Synthesis, Physical Characterisation and Chemical Properties of Methylsulphur Trifluoride, CH_3SF_3†

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Methylsulphur trifluoride, CH_3SF_3, has been synthesised by the reaction between AgF_2 and a solution of CH_3SCl in CCl_3F. It is a clear, viscous liquid which attacks glass, is hydrolysed rapidly, and decomposes at ambient temperatures to give CH_2FSF_3 and CH_2FSSCH_2F. The compound has been characterised by its ^1H and ^{19}F NMR and vibrational spectra, and a partial vibrational assignment is proposed. The chemistry of CH_3SF_3 is akin to that of SF_4. Thus, it functions as a fluoride ion donor much more readily than as a fluoride ion acceptor. It reacts with Pyrex glass to give $CH_3S(O)F$, is hydrolysed to $CH_3S(O)OH$, and effects O–F exchange with acetone to yield 2,2-difluoropropane.

While the methyl-substituted derivatives of phosphorus pentafluoride have received much attention as regards their physical and chemical properties,[1] very little is known about the corresponding derivatives of sulphur tetrafluoride. This situation is due in part to the comparative difficulty of synthesising such molecules, a problem compounded by their reactivity (especially towards glass apparatus) and limited thermal stability. Thus, methylsulphur trifluoride, CH_3SF_3, as identified by Gombler and Budenz[2] in 1976, was reported to react with glass at temperatures below 0 °C with the formation of methanesulphinyl fluoride, $CH_3S(O)F$. There have been no subsequent reports of the chemical properties of this compound. In 1984 Forster and Downs[3] reported that dimethylsulphur difluoride, $(CH_3)_2SF_2$, can be formed in solution, but that it decomposes rapidly at ambient temperatures; attempts to vaporise the compound without decomposition have proved fruitless.[3,4] Following the example of the monomethyl compound, $(CH_3)_2SF_2$ reacts with glass to give dimethyl sulphoxide.

We have determined recently the structure of the gaseous CH_3SF_3 molecule on the basis of its electron-diffraction pattern.[5] Here we describe its synthesis and some physical and chemical properties.

Results and Discussion

(*i*) *Synthesis of Methylsulphur Trifluoride.*—In order to prepare methylsulphur trifluoride from a sulphur(II) precursor, an oxidative fluorinating agent is required. Initial attempts using xenon difluoride or silver(II) fluoride and dimethyl disulphide, CH_3SSCH_3, were found to cause fluorination of the methyl groups.[6] Altogether more successful as a precursor is methanesulphenyl chloride, CH_3SCl. Treatment of a solution of CH_3SCl with silver(II) fluoride in either $CDCl_3$ or CCl_3F contained in fluorocarbon apparatus causes the reaction represented by equation (1) to proceed smoothly. Although it has proved impossible to separate CH_3SF_3 from $CDCl_3$ by fractional condensation *in vacuo*, such a separation from the more volatile CCl_3F is possible, using traps held successively at 240, 210 and 77 K. Pure CH_3SF_3 collects in the middle trap as a clear, viscous liquid with a melting point of 197 ± 2 K and can be stored in evacuated fluorocarbon apparatus at 77 K.

$$CH_3SCl + 2\,AgF_2 \xrightarrow[250\text{ K, 1 h}]{CDCl_3\text{ or }CCl_3F} CH_3SF_3 + AgF + AgCl \quad (1)$$

The perdeuteriated analogue CD_3SF_3 can be prepared in a similar manner from CD_3SCl. However, this isotopomer has physical properties significantly different from those of CH_3SF_3, as revealed by the following features: (*i*) at 211 ± 2 K, the melting point is some 14 K higher than that of the lighter isotopomer; (*ii*) the density of CD_3SF_3 is appreciably greater than that of CH_3SF_3, with the result that the latter floats on top of a saturated solution in CCl_3F, whereas the former makes up the *lower* layer in contact with a similar solution in CCl_3F; and (*iii*) CD_3SF_3 is significantly less volatile than CH_3SF_3, vacuum fractionation being effected most efficiently between traps held at 250, 222 and 77 K. Such noticeable differences imply a significant degree of hydrogen bonding in the condensed phases.

Methylsulphur trifluoride has limited thermal stability and the pure liquid has a half-life in the order of minutes at ambient temperatures. Under similar conditions and at a pressure of 5–10 mmHg, the vapour decomposes with a half-life of *ca.* 15 min; solutions of the compound in $CDCl_3$ or CCl_3F have a similar lifetime. The course of thermal decomposition is discussed later.

(*ii*) *Physical Characteristics of Methylsulphur Trifluoride.*—(*a*) *NMR spectra.* Proton and ^{19}F NMR spectra of a solution of CH_3SF_3 in CCl_3F are illustrated in Fig. 1; Table 1 lists the relevant parameters based on the results of the present, as well as earlier,[2,6] experiments. There are evidently significant variations in the NMR parameters depending on the conditions of the sample. The solvent dependence, and possibly also temperature and concentration dependences, is consonant with relatively strong intermolecular forces between the CH_3SF_3 molecules (*cf.* SF_4).[7] The inclusion of a few milligrams of CsF in the NMR sample permits ^1H–^{19}F coupling to be observed in the ^1H spectrum, but, in the absence of such an HF scavenger, only a singlet is discerned. No ^1H–^{19}F coupling could be observed in the ^{19}F NMR spectrum, the resonances being relatively broad in our experiments.

