

necessary excess of energy in passing the first hump, and conceptually the second hump would only be of significance if a mechanism existed to dissipate the internal energy of the complex before it reached its final σ -state. In the radical or free atom addition it is doubtful whether such a mechanism does exist.

One point, however, needs further discussion. If both π - and σ -complexes are feasible, does the transition state resemble a π - or a σ -complex? The transition state under consideration is the one described by the hump separating the π - and σ -complexes and not by a hump preceding the π -complex (if such a hump exists at all). Our studies of the addition of CF_3 radicals to unsubstituted aromatic hydrocarbons indicate that the transition state for this reaction resembles a σ -complex, *i.e.* even for this strongly electrophilic radical an incipient C-CF₃ bond is formed in the transition state. The addition of O-atoms may follow a different course, and, if this is the case, we suggest that the di-radical nature of O-atoms, and not their electrophilic character, may be responsible for such behavior.

The following point needs, however, further discussion. If both π - and σ -complexes are feasible, does the transition state resemble a π - or a σ -complex? The transition state under consideration is the one described by the hump separating the π - and σ -complexes and not by a hump preceding the π -complex (if such a hump exists at all). The addition of CF_3 radicals to benzene and some of its derivatives was studied recently by Whittle, *et al.*²¹ and their findings suggest that a covalent C-C bond is formed in this process. The results of our studies permit us to go further and claim that the incipient C-C bond is formed in the

(21) S. W. Chailles and E. Whittle, *Trans. Faraday Soc.*, **56**, 794 (1960); S. W. Chailles, J. T. Pearson and E. Whittle, *ibid.*, **57**, 1356 (1961).

transition state since the respective rate constants per reactive center were found to be related to the respective localization energies. This means that even for this strongly electrophilic radical the transition state resembles a σ - and not a π -complex. The addition of O-atoms may follow a different course, and, if this is the case, we suggest that the di-radical nature of O-atoms, and not their electrophilic character, may be responsible for such a behavior.

In conclusion we wish to emphasize that the electrophilic nature of a radical is reflected in its response to the presence of electron-donating or electron-withdrawing substituents in the substrate. Such a response is observed whether the addition leads directly to a σ -complex or proceeds *via* a π -complex. The electrophilic character of a radical might favor the formation of a π -complex, although such a complex need not necessarily be formed in every addition involving an electrophilic radical. Whenever a π - and σ -complex are formed in the same process, the formation of the former cannot be the rate determining step in the formation of the latter.

The transition state of the addition of a strongly electrophilic CF_3 radical to aromatic or olefinic substrates resembles a σ -complex. Relatively stable π -complexes probably are formed with extremely electrophilic radicals or free atoms. They are favored by reactions leading to relatively weak σ -bonds in the final adduct radical and by low temperature. The adducts observed by Abell and Piette are probably π -complexes.

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High-resolution Fluorine Magnetic Resonance Spectra of Some Perfluoroalkyl Derivatives of Sulfur Hexafluoride¹

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The high-resolution fluorine magnetic resonance spectra of a group of perfluoroalkyl derivatives of sulfur hexafluoride have been analyzed and the chemical shifts and spin-spin coupling constants determined. The fluorine chemical shifts are found to vary with the electronegativity of the substituents. Fluorine-fluorine coupling constants are observed between nuclei separated by three, four and five bonds, but the coupling constants do not vary in a coherent manner with a change in the number of bonds separating interacting nuclei. Our results are in agreement with the idea that coupling between fluorine nuclei separated by three or four single bonds is due to both through-space and through-bond interactions but that the importance of the through-bond interaction falls off rapidly with number of intervening bonds and the coupling is largely a through-space interaction when the nuclei are separated by five single bonds. The very small coupling constants observed for interaction between nuclei separated by three bonds in the $\text{CF}_3\text{-CF}_2$ and $\text{-CF}_2\text{-CF}_2\text{-}$ fragments would still appear to be anomalies possibly to be explained as resulting from rotational averaging of *trans* and *gauche* coupling constants of opposite signs.

