694. *The Infrared Spectra of Some Compounds containing the Trifluoromethylthio-group,* $CF_3·S·$.

By S. N. NABI and N. SHEPPARD.

The infrared spectra of $CF_3·S·S·CF_3$, $CF_3·SCl$, $CF_3·S·S·C_2H_5$, $(CF_3·S)_3P$, and $(CF_3·S)_2PH$ in the region 4000—400 cm.$^{-1}$ are presented and analysed. Characteristic frequencies of the trifluoromethylthio-group, $CF_3·S·$, are listed.

IN this paper we discuss the infrared spectra of a series of molecules containing the $CF_3·S·$ group. Examples are included in which the trifluoromethyl–sulphur group is attached to sulphur, chlorine, or phosphorus atoms. We first interpret a series of absorption bands that are common to the whole series of molecules and are, therefore, associated specifically with the $CF_3·S·$ group; other features in the spectrum of the individual molecules will then be discussed. Three typical spectra are shown in the Figure.

(*A*) *Characteristic Absorption Bands of the* $CF_3·S·$ *Group*.—All the compounds studied have prominent bands in the regions 1205—1155, 1135—1095, 765—750, 570—540, and 495—445 cm.$^{-1}$; these are listed in the Table (together with some less prominent, but persistent, overtone and combination bands) where they are compared with the closely analogous frequencies of CF_3Cl. The spectrum of trifluoromethyl chloride has been analysed in detail with the help of band contours in the infrared spectrum and polarisation measurements of the Raman lines.[1,2] It can, therefore, be used as a reliable guide for the assignments of the characteristic frequencies of the $CF_3·S·$ group to specific modes of vibration. The regularities in the spectral data are self-evident and the appropriate assignments of the bands to particular vibrations of the $CF_3·S·$ group are given in the Table. It should be noted, as in the case of CF_3Cl, that there is some mixing of the symmetrical CF_3 deformation and C–S (C–Cl) stretching modes of vibration. The frequencies of the $CF_3·S·$ group in the spectrum of $CF_3·S·S·CF_3$ have been discussed previously by

---

[1] Plyler and Benedict, *J. Res. Nat. Bur. Stand.*, 1951, **47**, 2245.

[2] Edgell and May, *J. Chem. Phys.*, 1954, **22**, 1808.

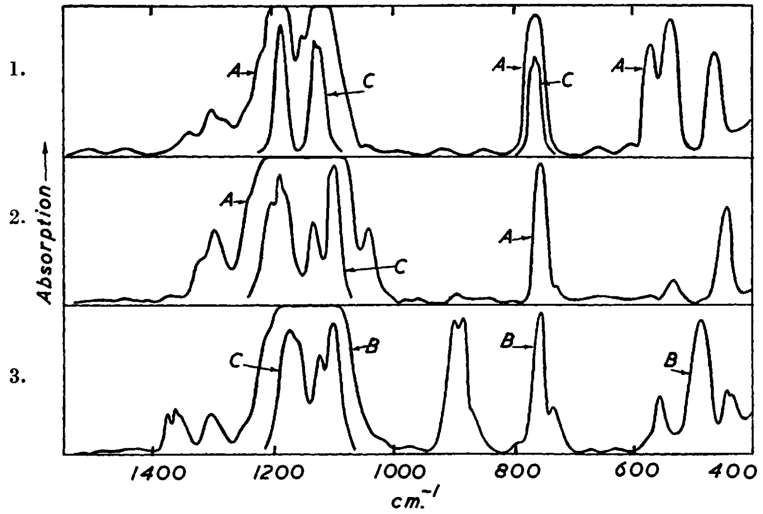
Characteristic frequencies in infrared spectra of $CF_3{\cdot}S{\cdot}$ *groups compared with those of* CF_3Cl.

Vibrational assignments	Frequencies (cm.$^{-1}$)					
	CF_3Cl *	$CF_3{\cdot}SCl$	$CF_3{\cdot}S{\cdot}S{\cdot}CF_3$	$CF_3{\cdot}S{\cdot}S{\cdot}C_2H_5$	$(CF_3{\cdot}S)_3P$	$(CF_3{\cdot}S)_2PH$
C–F stretch (asym), ν_4	1212	1189	1205 1109	1158	1180 1170	1177
C–F stretch (sym), ν_1	1104	1133	1133 1095	1117	1127 1095	1125 1103
CF_3 deform (sym), ν_2	782	764	755	750	755	755
CF_3 deform (asym), ν_5	562	570	540	543	560	558
C–S (C–Cl) stretch, ν_3	474	468	447	452	487	492
CF_3 rock, ν_6	356	← Region not investigated →				
$2\nu_4$	2417	2360	2400	—	—	—
$\nu_4 + \nu_1$	2315	2310	2290	2275	2260	2285
$2\nu_1$	—	2250	2230	2220	—	—
$\nu_4 + \nu_2$	1984	1948	1943	1960?	1940	—
$\nu_1 + \nu_2$	1887	1885	1887 1854	1870	1885 1850	1860
$\nu_2 + \nu_5$	1335	1305	1300	1285	1318	1302

* Mean values for fundamentals taken from references (1) and (2); overtones and combination frequencies from ref. (1).

