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SPECTROSCOPIC PROPERTIES OF FLUOROCARBONS AND FLUORINATED HYDROCARBONS

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ABSTRACT

Infrared spectra of 40 fluorinated compounds and Raman spectra of 25 of these compounds are presented. Complete or nearly complete vibrational assignments are proposed for $\text{CH}_2=\text{CF}_2$, $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CCl}_2$, $\text{CF}_2=\text{CFCl}$, CH_3-CF_3 , CH_3-CCl_3 , $\text{CF}_2=\text{CF}-\text{CF}_3$, and cyclic C_4F_8 . A partial assignment of fundamental frequencies for nine fluorinated aromatic hydrocarbons is also proposed.

Previous spectral data for fluorinated hydrocarbons are reviewed briefly and correlated with the present results. Application of spectral methods to analysis and determination of molecular structure is discussed. Olefinic $=\text{CF}_2$ groups are easily identified by characteristic vibrational frequencies in three spectral regions. Saturated CF_2 and CF_3 groups do not appear to have useful characteristic frequencies in saturated fluorocarbons, however, and no general basis has yet been found for the spectral identification of saturated cyclic and noncyclic structures. In the case of fluorinated aromatic hydrocarbons, the position and number of substituents in substituted benzenes can be determined by means of characteristic ring frequencies and fluorine and CF_3 group substituents can also be identified, either singly or together, by means of other characteristic frequencies.

Thermodynamic functions have been calculated from the spectral results for four fluorinated olefins, for methylfluoroform, and for cyclic C_4F_8 . The relationship between molecular forces and some of the observed spectral properties is discussed, and it is concluded that the C-F bond is highly ionic and, in the presence of other C-F or unsaturated linkages, tends to promote stabilizing resonant ionic structures. A normal coordinate treatment for cyclic C_4F_8 is given in an appendix.

PROBLEM STATUS

This is the first summary report on this problem; work is continuing and will be reported in future NRL reports and in University of Oklahoma reports under Contract N7onr-398-T.O.1 with the Office of Naval Research.

AUTHORIZATION

All work reported herein was authorized by NRL Problem N04-04R (NR474-040). In accordance with the provisions of the authorization, part of the work was performed at the University of Oklahoma under Contract N7onr-398-T.O.1 negotiated by the Office of Naval Research with the University of Oklahoma Research Institute. This report constitutes the final report for the period 30 April 1947 to 31 August 1949 on work under the contract (NR019-120).

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SPECTROSCOPIC PROPERTIES OF FLUOROCARBONS AND FLUORINATED HYDROCARBONS

INTRODUCTION

STATEMENT OF THE PROBLEM

The field of fluorine chemistry has developed rapidly in recent years, partly as a result of important practical uses that have been found for certain fluorinated compounds (e.g., the "Freon" refrigerants, and the tetrafluor- and trifluoromonochlor-ethylene polymers) and partly because of general interest in the unusual properties of many compounds containing fluorine, by far the most electronegative of the elements. In view of this rapid progress, it is most appropriate, if not necessary, that spectroscopists (as well as those engaged in the study and exploitation of certain other specialized methods or techniques) devote some attention to fluorine compounds and contribute to advancement in this field in a measure commensurate with the potentialities of their particular methods. Results from the study of the vibrational spectra of hydrocarbons, for example, have been of considerable importance to the petroleum industry, particularly with regard to spectral applications in connection with the fuel and rubber programs during the last war. It is to be expected, therefore, that the application of these same techniques to the study of fluorocarbons and other fluorine compounds will be of considerable help, either directly or indirectly, to the solution of many problems encountered in this field.

It has, however, not yet been shown that the spectral methods developed and results obtained in the study of hydrocarbons can be carried over directly to the analogous fluorocarbons. In hydrocarbons, for example, it has been found by empirical correlation of experimental data, frequently aided by theoretical calculations, that many molecular groups have "characteristic" vibrational frequencies which can be used to identify the groups in unknown molecules and thus to deduce structural information. Moreover, in the case of many molecular groups the nature of the vibrational motions associated with certain of these "characteristic" frequencies is known, and this, in turn, permits a more complete spectral interpretation to be made and more detailed conclusions to be reached. For fluorocarbons the data are insufficient for tracing detailed correlations, but it appears that the situation may be quite different from that in the hydrocarbon field.

Barnes et al (1)* give only one characteristic frequency for fluorine compounds, namely, a C-F stretching frequency which occurs in the spectral range 985 to 1400 cm^{-1} (7.15 to $10.15\text{ }\mu$). This correlation is obviously of little value, since all but a few very simple organic molecules will have at least one band in this broad spectral region. Thompson (2) has given slightly more detailed correlations, indicating that compounds with a single C-F

*All references appear at the end of the report.

linkage absorb in the range from 975 to 1100 cm^{-1} (9.10 to 10.25 μ), while those having a CF_2 group exhibit one band in the 1165 to 1350 cm^{-1} region (7.40 to 8.60 μ) and another in the range 1080 to 1200 cm^{-1} (8.34 to 9.26 μ). But even these correlations are too indefinite to be of much practical value. Although it is not certain that more detailed relationships exist, this question should be investigated so far at least as to determine whether or not it is possible to identify and to distinguish between various molecular groups (such as $-\text{CF}_3$, $>\text{CF}_2$, $=\text{CF}_2$) and various types of bonds (such as aromatic, aliphatic, and olefinic C-F).

Although the determination of molecular structure by means of spectral correlations is probably of greatest immediate value to fluorine chemistry, the application of spectral methods to the analysis of mixtures, to the identification of compounds, and as a criterion of purity, is also of importance to the chemist. This can easily be done if reference spectra of the compounds concerned are available. Since the development of spectral correlations as well as other types of information must also be based upon the experimental data, the determination of the spectra of known compounds is necessarily a preliminary step in the application of spectral methods to any problem. Most of the existing experimental data are for simple small molecules, such as the methane derivatives, and are frequently inaccurate or incomplete. Many additional molecules, particularly the larger ones of more complex structure, as well as some of the simpler ones, must be studied, therefore, before extensive use of spectral methods can be made.

Additional information can frequently be obtained from the results of spectral studies. It is sometimes possible (for simple molecules) to deduce values of the molecular dimensions in addition to molecular structure or shape, and this type of information is of value to the chemist in connection with steric hindrance or molecular strain. In cases where it is possible to obtain a complete assignment of the fundamental frequencies of the molecule, thermodynamic properties may be calculated for the compound in the gaseous state. These serve as a check on calorimetric measurements and are usually obtained with less effort and frequently with greater accuracy. Information of this type for certain refrigerant materials, for example, has been of some importance. Finally, a detailed interpretation of spectral data for a compound, or a series of structurally-related compounds, yields information concerning the forces which hold the various atoms in the molecular configuration. Information as to the types of forces which must be postulated in order to describe the molecular vibrations is closely related to the theory of valency and to the various conceptions of bond character (ionic and covalent) of interest to chemists. Moreover, the values of the force constants are related to bond strengths and bear upon the question of whether a useful relationship exists between the bond length and the energy of a bond. Such relationships are of interest, for they would provide a method for using an easily-measured quantity (the bond length) to determine bond energies.

Information which has been obtained from detailed spectral interpretations of fluorinated compounds is not very extensive. As in the case of empirical correlation data, most of the information pertains to methane derivatives and to other molecules of simple structure. Of the fluorinated hydrocarbons containing more than one carbon atom, only a few have been studied and some of the results need confirmation. In view of the recent growth of fluorine chemistry, and in consideration of the potentialities and relatively undeveloped status of spectral studies in this field, it is believed important that a broad program of spectroscopic work be initiated. Accordingly, the present project has been started having as its broad objective the determination of the molecular vibration spectra of fluorocarbons and fluorinated hydrocarbons and interpretation of these spectra to the fullest extent. More specifically, the aims of the present work are:

- (1) To obtain as complete and accurate infrared and Raman spectra of as many fluorocarbons and fluorinated hydrocarbons as possible.
- (2) To make complete assignments of fundamental frequencies whenever possible, particularly in the case of simpler symmetrical molecules where selection rules, polarization of the Raman lines, and contours of the infrared bands can be used to advantage.
- (3) To correlate the experimental data for the larger complex molecules, using as a basis the results obtained for simple molecules, and to develop insofar as possible spectral correlations which might be used for the determination of molecular structure in unknown samples.
- (4) To compute thermodynamic properties where a complete vibrational assignment for the molecule is possible and to determine the most suitable form of the potential function, together with an evaluation of its force constants, for various molecules or groups of structurally-related molecules; and to draw whatever conclusions seem reasonable on the basis of the spectral results concerning the molecular forces and their relationship with other physical or chemical properties of the molecule.
- (5) To effect experimental or theoretical developments, as necessary, for prosecution of the work.

PREVIOUS WORK

The molecular spectra of many compounds of fluorine combined with hydrogen, lithium, boron, nitrogen, oxygen, silicon, phosphorus, and other elements have already been studied. Although a review of the results would be of interest in connection with the bonding of the fluorine atom, such a discussion would appear to be an unnecessary preliminary to the topic of fluorocarbons. Accordingly, only previous work dealing with fluorocarbons and fluorinated hydrocarbons will be reviewed here. Since its main purpose here is to provide a background for further work, the review will not be comprehensive. It is intended only to show which compounds have been studied, to indicate the general nature of the molecular vibrations for various types of molecules, to show by comparison with data for structurally related molecules that the assignment of fundamental frequencies for several fluorinated compounds is known with a fair degree of certainty, and to summarize the previous work by making certain conclusions of possible use in the interpretation of spectral data for other molecules.

Fluoromethanes and Related Molecules

CX₄ Molecules of Symmetry T_d. Methane and its derivatives are believed to have a tetrahedral structure, and this has been confirmed by spectroscopic evidence (3). The normal modes of vibration consist (4) of a nondegenerate "breathing" mode, ν_1 , a doubly degenerate deformation mode ν_2 , and two triply degenerate modes ν_3 and ν_4 , as indicated in Figure 1. As shown in Table 1, two of the fundamentals should be infrared active, and all four should be Raman active.

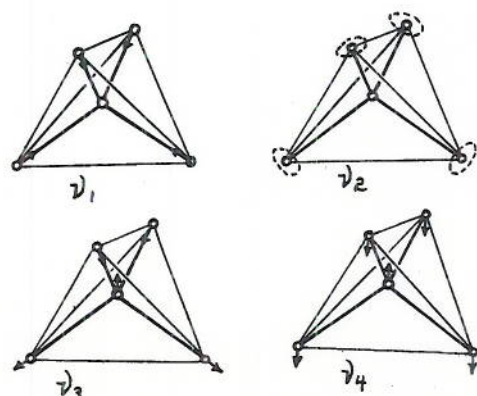


Figure 1 - Vibrational modes for CX_4 molecule

TABLE 1
Selection Rules for CX_4 Molecule

Symmetry	Mode	Species	Activity
T_d	ν_1	A_1	Ra, p.
	ν_2	E	Ra, dp.
	ν_3	F_2	Ra, dp.; I.R.
	ν_4	F_2	Ra, dp.; I.R.

The Raman spectrum of CF_4 has been studied by Yost et al* who find three lines for the liquid at -120° and one for the gas, and the infrared spectrum has been studied by Eucken* and by Bailey.* Kohlrausch (5) has summarized the assignments for CH_4 , CD_4 , CF_4 , CCl_4 and CBr_4 , as shown in Table 2, where parentheses are used to indicate values derived from combination frequencies but not observed as fundamentals.

TABLE 2
Fundamental Frequencies of CX_4 Molecules

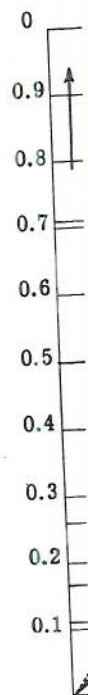
	ν_1	ν_2	ν_3	ν_4
CH_4 (gas)	2915	(1520)	3072	1304
CD_4 (gas)	2085	(1075)	2258	(985)
CF_4	904	437	1265	635
CCl_4	459	217	775	313
CBr_4	267	123	665	183

Kohlrausch (5, p. 150) has also shown that by using the frequency formulas of Nath (6) it is possible to predict the effect of changing the mass m of the atoms attached to the carbon ($M = 12$) by setting the constants f_{11} and d' equal to zero† and by making $f = 3.6 \times 10^5$ and $d = 0.36 \times 10^5$ dynes/cm. These results are shown in Figure 2 for comparison with the graphical representation of the observed frequencies shown in Figure 3. It may be noted that the frequencies ν_2 and ν_4 cross between CD_4 and CF_4 , as predicted, and that a good qualitative fit is found for the spread of frequencies in this series of molecules. This illustrates the use which can be made of correlations between structurally related molecules in identifying a few unknown fundamentals when most of the others are known.

Although a simple valence type potential function (as used to compute Figure 2) is useful for predicting the relative order and magnitude of the fundamental frequencies in CX_4 molecules, it may be emphasized that such a simple potential does not usually yield frequency values that agree closely with experiment. It can be used to account for the

*See Bibliography, page 19.

†In which case the formulas reduce to those of F. Lechner (7)



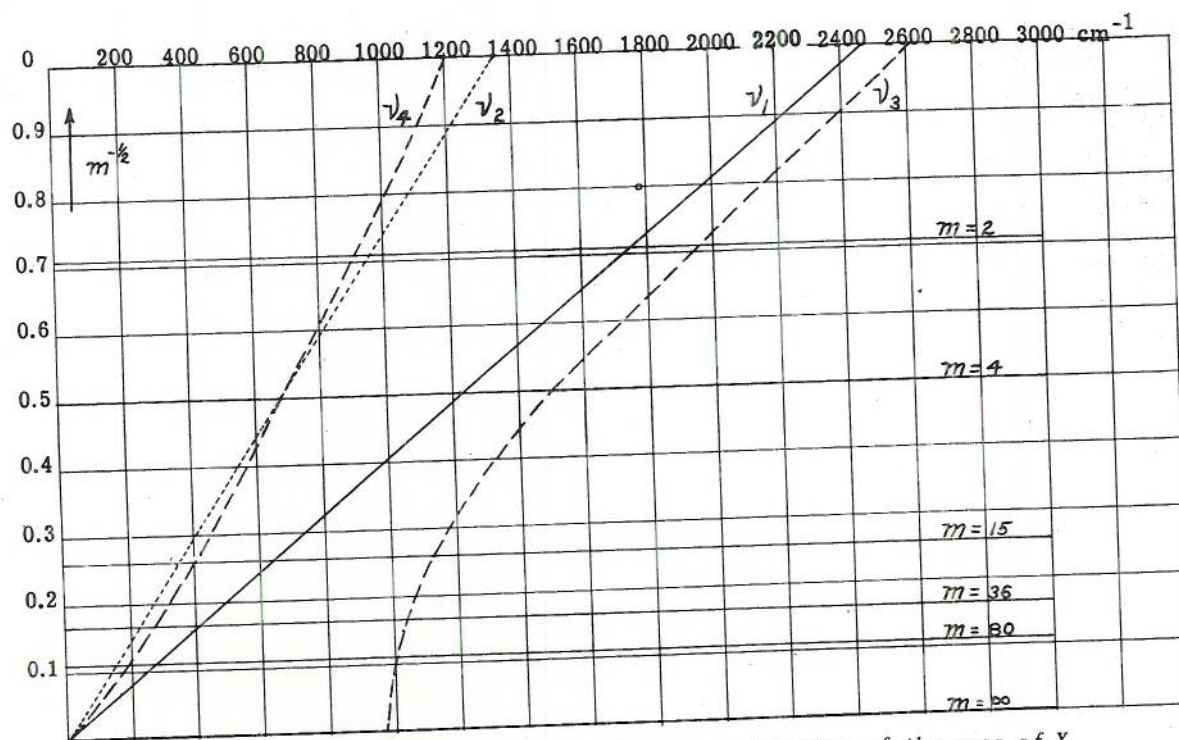


Figure 2 - Vibrational frequencies of CX_4 as a function of the mass of X

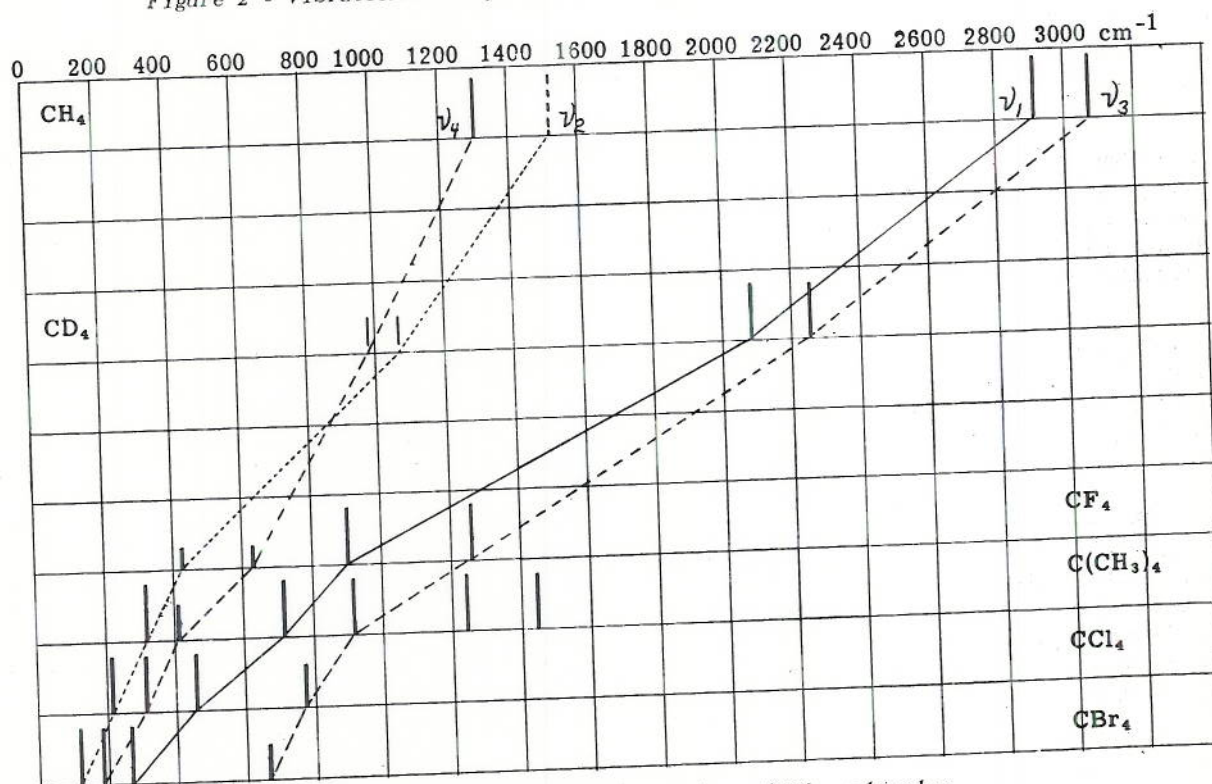


Figure 3 - Vibrational frequencies of CX_4 molecules.

frequencies of methane fairly satisfactorily, but for the heavier molecules in Table 2 it is very inadequate. Wu (4, p. 219) gives a potential containing both central and valence forces which is the most general form consistent with tetrahedral symmetry. For CF_4 better results are obtained by means of a pure central force potential (which is a modification of Wu's more general potential), the best agreement being obtained with the potential of Urey and Bradley (8) (which is also a modification of Wu's general potential). Various values of the force constant "f" for stretching of the C-X bond, as summarized by Wu (4, p. 232), and values of the bond length "r," as given by Kohlrausch (5, p. 151), are listed in Table 3 for CX_4 molecules.