Introduction

Although fluorine magnetic resonance spectra for a number of fluorocarbon derivatives have been

studied, much less systematic data for F^{19} chemical shifts and spin-spin coupling constants exist than

(2) Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut.

(3) Taken in part from the Ph.D. thesis of John D. Graham, Michigan State University, 1961.

(1) This research was supported by a grant from the Atomic Energy Commission.

are available from proton resonance spectra. A number of perfluoroalkyl derivatives of sulfur hexafluoride were studied by Muller, Lauterbur and Svatos⁴ at 40 Mc. and chemical shifts of the various non-equivalent groups of fluorine atoms were reported. At that time resolution was not sufficiently good to analyze most of the spin multiplets. We have now studied in the pure liquid state six compounds of the type RR^1SF_4 and RSF_5 , where R, R^1 are perfluoroalkyl groups, at spectrometer frequencies of 56.4 or 60 Mc. and from the well-resolved spin multiplets have determined and identified the spin-spin coupling constants. Chemical shifts for the various groups of fluorine atoms have also been recorded. Certain of our conclusions concerning the structures of these molecules have been mentioned by Dresdner and Young^{5,6} recently.

Some general conclusions concerning the chemical shifts and coupling constants have been drawn and our results should be of use in determining structures of new compounds of these types.

Experimental

Spectrometer.—A Varian Associates Model V-4300-2 spectrometer with model V-4311 fixed frequency RF unit and model V-4331A RF probe were used. The RF unit was modified by replacing the regular crystals with 56.445 Mc. crystals so the fluorine resonance could be obtained at a field of 14,100 gauss. Some fluorine resonance spectra were also obtained at 60.0 Mc. and at 40.0 Mc. (with V-4310C RF unit). A model V-4365 field homogeneity control and model V-3521 n.m.r. integrator were used at 56.445 Mc. For operation at 60.0 Mc. homemade electric shim coils were essential to obtain the desired resolution. Chemical shifts were measured by the sideband technique using a Hewlett-Packard 521A electronic counter and spectra were recorded on a Varian G-10 or Moseley 2-XY recorder.

Materials.—The compounds were the gift of Professors James A. Young and Richard D. Dresdner of the University of Florida and the preparation, purification and properties are described in their publications.^{5,6} As reported by them the boiling points and molecular weights of the materials we studied are as follows: $C_2F_5SF_5$, b.p. 14.3°, mol. wt. 246; $(C_2F_5)_2SF_4$, b.p. 70.0°, mol. wt. 346; $C_2F_5SF_4CF_3$, b.p. 47.1°, mol. wt. 297; $CF_3SF_4CF_2COOCH_3$, b.p. 123°; $C_4F_9SF_5$, b.p. 70.9°, mol. wt. 346; $CF_3SF_4CF_2SF_3$, b.p. 88°, mol. wt. 352.

Results

The fluorine resonance spectrum of $(CF_3CF_2)_2SF_4$ (I) consists of three multiplets. A quintet for CF_3 , and another for CF_2 , each arise from spin-spin coupling with the four equivalent fluorines of the SF_4 group; the third peak due to SF_4 consists of a complex multiplet arising from spin-coupling of the SF_4 fluorines to the six equivalent CF_3 fluorines ($J_{CF_3-SF_4} = 9.33$ c.p.s.) and with the four equivalent CF_2 fluorines ($J_{CF_2-SF_4} = 15.7$ c.p.s.). The spectrum calculated from first order perturbation theory for the latter peak agrees satisfactorily with experiment. The two are compared in an illustration in a recent review and details of the calculation are shown there.⁷ There is no measurable coupling between the CF_3 and CF_2 fluorine atoms, a phenomenon frequently observed in compounds containing perfluoroethyl groups. The

(4) N. Muller, P. Lauterbur and G. Svatos, *J. Am. Chem. Soc.*, **79**, 1043 (1957).

(5) R. D. Dresdner and J. A. Young, *ibid.*, **81**, 574 (1959).

(6) J. A. Young and R. D. Dresdner, *J. Org. Chem.*, **24**, 1021 (1959).

(7) Max T. Rogers, *Record of Chemical Progress*, **21**, 197 (1960).