Brandt, Emeléus, and Haszeldine[3] and Haszeldine and Kidd.[4] Except for the lower-frequency bands in the potassium bromide region for which more definite experimental data have now been obtained, the earlier assignments agree with the present ones. The C–S stretching frequency of the $CF_3{\cdot}S{\cdot}$ group (490 cm.$^{-1}$) may be compared with the value of 708 cm.$^{-1}$ in methanethiol.[5] Although the difference in frequency is considerable, the type of coupling of this vibration with others of the same symmetry is also markedly different in the two cases. For this reason no reliable conclusions on the relative force constants of the bonds can be made without detailed normal-co-ordinate calculations.

Infrared spectra of 1, $CF_3{\cdot}SCl$; 2, $CF_3{\cdot}S{\cdot}S{\cdot}CF_3$; *and* 3, $(CF_3{\cdot}S)_2PH$. *Curves labelled A are for a pressure of* 50 *mm., those labelled B for* 22 *mm., and those labelled C for* 1 *mm., or less in the case of curve* 1.



(*B*) *Features in the Infrared Spectra of Specific Molecules*.—(1) *Bistrifluoromethyl*

---

[3] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2549.

[4] Haszeldine and Kidd, *J.*, 1953, 3219.

[5] Scott and McCullough, *J. Amer. Chem. Soc.*, 1958, **80**, 3554.

disulphide, $CF_3{\cdot}S{\cdot}S{\cdot}CF_3$. Our spectrum (Figure) agrees well with that determined previously,[3,4] except that a previously reported band of medium strength at 1530 cm.$^{-1}$ (6·53 μ) is not present, and a better-defined spectrum has been obtained below 500 cm.$^{-1}$. No additional band is observed in the potassium bromide region of sufficient strength for a confident assignment to be made of the S–S stretching frequency.

(2) *Trifluoromethanesulphenyl chloride,* $CF_3{\cdot}SCl$. Our spectrum (Figure) agrees well with that previously recorded by Kidd [4,6] in the region 4000—650 cm.$^{-1}$. A strong band at 535 cm.$^{-1}$ additional to those listed in the Table can be assigned with confidence to the S–Cl stretching frequency. For comparison, the coupled S–S and S–Cl stretching frequencies of S_2Cl_2 occur at 538, 448, and 438 cm.$^{-1}$ [7] and the S–Cl frequency of $CCl_3{\cdot}SCl$ lies at 532 cm.$^{-1}$.[8]

(3) *Ethyl trifluoromethyl disulphide,* $CF_3{\cdot}S{\cdot}S{\cdot}C_2H_5$. In addition to the bands of the $CF_3{\cdot}S{\cdot}$ group listed in the Table a number of other medium or strong features appear which can be assigned as follows to vibrations of the $C_2H_5{\cdot}S{\cdot}$ group:[5] 2975, 2940, 2890 (C–H stretch); 1462, 1452 (δCH_3 asym. and δCH_2 bend); 1382 (δCH_3 sym.); 1315 (CH_2 twist); 1263 (CH_2 wag); 1045 (CH_3 rock?); 962 (C–C stretch); 643 (C–S stretch). A weak band at 520 cm.$^{-1}$ may represent the S–S stretching frequency but this is less certain.

(4) *Tris(trifluoromethylthio)phosphine,* $(CF_3{\cdot}S)_3P$. In addition to the $CF_3{\cdot}S{\cdot}$ frequencies in the Table a weak shoulder occurs at 467 cm.$^{-1}$ in the potassium bromide region which may be caused by a P–S stretching vibration.

(5) *Bis(trifluoromethylthio)phosphine,* $(CF_3{\cdot}S)_2PH$. The spectrum (Figure) shows additional bands at 2320 cm.$^{-1}$ (weak) and at 894 cm.$^{-1}$ (a doublet of spacing 13 cm.$^{-1}$, strong) which are almost certainly caused by P–H stretching and angle deformation modes of vibration respectively. In dimethylphosphine, $(CH_3)_2PH$,[9] and bistrifluoromethylphosphine, $(CF_3)_2PH$,[10] the P–H stretching frequencies are at 2290 and 2300 cm.$^{-1}$ and the PH deformation frequencies at 1000 and 850 cm.$^{-1}$ (a doublet) respectively. A medium-strength band at 440 cm.$^{-1}$ may represent a P–S stretching vibration frequency in $(CF_3{\cdot}S)_2PH$.

Experimental.—The method of preparation of the compounds is described elsewhere.[4,11] The spectra were recorded by use of a Perkin–Elmer Model 21 double-beam spectrometer with sodium chloride and potassium bromide prisms. The substances were examined as vapours in a 10 cm. cell having either sodium chloride or potassium bromide windows.

We thank Professor H. J. Emeléus, F.R.S., for his interest and encouragement. One of us (S. N. N.) is indebted to the Royal Commission for the Exhibition of 1851 for an Overseas Scholarship and also to the Government of Pakistan for supplementary grants.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, May 8th,* 1959.]

[6] Kidd, Ph.D. Dissertation, Cambridge, 1953.
[7] Bernstein and Powling, *J. Chem. Phys.*, 1950, **18**, 1018.
[8] Ketelaar and Vedder, *Rec. Trav. chim.*, 1955, **74**, 1482.
[9] Beachell and Katlafsky, *J. Chem. Phys.*, 1957, **27**, 182.
[10] Bennett, Ph.D. Dissertation, Cambridge, 1953.
[11] Emeléus and Nabi, forthcoming publication.