gives a free energy of hydration of -220 kJ mol^{-1} for the system $CH_3X + e^-$. For the transition states we estimate the radii to be 200 and 220 pm, respectively, resulting in hydration energies of 310 and 280 kJ mol^{-1}. This finally leads to barriers of 140 and 70 kJ mol^{-1} for dissociative electron attachment in aqueous solution for methyl fluoride and methyl chloride, respectively.

Thus, a conclusion from this work is that both CH_3F^- and CH_3Cl^- are discrete species in the gas phase. As for the liquid-phase mechanism, present estimates of the influence of solvation are too uncertain to allow for any firm conclusions to be drawn. The barrier for dissociative detachment does decrease when crude models of solvation are included, but one actually needs an extended molecular dynamics simulation of the solvent influence to see if the extreme limit of dissociative electron transfer without intervention of the radical anion[3] is a reasonable proposition.

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Received 18*th November* 1985; *Paper* 5/2018