935. *High-resolution Nuclear Magnetic Resonance Spectra of Pentafluorosulphur Compounds.*

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The ^{19}F nuclear magnetic resonance spectra of pentafluorosulphur phenoxide, SF_5OPh, and chloride, SF_5Cl, were examined as examples of the AB_4 nuclear magnetic system with markedly different values for the ratio of the coupling constant, J_{AB}, to the chemical shift, δ_{AB}. The nuclear magnetic resonance spectrum of a newly prepared molecule, probably $SF_5{\cdot}O{\cdot}SO_2F$, was consistent with that of an AB_4X system.

THE pentafluorosulphur (SF_5) group contains two different types of fluorine atom. The stereochemistry is based on a pyramid, and the unique atom at the apex is known as the axial fluorine. The other four fluorine atoms are stereochemically and magnetically equivalent, and are said to be equatorial; thus the SF_5 compounds studied in this work give spectra characteristic of the AB_4 nuclear magnetic system.[1] This system has been

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[1] Pople, Schneider, and Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, 1959.

studied theoretically by several authors,[2,3] usually using the symmetry properties to simplify the Hamiltonian. The theory has been applied to perfluoroalkyl derivatives of SF_6 containing the SF_5 group by Muller, Lauterbur, and Svatos.[4]

Experimental.—Pentafluorosulphur fluorosulphonate, $SF_5\cdot O\cdot SO_2F$, was obtained by photochemical reaction of disulphur decafluoride with sulphur dioxide.[5] The infrared spectrum in the range 4000—400 cm.$^{-1}$, the ^{19}F nuclear magnetic resonance spectrum, the molecular weight, and chemical analysis are consistent with the above formulation. The other two compounds were kindly supplied by Imperial Chemical Industries Limited, Alkali Division.

The spectra were obtained at 40 Mc./sec. by using a Varian Associates V4300A nuclear magnetic resonance spectrometer and 12″ electromagnet with flux stabilisation, sample spinning, and a Varian V4365 field homogeneity control unit. The compounds were dissolved in trichlorofluoromethane and sealed under a vacuum in Pyrex tubes of 5 mm. outside diameter. The concentrations obtained were ~80% by volume for pentafluorosulphur phenoxide, 60% for the chloride, and 16% for the fluorosulphonate. Positions of the unshifted A and B resonances are quoted relative to trichlorofluoromethane.[6] The separations between lines were measured by using side-bands of the compounds themselves, generated by a Muirhead–Wigan D695A decade oscillator. The sweep-rate was somewhat variable at the time that the measurements were made, so that line positions, and the parameters obtained, have the accuracies quoted in Tables 1 and 2. The values are, however, sufficiently accurate for a valid comparison of observed and calculated line positions.

Theoretical Considerations.—In this laboratory, the AB_4 system has been analysed by the "complex particle" method of Whitman *et al.*[7] Details of this analysis will be published later.[8] The basis of the method is that wave functions which are eigenfunctions of I_A^2 or I_B^2 (where I is the total spin angular momentum operator of the group designated) do not mix. The states with $J = 0, \frac{1}{2}, 1, \frac{3}{2}$, and 2 (where J is the eigenvalue of I) are known as singlet, doublet, triplet, quartet, and quintet states, abbreviated to S, D, T, Q, and Qt, respectively. Here the A group has only the D state, but the B group can occur in S, T, or Qt states. The possible overall states for this system are therefore D_AS_B, D_AT_B, and D_AQt_B. These have degeneracies 2, 3, and 1, respectively.[7,8] The matrix representing the Hamiltonian for each state can be written down, and the corresponding frequencies and intensities of transitions calculated separately.[7,8] The degeneracy factor means that DT lines are normally more intense than the others. The appearance of the spectrum (apart from scaling factors) depends solely on the ratio, R, of the coupling constant, J_{AB}, to the chemical shift, δ_{AB}.