The NMR properties reveal a 'rigid' CH_3SF_3 molecule with the structure **I** based on that of SF_4 but having the CH_3 group in place of one of the equatorial fluorine substituents. The relative intensities of the ^{19}F NMR resonances due to the solute and solvent suggest that the maximum solubility of CH_3SF_3 in CCl_3F at 250 K is *ca* 1.0 mol dm^{-3}.

(*b*) *Vibrational spectra.* Infrared spectra have been recorded for solid films of CH_3SF_3 and CD_3SF_3 at 77 K, for samples of

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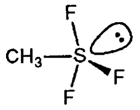
† *Non-SI units employed:* mmHg ≈ 133 Pa, atm = 101 325 Pa.

Table 1 NMR parameters for methylsulphur trifluoride, CH_3SF_3

Solvent, temperature/K	Chemical shift			Spin–spin coupling constant/Hz			Reference
	δ(CH_3)	δ(SF_2) (ppm)	δ(SF) (ppm)	$^2J(F_{ax}.F_{eq.})$	$^3J(F_{ax}.H)$	$^3J(F_{eq}.H)$	
CCl_3F, 293	3.78	+63.1	−52.8	71.4	14.9	11.7	This work
$CDCl_3$, 308	3.54	+60.6	−51.9	75.0	15.2	11.4	6
$CDCl_3$, 223	3.29	+59.3	−51.5	72.0	15.5	12.2	2



I

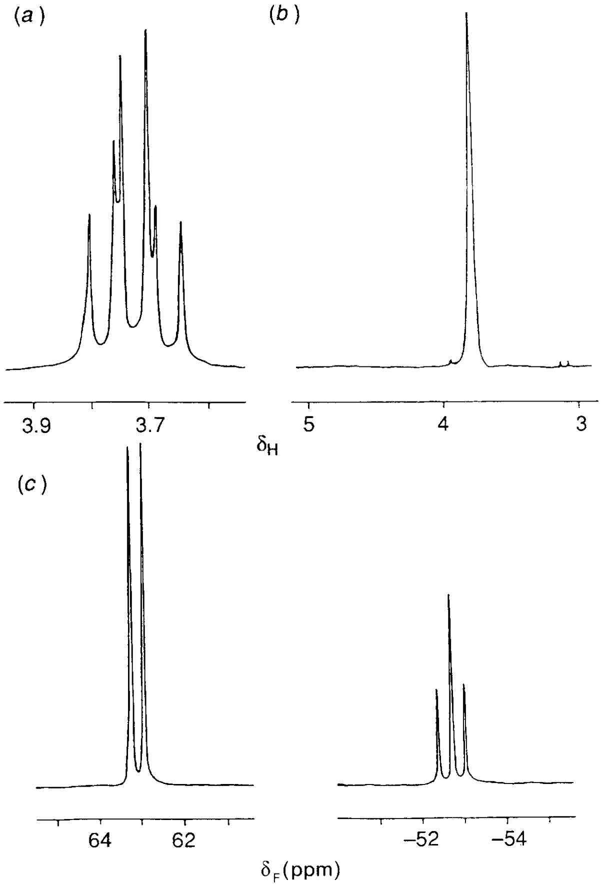


Fig. 1 Proton [(*a*),(*b*)] and ^{19}F (*c*) NMR spectra of CH_3SF_3 in CCl_3F solution at *ca.* 293 K (measured at 300 and 235 MHz, respectively). Samples: (*a*) and (*c*), contains CsF; (*b*) does not contain CsF.

the vapours isolated in inert-gas matrices at *ca.* 14 K, and for the vapours at *ca.* 293 K and a pressure of 5–10 mmHg. The Raman spectra of solid deposits of both isotopomers at 77 K have also been recorded, but attempts to measure the spectra of the liquids have been unsuccessful. Fig. 2 depicts the IR spectra of gaseous CH_3SF_3 and CD_3SF_3, and all the relevant vibrational frequencies are listed in Table 2.

The similarity of the IR spectra of CH_3SF_3 in the vapour, solid, and matrix-isolated states (notwithstanding the broadness of some of the absorptions in the spectrum of the solid), allied to the lack of significant changes in the spectrum of the matrix-isolated species when the matrix is annealed, argues for a discrete molecular, rather than an oligomeric or ionic, formulation in the condensed phases.

An electron-diffraction study of gaseous CH_3SF_3[5] has confirmed that the molecule adopts the structure **I**. Such a molecule has C_s symmetry, with the vibrational representation 11a′ + 7a″, and Table 3 lists the expected fundamental modes. By observing the effects of deuteriation on the vibrational spectra of CH_3SF_3, and by drawing on analogies with the vibrational spectra of related molecules, *e.g.* CH_3SH,[10] CH_3PF_4,[11] $(CH_3)_2PF_3$,[12] SF_4,[8] CF_3SF_3[13] and $FSSF_3$,[14] we have deduced for the molecules CH_3SF_3 and CD_3SF_3 a more or less complete assignment of the vibrational fundamentals with energies in the region 4000–400 cm^{-1}, the details being summarised in Table 3.