TABLE 3
Force Constant and Length of C-X Bond in CX_4 Molecules

	$f_{\text{C-X}}$	$r_{\text{C-X}}$
CH_4	$5.07^{(a)} \times 10^5$ dynes/cm	1.1 A
CF_4	$5.40^{(a)}$	$1.36^{(d)}$
	$3.99^{(b)}$	
	$3.08^{(c)}$	
CCl_4	$1.89^{(a)}$	1.76
CBr_4	$1.38^{(a)}$	2.0

(a) Using Wu's general valence and central force potential.

(b) Using Urey-Bradley potential.

(c) Using central force potential.

(d) Electron diffraction data of L. O. Brockway, *Rev. Mod. Phys.* **8**, 231 (1936)

The molecule $\text{C}(\text{CH}_3)_4$, neopentane, which has the structure CX_4 if the methyl groups are considered as point masses, has been included in Figure 3. Although the indicated assignment may not be correct,* it appears that the neopentane molecule should be placed below CF_4 in Figure 3, whereas the actual mass of the methyl group, being less than that of fluorine, would indicate that it should be placed above CF_4 .

YCX_3 Molecules of Symmetry C_{3v} . In view of the tetrahedral symmetry of CX_4 molecules, substitution of one or three atoms of a halogen in methane would be expected to produce a structure consisting of a triangular pyramid with the carbon atom at the apex and with the remaining atom directly above the apex. This structure, of symmetry C_{3v} , has been proven by spectral data (3, p. 312).

When the symmetry of the CX_4 model is partially destroyed by substitution of one or three of its atoms, part of the degeneracy of the normal vibrations is removed, each of the triply degenerate modes splitting into a nondegenerate and a doubly degenerate mode. There results six fundamental modes of vibration, three of species A_1 and three of species E (doubly degenerate), as shown in Figure 4 (4, p. 235). All six are both Raman and infrared active, the A_1 modes giving polarized Raman lines and parallel infrared bands and the E modes giving depolarized Raman lines and perpendicular infrared bands.

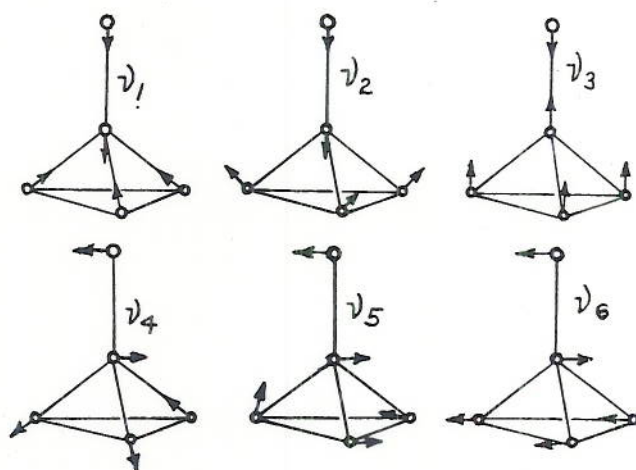
* The line at 1252 cm^{-1} , rather than that at 925 cm^{-1} , probably corresponds more nearly to ν_3 (9).

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Figure 4 - Vibrational modes for XYZ_3 molecules

CH_3F and the other methyl halides have been studied in the vapor phase by Bennett and Meyer* and by Barker and Plyler* in the infrared. The Raman spectra of these compounds have been discussed by Kohlrausch (5). Herzberg (3, p. 315) has summarized the assignments for the methyl halides, as shown in Table 4.

TABLE 4
Fundamental Frequencies of Methyl Halides

	CH_3F	CH_3Cl	CH_3Br	CH_3I
ν_1	2964.5 cm^{-1}	2966.2 cm^{-1}	2972 cm^{-1}	2969.8 cm^{-1}
ν_2	1475.3	1354.9	1305.1	1251.5
ν_3	1048.2	732.1	611	532.8
ν_4	2982.2	3041.8	3055.9	3060.3
ν_5	1471.1	1454.6	1445.3	1440.3
ν_6	1195.5	1015.0	952.0	880.1

More recently Yates and Nielsen* have studied the absorption of CH_3F under very high resolution and have shown that several of the previously observed bands are complex resonance states. Their assignments, using the frequency designation of Figure 4, are reproduced in Table 5 where the parentheses indicate resonance states, the first term listed in each case being the state to which the vibration would correspond if the resonance were removed.

The data of Table 4, together with those for the parent molecule, methane, are shown graphically in Figure 5, where it may be seen, as suggested by Figure 4, that ν_1 and ν_4 are essentially C-H valence vibrations, ν_3 and ν_6 correspond to stretching and bending, respectively, of the C-X bond, while ν_2 and ν_5 are C-H bending modes. The value of ν_2 does not remain constant for this series of molecules because of interaction with ν_3 , as explained by Herzberg (3). In fact, ν_2 changes from a C-H bending to a C-H stretching

*See Bibliography, page 19.

TABLE 5
Vibration Frequencies of CH_3F

Band Center	Identification	Character
1049.5 cm^{-1}	ν_3	parallel
1200.0	ν_6	perpendicular
1467.9	$(\nu_2:\nu_5)$	parallel-perpendicular
1469.7	$(\nu_5:\nu_2)$	perpendicular-parallel
2818.0	$(2\nu_5:2\nu_2:\nu_1)$	parallel
2862.9	$(\nu_1:2\nu_2:2\nu_5)$	parallel
2966.5	$(2\nu_2:2\nu_5:\nu_1)$	parallel
3009.1	ν_4	perpendicular

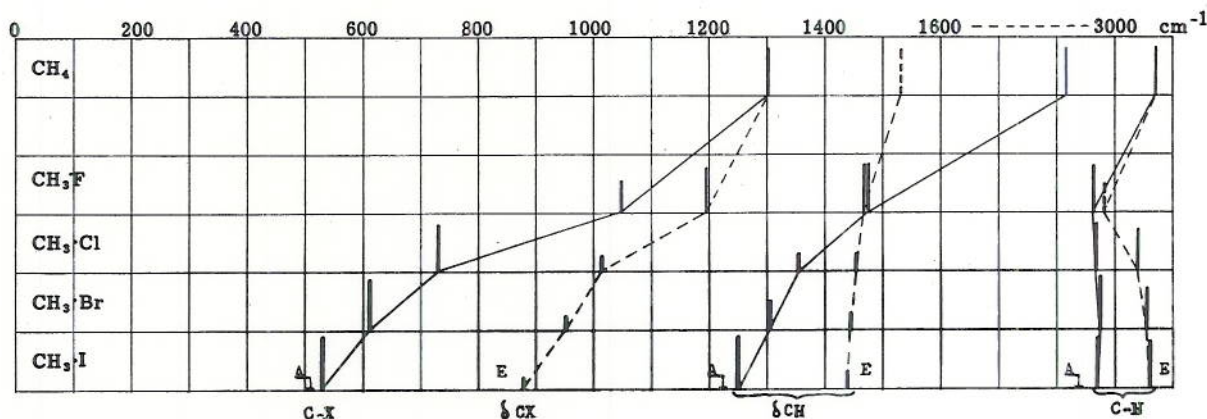


Figure 5 - Vibrational frequencies of CH_3X molecules

mode as the mass of X in CH_3X approaches that of hydrogen. The frequency pattern, as shown in Figure 5, corresponds very closely to that predicted solely on the basis of changing mass of X using a simple valence potential with constant values of the force constant (5, p. 144). It may be noted that, according to the more refined treatment of Yates and Nielsen, the frequencies ν_2 and ν_5 have already crossed for CH_3F (Table 5).

In Table 6 are shown values of the C-X stretching force constant which were obtained by Kohlrausch by assuming the CH_3X molecule to consist of two masses $\text{M}\cdot\text{X}$, where $\text{M} = \text{CH}_3 = 15$. These values are uniformly about 6 percent lower than those obtained for a valence force field when the actual structure of the molecule is taken into consideration (10).

As a result of recent work in microwave spectroscopy, the dimensions of the methyl halides are now known with greater accuracy than that previously obtained by conventional electron diffraction methods. The data, as summarized by Gordy (11), are those given in Table 6.

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TABLE 6
Force Constant and Bond Lengths in Methyl Halides

CH ₃ ·X	r _{C-X}	r _{C-H}	HCH Angle	f _{C-X}
CH ₃ ·F	1.38 ₄ A	1.11 ₂ A	110° 0'	5.04 x 10 ⁵ dynes/cm
CH ₃ ·Cl	1.77 ₉	1.10 ₉	110° 0'	3.12
CH ₃ ·Br	1.93 ₆	1.10 ₄	110° 15'	2.61
CH ₃ ·I	2.13 ₉	1.10 ₀	110° 58'	2.15

The Raman spectrum of HCF₃ has been studied by Glockler and co-workers and the absorption of the gas has recently been measured over the 2-15 μ region.* Wagner (12) has calculated the effect of changing the mass of X in type HCX₃ molecules, as shown in Figure 6, assuming tetrahedral angles and using $f_{C-H} = f_{C-X} = 3.6$, $d(HCX) = d(XCX) = 0.36 \times 10^5$ dynes/cm, and appropriate values for the masses. Kohlrausch (5, p. 148) has summarized the assignments for the HCX₃ molecules as given in Table 7. Herzberg (3, p. 316), gives slightly different values for HCCl₃. These data are shown graphically in Figure 7 for comparison with Figure 6. For the heavier molecules, ν_1 is essentially a C-H stretching vibration, ν_3 and ν_6 correspond to the symmetric and asymmetric deformations of the CX₃ group, while ν_2 and ν_5 correspond to the symmetric and asymmetric stretching of the C-X bonds and ν_4 to the bending of the lone C-H. The motions identified by ν_4 and ν_5 interchange when X changes from F to D.

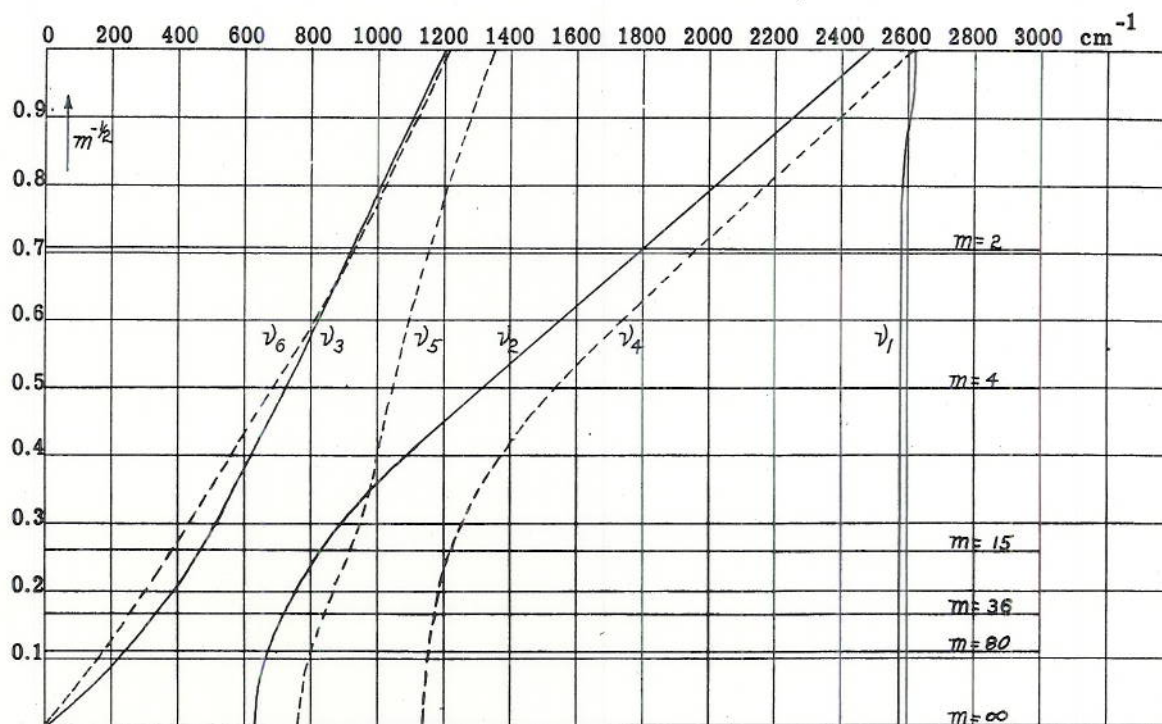
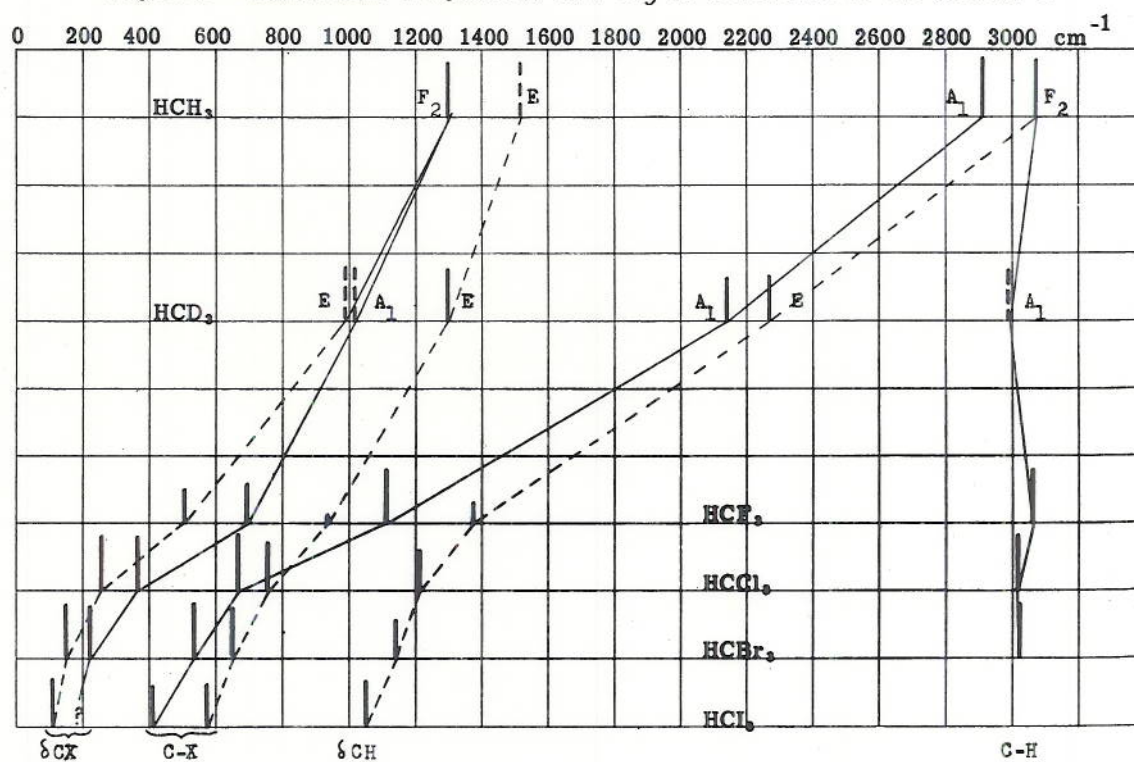
TABLE 7
Fundamental Frequencies of H·CX₃ Molecules

HCX ₃	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
HCD ₃	(2992)	2141	(1020)	2269	1299	(994)
HCF ₃	3062	1117	697	1376	937	508
HCCl ₃	3019	667	366	1216	762	261
HCB ₃	3022	539	222	1143	655	154
HCI ₃ †		416 ?		1053	576	112 ?