The spectra were assigned by a calculation in which an estimated value of R was used. The values of J_{AB} and δ_{AB} can then be measured separately and directly by using the DT and DS lines. The single DS line is at the unshifted resonance of the A nucleus, while lines 23 and 20, 19 and 16, 7 and 4, and 15 and 12 are symmetrically placed about the resonance position of the B nuclei,[9] the first-mentioned line in each case being that nearer to the A lines. The line notation is that of ref. 8, and as denoted in the Figures. Since lines 7 and 4 are sharper than the others (originating from DT state), and also clearly resolved for pentafluorosulphur phenoxide and fluorosulphonate, their centre was used as the unshifted resonance of the B nuclei. The chemical shift between the A and B nuclei was obtained by the equation

$$|\delta_{AB}| = E_1 - E_7 + \tfrac{1}{2}(E_7 - E_4),$$

where E_i is the position in cycles/sec. of the ith line. The coupling constant can be

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[2] Banerjee, Das, and Saha, *Proc. Roy. Soc.*, 1954, *A*, **226**, 490.
[3] Corio, *Chem. Rev.*, 1960, **60**, 363.
[4] Muller, Lauterbur, and Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1043.
[5] Emeléus and Packer, unpublished work.
[6] Filipovich and Tiers, *J. Phys. Chem.*, 1959, **63**, 761.
[7] Whitman, Onsager, Saunders, and Dubb, *J. Chem. Phys.*, 1960, **32**, 67.
[8] Chapman, unpublished work.
[9] Harris, unpublished work.

obtained by direct measurement from several different sets of four or five lines from the DS and DT states, the equations concerned involving no square-root terms. The most convenient proved to be:

$$3|J_{AB}| = 2(E_8 - E_3) - (E_7 - E_4).$$

Once J_{AB} and δ_{AB} have been measured, the complete spectrum can be calculated from the accurate value of R, and compared with the observed spectrum.

Pentafluorosulphur Phenoxide, $SF_5{\cdot}OPh$.—In this case the five-line A spectrum of the AX_4 case has been perturbed to give the theoretical nine lines of the AB_4 case. Likewise, the doublet characteristic of the X nuclei of the AX_4 case has split to give twelve lines. All 21 lines are clearly visible (Fig. 1), but none of the four combination lines is of sufficient intensity to be seen (calculations show that the strongest of these has only 2% of the intensity of the DS line). A value of R of 0·35 was estimated from the spectrum, and an approximate calculation quickly gave the assignment of the lines in the correct order, and with the expected intensity ratios. It can be seen that line 13 has crossed line 1 from its AX_4 position—this is the only example of such a crossing in the three molecules studied. Lines 1,3,4,7,and 8 were then used to measure J_{AB} and δ_{AB} directly. The complete calculated and observed spectra were in good agreement (Fig. 1 and Tables 1 and 2). The resonance of the equatorial fluorine nuclei occurred to high-field side of the axial nucleus; this is true also for the molecule $SF_5{\cdot}CF_2{\cdot}CF_3$ studied by Muller, Lauterbur, and Svatos,[4] but the opposite result is found for our chloride and fluorosulphonate.

Pentafluorosulphur Chloride, SF_5Cl.—The chemical shift, δ_{AB}, is here much greater than the coupling constant, so that the spectrum is much closer to the AX_4 case than is that of the phenoxide. Nevertheless, all nine lines of the A spectrum are clearly resolved (Fig. 2a). In the B spectrum, however, the lines overlap, so that each line of the original AX_4 doublet appears as a broad quartet (Fig. 2c). R was estimated at 0·06, and a calculation gave the assignment of the lines, as for the phenoxide. This shows that the four most intense peaks in the B spectrum can be assigned partly to the DT lines 7, 9, 4, and 2 (in order of proximity to the A lines), as expected by comparison with the phenoxide. The exact values of J_{AB} and δ_{AB} were then obtained by direct measurement as before.