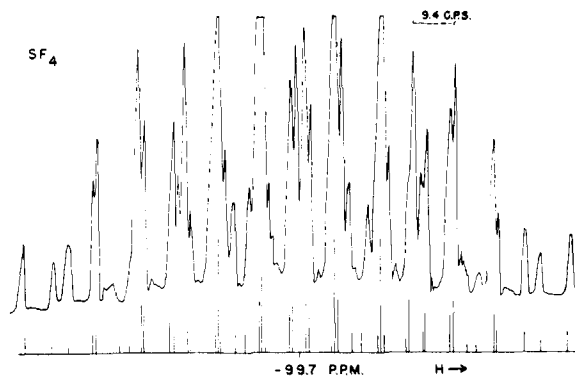
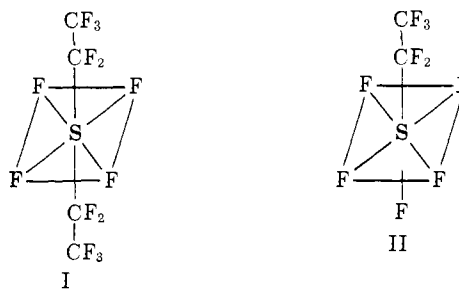


Fig. 1.—Fluorine magnetic resonance spectrum of the SF_4 group of $CF_3SF_4C_2F_5$ ($\nu_0 = 60.000$ Mc., reference is external CF_3COOH). The positions and intensities of the lines calculated by first order perturbation theory, using the J values of Table II, are shown below the experimental spectrum.

trans configuration of the C_2F_5 groups is established by the n.m.r. spectrum.

The fluorine resonance spectrum of $CF_3SF_4CF_2COOCH_3$ similarly consists of a pair of quintets for CF_2 and CF_3 and a twelve-line multiplet for SF_4 ; no proton-fluorine coupling is observed. The spectrum of $CF_3SF_4CF_2CF_3$ at 60.000 Mc. consists of three regular quintets, one for each of the three groups with fluorine attached to carbon, and a complex multiplet illustrated in Fig. 1 for the SF_4 group. The positions and intensities of the lines of the latter agree well with values computed from first-order perturbation theory using the J values found from the three quintets. The *trans* configuration of the perfluoroalkyl groups is again established by the n.m.r. spectrum.

The high-resolution fluorine n.m.r. spectrum of $C_2F_5SF_5$ (II) at 60.0 Mcs. shows four multiplets.



The CF_3 and CF_2 resonances are each simple multiplets (Fig. 2) while the four basal fluorine atoms of the SF_4 part of the SF_5 group give rise to a doublet, each component of which is an unresolvable multiplet (not shown). The resonance for the apex fluorine of the SF_5 group is chemically shifted from the resonance for the four basal fluorines and the SF_5 group therefore forms an AB_4 spin system. Splitting of the apex fluorine resonance by the four equivalent basal fluorines gives a nine line multiplet, $J_{SF_5-F_a} = 152.19$ c.p.s., $\delta_{SF_5-F_a} = 19.5$ p.p.m.; each line is again split into a triplet by spin coupling of the apex fluorine F_a to the CF_2 group ($J_{SF_5-CF_2} = 4.82$ c.p.s.) so that twenty-seven lines are observed for the apex fluorine resonance. The theoretical spectrum computed by the method of

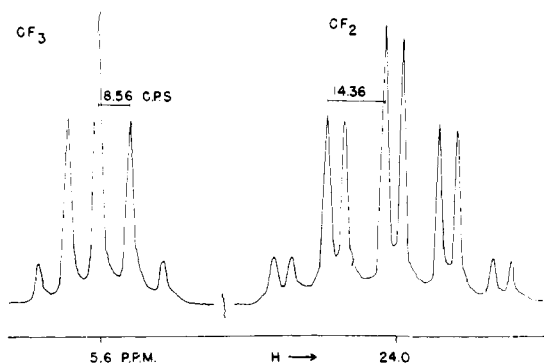


Fig. 2.—Fluorine magnetic resonance spectrum of the CF_3 and CF_2 groups of $\text{C}_2\text{F}_3\text{SF}_5$ ($\nu_0 = 60.000$ Mc., reference is external CF_3COOH). The spin of the axial fluorine of SF_5 is coupled to the CF_2 but not to the CF_3 spins.