† From data summarized by Wu (4, p. 243).

FCCL₃ has been studied in both the Raman and infrared. The assignment, together with that for BrCCl₃ is given in Table 8. Kohlrausch (5, p. 146) has also correlated these assignments with other X·CCl₃ molecules, as shown in Figure 8. This correlation is consistent with the requirement that vibrations of the same species must not cross. However, it must be remembered that a given mode of vibration does not necessarily correspond to the same motions throughout such a series of molecules. For example, the C-H and C-D stretching and bending modes go over into C-Cl stretching modes when X becomes large. Thus, when attempts are made to assign the fundamental modes to specific groups, it is found that crossing of modes of the same species sometimes occurs in correlating group frequencies.

* See Bibliography, page 19.

Figure 6 - Vibrational frequencies of $\text{H}\cdot\text{CX}_3$ as a function of the mass of XFigure 7 - Vibrational frequencies of $\text{H}\cdot\text{CX}_3$ molecules

X·C

F·C

Br·C

H·CC

D·CC

F·CC

Cl·C

Br·C

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TABLE 8
Fundamental Frequencies of $X\cdot CCl_3$ Molecules

$X\cdot CCl_3$	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(E)$	$\nu_5(E)$	$\nu_6(E)$
$F\cdot CCl_3$	1072	535	349	845	397	244
$Br\cdot CCl_3$	716	422	248	778	295	192
	C-X Valence	C-Cl Valence	C-Cl Deformation	C-Cl Valence	C-X Deformation	C-Cl Deformation

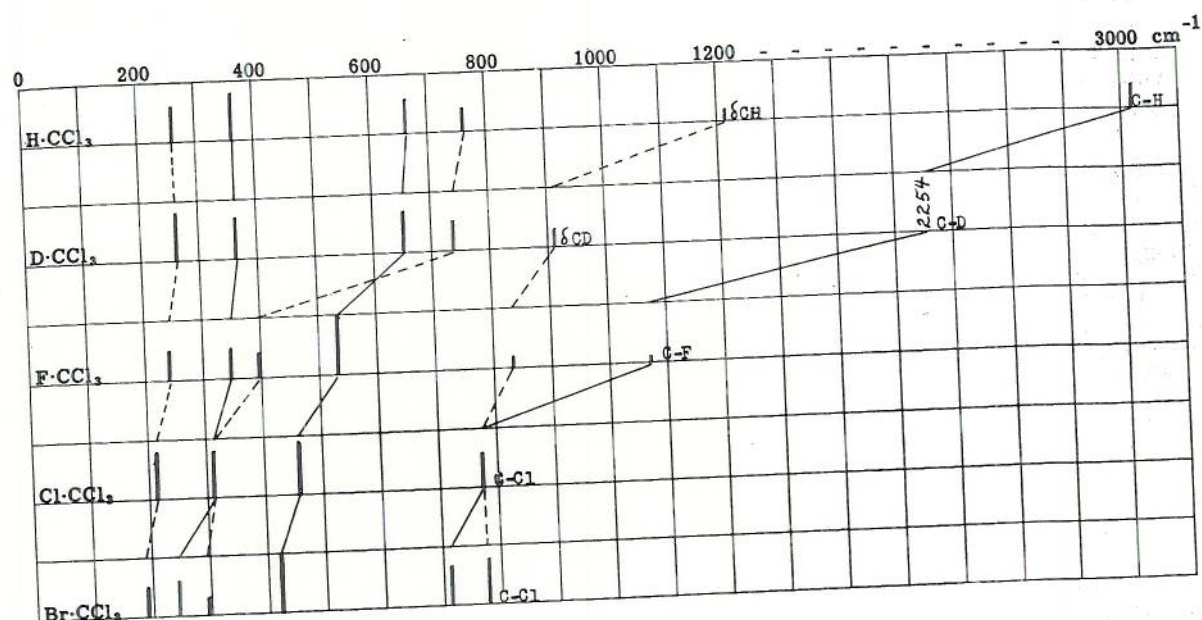


Figure 8 - Vibrational frequencies of $X\cdot CCl_3$ molecules

$ClCF_3$ has also been studied and the fundamental frequencies, along with those for CF_4 and HCF_3 are given in Table 9. These frequencies may be correlated as shown graphically in Figure 9. If the modes are correlated according to species, as is proper, it is observed that vibrations of the same species do not cross. However, if group frequencies are correlated, it is clear that the C-H valency in HCF_3 becomes the C-Cl valency in $ClCF_3$ and must cross the C-F valency mode of the same (A_1) species in so doing. Likewise, as the C-H bending mode changes over into the C-Cl bending, it must cross the C-F stretching mode of the same (E) species.

It is also of interest to note that the symmetric modes of the CF_3 group are higher than the corresponding asymmetric modes in HCF_3 , whereas the inverse is true for $ClCF_3$. It is probable that the pair of C-F deformation modes in HCF_3 and the pair of C-F valency modes in $ClCF_3$ correspond closely to the modes of a free CF_3 group, since in each case these frequencies are removed from those associated with the C-X part of the molecule.

TABLE 9
Fundamental Frequencies of $X\cdot CF_3$ Molecules

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$H\cdot CF_3$	3062 (A_1)	1117 (A_1)	697 (A_1)	1376 (E)	937 (E)	508 (E)
$F\cdot CF_3$	904 (A_1)	635 (F_2)		(1265) (F_2)	431 (E)	
$Cl\cdot CF_3$	1102 (A_1)	783 (A_1)	478 (A_1)	1210 (E)	560 (E)	356 (E)

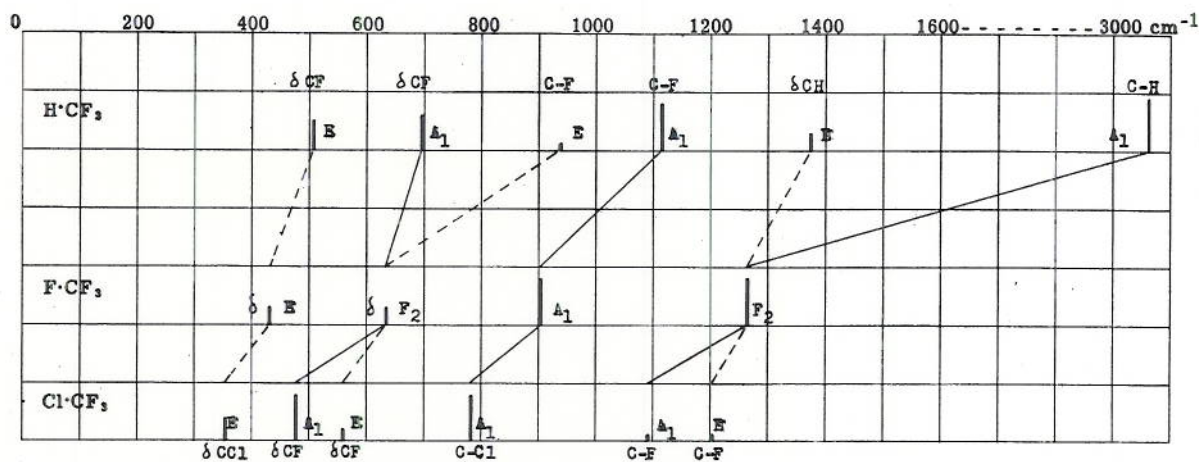


Figure 9 - Vibrational frequencies of $X\cdot CF_3$ molecules

The molecule $Br\cdot CF_3$ has not been studied, but Stepanov (13) has computed for the fundamental frequencies values which are probably accurate to within 30 to 50 cm^{-1} and which correlate nicely with the frequencies in Figure 9.

The fundamental frequencies of $F\cdot CH_3$, $F\cdot CF_3$, and $F\cdot CCl_3$ are shown in Tables 4, 2, and 8 and in Figures 5, 3, and 8 respectively. $F\cdot CBr_3$ has also been studied in the Raman effect* and the assignment is given in Table 10.

Other Molecules of Symmetry C_{2v} , C_s and C_i . H_2CF_2 , the only remaining fluoride of methane, has been studied by Glockler.* It has the symmetry C_{2v} ; and the species, activity, and description of the normal modes of vibration are shown in Table 11. Wagner (14) has computed the effect of changing only the mass of X on the fundamental frequencies using a simple valence-type system, as shown in Figure 10. Kohlrausch (5, p. 137) has summarized the assignments for H_2CX_2 molecules as shown in Figure 11. It may be noted that vibrations of the same species do not cross and that, although some of the assignments are incomplete and uncertain, the experimental frequency pattern conforms closely (but not exactly) with that calculated.

*See Bibliography, page 19.

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TABLE 10
Fundamental Frequencies of F·CBr₃

Mode	Species	Description	Frequency (cm ⁻¹)
ν_1	A ₁	C-F Stretch	1069
ν_2	A ₁	CBr ₃ Sym. Stretch	398
ν_3	A ₁	CBr ₃ Sym. Deformation	218
ν_4	E	CBr ₃ Asym. Stretch	743
ν_5	E	C-F Bending	306
ν_6	E	CBr ₃ Asym. Deformation	150

TABLE 11
Selection Rules for H₂CX₂ Molecules

Mode	Species	Activity	Description	H ₂ CF ₂
ν_1	A ₁	Ra (p), IR	Sym. C-H Stretch	2963
ν_2	A ₁	Ra (p), IR	CH ₂ Deformation	1509
ν_3	A ₁	Ra (p), IR	Sym. C-X Stretch	1079
ν_4	A ₁	Ra (p), IR	CX ₂ Deformation	532
ν_5	A ₂	Ra, ia	Twisting	1294
ν_6	B ₁	Ra, IR	Asym. C-H Stretch	3030
ν_7	B ₁	Ra, IR	CH ₂ Rocking	?
ν_8	B ₂	Ra, IR	CX ₂ Rocking	1509?
ν_9	B ₂	Ra, IR	Asym. C-X Stretch	1262

The molecules F₂CCl₂ and F₂CBr₂, also of C_{2v} symmetry, have both been studied in the Raman effect and the former in the infrared as well.* The fundamental frequencies (5, p. 140) are listed in Table 12. These data, together with those for other C_{2v} molecules containing the CF₂ group, are shown in Figure 12, where the vibrations are correlated according to species. Since, for lack of polarization measurements, the species of some of the F₂CBr₂ vibrations are unknown, the correlations for this molecule cannot be completed with certainty. The indicated descriptions of the F₂CCl₂ frequencies are probable but not certain. The two highest frequencies in F₂CCl₂ and in F₂CBr₂, however, are certainly C-F valence vibrations.

H₂CFCl, F₂CHCl, Cl₂CHF, Cl₂CBr, Br₂CHF, and Br₂CFCI have only a plane of symmetry, and HCFClBr has no symmetry. It is difficult, therefore, to make vibrational assignments and to describe the fundamentals in terms of group frequencies. Although the Raman spectra of these compounds have been studied, the data are incomplete because of lack of polarization data. Only Cl₂CHF has been studied in the infrared. The observed Raman frequencies are listed in Table 13.

*See Bibliography, page 19.

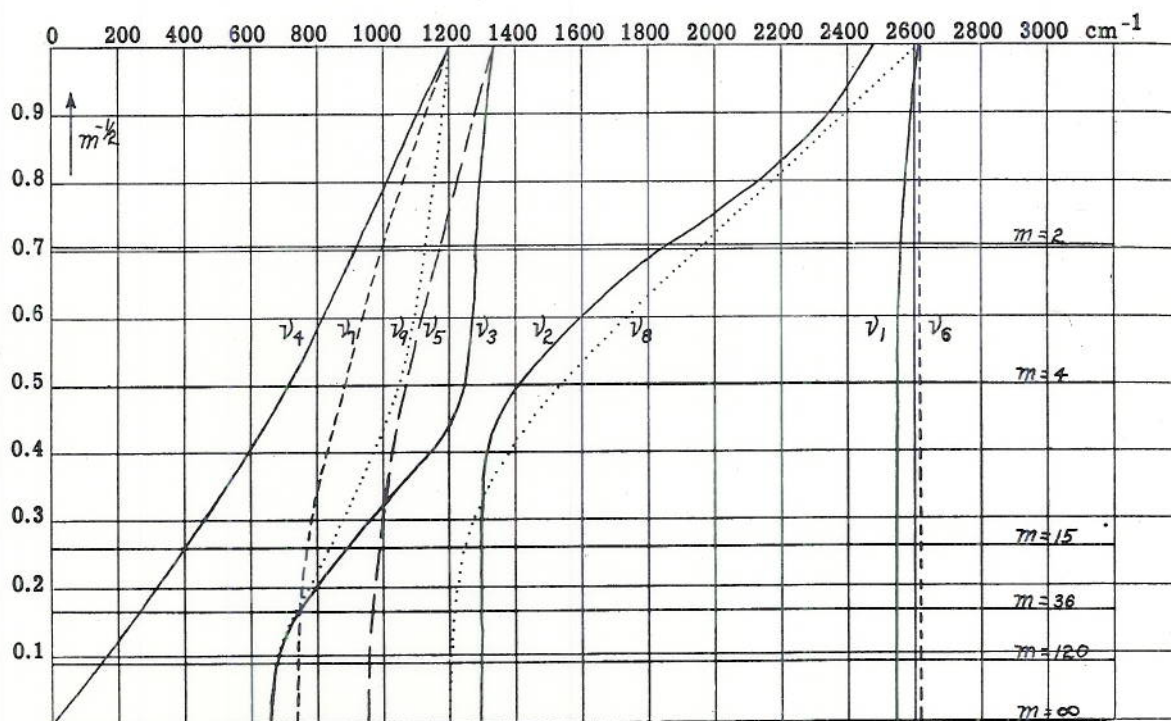
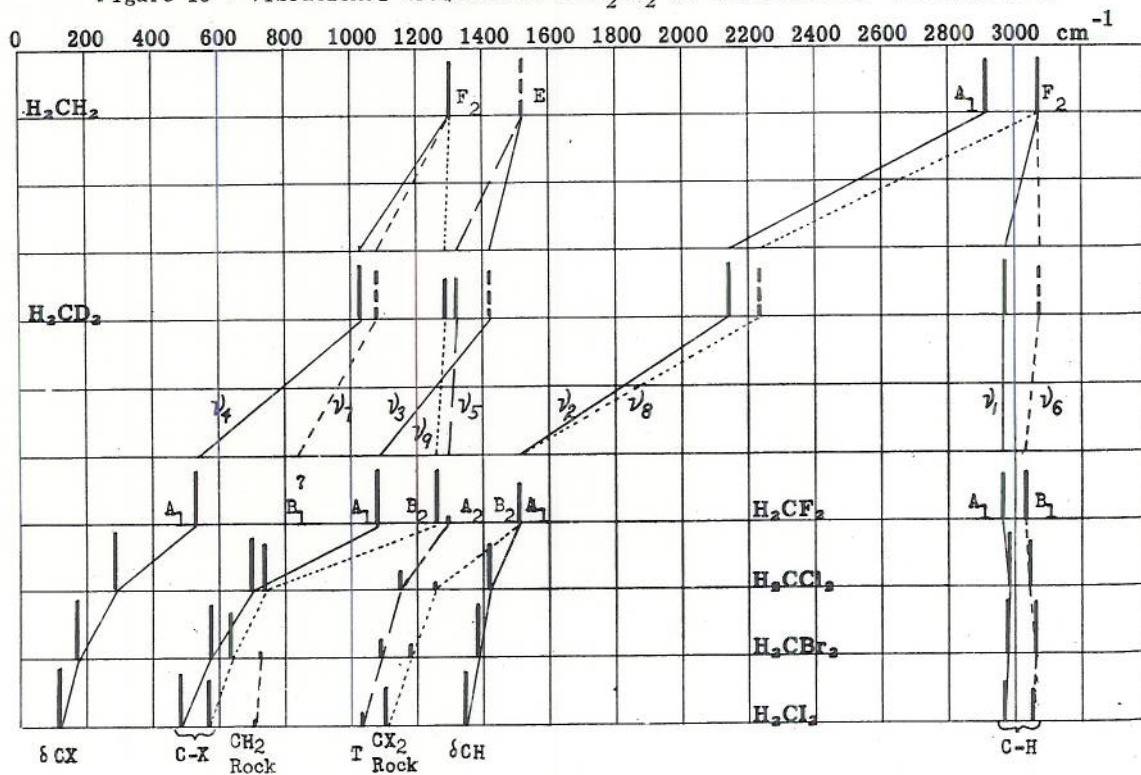
Figure 10 - Vibrational frequencies of H_2CX_2 as a function of the mass of XFigure 11 - Vibrational frequencies of H_2CX_2 molecules