Pentafluorosulphur Fluorosulphonate, $SF_5{\cdot}O{\cdot}SO_2F$.—This compound has only recently been prepared, and its identity was decided partly by its nuclear magnetic resonance spectrum. The nuclei form an AB_4X system, the chemical shift of the X nucleus (the fluorine of the SO_2F group) from A and B being very large compared with its coupling constants to these nuclei (Table 3). J_{AX} is small ($\sim$0·9 cycle/sec.) and, since the separations in the A spectrum are large, this splitting caused no complications. In the B spectrum, however, the splitting from X (7·2 ± 0·2 cycles/sec.) causes lines to overlap, but it is still no difficult matter to give a complete assignment (Fig. 3). The X spectrum occurs to high-field side of the A lines, and consists of a pentet of doublets, in accordance with the simplified theory. The AB_4 spectrum could be assigned by comparison with the phenoxide, and the values of J_{AB} and δ_{AB} measured as before. The presence of the pentafluorosulphur group was confirmed by the value of J_{AB} (Table 3).

Line Widths.—The line widths at half-maximum height are not the same throughout the spectrum of a given molecule of the AB_4 type. It was found that the DS line is always much sharper than the others, and this fact can be useful in the original assignment of the spectrum. Also, the DT lines are distinctly sharper than the DQt lines, so that peak heights are not good guides to relative intensities. This is well seen in Fig. 1, where the height of line 2 (DT state) is appreciably greater than that of line 11 (DQt state), although the calculated intensities are almost equal.

These observations cannot be explained by the effects of exchange processes or quadrupole relaxation, as in some other examples of line-width differences occurring in a single molecule.[10] Here the differences are probably due to the fact that DS, DT, and DQt

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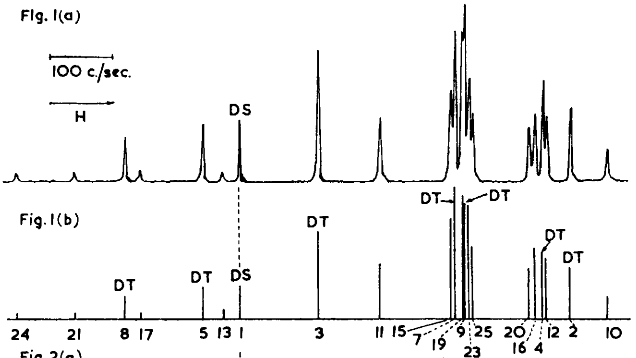
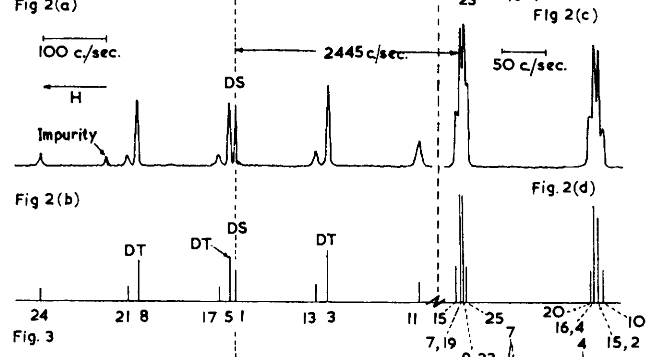
[10] Pople, *Mol. Phys.*, 1958, **1**, 168.

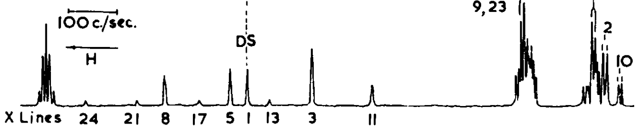
FIG. 1. (a) Observed and (b) calculated spectrum of $SF_5{\cdot}OPh$.

FIG. 2. (a) Observed and (b) calculated A spectrum of SF_5Cl. (c) Observed and (d) calculated B spectrum of SF_5Cl.

FIG. 3. Observed spectrum of $SF_5{\cdot}O{\cdot}SO_2F$.







In Fig. 1, *H* increases in the opposite direction from that of Figs. 2 and 3.

In Fig. 2, the scale of (c) and (d) is different from that of (a) and (b), both horizontally and vertically.

The unmarked lines in Figs. 1(b) and 2(b) arise from the DQt state.

The line numberings are in the notation of ref. 8.

The doublet splitting of the A and X lines of Fig. 3 cannot be observed on this scale.

The line heights are not directly proportional to line intensities owing to the rapid sweep rate.

TABLE 1.

A comparison of calculated and observed line separations[a] in the A spectrum.