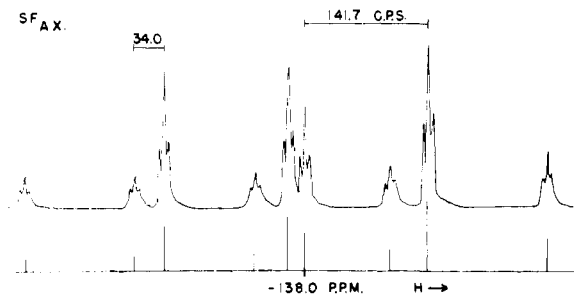


Fig. 3.—Fluorine magnetic resonance spectrum of the apex fluorine of the SF_5 group of $\text{C}_2\text{F}_3\text{SF}_5$ ($\nu_0 = 60.000$ Mc., reference is external CF_3COOH). The positions and intensities of the lines calculated for an AB_4 spectrum with $J/\delta = 0.13$ are shown below the experimental spectrum. Each component is further split into a triplet ($J = 4.82$ c.p.s.) by the fluorine nuclei of the CF_2 group.

Corio⁸ was computed and agrees well (Fig. 3) with the observed. The resonance due to the CF_2 group is split into a quintet by the SF_4 group ($J_{\text{SF}_4-\text{CF}_2} = 14.36$ c.p.s.) and again into doublets by the apex fluorine ($J_{\text{SF}_5-\text{CF}_2} = 4.82$ c.p.s.) but CF_3 - CF_2 spin-spin coupling is not detectable. The resonance due to the CF_3 fluorines is a simple quintet.

The fluorine resonance spectrum of $\text{C}_4\text{F}_9\text{SF}_5$ is more complex. We may identify the various CF_2 groups by the letters α, β, γ and distinguish the apex and basal fluorine atoms: $\text{CF}_3\text{CF}_2(\gamma)\text{CF}_2(\beta)\text{CF}_2(\alpha)\text{SF}_4\text{F}_a$. Then the six complex multiplets observed may be fairly completely analyzed and most of the coupling constants determined (Table II). The spin-coupling constants for fluorine nuclei in the CF_3CF_2 and CF_2 - CF_2 groups do not appear to be detectable. The SF_4 group gives rise to a broad doublet each component of which consists of seven (or more) lines with spacing 8–9 c.p.s., while each of these components is itself a complex multiplet; the approximately uniform spacing suggests that $J_{\text{CF}_2-\text{C}-\text{SF}_4} \cong 8 \pm 2$ c.p.s. since $J_{\text{CF}_2-\text{SF}_4} = 17.0$ c.p.s.

The structure $\text{CF}_3\text{SF}_4\text{CF}_2\text{SF}_5$ has been assigned to the compound of molecular weight 352 and b.p. 88 on the basis of the fluorine resonance spectrum

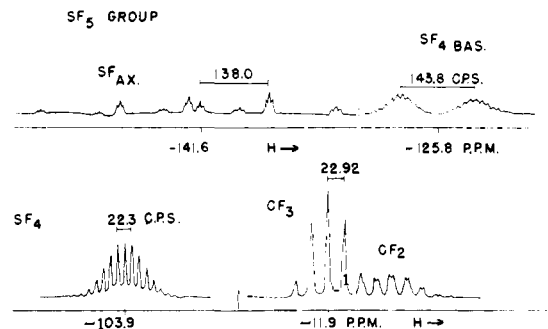


Fig. 4.—Fluorine magnetic resonance spectra of the axial and basal fluorines of the SF_5 group of $\text{C}_3\text{SF}_4\text{CF}_2\text{SF}_5$ (above). Below is shown the multiplet observed for the SF_4 group located between the carbon atoms as well as the first-order multiplets observed for the CF_3 and CF_2 groups. All chemical shifts are relative to external CF_3COOH and the spectrometer frequency is 56.445 Mc.