Because of the low (C_s) symmetry of the molecules, the descriptions of the modes given in Table 3 are at best only approximate. Several of the vibrations show evidence of strong coupling between different internal coordinates, and must be considered to be hybrid motions. For example, the a′ fundamental ν_6, assigned formally to the $S{-}F_{eq.}$ stretching mode is observed to *increase* in energy by about 3% on deuteriation, whereas the fundamental ν_7, assigned to the S–C stretching mode, displays a shift *larger* than expected on the basis of simple reduced-mass calculations. Such behaviour suggests that there is strong coupling of the relevant coordinates with CH_3 and/or CD_3 rocking coordinates. However, a fuller description of the vibrational properties must await further studies involving, ideally, ^{13}C- and ^{34}S-enrichment followed by a detailed normal coordinate analysis.

(*c*) *Vapour pressure.* As a result of the thermal instability of CH_3SF_3, its vapour pressure, *p*, can be measured only at low temperatures (<273 K). The measurements have been repeated with fresh samples to ensure consistency, and the results are listed in Table 4. Even within the (comparatively generous) limits of experimental error, the results do not give a linear plot of ln *p vs.* $1/T$. It is noteworthy that the vapour pressure/temperature data for HF over a comparable pressure range exhibit similar behaviour.[15] With a viscous liquid such as CH_3SF_3, it is quite possible that the degree of association in the liquid changes significantly as a function of temperature. Extrapolation of the straight line which reproduces best the measured vapour pressures at temperatures approaching 273 K suggests a normal b.p. of 363 ± 10 K. In contrast with the normal b.p.s of SF_4 (235 K[16]) and CF_3SF_3 (266 K[17]), this estimate would seem to leave little doubt that CH_3SF_3 is subject to appreciable hydrogen bonding in the liquid phase.

(*iii*) *Chemical Properties of Methylsulphur Trifluoride.*—The chemical properties of CH_3SF_3 established in the present exploration are summarised in Scheme 1. Of particular note is the extent to which the chemistry is dominated by the thermal frailty of the compound, so that only reactions which occur in the order of minutes at ambient temperatures can compete with decomposition. The following reactions warrant further discussion.

(*a*) *Thermal decomposition.* Samples of liquid CH_3SF_3 decompose completely over a period of minutes at ambient temperatures to give a white waxy solid insoluble in common solvents, together with hydrogen fluoride (identifiable by its IR spectrum[18]) as the only volatile product. The decomposition of CH_3SF_3 in either CCl_3F or CD_2Cl_2 solution, which proceeds to

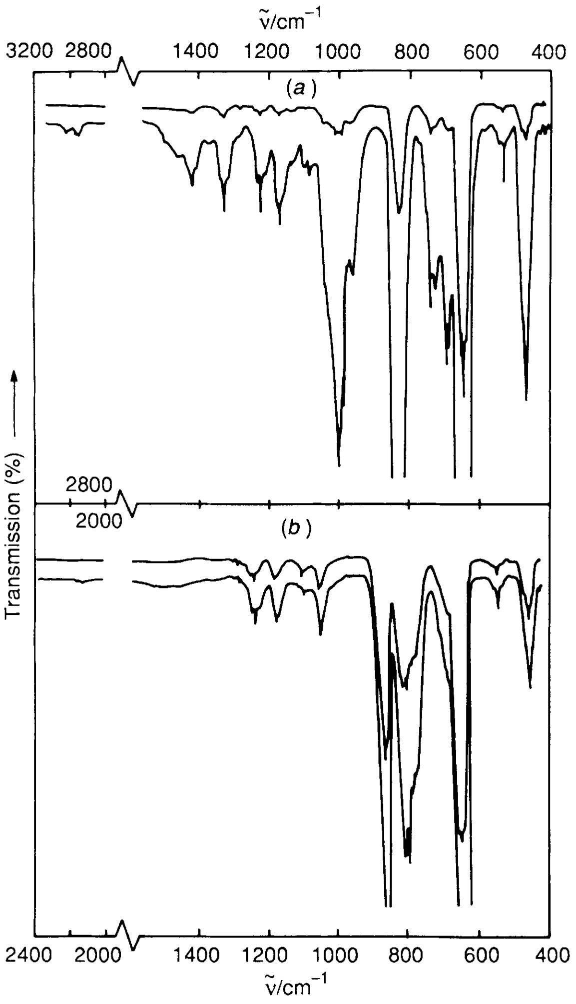
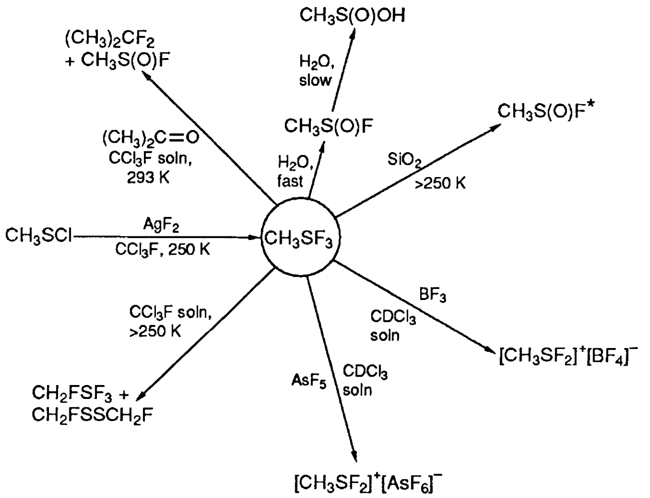


Fig. 2 IR spectra of the vapours of (*a*) CH_3SF_3 and (*b*) CD_3SF_3; pressure 2–10 mmHg, pathlength 10 cm and temperature *ca.* 293 K



Scheme 1 The formation and some reactions of CH_3SF_3. * Undergoes subsequent disproportionation (see text).

