CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

High-Resolution Nuclear Magnetic Resonance Spectra of the Pentafluorosulfur Group

BY C. I. MERRILL, S. M. WILLIAMSON, G. H. CADY, AND D. F. EGGERS, JR.

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High-resolution n.m.r. spectra have been obtained for a number of substances containing the pentafluorosulfur group ($-SF_5$). Because of a large coupling constant between fluorine atoms within this group, complex spin–spin interaction effects have been observed over a wide range of J/δ values. Line positions in these spectra are in excellent agreement with those calculated by the aid of an I.B.M. 709 computer using an AB_4 or square pyramidal model for the fluorine atoms in the pentafluorosulfur group. Graphs are given representing the experimental and calculated spectra. In addition, there is presented a graphical method of estimating rather precisely the values of δ, J/δ, and line positions in the spectra of AB_4 n.m.r. systems having J/δ values in the range 0.15 to 0.7.

Muller, Lauterbur, and Svatos[1] found that the n.m.r. spectrum for the pentafluorosulfur group in various perfluoroalkyl derivatives of sulfur hexafluoride was more complex than would be expected for a first order spin–spin interaction between two types of fluorine atoms in a square pyramidal arrangement. The expected spectrum from simple considerations would consist of two multiplets, one a doublet with a separation of J (spin coupling constant) cycles per second and the other a quintet with a separation of J c.p.s. The separation of the two multiplets would be the chemical shift, δ, between the two types of magnetically non-equivalent fluorine atoms. The above authors observed and explained, by calculation using the method of McConnell, McLean, and Reilly,[2] nine resonance frequencies for which the apex fluorine atom was responsible, and two broad resonance frequencies for which the fluorine atoms of the base of the square pyramid were responsible.

We also have observed for the AB_4 n.m.r. system both in experimental and calculated spectra of $-SF_5$ derivatives nine distinct resonances due to the apex (or A) fluorine atom and we have found that each part of the doublet due to the four equivalent base (or B) atoms is further split into six "peaks" to give a total of 21 discrete resonance frequencies. The calculations of the n.m.r. spectra for the AB_4 model were accomplished by the use of a generalized seven-spin program written for the I.B.M. 709 high speed digital computer.[3a] The data obtained from this program were in the form of single frequency lines of computed intensity.[3b]

Experimental

A Varian Model 4311B high-resolution n.m.r. spectrometer employing a 40 Mc. oscillator was used to acquire all of the spectra presented here. Samples for this study were placed in sealed 5-mm. o.d. Pyrex tubing. Some caution had to be exercised in sealing and using the sample tubes because the internal standard, sulfur hexafluoride, can develop about 25 atm. vapor pressure at the temperature (~25°) at which the spectra were taken.

Discussion

In order to readily analyze an experimental n.m.r. spectrum of an $-SF_5$ derivative, theoretical spectra first were computed for various values of the J/δ ratio using a constant value of J of 150 c.p.s., which is nearly the correct value for J_{AB} for the $-SF_5$ group. In order to identify the lines an arbitrary numbering system was set up, so that when all 21 lines were distinct at about $J/\delta = 0.25$ the extreme line due to the apex (or A) fluorine atom was line 1. The others were numbered in increasing order in the direction going toward the lines caused by the four equivalent (or B) fluorine atoms. When making computations the value zero on the c.p.s. scale was taken as the center of the resonance "peaks" due to the four B fluorine atoms.

An examination of a theoretical, computed spectrum showed that line 6 was the center of the

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[1] N. Muller, P. C. Lauterbur, and G. F. Svatos, *J. Am. Chem. Soc.*, **79**, 1043 (1957).

[2] H. M. McConnell, A. D. McLean, and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

[3] (a) Program furnished by Prof. K. B. Wiberg, University of Washington; (b) after submission of this article for publication, R. K. Harris and K. J. Packer published results [*J. Chem. Soc.*, 4736 (1961)] obtained from the n.m.r. spectra of $C_6H_5OSF_5$, SF_5Cl, and SF_5OSO_2F. Their values of J and δ for the latter two examples are similar to those given in this paper.

A fluorine atom resonance. Its computed position was equal to the value of the chemical shift, δ, that was used in the computation. It also was found that lines 14 and 16, 12 and 17, 11 and 18, and 10 and 19 were symmetrically positioned about the zero point. From this it followed that the identification of any set or sets of these lines in an experimental spectrum readily gave zero on the scale. The identification of line 6 consequently gave the chemical shift.