TABLE 12
Fundamental Frequencies of F_2CCl_2 and F_2CBr_2

F_2CCl_2	260	320	433	455	664	877	919	1082	1147
F_2CBr_2	165	282	330	340	367	623	816	1077	1142

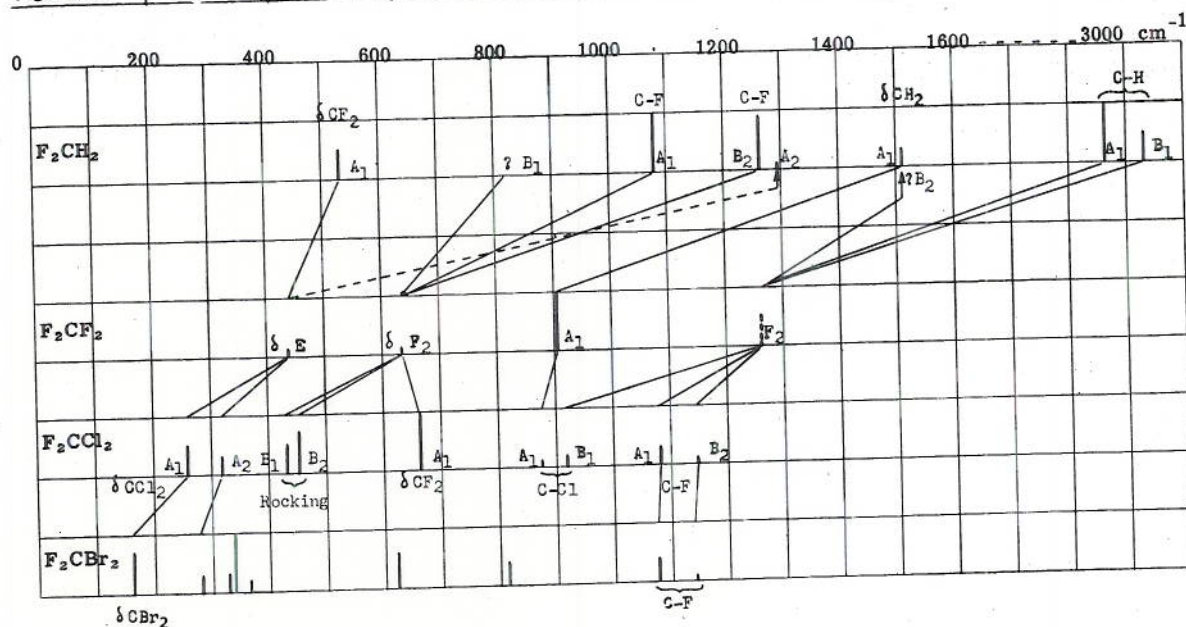


Figure 12 - Vibrational frequencies of F_2CX_2 molecules

TABLE 13
Raman Frequencies* of Other Methane Derivatives

H_2CFC1	F_2CHCl^\dagger	Cl_2CHF^\dagger	Cl_2CFBr	Br_2CHF	Br_2CFCl	$HCFC1Br$
385 (1)	369 (7)	277 (8)	203 (4)	93 (6)	160 (10)	225 (10)
743 (10b)	409 (1)	366 (4)	215 (5)	171 (9)	195 (4)	313 (9)
1004 ($\frac{1}{2}$)	416 (10b)	457 (10)	303 (9)	295 (5)	267 (20)	425 (9)
1046 (2b)	436 ($\frac{1}{2}$)	727 (8)	334 (2)	358 (9)	306 (3)	649 (6)
1353 (2)	456 (1)	738 (5)	390 (1)	560 (3)	340 (3)	659 (10)
1468 (2)	597 (8)	795 (2)	501 (10)	619 (10)	462 (10)	735 (2)
2911 (4)	800 (9b)	1067 (0)	779 (5)	701 (1)	741 (5)	773 (5b)
2993 (10b)	831 (3)	1255 (0)	825 (1)	3017 (2)	790-802 (1)	1063 (3d)
3049 (6b)	1085 ($\frac{1}{2}$)	1310 (1)	1069 (0)	[3059 (2) ?]	1063 (0)	1205 (4)
	1228 ($\frac{1}{2}$)					1302 (5)
	1311 (4)					3018 (7b)
	1354 (3)					
	3032 (8b)					

* Intensities are given in parentheses.

† The Raman photographs have been remeasured and the revised frequencies assigned to the fundamental modes by G. Glockler and W. F. Edgell, *J. Chem. Phys.* **9**, 224, (1941). The specific heat was calculated over the range 250-650°K, and accurate formulas were developed. The spectral sequence $CHClBr_2 \rightarrow CHClBrF \rightarrow CHCl_2F \rightarrow CHClF_2$ is also shown.

The foregoing results for methane derivatives may now be summarized. Although several of the fluorinated compounds have not yet been studied in the infrared,* the Raman spectra of most of them are known and the fundamental frequencies appear to be assigned correctly in most instances, as indicated by the data in Figures 2 through 12. It is apparent that the C-F bond does not have a single "characteristic" stretching frequency in all molecules; instead, the stretching frequency (or frequencies) depends upon the number of C-F bonds present and upon the other substituents on the carbon atom, and in general it falls within a rather broad spectral region extending from about 935 to 1250 cm^{-1} , as indicated by the collected data in Table 14.

TABLE 14
C-F Stretching Frequencies

Molecule	Frequency (cm^{-1})
$\text{CH}_3\text{-F}$	1048
F-CCl_3	1072
F-CBr_3	1069
H_2CF_2	1079, 1262
Cl_2CF_2	1082, 1147
Br_2CF_2	1077, 1142
HCF_3	937, 1117
ClCF_3	1102, 1210
H_2CFCl	1046
HCFCl_2	1067 (1255 ?)
BrCFCl_2	1069
HCFBrCl	1063 (1205)
HCFBr_2	701 ?
ClCFBr_2	1063
F_2CHCl	1085, 1228

However, it appears that this broad region may be divided into narrower regions under certain conditions as, for example, in the case of compounds containing only one C-F bond. The C-F stretching frequency in $\text{CH}_3\text{-F}$ appears at 1048 cm^{-1} , which value undoubtedly corresponds very closely to the "natural" frequency of a C-F bond, as would be observed in a free C-F group. All but one of the nine compounds having only one C-F bond display a band in the region 1045 to 1072 cm^{-1} . In this region there is no frequency reported for HCFBr_2 , but it is probable that it has been missed. Delwaille and Francois (15), in a detailed summary of the Raman spectra of tetrahedral pentatomic molecules, conclude that for completely halogenated methanes the C-F bond in monofluoro compounds is characterized by a polarized Raman line in the narrow region 1063 to 1071 cm^{-1} . But when hydrogen-containing compounds are included in the correlation, it is clear that this region must be broadened to include frequencies as low as 1048 cm^{-1} .

*See Bibliography, page 19.

A free CF_2 group would evidently have stretching frequencies near the values 1079 and 1262 cm^{-1} found for H_2CF_2 . In view of the frequencies found for F_2CCl_2 , F_2CBr_2 , and F_2CHCl (Table 14), it appears that the CF_2 group is characterized by one band in the region 1075 to 1085 cm^{-1} and another in the region 1140 to 1265 cm^{-1} . In the special case that no hydrogen is present, the corresponding regions are 1075 to 1085 cm^{-1} and 1140 to 1150 cm^{-1} .

The CF_3 group also has two C-F stretching frequencies, one of which is doubly degenerate. These will normally appear near 937 and 1117 cm^{-1} , as in HCF_3 . In ClCF_3 , these frequencies appear at 1102 and 1210 cm^{-1} , and they may be expected at about the same place in BrCF_3 according to the calculations of Stepanov (13).

It hardly needs to be mentioned that the deformation frequencies of CF_2 and CF_3 groups depend upon the rest of the molecule to an even greater extent than do the valence vibrations and are accordingly spread over a wide range of low frequencies.

The values of force constants and the form of the potential function for methane derivatives are also of interest in connection with further work. Although the data are too scant to permit conclusive results, it appears that in molecules containing only one C-F bond, as in $\text{CH}_3\text{-F}$ which approximates a diatomic molecule, the C-F bond distance is only slightly shorter than Pauling's covalent bond distance (1.38\AA vs. 1.41\AA), and a valence type potential employing a force constant $f_{\text{C-F}} = \text{approximately } 5.4 \times 10^5 \text{ dynes/cm}$ is suitable, at least for CH_3F . When more than one fluorine are attached to a carbon atom, the C-F bond distances are reduced to about $1.32 - 1.36\text{\AA}$, as has been pointed out by several investigators. This may be associated with the fact that in all cases at least one of the two C-F stretching frequencies is considerably greater than the "normal" value of 1050 cm^{-1} . It also appears that valence type forces cannot accurately account for the vibrational frequencies, this being certain in the case of CF_4 and other molecules of tetrahedral symmetry.

For CF_4 the C-F stretching force constant values range from about 9.10 to 3.08×10^5 dynes/cm, depending on the number and type of forces used in addition to the valence force. When simple valence forces are used, the calculated frequencies differ from the observed by as much as 42 percent; when additional forces, allowing for a sixth power repulsion between like atoms, are used, the agreement is within from 3.0 to 0.3 percent. Since this situation also occurs for other CX_4 molecules, it is not yet definite from work on methane derivatives whether fluorine-containing compounds, particularly the fluorocarbons, require special methods for the interpretation of their spectral properties.

Fluorocarbons Containing Two or More Carbon Atoms

Spectral data for only a very few larger fluorocarbon and fluorinated hydrocarbon molecules are found in the literature, and in practically all instances interpretation is either incomplete or entirely lacking.

The Raman spectrum of liquid hexafluoroethane, C_2F_6 , has been obtained by Rank and Pace (16), and the infrared spectrum of the gas has been studied by Nielsen et al. (17). The latter authors have made a satisfactory assignment of all but one of the fundamental frequencies, as shown in Table 15, and have given an essentially complete interpretation of the spectra. They have concluded that the molecule has the "staggered" configuration of symmetry D_{3d} , rather than the "eclipsed" configuration, and that in making a normal coordinate treatment, it is necessary to allow for repulsive forces between the F atoms in the CF_3 groups. Brockway and Livingston (18) have also eliminated the nonstaggered

or "eclipsed" model on the basis of electron diffraction results and find the most probable dimensions of the molecule to be: $C-C = 1.45 \pm 0.06$ A, $C-F = 1.35 \pm 0.02$ A, angle $FCF = 107\frac{1}{2} \pm 1\frac{1}{2}^\circ$. Pace (19) has used these dimensions and the assignment of Nielsen et al to derive the force constants for the C_2F_6 molecule listed in Table 16.

TABLE 15
Fundamental Vibration Frequencies of Hexafluoroethane

	Character*	Species	Activity	Frequency	Spectrum
ν_1	C-F Stretch	A_{1g}	Ra·p	1420 cm^{-1}	R (liq.)
ν_2	C-C Stretch	A_{1g}	Ra·p	809	R (liq.)
ν_3	CF_3 Deformation	A_{1g}	Ra·p	349	R (liq.)
ν_4	Torsion	A_{1u}	Inactive	—	—
ν_5	C-F Stretch	A_{2u}	IR·	1117	IR (g)
ν_6	CF_3 Deformation	A_{2u}	IR·	714	IR (g)
ν_7	C-F Stretch	E_u	IR·	1250	IR (g)
ν_8	CF_3 Deformation	E_u	IR·	522	IR (g)
ν_9	CF_3 Rock	E_u	IR·	216	IR (g)
ν_{10}	C-F Stretch	E_g	Ra·dp	1237	Ra (liq.)
ν_{11}	CF_3 Deformation	E_g	Ra·dp	620	Ra (liq.)
ν_{12}	CF_3 Rock	E_g	Ra·dp	380	Ra (liq.)

*The terms in this column have only very rough meaning.

TABLE 16
Force Constants for Hexafluoroethane

f_{C-F}	$= 9.15 \times 10^5$ dynes/cm
f_{FCF}	$= 0.71$
$f_{C-F, FCF}$	$= 1.13$
$f_{C-F, FCC}$	$= 1.35$
f_{FCC}	$= 0.80$
f_{C-C}	$= 5.45$
$f_{C-C, FCF} - f_{C-C, FCC}$	$= -0.28$.

The first three constants in Table 16 are those derived for CF_4 . When they are used to calculate CF_4 frequencies, the values obtained differ from those observed by as much as 18 percent, and it may be noted that the f_{C-F} value is considerably higher than those listed in Table 3. The remaining constants were adjusted so as to obtain the best fit with the observed frequencies for C_2F_6 . With these constants, all of the observed frequencies except those of species E_u (Table 15) are reproduced to within 5 percent—which is a considerable improvement over a simple valence force field treatment. Somewhat greater discrepancies were found for the E_u frequencies because no interaction between the CF_3 groups was

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assumed. As pointed out by Pace, the short C-C distance (1.45A as compared to the value 1.54A in saturated hydrocarbons) is accompanied by a rather high value of the C-C force constant in this molecule.

Torkington and Thompson (20) have measured the infrared spectra of gaseous $\text{CH}_2=\text{CHF}$, $\text{CH}_2=\text{CF}_2$, $\text{CH}_2=\text{CFCl}$, $\text{CCl}_2=\text{CF}_2$, and $\text{CF}_2=\text{CF}_2$ over the 2-20 micron range. Their results for all but the first of these ethylene derivatives will be reviewed later in this report in connection with more detailed results to be presented for these molecules. The fundamentals of vinyl fluoride, $\text{CH}_2=\text{CHF}$, together with previous results for the other vinyl halides (21) are listed in Table 17. Here there is a uniform decrease in frequency with increasing mass of X, except for the two out-of-plane vibrations ν_{11} and ν_{12} which involve bending of C-H bonds and for ν_8 which also involves C-H bendings. Thus, there is nothing unusual about the spectrum of vinyl fluoride in comparison with the other halides, according to these assignments. The C-F stretching frequency (1153 cm^{-1}) in this olefin is somewhat higher than the value ($\sim 1050\text{ cm}^{-1}$) found for most methane derivatives containing a single fluorine atom, but, as pointed out by Torkington and Thompson, this also occurs in the case of the analogous compounds of chlorine, bromine, and iodine.

TABLE 17
Fundamental Vibration Frequencies of Vinyl Halides, $\text{CH}_2=\text{CHX}$

	Description	Fluoride	Chloride	Bromide	Iodide
ν_1	CH_2 Sym. Stretch	3080	3030	3014	3000
ν_2	CH Stretch	3110	3080	3076	3060
ν_3	CH_2 Asym. Stretch	3135	3130	3100	3110
ν_4	C=C Stretch	1650	1610	1605	1593
ν_5	C-X Stretch	1153	724	615	535
ν_6	C-X Bend	500	395	345	309
ν_7	CH_2 Deformation	1393	1370	1377	1376
ν_8	CH_2 Rock	924	1030	1008	990
ν_9	CH Rock	1306	1280	1262	1229
ν_{10}	Twisting	715	622	497	435
ν_{11}	CH_2 Wag	732*	895	902	909
ν_{12}	CH Wag	860*	940	940	946

*These frequencies should be interchanged, according to recent results reported privately by Dr. H. W. Thompson.

Torkington and Thompson also make the following observations on the basis of their results for the other ethylene and methane derivatives. First, a single fluorine atom attached to an olefinic carbon has no unusual effect upon the C=C stretching frequency, but when two fluorines are attached this frequency is enhanced by approximately 100 cm^{-1} . It is also suggested that the appreciable lowering of the C-H bending frequencies of the $=\text{CH}_2$ group when fluorine is attached to the other carbon atom must be due to some effect transmitted through the double bond. Secondly, the infrared absorption associated with C-F stretching vibrations is strong in comparison with the intensity of the corresponding

Raman bands, and this effect is several times greater in compounds containing a CF_2 group than in those containing only one C-F bond.

No previous information concerning the force constants for fluorinated olefinic hydrocarbons is available, since normal coordinate treatments have not been made.

Some spectral and structural data are available for $\text{CH}_3\text{-CF}_3$ and a few larger fluorinated hydrocarbons, and as in the case of the other ethylenederivatives, these will be reviewed in connection with the discussion of these compounds in the following parts of this report. The results of previous work summarized here, together with results from the spectral interpretations in this report, will be used in an attempt to explain qualitatively the spectra of other larger molecules and in developing relationships which may provide useful structural information through spectral studies on unknown fluorinated hydrocarbon samples. (See Applications, p. 140.)

METHOD OF ATTACK

In view of the results available from previous work on fluorinated hydrocarbons, the present study has been concerned only with compounds of higher molecular weight containing two or more carbon atoms. All samples were collected by the Naval Research Laboratory where all the experimental infrared measurements were made. All Raman spectra were obtained at the University of Oklahoma, and the infrared and Raman data were then exchanged. Parts of the work on the interpretation of data were done independently by one or the other of the two laboratories, and other parts were done jointly through close cooperation.