The separations of the DQt lines from the unshifted A resonance are given in cycles/sec.

	$SF_5{\cdot}OPh$		SF_5Cl		$SF_5{\cdot}O{\cdot}SO_2F$ [b]	
Line no.	Calc.	Obs.[c]	Calc.	Obs.	Calc.	Obs.[c]
11	222·6	223	290·3	289	260·2	260
13	25·1	26	126·6	126	46·1	46·5
17	156·9	157	26·6	27	105·1	105
21	262·4	264	169·8	171	229·9	229
24	353·2	354	308·2	308	338·9	338

[a] Magnitudes given only. [b] The positions are for the centres of doublets produced by coupling the F atom of the SO_3F group. [c] ±1·5 cycles/sec.

TABLE 2.

Some calculated and observed line separations [a] in the B spectrum [d] in cycles/sec.

State	Line separations	$SF_5 \cdot OPh$ Calc.	$SF_5 \cdot OPh$ Obs.[c]	$SF_5 \cdot O \cdot SO_2F$ [b] Calc.	$SF_5 \cdot O \cdot SO_2F$ [b] Obs.[c]
DT	E_2—E_4	44·1	43·5	24·7	24·5
DT	E_9—E_7	14·6	14·5	12·2	12·0
DQt	E_{10}—E_4	103·6	103·0	56·2	56·0
DQt	E_{25}—E_7	26·6	26·6	22·5	22·5

[a, b] See Table 1. [c] ±1 cycle/sec. [d] Owing to overlapping lines, comparison of observed and calculated positions in the B spectrum of SF_5Cl are best shown in Fig. 2c & d.

TABLE 3.

Nuclear magnetic resonance parameters of pentafluorosulphur compounds.

Compound	J_{AB} (cycles/sec.) *	δ_{AB} (cycles/sec.)	Chemical shift [b] from CCl_3F in parts per million † A	B	$R(=J_{AB}/\delta_{AB})$
SF_5OPh	158·5	410 ± 2	−72·7	−62·6	0·386
SF_5Cl	150	2520 ± 5	−62·3	−125·2	0·0596
$SF_5 \cdot O \cdot SO_2F$ [a]	156	650 ± 2	−55·6	−71·9	0·238
$SF_5 \cdot CF_2 \cdot CF_3$ [4]	145	752	−61·0	−42·2	0·193

* ±1·5 cycles/sec. † ±0·15 p.p.m.

[a] The fluorine atom of the SO_2F groups gives a spectrum centred at −45·1 p.p.m. from CCl_3F. The coupling constant to the axial F atom is 0·9 cycle/sec., and to the equatorial atoms 7·2 cycles/sec. The marked difference between these two coupling constants is probably due to the importance of direct terms (through space rather than through bonds) in fluorine couplings (Petrakis and Sederholm, private communication). [b] It is noteworthy that the resonance position of the equatorial nuclei is much more variable than that of the axial nucleus.

states have different values of T_1, the spin-lattice relaxation time. This time T_1 depends on the probability (per unit time) of a transition's being induced by the random perturbing field, $H(t)$. It can be shown that this probability is a function of $(\psi_2|H|\psi_1)^2$ for a transition from eigenstate ψ_1 to eigenstate ψ_2 (ref. 1, appendix) and will therefore vary with the total spin angular momentum operator, I, of the molecule. Thus, T_1 will differ for the states DS, DT, and DQt, decreasing as I increases.[11, 12] This would account for the observed line-width differences. In general, in an AB_n system, if n is even, there will be a single line in the A spectrum, narrower than the others, arising from the D_AS_B state. The extreme sharpness of such a DS line has been noted by several authors.[7, 11, 13] For the A_mB_n system, this situation will occur if either m or n is even. If both are even, there will be such a line in both the A and the B part of the spectrum. These facts can be of great use in analysing such a spectrum, if the separate lines are resolved.

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[11] Anderson and Arnold, *Discuss. Faraday Soc.*, 1955, **19**, 226.

[12] Abragam, " The Principles of Nuclear Magnetism," Oxford Univ. Press, 1961.

[13] Sheppard and Turner, *Mol. Phys.*, 1960, **3**, 168.