The spin–spin coupling constant, J_{AB}, was not directly determinable from an experimental spectrum. From the computed spectra it was found that the ratio of the difference in c.p.s. between lines 8 and 10 and lines 6 and 10 was a fairly sensitive function of J/δ. Lines 6, 8, and 10 also were chosen because they were present with fairly large intensities. A plot of log (J/δ) *vs.* the above ratio gave a smooth curve with J/δ ranging from 0.15 to 0.7 (Fig. 1). From this curve the value of J/δ and, consequently, J_{AB} for a compound could be determined. Using the determined values of J and δ, the spectrum of the compound then was computed. Close agreement with the experimental spectrum was considered to confirm the validity of the values of J and δ, and the basic model, AB_4.[4–12]

A check on the values of J and δ also may be accomplished without computing a spectrum for the particular values, by comparison of the experimental spectrum with a spectrum plotted from graphs of the computed line positions as a function of J/δ (Fig. 2).[13] Since the data for the graphical method of analysis were obtained for $J = 150$ c.p.s., the line positions as determined from graphs for an experimental value of J/δ were corrected to the experimental value of J by multiplying the line position by the factor of the experimental J divided by 150. If δ be negative, the signs of the line positions in Fig. 2 are reversed.

When experimental resolution was adequate to differentiate all of the resonance frequencies, the computed intensities of the lines agreed reasonably well with the experimentally observed intensities. When inadequate, the experimental intensities appeared more or less as the sum of the individual intensities.

Other fluorine atoms in the molecule perturbed the resonance frequencies of the $-SF_5$ group with added splittings, but the basic line positions remained unaffected. Muller, Lauterbur, and Svatos[1] reported that the n.m.r. spectra for $C_2F_5SF_5$, $C_3F_7SF_5$, and $C_4F_9SF_5$ did not show additional splitting due to interaction of fluorine atoms in the difluoromethylene group $(-CF_2-)$ with those of the $-SF_5$ group. We observed that in the spectrum of CF_3SF_5 all resonances of the $-SF_5$ group were split into quartets by interaction of the fluorine atoms in the trifluoromethyl group (CF_3). The values for the coupling constants were 6.4 and 22 c.p.s., respectively, between the fluorine atoms of the $-CF_3$ group and the A and B fluorine atoms attached to the sulfur atom. We also observed for $C_2F_5OSF_5$[8] that the interaction of the fluorine atoms of the $-CF_2-$ group, even though separated by an added oxygen atom, was large enough to split all fluorine resonances of the $-SF_5$ group into triplets. The coupling constants were 3 and 10 c.p.s., respectively, between the fluorine atoms of the $-CF_2-$ group and the A and B fluorine atoms of the pentafluorosulfur group. However, it also was observed that for $FCH_2CH_2OSF_5$[8] the protons of the $-CH_2-$ group did not interact sufficiently with the fluorine atoms of the $-SF_5$ group to cause any further splitting. Lack of resolution in the spectra of Muller, Lauterbur, and Svatos must have prevented the identification of the coupling constants between the fluorine atoms of the $-CF_2-$ groups with those of the $-SF_5$ group.

Figure 3 shows the experimental n.m.r. spectra of the compounds used in this study and gives the spin–spin coupling constants, chemical shifts, and spectra that were computed by use of experimental values. Superscripts following the chemical formulas of these compounds refer to the references giving the source of the compounds, method of preparation, or type of calculation of the computed spectrum.

Since the computer program used was inadequate for handling eight-spin systems, the fluorine atoms of $-CF_3$ groups were in three instances

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(4) C. I. Merrill, to be published.

(5) H. L. Roberts, British Patent Appln. 2543(1959).

(6) G. A. Silvey and G. H. Cady, *J. Am. Chem. Soc.*, **72**, 3624 (1950).

(7) Computed spectrum calculated as a six-spin n.m.r. system.

(8) S. M. Williamson, to be published.

(9) L. C. Duncan, to be published.

(10) S. M. Williamson, new method of preparation to be published.

(11) C. I. Merrill and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 298 (1961).

(12) K. G. Denbigh and R. Whytlaw-Gray, *J. Chem. Soc.*, 1346 (1934).

(13) The data from which Figure 2 was constructed have been deposited as Document number 7066 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be received by citing the Document Number and remitting $1.25 for photoprints or for 35 mm. microfilm, in advance by check or money order payable to Chief, Photoduplication Service.