shown in Fig. 4. The five multiplets are satisfactorily accounted for on the basis of this arrangement and all the spin coupling constants may be found. The characteristic nine line spectrum for the apex fluorine and doublet for the four basal fluorines reveal the presence of an SF_5 group with $J_{\text{SF}_4-\text{SF}_5} = 145.96$ c.p.s. when analyzed as an AB_4 system. Each line of the nine is further split into a triplet, $J_{\text{CF}_2-\text{SF}_5} = 5.28$ c.p.s., by the CF_2 group. The fluorine resonance peak for CF_3 is a quintet ($J_{\text{SF}_4-\text{CF}_3} = 22.92$) while that for the CF_2 group is a multiplet of nine lines due to splitting by the eight roughly structurally equivalent SF_4 fluorine nuclei ($J_{\text{SF}_4-\text{CF}_2} = 21.41$) each of which is further split into a doublet by the single apex fluorine; the CF_3 and CF_2 multiplets partly overlap. The SF_4 peak is a multiplet of 15 lines with nearly equal spacing. The quartet ($J_{\text{CF}_3-\text{SF}_4} = 22.92$ c.p.s.) of triplets ($J_{\text{CF}_2-\text{SF}_4} = 21.41$ c.p.s.) would lead to twelve lines which probably would only show as six rather broad lines with average spacing about 22 c.p.s. If each of these is split into a quintet by coupling with the other SF_4 group, $J_{\text{SF}_4-\text{SF}_4} \cong 11$ c.p.s., the observed 15 line multiplet would be accounted for. The uncertainty in $J_{\text{SF}_4-\text{SF}_4}$ estimated this way is about ± 1 c.p.s. Unfortunately an erroneous conclusion was drawn earlier⁶ on the basis of a low-resolution spectrum which failed to resolve the spin multiplets.

The chemical shifts and spin-coupling constants found from the n.m.r. spectra are shown in Tables I and II, respectively.

Discussion

Our chemical shift data agree well with those reported previously.⁴ The data tend to show that similar groups have characteristic chemical shift values in the various perfluoroalkyl derivatives of sulfur hexafluoride. Thus, a CF_2 group adjacent to sulfur has a chemical shift (relative to external CF_3COOH) varying between 12.1 and 24.0 p.p.m. in five compounds. However, in $\text{CF}_3\text{SF}_4\text{CF}_2\text{SF}_5$ where the CF_2 occupies a unique position between two sulfur atoms the value of δ is unusually low (-10.3 p.p.m.).

(8) P. L. Corio, *Chem. Revs.*, **60**, 363 (1960).

TABLE I
FLUORINE CHEMICAL SHIFTS IN PERFLUOROALKYL DERIVATIVES OF SULFUR HEXAFLUORIDE
Chemical shifts are given in parts per million (p.p.m.) from external CF_3COOH

Compound	$\delta_{\text{SF}_a}^a$	δ_{SF_b}	$\delta_{\text{CF}_3-\text{S}}$	$\delta_{\text{CF}_2-\text{S}}$	$\delta_{\text{CF}_3-\text{C}}$	$\delta_{\text{CF}_2\text{C}-\text{S}}$	$\delta_{\text{CF}_2\text{CC}-\text{S}}$
$(\text{CF}_3\text{CF}_2)_2\text{SF}_4$		-105.0		21.0	4.5		
$\text{CF}_3\text{SF}_4\text{CF}_2\text{CF}_3$		-99.7	-11.4	21.4	4.5		
$\text{CF}_3\text{SF}_4\text{CF}_2\text{COOCH}_3$		-99.7	-12.7	12.1			
$\text{CF}_3\text{CF}_2\text{SF}_5$	-138.0	-118.5		24.0	5.6		
$\begin{matrix} \gamma & \beta & \alpha \\ \text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{SF}_5 \end{matrix}$	-136.9	-119.5		17.8(α)	5.0	46.2(β)	48.7(γ)
$\text{CF}_3\text{SF}_4\text{CF}_2\text{SF}_5$	-141.6	-103.9	-11.9	-10.3			
		-125.8 ^b					

^a Chemical shift of apex fluorine atom of the SF_5 group. ^b Chemical shift of base fluorine atoms of SF_5 group.