Because of the order in which samples became available, the initial work was done on the most complicated molecules, the aliphatic fluorocarbons containing five- and six-atom rings, rather than upon the smaller symmetrical molecules. This early experimental work pointed to the necessity for development of more powerful Raman excitation equipment—a development which was carried out next along with the development of certain theoretical results for later use in the spectral interpretations. Since then the work has been centered mainly upon determination and interpretation of the spectra of fluorinated ethylenes, cyclic C_4F_8 , and fluorinated aromatics. These results, together with some limited results for several other molecules, are presented in the following section. Application of the spectral results (the experimental data and their interpretation) to the solution of chemical problems (identification and analysis, determination of structure, calculation of thermodynamic data, etc.) is discussed in the concluding topic.

The results of work on determination of a suitable potential function for ethylene molecules, and evaluation of its force constants which is now in progress but not yet completed, will be reported later along with further experimental results for other molecules not included here.

EXPERIMENTAL

MATERIALS

All samples collected as of 31 May 1949, those which have been studied and those which have not, are listed in Table 18, together with the source and available physical properties. Each sample has been given a serial number which is used throughout the text in referring to the table. In the case of samples for which no physical properties were supplied, data for the compound as taken from the literature are enclosed in parentheses. The type of spectral data obtained for various samples is indicated, so that Table 18 summarizes the status of the project as of 31 May 1949.

Available information regarding the purity of the samples studied is to be found in the text under the discussion of the results for the respective compounds. All of the samples studied were used as received, without further purification except for distillation into the Raman tubes.

INFRARED EQUIPMENT AND PROCEDURES

All infrared spectra were obtained with a large research-type instrument already discussed (22). Interchangeable prisms (60° , 100 x 150 mm faces) of LiF, NaCl, and KBr were used over the ranges 2-6, 6-15 and 15-22 μ , respectively. Radiant energy from a Nernst source, after dispersion by the spectrometer having Wadsworth-Littrow optical arrangement, was detected by a compensated vacuum thermocouple. The thermocouple signal was measured with a galvanometer, amplified photoelectrically, and recorded as a function of wavelength on a Speedomax potentiometer-type recorder. Corresponding recorder traces obtained with sample cell and dummy cell in front of the entrance slit were measured by hand, and percent transmittance was plotted on standard spectral charts. Percent transmittance is generally reproducible to within 2 to 3 percent, and the wavelength measurements over most of the spectral range are accurate to within $\pm 0.01 \mu$. In certain instances (when calibration was checked) they are probably correct to within $\pm 0.001 \mu$ for sharp absorption maxima.

All samples were measured at room temperature (approximately 25°C) either as liquid, or gas, or both. Liquid samples were measured in the same set of four sealed absorption cells similar to those described by Smith and Miller (23), having thicknesses of 0.0104, 0.0576, 0.2398, and 0.955 mm. The spectral curves for the respective cell thicknesses are indicated by dashed, broken, solid, and dashed-broken lines. In regions where the absorption was too strong with the thinnest cell, the sample was measured as a capillary film between KBr plates without spacer, and the results were recorded as dotted lines. All vapor spectra were obtained using a 10-cm pyrex cell* with KBr windows. Solid curves are used for sample pressures in the range 800-600 mm Hg, broken curves for the range 400-200 mm, dashed for the range 100-25 mm, and dotted curves for sample pressures

* $\text{CH}_3\text{-CCl}_3$, because of its low vapor pressure, was also measured in a 69-cm cell (solid curve, Figure 33, page 125).

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below 25 mm. In order to obtain sample pressures less than 25 mm, the samples were diluted with dry air to a total pressure of 100 mm and then evacuated to 25 mm. The partial pressure of the sample is recorded in mm Hg on all spectral curves, partial pressures under 25 mm being given as fractional parts of the total cell pressure.

Although the cell pressure was measured to within ± 1 mm Hg or better, there was in certain instances evidence of contamination by air (or other impurities) so that the accuracy of the partial pressure is not definitely known. Also, in the case of some olefinic compounds there was evidence that the sample tended to dissolve in the beeswax-and-rosin wax used for attaching the cell windows, especially when the sample was allowed to remain in the cell for several days. Recent work (24) has indicated that Fluorothene-W, a polymeric wax of trifluoromonoethylenylene, may be a more satisfactory sealing compound.

The infrared spectral curves are grouped together in Figures 32 to 40, pages 122 to 139 for easy comparison. It will be noted that the wavelength scale changes at 14 μ , causing the curves to be discontinuous at that point. Also, in some cases the transmittance values obtained with NaCl and KBr prisms at 14 μ were not quite equal. Positions of the infrared absorption maxima are given in the tables opposite the spectral curves. Shoulders and inflexions due to unresolved bands are not included in these tables, and the positions of the absorption maxima do not necessarily correspond to band centers.

RAMAN EQUIPMENT AND PROCEDURE

Spectrograph

The spectrograph used was manufactured by the Lane-Wells Company. Designed especially for Raman spectroscopy, it combines a large aperture with high dispersion. The collimator lens is an uncemented achromat having a focal length of 900 mm and a diameter of 100 mm. All four lens surfaces are covered with a low-reflection coating. The dispersive system consists of three 60-degree prisms of extra-dense flint glass with faces 153 mm wide and 75 mm high having low-reflection coating.

The photographic camera resembles the Schmidt type. The correcting plate, designed by P. Swings, is a crown-glass shell placed immediately behind the third prism. The spherical mirror, with a radius of curvature of 737 mm and a diameter of 200 mm, is made of Pyrex glass, is aluminized, and is provided with a protective coating.

The spectrum is focused on a film held in a curved film holder so constructed as to eclipse only about ten percent of the light. A narrow mask was added to prevent the 4358 mercury light from striking the film. The linear dispersion is 15 Å/mm near 4358 Å and 34 Å/mm at 5000 Å. The height of the spectrum is 5 mm or less, and the spectrum from 4358 to 5000 Å extends over 38 mm. To eliminate temperature changes during long exposures, the entire spectrograph is enclosed in a thermostated box.

The spectrograph has proved highly satisfactory except for the fact that spurious light may hinder the observation of weak Raman bands with shifts of less than 170 cm^{-1} . The spurious light appears on each side of the strong mercury lines, especially at about 131 cm^{-1} toward long wavelengths from the 4358 Å mercury line and at 150 cm^{-1} toward long wavelengths from the 4916 Å line.

Elimination of the spurious light would have been desirable, since many of the fluorocarbons have fundamental frequencies below 200 cm^{-1} . Masking the collimator lens down to half its diameter reduced the spurious light somewhat but did not eliminate it. The

TABLE 18
 Fluorocarbon Project Status (31 May 1949)

Compound	Serial Number	Source	Spectral Data ⁽¹⁾		Frequency Assignment	Physical Properties
			I.R.	Raman		
CF ₄	362	K. Chem. ⁽¹⁾				b.p. -128.0; m.p. -183.5°C
CF ₃ Cl	361	K. Chem.				b.p. - 82; m.p. -182
CF ₂ Cl ₂	360	K. Chem.				b.p. -29.8; m.p. -158
CFCl ₃	359	K. Chem.				b.p. 23.8; m.p. -111
CF ₃ H	364	K. Chem.				b.p. -84.4; m.p. -160
CF ₂ H ₂	363	K. Chem.				b.p. -51.7
CF ₂ =CF ₂	300	du Pont ^(a)	G	G (p)	No Torsion	(b.p. -76.3; m.p. -142.3)
CF ₂ =CF ₂	394	du Pont	G	G		Very pure sample
CF ₂ =CH ₂	299	du Pont	G	G	Complete	(b.p. - 82°C)
CF ₂ =CH ₂	370	du Pont				Examined by E. K. Plyler, National Bureau of Standards
CF ₂ =CCl ₂	325	du Pont	G	G, L (p)	Complete	(b.p. +19; m.p. -116)
CF ₂ =CFCl	379	du Pont	G	L	Complete	(b.p. -27.9; m.p. -157.5)
CF ₃ -CF ₃						Studied previously; See page 17
CH ₃ -CF ₃	298	du Pont	G	G	Complete	(b.p. -47.5; m.p. -111)
CH ₃ -CF ₂ H	371	du Pont	G			(b.p. -24.7; m.p. -117)
CH ₃ -CF ₂ Cl	373	du Pont				(b.p. -9.0)
CH ₃ -CFCl ₂	372	du Pont				(b.p. +32.0; m.p. -103.5)
CF ₃ -CH ₂ Cl	375	du Pont				(b.p. +6.1; m.p. -105.6)
CF ₂ Cl-CF ₂ H	377	du Pont				(b.p. -10.0; m.p. -117)
CF ₃ -CCl ₃	366	K. Chem.	G		Partial	b.p. +45.7; m.p. +14
CH ₃ -CCl ₃	365	du Pont	G			b.p. +74.1; m.p. -30.4
CF ₂ Cl-CF ₂ Cl	329	Colorado ^(b)	G			b.p. +4°C
CF ₂ Cl-CF ₂ Cl	368	K. Chem.	G			
CF ₂ Cl-CFCl ₂	330	Colorado	L			b.p. 28°C
CF ₂ Br-CF ₂ H	391	Colorado				b.p. 282.1 ± 0.4° A at 760 mm
CF ₂ Br-CCl ₂ H	392	Colorado				b.p. 363.2 ± 0.1° A at 760; N _D ²⁰ 1.4349
CF ₂ Br-CFClH	393	Colorado				b.p. 325.9 ± 0.2° A at 760; N _D ²⁰ 1.3685
CF ₃ -CF=CF ₂	327	du Pont	G	G	Partial	(b.p. -29.4; m.p. -156.2°C)
CF ₃ -CF=CF ₂	358	du Pont	G			
CF ₃ -CF ₂ -CF ₃	326	K. Chem.	G	G		(b.p. -38°C; m.p. -183°C)
CF ₃ -CF ₂ -CF ₃	328	3M ^(c)	G			b.p. -37°C
CF ₃ -CFH-CF ₃	369	3M				
CF ₃ -CH ₂ -CH ₃	367	du Pont				b.p. -13°C
Cyclic C ₆ F ₆	324	K. Chem.	G	G, L (p)	Complete	(b.p. -5; m.p. -40)
CF ₂ =CCl-CCl=CF ₂	353	Miller ^(d)				b.p. 61.2°C/740
CF ₂ =CCl-CCl=CFCl	351	Miller				b.p. 104.5°C/738
CFCl=CCl-CCl=CFCl	349	Miller				b.p. 140.6°C/740
CClF ₂ -CCl ₂ -CCl ₂ -CClF ₂	352	Miller				b.p. 135.0°C/100
CClF ₂ -CCl ₂ -CCl ₂ -CCl ₂ F	350	Miller				b.p. 124.2°C/20
CCl ₂ F-CCl ₂ -CCl ₂ -CCl ₂ F	348	Miller				b.p. 152.5°C/20
Cyclic C ₆ F ₁₀	356	Cady ^(e)	G	L (p)		(b.p. 22.5°C)
Cyclic C ₆ F ₈ H	357	Cady				(b.p. 37.8 - 38.2°C)
n-C ₆ F ₁₂	354	Cady	G	L (p)		(b.p. 29.3°C; m.p. -125.4°C)
iso-C ₆ F ₁₂	355	Cady	G, L			(b.p. 30.1°C; m.p. -96.7°C)
n-C ₇ F ₁₆	277	Hopkins ^(f)	L	L		b.p. 82.4°C, N _D ²⁰ 1.2617 (m.p. -52.6°C)

TABLE 18 (Cont.)
Fluorocarbon Project Status (31 May 1949)

Compound	Serial Number	Source	Spectral Data ⁽¹⁾		Assignment Frequency	Physical Properties
			I.R.	Raman		
	276	Hopkins	L	L		b.p. 76.3°C; n_D^{20} 1.2815
	287	Hopkins	L	L		b.p. 75.1°C; n_D^{20} 1.2772
	286	Hopkins	L	L		b.p. 100.5°C; n_D^{20} 1.2896
	285	Hopkins	L	L		b.p. 102.1 - 102.4°C; n_D^{20} 1.2922
	275	Hopkins	L	L		b.p. 124.9°C; n_D^{20} 1.2988
Fluorobenzene	309	Finger ^(d)	L	L	Partial	b.p. 84.5°C
1,4-Difluorobenzene	310	Finger	L	L	Partial	b.p. 89°C
1,2,4-Trifluorobenzene	311	Finger	L	L	Partial	b.p. 90°C
1,2,4,5-Tetrafluorobenzene	317	Finger	L,G	L	Partial	b.p. 86.5 - 87.0°C; m.p. approx. +4°C
Benzotrifluoride	314	Finger	L	L	Partial	b.p. 102.2°C
m-Fluorobenzotrifluoride	315	Finger	L	L	Partial	b.p. 100.5°C
2,5-Difluorobenzotrifluoride	316	Finger	L	L	Partial	b.p. 109.5°C
o-Fluorotoluene	312	Finger	L	L	Partial	b.p. 114.5°C
p-Fluorotoluene	313	Finger	L	L	Partial	b.p. 116.5°C
1,4-Di(trifluoromethyl) benzene	388	Saylor ^(h)				b.p. 116.17 - 116.23°C/760
CH ₃ -O-CF ₂ -CHFCI	331	Colorado	L			(b.p. 64.4°C/630; n_D^{20} 1.33381)
C ₂ H ₅ -O-CF ₂ -CHFCI	332	Colorado	L			(b.p. 82.0°C/630; n_D^{20} 1.34787)
n-C ₃ H ₇ -O-CF ₂ -CHFCI	333	Colorado	L			(b.p. 102.3°C/630; n_D^{20} 1.35751)
n-C ₄ H ₉ -O-CF ₂ -CHFCI	334	Colorado	L			(b.p. 124.5°C/630; n_D^{20} 1.36796)
(C ₄ F ₉) ₂ O	389	3M	L			
(C ₄ F ₉) ₂ N	390	3M	L			

(a) E. I. du Pont de Nemours & Co., Wilmington, Delaware.

(b) Drs. J. R. Lacher and J. D. Park, University of Colorado, Boulder, Colorado.

(c) Research Department, Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.

(d) Prof. W. T. Miller, Cornell University, Ithaca, New York.

(e) Prof. G. H. Cady, University of Washington, Seattle, Washington.

(f) Johns Hopkins University, Baltimore, Maryland; samples from this source were purified at NRL.

(g) Dr. O. C. Finger, Illinois Geological Survey, Urbana, Illinois.

(h) Prof. J. H. Saylor, Duke University, Durham, North Carolina.

(i) G means gaseous phase, L means liquid phase, (p) means polarization measurements for Raman lines.

(j) Kinetic Chemicals, Inc., Wilmington, Delaware.

spurious light was not observed when an older irradiation apparatus was used in which the Raman tube was placed at considerable distance from the spectrograph slit and the scattered light was focused on the slit with a condensing lens. With the irradiation apparatus used in the present investigation, in which the window of the Raman tube was placed very close to the slit, the spurious light was somewhat reduced when the condensing lens between the Raman tube and the slit was removed.

Photographic Emulsions

Photographic emulsions used in Raman spectroscopy must be fast, but for good photometry it is also desirable that they be as fine-grained as possible. At the beginning of the present work, Triple S Ortho films and Agfa 47 developer were used. Later, on the basis of data supplied by the manufacturers, five emulsion types and four developers were chosen as most suitable. These were compared in all combinations with respect to spectral sensitivity and grain size.* From the emulsions tested, Eastman Tri X Panchromatic was chosen as most satisfactory for general Raman work. It is as fast as any of the emulsions tested and has the advantage of very nearly constant sensitivity over the range from 4358 to 5000 Å when used in the Lane-Wells spectrograph. Kodak Dk60a developer was used generally. However, since it produces finer grain than any of the other developers tested, Microdol developer was found most satisfactory for microphotometry, although longer exposure times are required when this developer is used.

Irradiation Apparatus and Procedures for Gases

Rank and Pace (16) observed that the Raman spectrum of hexafluoroethane is only about one-tenth as intense as that of ethane. In the first work at the University of Oklahoma with liquid fluorocarbons, similar results were found. Thus, the over-all intensities of the Raman spectra of perfluoromethylcyclohexane and methylcyclohexane were found to be about equal when the fluorocarbon was exposed nine times as long as the hydrocarbon. It is clear, therefore, that to observe the Raman spectra of fluorocarbons, especially in the gaseous state, very powerful irradiation is required.

After considerable experimentation with various designs of mercury lamps, a satisfactory irradiation apparatus for gases was developed. It employs two high-current low-pressure Pyrex mercury lamps constructed as shown in Figure 13. The arcs are folded, so as to have two effective straight columns. This arrangement has the added advantage that the front end of the irradiation apparatus, i.e., the end opposite to the electrodes, can be placed close to the slit of the spectrograph. This makes it possible to place the window of the Raman tube very near the slit, thus facilitating the alignment.

The most essential feature of these lamps is the internal water-cooling of the mercury pools and the mercury vapor, shown in detail in section AA of Figure 13. This type of water-cooling, first used by H. L. Welsh and M. F. Crawford† of the University of Toronto, makes possible the use of very high arc currents without introducing any continuous background or broadening of the mercury lines. The arc current that can be used is limited largely by the facilities for dissipating the heat generated in the luminous column. The back

* Cf. *Spectroscopic Properties of Fluorocarbons*, University of Oklahoma Technical Report 1 on ONR Contract N7onr-398-T.O.1, 15 May 1948.