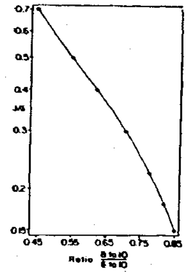

Fig. 1.—Determination of J/δ by ratio of 8 to 10 distance to 6 to 10 distance.

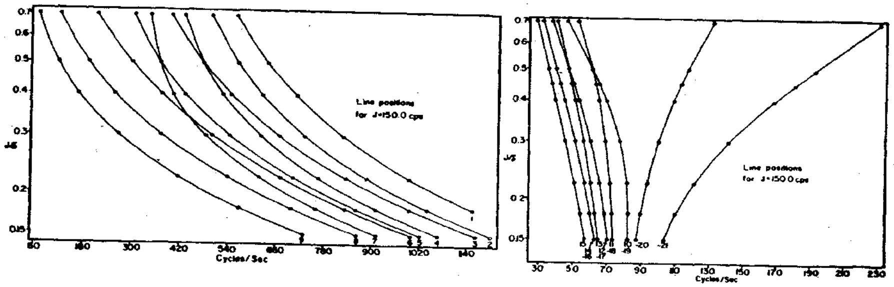

Fig. 2.—Line positions as a function of J/δ.

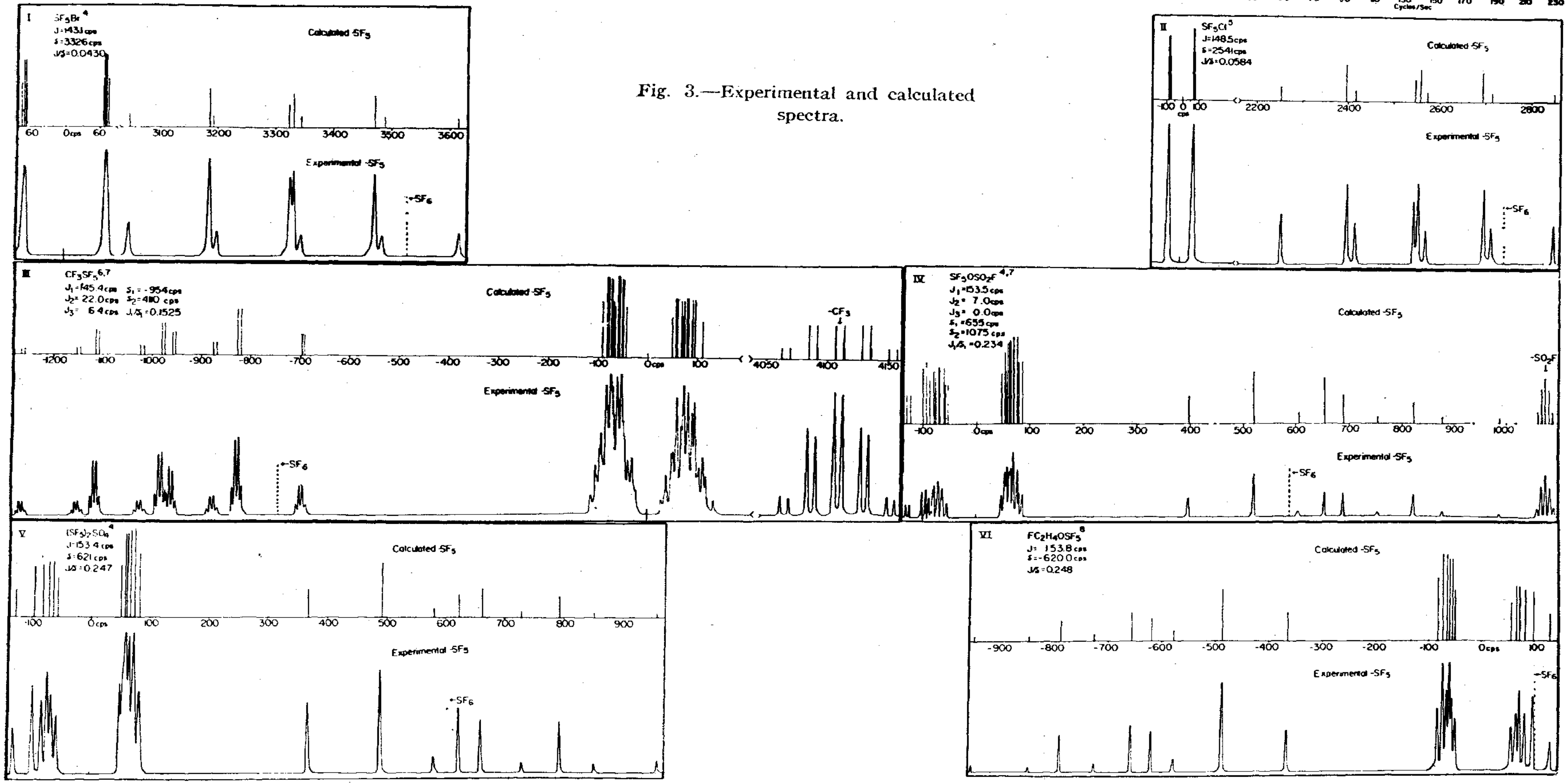

Fig. 3.—Experimental and calculated spectra.