In general the variations within such a set show that as the electronegativity of the substituent on an atom to which fluorine is bonded increases the given fluorine becomes less shielded. Thus, the CF_2 group in $\text{CF}_3\text{SF}_4\text{CF}_2\text{SF}_5$ is bonded to two SF_4 groups and the fluorine resonance is shifted downfield from, say, CF_2 in $\text{CF}_3\text{CF}_2\text{SF}_5$. Also, the CF_2 resonance in $\text{CF}_3\text{SF}_4\text{CF}_2\text{COOCH}_3$ lies between two electronegative groups and is shifted somewhat downfield from CF_2 in $\text{CF}_3\text{SF}_4\text{CF}_2\text{CF}_3$. The variation in CF_3 attached to sulfur (-11.4 to -12.7 p.p.m.) and in terminal CF_3 of a fluorocarbon group (4.5 to 5.6 p.p.m.) is quite small; similarly the fluorines attached to sulfur have fairly constant chemical shifts in $\text{RR}'\text{SF}_4$ and also within the series RF_5 , the effect of the substituent groups being small. The apex fluorine in SF_5 is always less shielded than the SF_4 basal fluorines (δ varies from 15.8 to 19.5 p.p.m. in the compounds of Table I) indicating that the SF_a bond is more covalent than the SF_b bond if the theory of Saika and Slichter⁹ is applied. The chemical shift between the apex and base fluorines of the SF_5 group varies considerably with substituent, being very large for $\text{SF}_5\text{-Cl}$ ¹⁰ ($\delta=63$ p.p.m.) and rather small in $\text{SF}_5\text{OC}_6\text{H}_5$ ($\delta=10.2$).¹⁰

The spin-spin coupling constants are of particular interest. The monotonic decrease in coupling constants with number of intervening bonds which is observed for proton-proton couplings in saturated molecules is absent here. Fluorine-fluorine couplings between nuclei separated by three chemical bonds vary from nearly zero ($J_{\text{CF}_2-\text{CF}_2} \leq 1$ c.p.s. and $J_{\text{CF}_2-\text{CF}_2} < 2$ c.p.s.) to 24.0 c.p.s. ($J_{\text{CF}_3-\text{SF}_4}$) and couplings between fluorine nuclei separated by four bonds vary from nearly zero ($J_{\text{CF}_3-\text{C}-\text{SF}_a} \leq 1$ in $\text{C}_2\text{F}_5\text{SF}_5$) to 10.8 c.p.s. in the $\text{CF}_3-\text{CF}_2-\text{CF}_2-$ group. It has been suggested that rotational averaging of *trans* and *gauche* F-C-C-F couplings of opposite sign^{11,12} leads to the essentially zero value observed for $J_{\text{CF}_3-\text{CF}_2}$.

Our results provide partial support for the suggestion of Petrakis and Sederholm¹³ that through-bond fluorine-fluorine couplings are small when the coupling is through three or more bonds and that

the long-range couplings observed are probably principally through-space couplings which only become appreciable when the F-F non-bonded distances are short enough. We will use the term through-space coupling to indicate the contribution to the spin coupling due to non-classical structures with F-F "long-bonds"; this would arise from both two-electron and contact terms primarily since the one-electron terms will presumably be small in these cases. We observe that $J_{\text{CF}_2-\text{C}-\text{SF}_3}$ in $\text{CF}_3\text{SF}_4\text{C}_2\text{F}_5$ and $\text{CF}_3\text{SF}_4\text{CF}_2\text{COOH}$, $J_{\text{CF}_3-\text{C}-\text{S}-\text{CF}_3}$ in $\text{CF}_3\text{SF}_4\text{-C}_2\text{F}_5$, and $J_{\text{CF}_3-\text{C}-\text{SF}_a}$ in $\text{C}_2\text{F}_5\text{SF}_5$ are all ≤ 1 . Since the octahedral arrangement of groups about sulfur should reduce through-space coupling for groups *trans* to one another, one might attribute the observed J values, as a first approximation, to through-bond coupling which would therefore be ≤ 1 c.p.s. when fluorines are separated by five bonds; even for fluorines separated by four bonds the largest *trans* coupling observed is 2.47 c.p.s. ($J_{\text{CF}_2-\text{C}-\text{SF}_a}$ in $\text{C}_4\text{F}_9\text{SF}_5$). When fluorine atoms are separated by only three bonds there is appreciable coupling even when the atoms are in groups *trans* to one another ($J_{\text{CF}_2-\text{SF}_a} \cong 5$ c.p.s.).