† Private communication to J. Rud Nielsen.

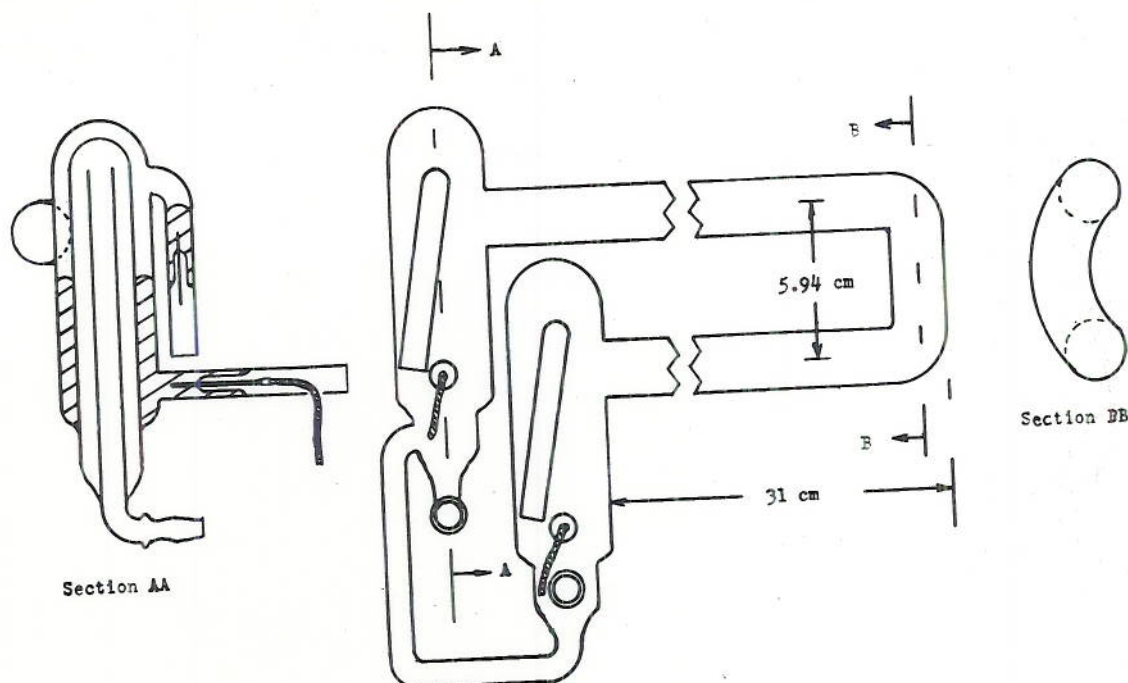


Figure 13 - Mercury lamp with water-cooled mercury-pool electrodes

of the reflector and the electrode ends of the lamp are enclosed in a box, and air is drawn through the reflector and out of the box by a centrifugal blower. In this instance the hot exhaust air from the blower was piped to another room, so as not to heat the room in which the spectrograph was set up and to permit cool air to enter the irradiation apparatus near the slit of the spectrograph. With the present design the maximum arc current that could be used was about 15 amperes.

The arcs operate on 110 volts direct current with two or three ohms resistance in series. The upper auxiliary electrodes are used only for starting the lamps. They are connected to the terminals of a small induction coil. The induction-coil lead to the cathode end is also connected to a tinfoil strip (not shown in Figure 13) that encircles the glass of the lamp just above the surface of the mercury pool. A momentary operation of the induction coil usually starts the arc. When the room is abnormally cool, or when the lamp is not free of air, it may be necessary to blow warm air over the lamp for about a minute before applying the induction coil.

The mercury lamps were constructed by Mr. R. C. Wyckoff, glass blower at the University of Oklahoma. They were cleaned with chromic acid, and the oxide coating was then removed from the tungsten electrodes by passing a small alternating current from one electrode to the other through a potassium hydroxide solution for one or two minutes. After rinsing with acetic acid and repeated rinsing with distilled water, the lamps were placed in an oven and sealed to a vacuum system. With forepump and mercury diffusion pump operating, the lamps were baked out at 450°C for four hours or more, cooled, filled with mercury by distillation from a still incorporated in the vacuum system, and finally sealed off.

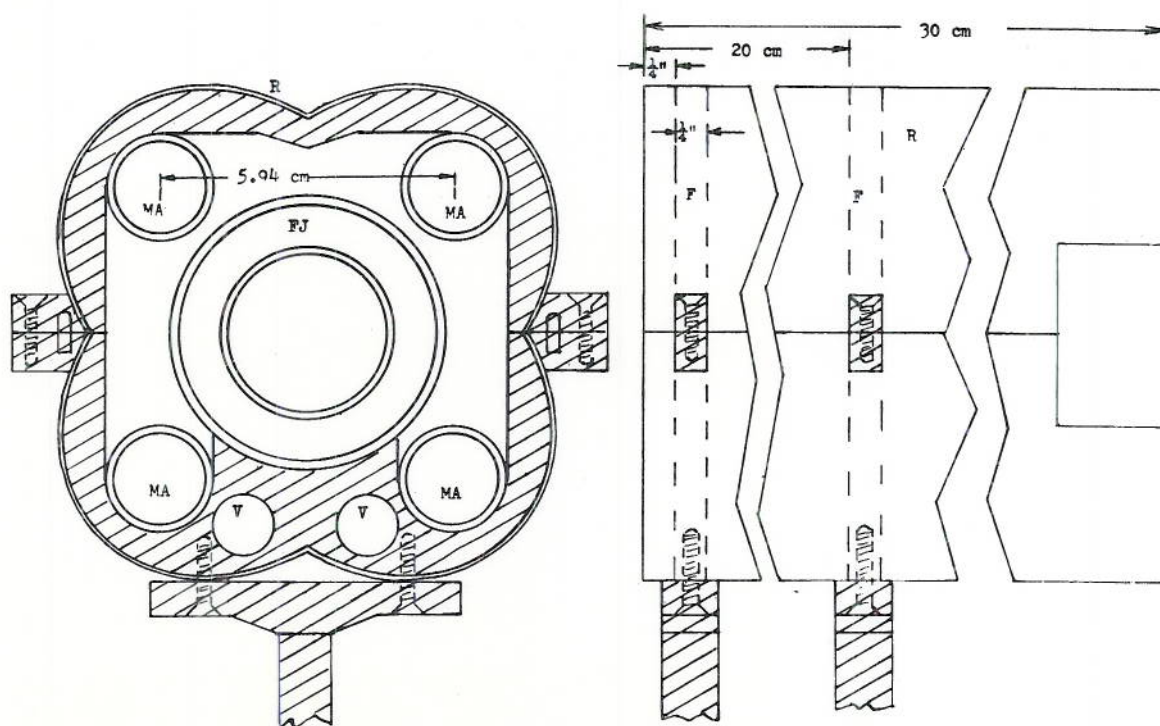


Figure 14 - Raman irradiation apparatus

Pyrex mercury lamps darken with prolonged use, so that after 1000 hours their light output has decreased considerably. It was discovered in this work that such old lamps recover their clear appearance when they are baked at 450°C for 8 to 12 hours after being emptied of mercury.

Figure 14 shows the reflector and lamp support used for gases. The cylindrical reflector, R, is of polished aluminum sheet. Its cross-section is made up of four segments of ellipses, each having one focus at the center of the filter jacket and one at the center of the appropriate mercury arc column. The reflector is held by two $1/4$ -inch aluminum frames, F. These also support the filter jacket, FJ, and the mercury lamps, MA. The holes, V, in the frames are for ventilation. Rectangular sections are cut out of the reflectors at the front end, as shown at the right in Figure 14, to accommodate the short connecting parts of the mercury arcs which are curved outward around the filter jacket.

A number of the gases studied in the present work had vapor pressures at room temperature of less than 8 atmospheres. These were studied in both the gaseous and liquid states in the same irradiation apparatus. The Pyrex Raman tubes used for gases and for liquids are illustrated in Figure 15. All of the gas tubes were of approximately the same size, except that the size of the window varied somewhat. They fit loosely inside the filter jacket. The tubes for liquids varied considerably in both diameter and length, depending on the amount of sample available. They were supported at the axis of the filter jacket by means of collars. It was found that Raman tubes as small as 6 mm outside diameter and up to 30 cm in length could be used for liquids with good results. For gases, however, it is important to have the diameter large to prevent the collimator lens from "seeing" the walls of the tube. All but the straight effective part of the Raman tubes was painted black. In

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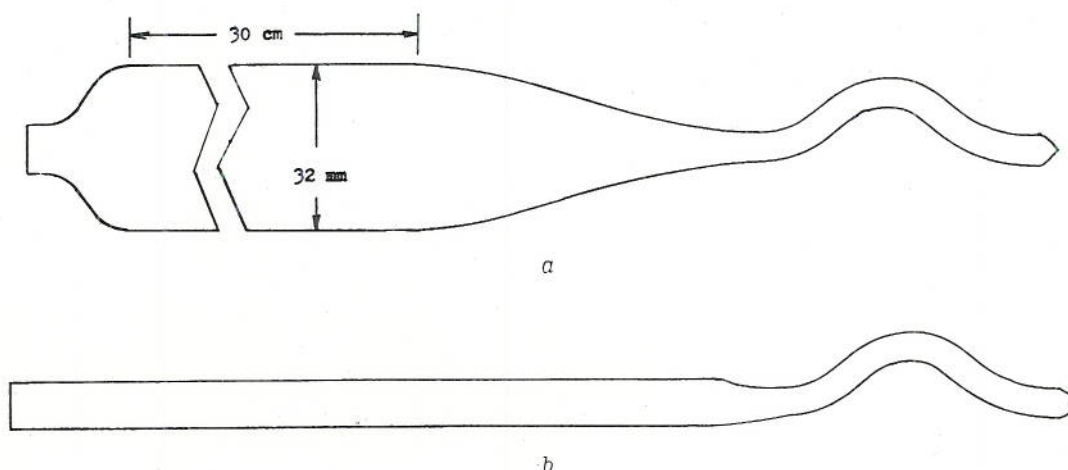


Figure 15 - Raman sample tubes: a, for gases; b, for liquids

some cases the blackened part was covered with tinfoil to decrease the absorption of light and thus decrease the heating. The plane windows used in these tubes, purchased from the American Instrument Company, were obtained sealed to short lengths of tubing. They are flat and perpendicular to the tube axis to within one-half degree.

The Raman tubes used for the light gases were filled to a pressure of 8 atmospheres, or somewhat less. To fill a tube, the tip of the horn was sealed to a vacuum system containing a bulb whose volume was seven times that of the Raman tube. The system was evacuated up to the needle valve of the sample cylinder, the needle valve being opened until the pressure in the system had risen to one atmosphere and then closed. Practically all of the sample was then condensed into the Raman tube by cooling the window end with liquid nitrogen. Thereupon, the Raman tube containing the condensed gas was sealed off, this procedure insuring that, when the tube came to room temperature, the pressure would rise no higher than 8 atmospheres. Deviations from the ideal gas laws would be in a direction to give a resultant pressure less than 8 atmospheres.

Before filling the tubes with sample, they were usually tested for strength by filling with ammonia in the same way except that more ammonia was introduced so that some liquid would be left in the sealed-off tube even at room temperature. The vapor pressure of ammonia is approximately 12 atmospheres at 30° C. Having withstood this pressure for several days, a tube can be assumed to be safe enough for use with a sample of gas at 8 atmospheres.

To fill a Raman tube with a liquified gas, the tube and an ampoule were sealed to the vacuum system. After evacuation, the sample was condensed into the ampoule by cooling it and opening the sample cylinder valve. After condensing slightly more than enough to fill the Raman tube, the ampoule and the Raman tube together were sealed off from the vacuum system. The sample was distilled into the Raman tube slowly at near room temperature. The whole was then cooled slowly and uniformly (to prevent further transfer of sample) to the temperature of dry ice or of liquid air, and the Raman tube was sealed off.

Irradiation Apparatus and Procedures for Liquids

The design of the lamps generally used for liquids is shown in Figure 16. The water-cooled electrode ends are similar to those of the lamps used in the irradiation apparatus for gases. The arcs are triply folded, each straight part having a length of 15 cm. Two such lamps are mounted in the circular reflector shown in Figure 17. Each lamp is operated at a current of 10 amperes on a 110-volt direct-current line. The mercury lamps were started by means of induction coils in the same manner as the lamps used in the irradiation apparatus for gases. They are cooled by air drawn through the reflector.

The straight portion of the Raman tubes was 15 cm long and had an outside diameter of 12 mm. The window of the Raman tube is placed immediately in front of the spectrograph slit, the filter jacket and a rubber gasket attached to the slit assembly forming a light-tight seal. In most cases no condensing lens was used.

The first liquid samples (all fluorocarbons) were distilled at atmospheric pressure in a still having a long condensing column filled with short pieces of capillary tubing in order to prevent mechanical carry-over of colloidal particles. Good Raman spectra were obtained, but the great intensity of the mercury lines indicated that some colloidal impurity was still present in the sample. Later, vacuum distillation was resorted to. The Raman tube is sealed to a small flask, and Raman tube and flask are cleaned with chromic acid cleaning solution, washed, and dried. The sample is transferred to the flask and cooled by a mixture of dry ice and alcohol. The assembly is then evacuated and sealed off. The cooling mixture is removed from the flask and applied to the Raman tube while the flask is heated slightly by the radiation from a light bulb. The sample distills over a period of several hours. When the Raman tube is filled, it is sealed off from the flask. The Raman

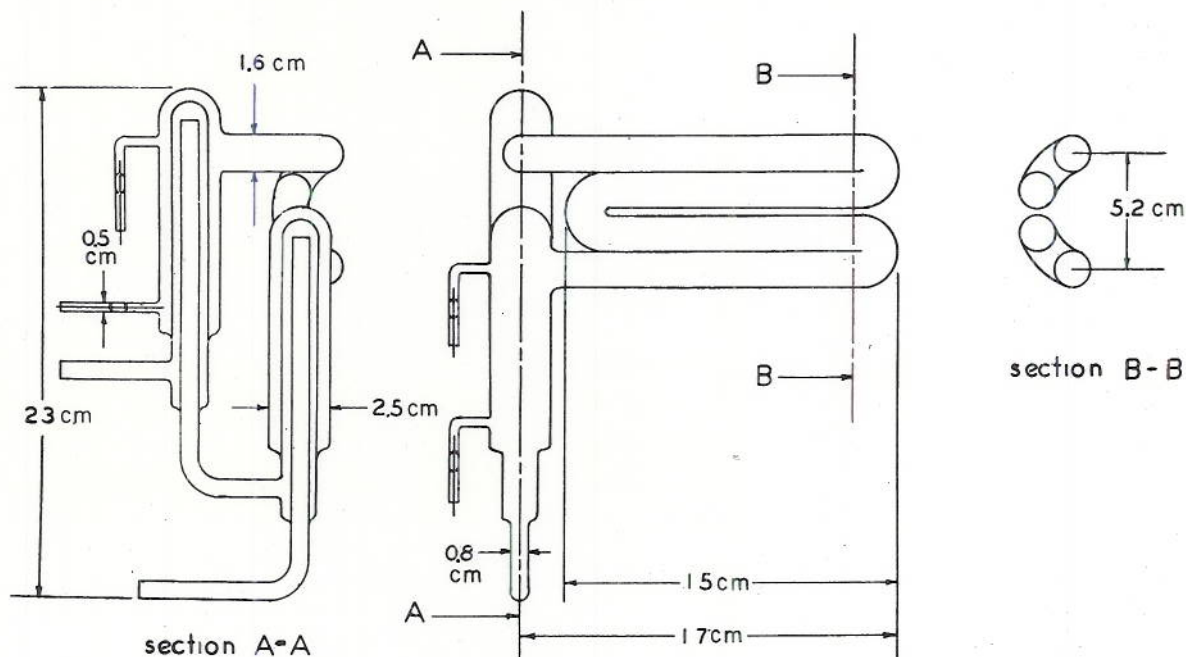


Figure 16 - Water-cooled mercury lamp

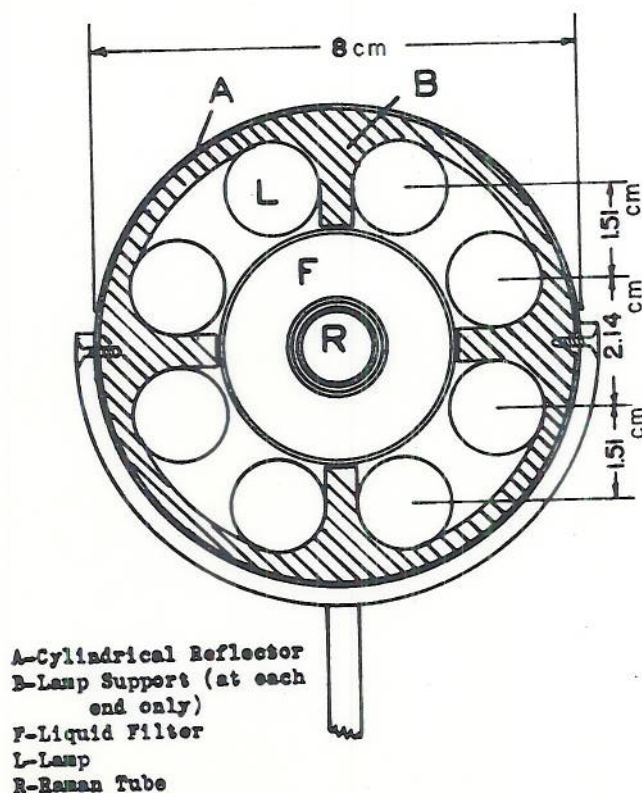


Figure 17 - Reflector and lamp support

spectra of samples prepared in this manner had very little background, and the intensity of the mercury lines was greatly reduced.