Fig. 3.—(continued)

(spectra III, XI, and XII) entered into computation as a single nuclear spin interaction. This six-spin approximation gave good correspondence between the major lines in the experimental quartets and the calculated doublets in the $-SF_5$ group resonances.

Spectra XIII, XIV, and XV are very complicated spectra and appear to be examples of ten-spin n.m.r. systems. A five-spin computation is given with spectrum XIII that shows the strong resemblance of the experimental spectrum to an AB_4 system.

TABLE I

CHEMICAL SHIFTS[a] IN P.P.M., REFERRED TO INTERNAL SF_6, AND THE SPIN-SPIN COUPLING CONSTANT, *J*, IN C.P.S. BETWEEN APEX AND BASAL FLUORINE ATOMS

Compound	Basal F	Apex F	*J*
SF_5Br	−88.2	−5.00	143.1
SF_5Cl	−68.4	−4.88	148.5
CF_3SF_5	18.4	−5.43	145.4
SF_5OSO_2F	−14.8	1.63	153.5
$(SF_5)_2SO_4$	−15.1	0.43	153.4
$FC_2H_4OSF_5$	−2.48	−17.98	153.8
$FClC_2H_3OSF_5$	−2.69	−15.93	154.7
$C_2F_5OSF_5$	−15.2	−3.35	152.8
$C_5F_9OSF_5$	−14.7	−4.00	154.9
$FC_2Cl_4OSF_5$	−14.8	−6.37	154.9
CF_3OSF_5	−11.4	−4.23	153.0
SF_5OSF_5	−14.0	−4.53	150
SF_5OOSF_5	0.75	0.16	

[a] Chemical shifts given here were obtained in about 50% SF_6 solution and thus may have small errors associated with them. However, the related compounds SO_3F_2 and SF_5OF show less than 0.3 p.p.m. in shift in proceeding from 10 to 90 mole % SF_6. Positive shifts are at increased magnetic field from SF_6.

The spin–spin coupling constants, *J*, in Table I are all remarkably constant; they fall close to the value 150 c.p.s., with a range of only twelve cycles. We believe this *J* should characterize all substituted SF_5 compounds. Constancy in coupling constants has been observed previously in six-coordinated systems.[14] In a *cis* disubstituted compound, $SF_4(SO_3F)_2$,[15] *J* was found to be 156 cycles. The value reported for another *cis* disubstituted compound, $\overline{CF_2CF_2OCF_2CF_2SF_4}$,[1] was only 93 cycles; however, the substitution forms a cyclic system, including the sulfur, and possibly causes changes in the SF_4 geometry.

The chemical shifts listed in Table I all are referred to SF_6 as an internal standard. The shifts are for the most part negative; *i.e.*, replacement of one fluorine in SF_6 by other halogens or oxygen causes the fluorine resonance to center about a lower value of magnetic field. Since the fluorine is replaced by a less electronegative atom, this should cause a decrease in the effective electronegativity of the sulfur and give a positive δ.[16] The experimental evidence thus shows that electronegativity change is certainly not the dominant factor, though it may be in CF_3SF_5 with a positive δ for the basal fluorine atoms. For the first two compounds, SF_5Br and SF_5Cl, the basal shifts are an order of magnitude larger than for any of the other compounds. This then might be due to the presence of low-lying excited electronic states.[17]

The chemical shifts of the apex fluorine are generally smaller in magnitude than the basal shifts. This is especially true of the first three compounds; the basal shifts extend over 106 p.p.m. while the apex shifts cover only 0.55 p.p.m. The sulfate and fluorosulfonate are out of line to positive δ values, and the compounds containing the $-CH_2-$ group lie to larger negative δ values. It is apparent that further study of related compounds will be necessary before the origins of these shifts are understood.

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(14) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

(15) J. M. Shreeve and G. H. Cady, to be published.

(16) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(17) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).