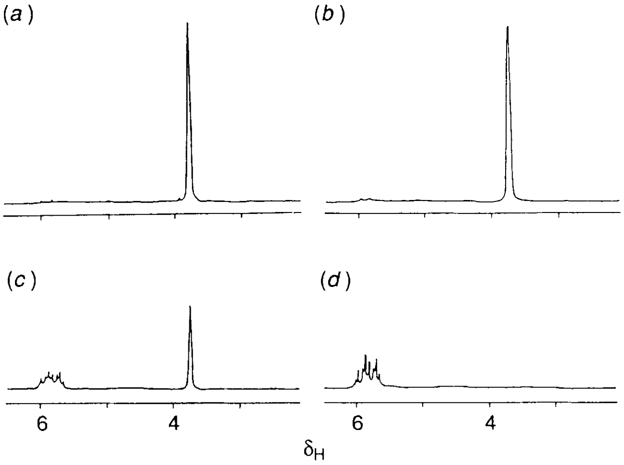


Fig. 3 Thermal decomposition of CH_3SF_3 in CCl_3F solution at 293 K as revealed by the ^1H NMR spectrum (300 MHz): (*a*) initially, (*b*) after 5, (*c*) after 10 and (*d*) after 15 min

completion over a period of *ca.* 15 min at 293 K, can be observed conveniently by ^1H NMR measurements (see Fig. 3). The lifetime of such a solution can be extended somewhat by the inclusion of a small amount of CsF to minimise the effects of HF-induced catalysis. Table 5 lists the ^1H and ^{19}F NMR parameters associated with the decomposition products. Hence it appears that the products are CH_2FSF_3, not reported previously, and CH_2FSSCH_2F formed presumably in accordance with equation (2). The compound CH_2FSF_3, whose NMR

$$\begin{tikzcd} CH_3SF_3 \arrow[r, "slow", "-HF"'] & {[CH_2{=}SF_2]} \arrow[r, "fast"] & CH_2FSF \arrow[d, "fast"', "disproportionation"] \\ & & \tfrac{1}{3}CH_2FSF_3 + \tfrac{1}{3}CH_2FSSCH_2F \end{tikzcd} \quad (2)$$

properties imply a structure analogous to that of CH_3SF_3, appears to be long lived in solution at ambient temperatures, but decomposes to a white waxy solid on removal of the solvent.

(*b*) *Reactions with glass and water.* As monitored by NMR and IR spectroscopic measurements, the reaction of CH_3SF_3 with glass at temperatures >250 K is rather complex, the methanesulphinyl fluoride produced initially disproportionating into methanesulphonyl fluoride and methanesulphenyl fluoride [equation (3)].[21] The extremely reactive and thermally unstable

$$2\,CH_3S(O)F \longrightarrow CH_3SO_2F + [CH_3SF] \quad (3)$$

sulphenyl fluoride could not be recognised as such, but was presumed to be responsible for the formation of several other unidentified products *via* further disproportionation [*cf.* equation (2)] and /or reactions with glass. Similar methods have also been used to chart the hydrolysis of CH_3SF_3 using a limited supply of water, which has been shown to proceed in two stages, as in equation (4).[21,22]

$$CH_3SF_3 \xrightarrow[\text{fast, }-2HF]{H_2O} CH_3S(O)F \xrightarrow[\text{slow, }-HF]{H_2O} CH_3S(O)OH \quad (4)$$

(*c*) *Reactions with fluoride ion donors and acceptors.* The powerful Lewis acids BF_3 and AsF_5 abstract a fluoride ion from CH_3SF_3 to yield the difluoro(methyl)sulphonium cation, $[CH_3SF_2]^+$. The reactions, carried out typically in $CDCl_3$ solution at ambient temperatures, yield white solids with the composition $CH_3SF_3{\cdot}A$ (A = BF_3 or AsF_5) which are long lived and have negligible dissociation pressures at room temperature. The formation of the cation $[CH_3SF_2]^+$ is demonstrated clearly by the ^1H and ^{19}F NMR spectra of solutions, for example in anhydrous hydrogen fluoride, as illustrated in Fig. 4, and with the parameters listed in Table 6.

For a fuller characterisation of the adducts $CH_3SF_3{\cdot}A$ in the solid state and in hydrogen fluoride solution, we have examined their vibrational spectra, and the results are summarised in Table 7. In practice, the Raman spectra of the samples, contained in Teflon-FEP cells, provided the more reliable

Table 2 Vibrational spectral data ($\tilde{\nu}$/cm^{-1}) for CH_3SF_3 and CD_3SF_3 in the region 4000–200 cm^{-1} *