Light Filter

In either irradiation apparatus, the filter jacket was usually filled with a solution of 400 g of sodium nitrite in a liter of water. This solution was circulated through the filter jacket and a length of water-cooled glass tubing by means of a small centrifugal pump made of stainless steel. The connections on the filter jacket are on the end away from the spectrograph, and the tube through which the solution enters the filter jacket extends inside to within a few millimeters of the other end of the filter jacket. In addition to removing the 4047 Å and other mercury lines from the incident light, the filter solution serves to keep the sample cool.

Elimination of Raman bands excited by 4047 Å and 4078 Å was not complete. Hence, for partly fluorinated hydrocarbons, at least one exposure was made with water in the filter jacket, and the Raman bands enhanced in this exposure were noted. For completely fluorinated hydrocarbons, this procedure is not necessary since, for these compounds all but a few extremely faint Raman bands lie below 1400 cm^{-1} .

Measurement of Films

To facilitate the measurement of the Raman shifts, an iron arc spectrum was photographed adjacent to each Raman spectrum. A "positive" print of each film, enlarged 22.5 times, was made by first making an enlarged negative on a 2 x 10 inch medium-contrast lantern-slide plate and then enlarging this further on Kodabromide F-2 paper. With the proper exposure and developing time, all details that can be seen on the original films appear on such enlargements. The enlarged print is taped to a special drawing board having a fixed millimeter scale. The positions of the Raman bands and of the neighboring iron lines are measured relative to the fixed scale by means of a transparent T-square with a finely ruled line on the underside. The known iron frequencies are plotted on a graph having a scale of $1 \text{ cm}^{-1} = 0.5 \text{ mm}$ on one side and $0.1 \text{ mm} = 1 \text{ mm}$ on the other. The Raman shifts are then determined from this graph.

This method is essentially one of linear interpolation, since the segments of the curve that can be drawn on the 20-inch-wide roll of graph paper are practically straight. The graphical method, however, has the advantage that mistakes are less easily made than when numerical methods are employed. The master graphs have the coordinates inked in, as well as vertical lines showing the frequencies of all the useful iron lines. The iron lines are identified during plotting by arbitrarily assigned small numbers rather than by frequencies, so that the method is quite fast. The actual curves are drawn on tracing paper placed on the master graphs.

The resolution of the spectrograph and the accuracy of the measurements are such that the sharper Raman bands, when measured by two observers, usually agree to within 0.4 cm^{-1} or less. Measurements of diffuse or extremely weak bands, however, may differ by one or more cm^{-1} . In reporting frequencies, some bands are given to the nearest 0.1 cm^{-1} while others are given only to the nearest cm^{-1} . Each Raman band was usually measured on two or more different exposures, the most intense band being measured on the shorter exposures and the least intense band on the longer exposures. The weakest bands could be measured only on the longest exposures. The reported values are averages, the individual measures being weighted according to their estimated accuracy.

Polarization Measurements

The apparatus for obtaining the depolarization of the Raman bands is similar to that described by Crawford and Horwitz (25). The Raman tube is illuminated from all sides, but baffles are used to restrict the light to directions nearly perpendicular to the axis. Two exposures are taken. In the first, the Raman tube is encircled by a cylinder of Type H polaroid sheet transmitting light with electric vector parallel to the axis of the Raman tube; in the second, a cylinder of polaroid is used that transmits light with electric vector perpendicular to the axis of the Raman tube.

If the intensities of a Raman band in the first and second exposures are denoted by I_{\parallel} and I_{\perp} , respectively, then, as discussed by Edsall and Wilson (26), the ratio I_{\parallel}/I_{\perp} is equal to the depolarization for unpolarized incident light. Its values may range from 0 to $6/7$; bands with $\rho = 6/7$ are called depolarized, and bands with $\rho < 6/7$ are called polarized.

The polarization apparatus is in general design similar to the irradiation apparatus described above. To provide space in the polarization apparatus for the light baffles, the dimensions, as well as the mechanical details, of the reflectors and of the lamps are rather different from what they are in the other apparatus. The length, however, is the same,

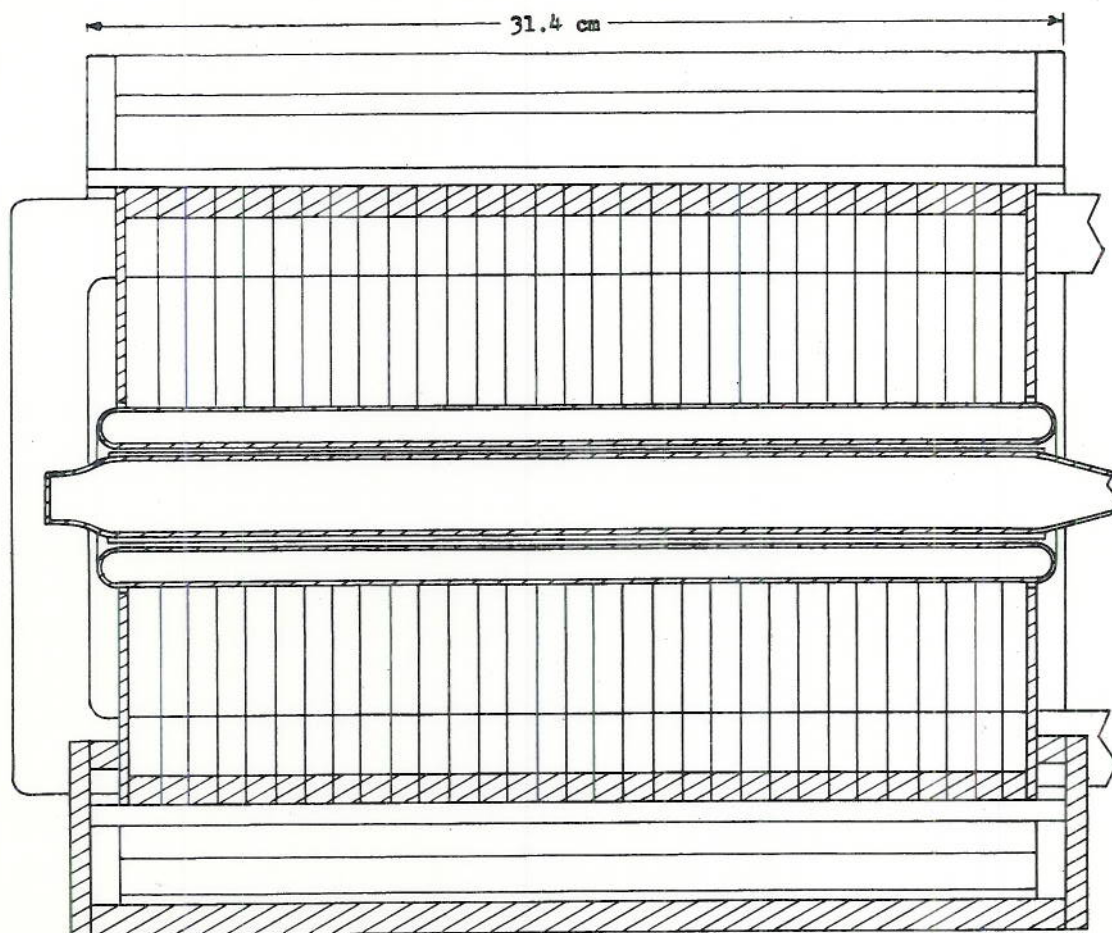


Figure 18 - Irradiation apparatus for polarization measurements, longitudinal section

so that the filter jacket and the Raman tubes are interchangeable. The polarization apparatus is shown in two sections in Figures 18 and 19, where the water-cooled mercury-pool electrodes of the lamps are omitted since they are essentially the same as those of the lamp shown in Figure 13. The baffles between the lamp columns and the filter jacket are blackened copper washers, 0.020 inch thick. The reflectors are elliptical in section, as in the other apparatus.

The spacing of 1 cm for the baffles was designed to give the same degree of collimation as in the apparatus described by Crawford and Horwitz (25). This spacing restricts the light to within 8 degrees from the perpendicular to the axis. Crawford and Horwitz calculated that the error in the depolarization factors due to lack of perpendicular incidence was less than 0.01 and hence could be neglected.

To reduce the long exposure times necessary for fluorocarbons, alternate baffles were removed from the apparatus so that the light was restricted to within 15 degrees from the perpendicular. From the theory of Gans (27) one would expect this change to increase the error by a factor of roughly 4. It would still be small enough, however, to permit picking out the polarized bands unless their depolarization factors are very close to 6/7.

EXPERIMENTAL

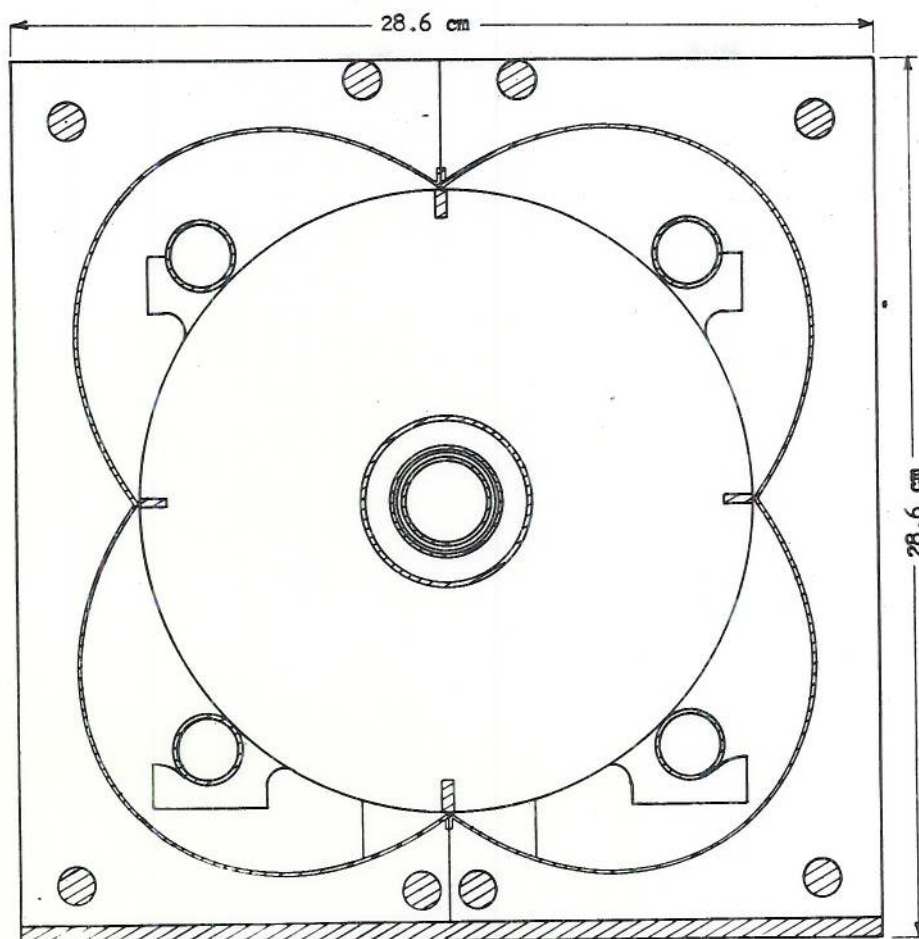


Figure 19 - Irradiation apparatus for polarization measurements, cross-section

The polaroid cylinders inserted inside the filter jacket are of the new type H which transmits approximately 35 percent and polarizes almost completely at 4358 Å. The flat sheets obtained from the Polaroid Corporation are rather resistant to bending. It was found that such a sheet could be given a permanent cylindrical shape by bending it tightly around a glass tube of appropriate size, wrapping a string along the whole length, and heating in an oven for one to two hours at 75°C. The polarizing properties are not affected by this treatment.

In making polarization measurements great care is necessary to keep conditions the same for the two exposures that are to be compared. Small variations in lamp current and in temperature of the apparatus cannot be avoided completely. To correct for such deviations an intensity integrator, the circuit diagram for which is shown in Figure 20, was designed and built.

In principle this device consists of a glow-tube relaxation circuit in which the resistance in series with the condenser is furnished by a photo-tube and is a function of the light intensity falling on the photo-tube surface. The condenser charges at a rate determined by the voltage applied across the condenser and the photo-tube and the intensity of the light

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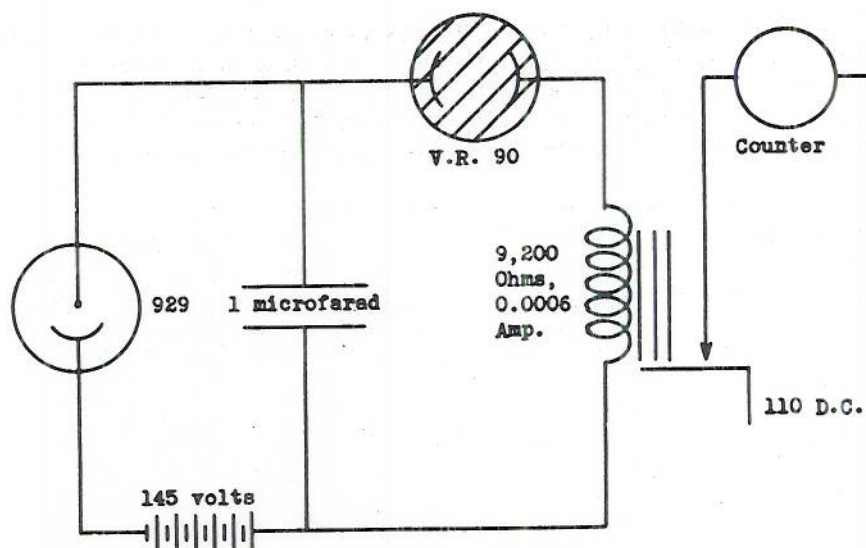


Figure 20 - Circuit diagram for intensity integrator

on the photo-tube. The voltage across the 1-microfarad condenser may be expressed by the equation

$$V = E_{\text{batt}} \times (1 - e^{-t/RC}),$$

where $R = F(I)$. When the condenser voltage becomes equal to the breakdown voltage of the glow tube, the tube breaks down and the condenser discharges through a sensitive relay which activates a mechanical counter. When the voltage has fallen to the extinction voltage of the glow tube, the discharge stops and the condenser begins to charge again. The photo-cell is a 929 and is sensitive in the violet region of the spectra. It is mounted, with appropriate shielding, above the reflector in the polarization apparatus, with suitable holes drilled in the reflector that transmits light from both arcs to the photo cell.

To make two exposures equal, both are exposed for the same number of counts. The light falling on the photo-tube is such that, when both lamps are operating at approximately 17 amperes, the time between counts is about 17 seconds. At this counting rate the integrator is very nearly linear, since the glow-tube dark current is very small and the glow-tube recovery time is a small fraction of the time required to produce one count. The integrator has been tested for short exposures of one hour or less in which the currents in the lamps were varied from 12 amps to 9 amps in steps of one ampere. The resulting four exposures gave line intensities whose ratios varied no more than the ratios of the line intensities on the same film. On long exposures,* however, the integrator slows down, and at this writing it is not definitely determined whether this is a fault in the integrator or whether the effect is caused by the darkening of the lamps.

Film calibration spectra for determining relative intensities were made on a separate spectrograph. This made it possible to expose the calibration spectra at the same time as the Raman spectra. The calibration spectrograph is a three-prism glass instrument with

* Two of 60 hours each were made.

a dispersion nearly as great as that of the Raman spectrograph. Continuous spectra from a tungsten lamp source were photographed with the use of a step sector, for calibration, placed directly in front of the slit. A lens just in front of the step sector focused the source on the collimator of the spectrograph. The photometry of the Raman spectra was carried out by means of a Leeds and Northrup Knorr-Albers photoelectric microphotometer.

In making polarization measurements, two exposures were made of equal integrated light intensity as indicated by the photo-cell counter. One was made with the polaroid cylinder transmitting light parallel and the other perpendicular to the axis. At the same time two step-sectored continuous light spectra were exposed in the other spectrograph using slit widths of 50 and 180 microns respectively. The films for such a set of exposures were cut from the same sheet and developed simultaneously with continuous rocking of the tray during development.

Microphotometer traces were made of the two Raman spectra in the usual way by scanning along the spectral range. The sectored spectra were scanned across the steps at each spectral position at which a Raman band occurred. For each Raman band (or for a group close together) an H and D curve was drawn giving the relation between optical density of the film and light intensity. This curve was used to obtain the relative intensities of the maxima of the particular Raman band on the two exposures. Correction was made for background by drawing a smooth background curve on the microphotometer trace and subtracting the intensity of the background at the center of the Raman band. The depolarization factor for a Raman band was then obtained by taking the ratio of the two corrected intensities.