However, there is an increase in J in every case on going from the *trans* to the *cis* arrangement and for the latter through-space coupling becomes more important. Thus, using averages of several values, we find $J_{\text{CF}_2-\text{SF}_4} \cong 16.2$ and $J_{\text{CF}_3-\text{C}-\text{SF}_4} \cong 9.1$ c.p.s.; also $J_{\text{CF}_2-\text{C}-\text{SF}_4} \cong 8.5$ c.p.s. (in $\text{C}_4\text{F}_9\text{SF}_5$). The through-space coupling could be considered to contribute the differences between these values and the corresponding coupling constants for the same groups when *trans* as quoted in the paragraph above; these differences are about 11.2 c.p.s. for fluorine nuclei separated by three bonds and 6-8 c.p.s. for nuclei separated by four bonds. It is also interesting that $J_{\text{SF}_4-\text{C}-\text{SF}_a} \cong 11$ c.p.s. in $\text{CF}_3\text{SF}_4\text{CF}_2\text{SF}_5$; this value is larger than expected for through-bond coupling through four bonds. The geometry suggests that through-space coupling could be quite appreciable here as is apparently the case.

The above numbers have only limited significance, however, since the effect of geometry on the through-bond couplings in octahedral molecules is unknown, as are the effects of rotational averaging. The fact that $J_{\text{CF}_2-\text{SF}_4} > J_{\text{CF}_2-\text{SF}_a}$ may be partly due to the change in C-S-F_a angle from 90 to 180° and to the absence of rotational averaging effects in the CF_2-SF_a case.

Since $J_{\text{CF}_3-\text{S}-\text{F}_a} \cong 5$ c.p.s. for a case where the coupling presumably is due to interaction through

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

(10) R. K. Harris and K. J. Packer, *J. Chem. Soc.*, 4736 (1961).

(11) P. T. Narasimhan, private communication, has had some success in developing a quantitative theory along these lines.

(12) See, for example, L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961). See also, J. I. Musher, *ibid.*, **36**, 1086 (1962); and L. Petrakis and C. H. Sederholm, *ibid.*, **36**, 1087 (1962). H. S. Gutowsky, C. G. Belford and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).

TABLE II
 SPIN-SPIN COUPLING CONSTANTS IN PERFLUOROALKYL DERIVATIVES OF SULFUR HEXAFLUORIDE^a

Compound	$J_{\text{CF}_3-\text{SF}_4}$	$J_{\text{CF}_2-\text{SF}_4}$	$J_{\text{CF}_3\text{C}-\text{SF}_4}$	$J_{\text{CF}_3\text{C}-\text{CF}_2}$	$J_{\text{CF}_3\text{CC}-\text{CF}_2}$	$J_{\text{CF}_2-\text{SF}_6}^b$	$J_{\text{CF}_2-\text{SF}_6}^b$	$J_{\text{SF}_6-\text{F}_6}^c$	$J_{\text{CF}_3-\text{CF}_2}$
(CF ₃ CF ₂)SF ₄		15.70	9.33						∞
CF ₃ SF ₄ CF ₂ CF ₃	24.00	15.10	9.40						
CF ₃ SF ₄ CF ₂ COOCH ₃	23.50	13.60							
CF ₃ CF ₂ SF ₅		14.36	8.56			4.82		152.19	∞
CF ₃ CF ₂ CF ₂ CF ₂ SF ₅ ^d		17.0		10.80	2.42	4.93	2.47	145.96	∞
CF ₃ SF ₄ CF ₂ SF ₅ ^e	22.92	21.42				5.28		151.87	