CH_3SF_3						CD_3SF_3				
	Solid matrix at *ca.* 14 K		Solid at 77 K				Solid matrix at *ca.* 14 K		Solid at 77 K	
Vapour, IR	IR (Ar)	IR (N_2)	IR	Raman	Assignment	Vapour, IR	IR (Ar)	IR (N_2)	IR	Raman
3022vw			3070w	3066s	ν(C–H)/ν(C–D)	2363vw		2306w	2305w	2301s
			3034w	3033s				2273w	2275w	2277s
2932vw			2955w	2947s		2325vw		2155w	2153w 2139w	2154s
2061w			2052w		1329 + 735					
					$CD_3S(O)F$ imp.	1223w	1210w	1211w		
1426w	1418w	1415w	1415w	1415m	δ(CH_3)/δ(CD_3)	1164w	1133w	1128w	1140w	
1341w						1038m	1035m	1039m	1035m	1032w
1329w	1324w	1329w	1329w			1032m	1020m	1019m	1020m	1023w
1224w	1211w	1210w			$CH_3S(O)F$ imp.					
					ν(S–C) + ν(S–F$_{eq.}$)	855s	847s	857s	841s	820m
1006m	1003m	1003m	1012m	1011w	ρ(CH_3)/ρ(CD_3)	801s	790s	790s	795s	
987m	982m	985m	988m	992w		787s	773s	772s	769s	767s
827s	823s	821s	813s	834m 816m	ν(S–C) + ν(S–F$_{eq.}$)					
735w	728w	728w	730w	731vs	ν(S–C) + ν(S–F$_{eq.}$)	669w		668w	672w	669vs
668m	665m	660m			2 × 335					
647vs	623vs	618vs	577vs (br)		ν(S–F$_{ax.}$)	641vs	619vs	613vs	559vs (br)	556w
527w	516w	519w	489w	521m		526w		511w	490m	529m 500m
463m	455m	458m	448s	494m 474s 452m	δ(CSF_3) and ρ(CSF_3)	437m	432m	434m	425s	467s 451m 428m
	338w	340w		394m 330m 241m			336m	336m		355m 234m

* s = Strong, m = medium, w = weak, v = very, br = broad and imp. = impurity.

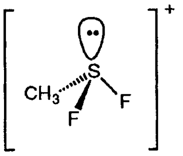
Table 3 Proposed assignment of the vibrational fundamentals of the molecules CH_3SF_3 and CD_3SF_3

			$\tilde{\nu}^a$/cm^{-1}		
Symmetry class	Approximate description of mode	Number	CH_3SF_3	CD_3SF_3	$\tilde{\nu}_H/\tilde{\nu}_D$
a′	Antisym. ν(C–H)/ν(C–D)	ν_1	3022	2363	1.279
	Sym. ν(C–H)/ν(C–D)	ν_2	2932	2325	1.261
	Antisym. δ(CH_3)/δ(CD_3)	ν_3	1426	1164	1.225
	Sym. δ(CH_3)/δ(CD_3)	ν_4	329	1032	1.288
	ρ(CH_3)/ρ(CD_3)	ν_5	1006	801	1.256
	ν(S–F$_{eq.}$) + ν(S–C)	ν_6	827	855	0.967
	ν(S–C) + ν(S–F$_{eq.}$)	ν_7	735	669	1.099
	Sym. ν(S–F$_{ax.}$)	ν_8	527	526	1.002
	δ(F$_{eq.}$–S–C) + δ(F$_{ax.}$–S–F$_{ax.}$)	ν_9	463	437	1.059
	CSF_3 rocking	ν_{10}	338^b	336^b	1.006
	δ(F$_{ax.}$–S–F$_{ax.}$) + δ(F$_{eq.}$–S–C)	ν_{11}	241^b	234^b	1.030
a″	Antisym. ν(C–H)/ν(C–D)	ν_{12}	3022	2363	1.279
	Antisym. δ(CH_3)/δ(CD_3)	ν_{13}	1341	1038	1.292
	ρ(CH_3)/ρ(CD_3)	ν_{14}	987	787	1.254
	Antisym. ν(S–F$_{ax.}$)	ν_{15}	647	641	1.009
	F$_{eq.}$–S–C wagging	ν_{16}	*ca.* 400^c	*ca.* 400^c	—
	CSF_3 twisting	ν_{17}	*ca.* 400^c	*ca.* 400^c	—
	CH_3/CD_3 torsion	ν_{18}	*ca.* 200^c	*ca.* 200^c	—

^{a} Spectra of the vapours unless indicated otherwise. ^{b} Spectra of the solids. ^{c} Not observed; estimated value based on the results of refs. 8 and 9.

results; for solid samples sandwiched between AgCl windows only was it possible to record any IR spectra and these were invariably of relatively poor quality, with broad and rather ill defined absorptions. There is no doubt that certain bands in both the Raman and IR spectra originate in vibrations of the anions $[BF_4]^-$[26] and $[AsF_6]^-$[27] and that the remaining features are more or less common to all the samples studied. Several of these features arise from internal vibrations of the methyl group which can be identified by analogy with spectroscopically well characterised species such as CH_3SH[7] and CH_3PF_2.[9] Of more immediate interest, however, are the vibrational properties of the CSF_2 skeleton of the $[CH_3SF_2]^+$ unit.