^a Coupling constants are given in units of cycles per second. ^b SF₆ indicates the apex fluorine atom of the SF₆ group. ^c $J_{\text{SF}_6-\text{F}_6}$ is the coupling constant between the apex and base fluorine atoms in the SF₆ group. ^d $J_{\text{CF}_2-\text{C}-\text{SF}_4}$ must be about 8–9 c.p.s. in this compound to account for the SF₄ multiplet observed. Some assumptions concerning the relative magnitudes to be expected for certain of these coupling constants have been made in assigning them to particular pairs of groups. ^e $J_{\text{SF}_4-\text{C}-\text{SF}_4}$ must be about 10–12 c.p.s. in this compound to account for the SF₄ multiplet at –103.9 p.p.m. in Fig. 4.

three bonds, one would also expect the through-bond coupling in the F–C–C–F fragment to be appreciable. It has indeed been found¹³ that $J_{\text{trans}} = 18.6$ c.p.s. and $J_{\text{gauche}} = 16.2$ c.p.s. for CF₂Br–CFBr₂ and, at least for the *trans* isomer, the through-space coupling should be small here. The hypothesis of Petrakis and Sederholm¹² that through-bond coupling is essentially zero for interaction through three single bonds therefore seems untenable and some other explanation of the low values for $J_{\text{CF}_3-\text{CF}_2}$ and $J_{\text{CF}_2-\text{CF}_2}$ must be sought. If the *trans* and *gauche* coupling constants were of opposite sign, then rotational averaging might indeed lead to the observed results. Unfortunately

(13) S. L. Manatt and D. D. Elleman, *J. Am. Chem. Soc.*, **84**, 1305 (1962).

the only study of relative signs of F–F coupling constants which has been made¹³ indicates that both *trans* and *gauche* coupling constants in CF₂Br–CFBr₂ have the same sign. Accidental mutual cancellation of through-bond and through-space interaction terms might also result in low J values but the problem remains a puzzling one.

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Hot Bands in the Infrared Spectra of Acetylenes in Solution

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The side band accompanying the acetylenic C–H stretching infrared band in solutions of acetylenes is shown to be a "hot band" absorption resulting from molecules in the first excited state with respect to the C–H bending mode. This appears to be the first reported observation of infrared hot bands in solution.

Splitting of the acetylenic carbon–hydrogen stretching band has been noted in recent infrared spectral studies of acetylenes.^{1–3} A weak side band usually appears about 20 cm.^{–1} lower in frequency than the main band. Previous workers have suggested that this vibrational doubling is due to Fermi resonance between the acetylenic C–H fundamental and a summation tone.^{2,3} To investigate the nature of the side band more fully, we have investigated the spectral absorption of a number of acetylenes as a function of temperature, in the region of the C–H fundamental and first overtone.

Experimental

The methods of purification and preparation of the acetylenes and their physical constants have been described elsewhere.⁴ Methylacetylene (Matheson Compressed

Gases; 95% min. purity) was used without purification. Reagent grade carbon tetrachloride and 2,2,4-trimethylpentane from freshly opened bottles were used as solvents.

Infrared spectra in the C–H stretching region were determined with a Perkin–Elmer Model 112 spectrophotometer employing a lithium fluoride prism. The temperature of the 1 mm. cell employed was maintained to within ±0.5°. Slit widths were 0.085–0.10 mm. The same instrument, with a cesium bromide prism, was used for studies in the 400–700 cm.^{–1} region. Spectra in the 5000–7000 cm.^{–1} region were obtained with a Cary Model 14M Spectrophotometer equipped with thermostated cell blocks. The temperature was constant to ±0.1°. The path length used was 10 cm. and the slit widths were 0.2–0.32 mm. for slit heights of 20 mm. The scanning speed was 5 Å./sec.

The values of n/n_0 used in the calculations are optical density ratios for the side band compared to the main band; The optical density of the side band was taken to be the maximum difference between the actual absorption curve and the approximated low frequency wing of the main band; the latter was obtained by reflection of the main band about its center. Ratios of n/n_0 for the spectra in the fundamental region are $\log I'/I_0$ values.

Discussion

A weak band is present approximately 20 cm.^{–1} lower in frequency than the main acetylenic carbon–hydrogen stretching fundamental, in each of

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