In common with the isoelectonic species CH_3PF_2, the $[CH_3SF_2]^+$ ion may be expected to have a trigonal pyramidal framework **II** with C_s symmetry. In these circumstances the CSF_2 skeleton has six vibrational fundamentals spanning the representation 4a′ + 2a″. We have been guided by the



II

assignments proposed for the CH_3PF_2 molecule by Durig *et al.*[9] on the basis of studies encompassing the vapour and condensed phases and a normal coordinate analysis. In energy terms, the fundamentals of the cation $[CH_3SF_2]^+$ are expected to be similar to, if anything slightly higher than, the corresponding modes of CH_3PF_2, although the picture is clouded somewhat by the effects of solvation and of fluorine bridges linking the cation and anion in the solid adducts.[3,28] Such an analogy suggests that the scattering at 860–910, 700–720 and 600–620 cm^{-1} in the Raman spectra of the CH_3SF_3 adducts corresponds mainly to the three stretching vibrations of the CSF_2 skeleton. Detailed assignments are complicated by mixing, not only between the S–C and symmetric S–F stretching fundamentals (both of a′ symmetry), but also between the skeletal stretching and CH_3 rocking fundamentals (in both a′ and a″ symmetry).[9] It follows that any simple description of the modes relates, at best, to the coordinate making the major contribution to the potential energy. The remaining (low-energy) fundamentals involve three deformation modes of the CSF_2 skeleton (2a′ + a″) and the CH_3 torsional mode (a″); tentative assignments are given in Table 7. Our interpretation is broadly in line with the vibrational analysis of CH_3PF_2,[9] although confirmation must await more detailed studies, including, ideally, information about the deuteriated adducts CD_3SF_3·A (A = BF_3 or AsF_5) as well as normal coordinate analysis calculations.

Fluoride ion abstraction from CH_3SF_3, as from the parent SF_4, is more easily engineered than fluoride ion donation to the molecule. Attempts to generate the tetrafluoro(methyl)sulphate(1 −) anion, $[CH_3SF_4]^-$, by the reaction of CH_3SF_3 with various fluoride sources, *e.g.* tetraalkylammonium fluorides or nitrosyl fluoride, have so far failed to yield conclusive and reproducible evidence of its existence.

Table 4 Vapour pressure (*p*) *vs.* temperature (*T*) measurements for liquid CH_3SF_3

T/K	$T^{-1}/10^{-3}$K^{-1}	p/mmHg	ln p
228.1	4.384	1.2	0.182
240.1	4.165	2.6	0.956
249.6	4.006	4.5	1.504
260.1	3.845	5.9	1.775
273.1	3.662	8.1	2.092

(*d*) *Reaction with acetone.* One of the most useful reactions of SF_4 in synthetic terms is its ability to effect difluorination of organic carbonyl groups.[29] Phenylsulphur trifluoride, $C_6H_5SF_3$, is also capable of such a reaction at ambient temperatures.[30] The reaction with acetone therefore offers a suitable test of whether CH_3SF_3 has the capacity to undergo any 'useful' chemistry before the onset of decomposition.

We have found that CH_3SF_3 reacts with acetone in CCl_3F solution [the sample having the composition $CH_3SF_3:(CH_3)_2CO:CCl_3F$ = *ca.* 1:5:30] at room temperature. The ^1H and ^{19}F NMR spectra of the solution show, over a period of *ca.* 1 h, the decay of the resonances due to CH_3SF_3 with the simultaneous appearance and growth of features associated with two products, X [characterised by δ_H 1.90, δ_F −92.1 ppm, and ^3J(FH) 17.9 Hz] and Z [characterised by δ_H 3.73, δ_F −10.5 ppm, and ^3J(FH) 17.4 Hz]. The NMR properties serve to identify X as 2,2-difluoropropane, $(CH_3)_2CF_2$,[31] and Z as methanesulphinyl fluoride, $CH_3S(O)F$,[21] formed in equimolar proportions in accordance with equation (5). Additional weak resonances in the ^1H NMR spectrum in the region δ 5.5–6.0 attest to the fact that decomposition competes to some extent under these conditions with the metathesis (5).

$$\mathrm{CH_3SF_3 + CH_3COCH_3 \xrightarrow{CCl_3F,\ 293\ K} CH_3S(O)F + CH_3CF_2CH_3} \quad (5)$$

Experimental

Apparatus.—All manipulations were carried out in a vacuum system constructed in Teflon-FEP tubing with Teflon-PTFE couplings and needle valves (Production Techniques Ltd.). The apparatus was conditioned prior to use by exposure for 8–12 h to fluorine gas at a pressure of 1 atm. A conventional glass vacuum system was available for the purification of $CFCl_3$, $CDCl_3$ and CD_2Cl_2 (all supplied by Aldrich). A nitrogen-

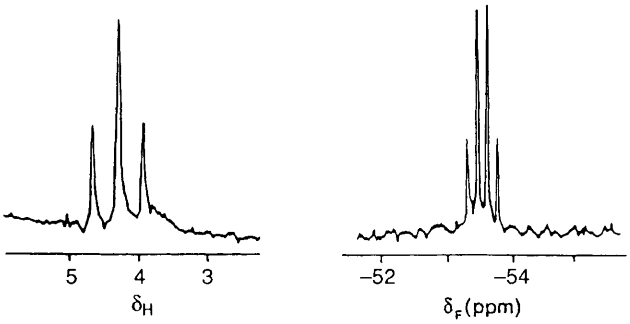


Fig. 4 Proton (*a*) and ^{19}F (*b*) NMR spectra of $[CH_3SF_2]^+[BF_4]^-$ in HF solution at *ca.* 305 K (measured at 60 and 84.6 MHz, respectively)

Table 5 NMR properties of the primary decomposition products of CH_3SF_3

Compound	Conditions	δ(H)	δ(F) (ppm)	^2J(FH)/Hz	^2J(FF)/Hz	Reference
CH_3SF_3	CCl_3F soln., 293 K	3.78	−52.8 (SF) +63.1 (SF_2)	—	71.4	This work
Decomposition product 1 (CH_2FSF_3)	CCl_3F soln., 293 K	5.88	−192.6 (CH_2F) −57.8 (SF) +39.0 (SF_2)	52.0	78.6	This work
Decomposition product 2 (CH_2FSSCH_2F)	CCl_3F soln., 293 K	5.88	−192.8 (CH_2F)	53.0	—	This work
CH_2FSSCH_2F	Neat liquid, 223 K	5.62	−182.6 (CH_2F)	51.3	—	19
CF_3SF_3	Neat liquid, 300 K	—	−70.3 (CF_3) −48.3 (SF) +44.1 (SF_2)	—	65.8	6,20
SF_4	Neat liquid, 223 K	—	+34.1 ($SF_{eq.}$) +88.4 ($SF_{ax.}$)	—	78.7	7

Table 6. NMR parameters for the difluoro(methyl)sulphonium cation, $[CH_3SF_2]^+$, and related species

Species	Conditions	δ(H)	δ(F)/(ppm)	J(FH)/Hz	Reference
$[(CH_3)_3S]^+$	D_2O soln., room temperature	2.96	—	—	23
$[(CH_3)_2SF]^+$	HF soln., 300 K	3.73	−190.7	20.7	3
$[CH_3SF_2]^+$	HF soln., 300 K	4.3	−53	24	This work
$[SF_3]^+$	HF soln., 183—298 K	—	−25 to −30	—	24
CH_3PF_2	Neat liquid, room temperature	1.41	−92.9	20	25

Table 7 Vibrational spectral data ($\tilde{\nu}$/cm^{-1})[a] for the adducts $CH_3SF_3{\cdot}BF_3$ and $CH_3SF_3{\cdot}AsF_5$

CH_3PF_2[b]	$CH_3SF_3{\cdot}BF_3$			$CH_3SF_3{\cdot}AsF_5$		
IR + Raman	HF soln., Raman	Solid, Raman	Solid, IR	Solid, Raman	Solid, IR	Assignment
2992, 2996	3040w	3026w	3040m	3021m	3036m	Antisym. ν(C–H), ν_1 (a′), ν_{10} (a″)
2915	2940s	2930m	2940w	2936m	2938w	Sym. ν(C–H), ν_2 (a′)
			2630w			2 × 1314
					2550w (br)	1315 + 1251
			2189w			$[BF_4]^-$, $2\nu_3$
			2023w			1401 + 620
1417, 1405			1401m		1397m	Antisym. $\delta(CH_3)$, ν_3 (a′), ν_{11} (a″)
1292			1314m		1315m	Sym. $\delta(CH_3)$, ν_4 (a′)
			1288m			$[BF_4]^-$, $\nu_1 + \nu_4$
					1251m (br)	$[AsF_6]^-$, $\nu_1 + \nu_2$
					1123m	$[AsF_6]^-$, $2\nu_2$
			1084s (br)			$[BF_4]^-$, ν_3
889					983m	$\rho(CH_3)$, ν_5 (a′)
					956w	$[AsF_6]^-$, $\nu_2 + \nu_5$
					928w	492 + 423
859	905s		901s	894m	876m	$\rho(CH_3)$, ν_{11} (a″)
812		865m (br)	866s		825m	Sym. ν(S–F), ν_6 (a′)
	780m	761m	765m			$[BF_4]^-$, ν_1
800	700w	715s	720m	736s		Antisym. ν(S–F), ν_{13} (a″)
					707s	$[AsF_6]^-$, ν_3
				685w		$[AsF_6]^-$, ν_1
701	602s		620m		610w	ν(S–C), ν_7 (a′)
				579w	560m	$[AsF_6]^-$, ν_2
	530w	526w	518s			$[BF_4]^-$, ν_4
405		470m			492m	SF_2 wag, ν_8 (a′)
321	430w	433w		442w	458m 423m	SF_2 scissors, ν_9 (a′)
				387m (br)		$[AsF_6]^-$, ν_5
		344w				$[BF_4]^-$, ν_2
278				301w		SF_2 twist, ν_{14} (a″)
192		215s				CH_3 torsion? ν_{15} (a″)

[a] s = Strong, m = medium, w = weak, v = very and br = broad. [b] Ref. 9.

purged glove-box was used for the storage and transfer of solid materials.

IR spectra of gaseous samples were recorded with the vapour contained in a pre-conditioned stainless-steel cell equipped with Teflon-PTFE O-rings and AgCl windows to give a pathlength of 10 cm. Solid deposits of volatile materials were presented for spectroscopic analysis by allowing the vapour to condense on a CsI window (for IR measurements) or a copper block (for Raman measurements) contained in an evacuated glass shroud and maintained at 77 K. Cryogenic matrices were deposited on a CsI window the temperature of which was controlled by a 'Displex' closed-cycle refrigerator (Air Products model CS 202). The temperature of such a sample (typically *ca.* 14 K) was monitored by a hydrogen vapour bulb and/or a chromel *vs.* iron-doped gold thermocouple, and regulated by an Air Products ADP-IC2 temperature control unit. Solids and liquids at ambient temperatures destined for Raman studies were contained in thin-walled Teflon-FEP tubing, due allowance being made for the scattering due to the container.[26a] IR spectra were measured with a Perkin-Elmer model 1710 FTIR or a 580A dispersive spectrometer, with a resolution typically better than 2 cm^{-1}. Raman spectra were excited at λ = 514.5 nm using the output from a Spectra-Physics model 165 Ar^+ laser and measured with a Spex Ramalog 5 spectrophotometer in conjunction with a Glen-Creston SCADAS data-handling system; the resolution was normally *ca.* 5 cm^{-1}.

NMR samples were each sealed in a section of Teflon-FEP tubing 5–10 cm long and 3 mm in external diameter which was inserted into a standard 5 mm precision NMR tube.[32] The spectra were recorded with the aid of four spectrometers, namely a Brüker WH300 (^{1}H, 300 MHz), a JEOL PMX-60 (^{1}H, 60 MHz), a Perkin-Elmer R32 (^{19}F, 84.6 MHz) and a Brüker AM250 (^{1}H, 250 MHz; ^{19}F, 235 MHz), the last of these being used for low-temperature measurements. Chemical shifts were referenced to internal CCl_3F (^{19}F) or to an external 'locking' solvent introduced into the sample (^{1}H or ^{19}F).

Vapour-pressure measurements were made using a 'Baratron' pressure sensor (MKS Instruments, Inc.).

Chemicals.—Methanesulphenyl chloride was prepared by the reaction of dimethyl disulphide with elemental chlorine.[33] [$^3H_6$]Dimethyl disulphide, used as the precursor to [$^2H_3$]-methanesulphenyl chloride, was prepared from [$^2H_4$]methanol and thiourea.[34] Xenon difluoride was synthesised by exposure to sunlight of an equimolar xenon–fluorine mixture,[35] arsenic pentafluoride by the action of elemental fluorine on metallic arsenic in a Monel bomb[36] and nitrosyl fluoride by the action of potassium fluoride on nitrogen dioxide.[37] Acetone (BDH) was purified by an established method involving the formation of an adduct with sodium iodide,[38] and hydrogen fluoride (BDH, 99.8%) by double distillation from Teflon-FEP traps held at 210 K. Otherwise the following chemicals were all used as supplied: elemental fluorine (Air Products), chlorine (BOC), xenon (BOC), boron trifluoride (BDH), nitrogen dioxide (BDH), arsenic (BDH), silver(II) fluoride (Aldrich), red phosphorus (Aldrich), iodine (BDH), thiourea (Aldrich), caesium fluoride (Alfa), potassium fluoride (BDH), dimethyl disulphide (BDH), aniline (BDH) and [$^2H_4$]methanol (Aldrich).

Analysis.—Elemental analyses were performed by the Analytische Laboratorien, Engelskirchen, West Germany on samples sealed *in vacuo* in Teflon-FEP ampoules.

Preparation of Methylsulphur Trifluoride.—In a typical experiment CH_3SCl (500 mg, 6.0 mmol) dissolved in CCl_3F (*ca.* 5 cm^3) reacted with solid AgF_2 (*ca.* 5 g, 35 mmol) in the presence of dry CsF (*ca.* 10 mg) as an HF scavenger, the mixture being maintained at *ca.* 250 K. The initial orange colour of the solution was discharged rapidly with shaking, and there was a simultaneous change in the colour of the solid charge from black to a 'dirty off-white.' Methylsulphur trifluoride was observed to separate out as oily droplets which floated on top of the CCl_3F solution. The liquid was filtered from the solid AgF_2–AgF–AgCl residue *via* a PTFE frit and fractionated *in vacuo* to produce samples of CH_3SF_3 shown to be free from detectable impurity on the evidence of (*i*) the ^1H and ^{19}F NMR spectra of CCl_3F solutions and (*ii*) the IR spectrum of the vapour. Based on equation (1) and the amount of CH_3SCl taken, the yield of pure CH_3SF_3 was 80–90%.

Preparation of $CH_3SF_3{\cdot}BF_3$.—An excess of BF_3 was co-condensed with a solution of CH_3SF_3 in $CHCl_3$. Warming the reaction mixture yielded a white solid which could be separated from the liquid by filtration and freed from volatile materials by pumping [Found: C, 6.8; H, 1.6; B (by difference), 6.8; F, 66.1; S, 18.6. $CH_3SF_3{\cdot}BF_3$ requires C, 7.0; H, 1.8; B, 6.3; F, 66.3; S, 18.6%]. Under rigorously dry conditions, the solid was stable indefinitely, with a negligible dissociation pressure, at room temperature.

Preparation of $CH_3SF_3{\cdot}AsF_5$.—A procedure analogous to that used for the preparation of the BF_3 adduct was adopted with AsF_5 in place of the BF_3. This also gave a white solid which was stable at room temperature, but it was appreciably less soluble in HF than the BF_3 adduct [Found: C, 4.4; H, 1.1; As (by difference), 27.7; F, 55.3; S, 11.6. $CH_3SF_3{\cdot}AsF_5$ requires C, 4.4; H, 1.1; As, 27.3; F, 55.5; S, 11.7%].

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