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RESULTS AND DISCUSSION

FLUORINATED ETHYLENES

 $\text{CH}_2=\text{CF}_2$ (Vinylidene Fluoride)

Previous Work. The infrared spectrum of $\text{CH}_2=\text{CF}_2$ has been studied by Torkington and Thompson (20) who made a partial assignment of fundamental frequencies. As will be mentioned later, their sample must have been impure. Very recently Edgell and Byrd (28) have obtained the Raman spectrum of this compound in the liquid state and have proposed a complete assignment of fundamentals.

Experimental Results. The infrared absorption of 1,1-difluoroethylene gas (Serial No. 299, Table 18) from 2 to 22.7 microns is shown in Figure 32. The wave number values for the observed absorption maxima are given in the first column of Table 19, and the relative intensities are indicated under the heading "Description." For bands having more or less typical contours, the contour type in Badger and Zumwalt's notation (29) is also given in this column. Type A bands have a moderately intense zero branch in addition to the rotational branches. Type B, or doublet bands, have no zero branch and fairly closely spaced rotational branches. Type C bands have a very intense, and often somewhat broadened, zero branch and rather widely separated rotational branches.

The Raman spectrum of $\text{CF}_2=\text{CH}_2$ gas (Serial No. 299) at about 7 atmospheres was investigated by the procedure described previously, exposure times up to 70 hours being used. The observed Raman shifts are listed in Table 20. In the second column are given rough estimates of the relative intensities of the bands with the abbreviations s, strong; m, medium; w, weak; and vw, very weak. Unusually sharp or diffuse bands are designated as sh, d, or vd (very diffuse), also in this column.

Molecular Structure Considerations. If the $\text{CF}_2\text{:CH}_2$ molecule has a planar structure of symmetry C_{2v} , the normal vibrations divide themselves into symmetry species as follows. There are five fundamentals of species A_1 , one of species A_2 , four of species B_1 , and two of species B_2 . All of the fundamentals are active in the Raman effect, the five totally symmetrical vibrations giving rise to polarized bands and the other vibrations to depolarized bands. With the exception of the single fundamental of species A_2 (the twisting mode), all of the fundamental vibrations are active in infrared absorption.

The vibrations of species B_2 , in which the atoms move perpendicular to the plane of the molecule (i.e., parallel to the axis of greatest moment of inertia), give rise to infrared absorption bands of Type C. The contours of the bands belonging to species A_1 and B_1 will depend on whether the C=C bond is the axis of least or intermediate moment of inertia. As first pointed out by Torkington and Thompson (20) it is difficult to assign the A_1 and B_1 C-F stretching modes, unless it is assumed that the C=C bond is the axis of least moment of inertia. This assumption was therefore made here, and it was further assumed that the $\text{CF}_2=\text{CH}_2$ molecule is definitely an asymmetrical top.

After the completion of the present work, Roberts and Edgell (30), on the basis of microwave observations, have reported the following moments of inertia for the $\text{CF}_2\text{:CH}_2$

RESULTS AND DISCUSSION

TABLE 19
Infrared Spectrum of CF_3CH_3 (Gas)

Wave Number	Description	Interpretation	Wave Number	Description	Interpretation
429)* cm^{-1}	m	B_1 Fundamental	1896		
448)*			1909	s Type A?	$2 \times 955 = 1910 (A_1)$
~539			1913		
550	m Type A	A_1 Fundamental	1921		
~563					
593			1981	vw	$550 + 1414 = 1964 (A_1)?$
611			1996	vw	
630	vw Type C	B_2 Fundamental	2000	vw	
708	vw Type C	$1302 - 590 = 712 (B_2)$	2004	vw sh	$611 + 1414 = 2025 (B_2)$
735	vw	$550 + 803 - 611 = 742 (A_1)$	2023	vw	$438 + 2 \times 803 = 2044 (B_1)$
743			2045	vw	
749	w Type B	$1302 - 550 = 752 (B_1)$	2155}	vw	$438 + 1728 = 2166 (B_1)$
784			2174}		
796			2208	w	
797			2216	w sh	$803 + 1414 = 2217 (B_2)$
803	vs Type C	B_2 Fundamental	2222	m	$925 + 1302 = 2227 (B_1)$
810			2234	m	
822			2251	m sh	$955 + 1302 = 2257 (A_1)$
864	vw	$1414 - 550 = 864 (A_1);$ $1302 - 438 = 864 (A_1)$	2263	m	
914			2285	vw sh	$550 + 1728 = 2278 (A_1)?$
923			2290	vw sh	$438 + 550 + 1302 = 2290 (A_1);$ $2 \times 438 + 1414 = 2290 (A_1)$
926	vs Type A	A_1 Fundamental	2319		
940			2331	vw Type C	$925 + 1414 = 2339 (A_1);$ $611 + 1728 = 2339 (B_2)$
952}	s Type B	B_1 Fundamental	2344	vw sh	
958}			2425	vw sh	$550 + 925 + 955 = 2430 (B_1)$
1048	vw Type C?	$438 + 590 = 1028 (B_2)?$	2441	vw sh	$3059 - 611 = 2448 (B_1)$
1156	vw	$550 + 611 = 1161 (B_2)$	2467	vw sh	$2 \times 955 + 550 = 2460 (A_1)$
~1170	vw	$1728 - 550 = 1178 (A_1)$	2533	vw sh	$803 + 1728 = 2531 (B_2)$
~1180	vw	$2 \times 590 = 1180 (A_1)$	2584	w	$2 \times 590 + 1414 = 2594 (A_1)$
1208			2593	m sh	$2 \times 1302 = 2604 (A_1)$
1218	m Type A	$2 \times 611 = 1222 (A_1)$	2606	m	$3058 - 438 = 2620 (B_1)$
1232			2648	m	$925 + 1728 = 2653 (A_1)$
1294			2661	m sh	$3100 - 438 = 2662 (A_1)$
1299}	vs Type B	B_1 Fundamental	2709	vw sh	$1302 + 1414 = 2716 (B_2)?$
1305}			2767	vw	$3 \times 925 = 2775 (A_1); 550 + 925$ $+ 1302 = 2777 (B_1)$
1314			2779	vw	$438 + 925 + 1414 = 2777 (B_1)$
1361	w	$550 + 803 = 1353 (B_2)$	2817	vw	$2 \times 1414 = 2828 (A_1)$
1376	w Type B?	$438 + 925 = 1363 (B_1)$	2844	vw	$3 \times 955 = 2865 (B_1)?$
1404			2929	vw d	$590 + 611 + 1728 = 2929 (B_1)$
1414	m Type A	A_1 Fundamental	3049	m Type A?	A_1 Fundamental
1425			3060	m Type C?, A?	$550 + 803 + 1728 = 3081 (B_2)$
1475	vw sh	$550 + 925 = 1475 (A_1)$	3072	m	B_1 Fundamental
1493	vw	$550 + 955 = 1505 (B_1)$	3088	m	
1522	vw	$611 + 925 = 1536 (B_2)$	3099	m	
1602			3109	w	
1611	s Type A	$2 \times 803 = 1606 (A_1)$	3147	w	$1414 + 1728 = 3142 (A_1); 803 + 925$ $+ 1414 = 3142 (B_2)$
1623			3160	w	$438 + 1302 + 1414 = 3154 (A_1)$
1720			3453	w	$2 \times 1728 = 3456 (A_1)$
1724			3464	w	$438 + 3058 = 3496 (B_1)$
1728	vs Type A?	$803 + 925 = 1728 (B_2)$	4030	vw	$925 + 3100 = 4025 (B_1)?$ $955 + 3100 = 4055 (A_1)$
1733		A_1 Fundamental	4120	w	$2 \times 550 + 3058 = 4158 (A_1)?$
1738			4390	w	$1302 + 3100 = 4402 (A_1)$
1740	vs sh	$438 + 1302 = 1740 (A_1)$	4500	w	$1414 + 3100 = 4514 (B_1);$ $1414 + 3058 = 4472 (A_1)$
1804	vw Type C?	$2 \times 438 + 925 = 1801 (A_1)$	4740	w	$1728 + 3058 = 4786 (A_1)$
1849	m sh	$2 \times 925 = 1850 (A_1); 550 + 1302 =$ $1852 (B_1); 438 + 1414 = 1852 (B_1)$			
1863	m	$925 + 955 = 1880 (B_1)$			
1877	m sh	$590 + 1302 = 1892 (B_2)$			

* Observed by Dr. E. K. Plyler of the National Bureau of Standards.

TABLE 20
Raman Spectrum of $\text{CF}_2\text{:CH}_2$ (Gas)

Wave Number	Description	Interpretation
$\sim 440 \text{ cm}^{-1}$	vw vd	B_1 Fundamental
590	vw vd	A_2 Fundamental
~ 615	vw d	B_2 Fundamental
799	vw vd	B_2 Fundamental
925.3	vs sh	A_1 Fundamental
1358.7	vw	$438 + 925 = 1363 (B_1);$ $550 + 803 = 1353 (B_2)$
~ 1405	w vd	A_1 Fundamental
1479.5	vw	$550 + 925 = 1475 (A_1)$
1610	vw	$2 \times 803 = 1606 (A_1)$
1728.5	s sh	A_1 Fundamental*
1740.6	s sh	$438 + 1302 = 1740 (A_1)$
3058.3	s sh	A_1 Fundamental
3085.4	w	
3099.8	m	B_1 Fundamental
3112.2	w	

*Coincides with $803 + 925 = 1728 (B_2)$.

molecule: $76.28, 80.47$, and $156.99 \times 10^{-40} \text{ g cm}^2$, the smallest moment belonging actually to an axis coinciding with the C=C bond.† Badger and Zumwalt's parameters,

$$\rho = (a - b)/b \text{ and } S = (2b - a - c)/(a - c),$$

where a , b , and c are the reciprocals of the smallest, intermediate, and largest moments of inertia respectively, then have the values $\rho = 0.54$ and $S = 0.80$. Using Badger and Zumwalt's curves for $\rho = 1/2$ and $S = 1/2$, extrapolation to $S = 0.8$ gives for the spacing $\nu - \nu_0$ from the band center to the maxima of the rotational branches the values 13 cm^{-1} for Type A, 2.9 cm^{-1} for Type B, and 18 cm^{-1} for Type C bands, in excellent agreement with the observed spacing.

Assignment of Fundamentals. The fairly strong Type A infrared band at 550 cm^{-1} , although not observed in the Raman effect, is undoubtedly an A_1 fundamental. The corresponding vibration may be characterized roughly as a CF_2 deformation. The very intense band at 926 cm^{-1} definitely has Type A contour and is observed as a very strong

† This is in excellent agreement with preliminary electron diffraction results recently obtained by Drs. Jerome and Isabella Karle at the Naval Research Laboratory. The molecule appears to be planar, having the dimensions C-C = 1.31 \AA , C-F = 1.32 \AA , C-H = 1.07 \AA , FCF = 110° , and HCH = 120° .

sharp band in the Raman effect. It must be a fundamental belonging to species A_1 and can be designated very roughly as a symmetrical C-F stretching mode.

Going towards higher wave numbers, the A_1 CH_2 deformation fundamental must next be accounted for. In ethylene the symmetrical and unsymmetrical CH_2 deformation frequencies lie at 1342 and 1444 cm^{-1} respectively (3, page 326). In isobutene Kilpatrick and Pitzer (31) have assigned 1390 cm^{-1} to this mode, and for $CCl_2:CH_2$ Kohlrausch (5, page 305) has assigned a value of approximately 1400 cm^{-1} . Most hydrocarbons of the form $CH_2:CHR$ have a characteristic frequency very close to 1416 cm^{-1} (32). Thus, there can be no doubt that the Type A infrared band at 1414 cm^{-1} and the weak and very diffuse Raman band with a maximum at approximately 1405 cm^{-1} represent the A_1 fundamental associated with the CH_2 deformation. It is somewhat disturbing, nevertheless, that these bands could also be explained as $611 + 803 = 1414$ (A_1).

While all olefinic hydrocarbons have a frequency near 1640 cm^{-1} , ascribed to a C=C stretching mode, it has been found by Hatcher and Yost (33), by Torkington and Thompson (20), and in the present work that the corresponding frequency in fluorinated olefins lies at considerably higher values. In $CF_2:CH_2$, a very intense infrared band is observed at 1728 cm^{-1} , but its abnormal contour indicates that it is not a single band. In the Raman spectrum two strong and sharp bands occur at 1728.5 and 1740.6 cm^{-1} respectively. One of these must be the A_1 fundamental in question. Since the lower value is the more useful in accounting for combination bands, and since the higher value can readily be explained as an A_1 combination band, $477 + 1302 = 1749$, it appears certain that 1728.5 cm^{-1} is the A_1 fundamental associated with C=C stretching. The fact that the band at 1740 cm^{-1} is about as intense as the fundamental may be explained by the proximity of the two A_1 bands. The complexity of the infrared contour is even greater than would be expected for two close A_1 bands. This appears to be the result of overlapping with a combination band $803 + 925 = 1728$ cm^{-1} of species B_2 .

The last A_1 fundamental is essentially a C-H stretching mode and should lie between 2980 and 3080 cm^{-1} . It must be identified with the strong sharp Raman band at 3058 cm^{-1} . This probably corresponds to the infrared absorption maximum at 3060 cm^{-1} rather than to the somewhat more intense maximum at 3072 cm^{-1} which appears to result from a B_2 combination band.

The assignment of the B_1 fundamentals presents little difficulty. The two most intense infrared bands with Type B contours, at 1302 and 955 cm^{-1} , must be fundamentals of species B_1 . They may be characterized roughly as C-F stretching and CH_2 rocking modes. Although the higher frequency lies closest to the values for the CH_2 rocking frequency found for olefins, the greater intensity of the band at 1302 cm^{-1} would indicate that it is associated with a motion in which the fluorine atoms participate strongly. The fairly weak doublet band at 438 cm^{-1} is undoubtedly also a B_1 fundamental, associated roughly with a CF_2 rocking motion. It is observed in the Raman spectrum as a very diffuse and weak band with maximum near 440 cm^{-1} .

The remaining B_1 fundamental, which can be characterized rather accurately as the unsymmetrical C-H stretching mode, must lie somewhat higher than the corresponding A_1 fundamental. It must undoubtedly be identified with the medium intense Raman band at 3099.8 cm^{-1} . In the infrared, absorption maxima have been observed at 3088, 3098 and 3109 cm^{-1} . Because of the low dispersion in this region and the proximity to the A_1 fundamental at 3058 cm^{-1} , and apparently also because of overlapping of combination bands, it is not possible to ascertain the band contour and obtain thereby an accurate frequency value from the infrared spectrum.

The single fundamental of species A_2 , which corresponds to a twisting of the molecule, is active only in the Raman effect. If it is observed, it must be 590 cm^{-1} , a value which seems quite reasonable. In fact, if the twisting frequency for ethylene is taken to be 825 cm^{-1} (3, p. 326), and if it is assumed that $\text{CF}_2=\text{CH}_2$ has the same configuration and the same torsional force constant as $\text{CH}_2=\text{CH}_2$, a simple calculation gives a value of 590 cm^{-1} for the twisting frequency of $\text{CF}_2=\text{CH}_2$ *. Moreover, no other interpretation seems possible for the Raman band at 570 cm^{-1} . It is therefore assumed to be the A_2 fundamental. However, Edgell and Byrd (28) have recently observed a very weak Raman band at 714 cm^{-1} in liquid $\text{CF}_2=\text{CH}_2$ and have interpreted this as the A_2 fundamental. The value of this fundamental must therefore at present be regarded as uncertain.

There remain the two fundamentals of species B_2 . One of these is certainly 803 cm^{-1} , which occurs as a very intense Type C band in the infrared and as a faint very diffuse band in the Raman effect. This frequency must be associated with a wagging motion of the CH_2 group. While the contour of the infrared band at 803 cm^{-1} is undoubtedly of Type C, the band appears to have two, or perhaps four, secondary zero branches, for which no explanation is given here.

The other B_2 fundamental must lie below 803 cm^{-1} . The strongest Type C band observed here is the very weak band at 611 cm^{-1} . This could be interpreted as a difference band, $1414 - 803 = 611\text{ cm}^{-1}$ (B_2). However, this is not a plausible interpretation, especially since Edgell and Byrd have found a strong Raman band at 603 cm^{-1} in liquid $\text{CF}_2=\text{CH}_2$ at a low temperature. The possibility that the absorption maximum found by Plyler at 429 cm^{-1} is the B_2 fundamental has been considered, but its interpretation as one component of a Type B band seems more plausible. Thus, the infrared band at 611 cm^{-1} , and the very weak and diffuse Raman band at 615 cm^{-1} , are assigned as the second B_2 fundamental.

The infrared and Raman frequencies interpreted here as fundamental vibration frequencies for $\text{CF}_2=\text{CH}_2$ are listed in Table 21. As already pointed out, the characterization of the vibration mode given in the second column has only very rough significance, except for vibrations limited largely to the CH_2 group.

Six of the fundamentals listed here were previously assigned by Torkington and Thompson (20). Two other bands, at 677 and 1133 cm^{-1} , observed and assigned as fundamentals by them, were not found in the present work and therefore must have been caused by impurities. When the differences in some of the frequency values are disregarded, the present assignment agrees with that of Edgell and Byrd, except for the A_2 fundamental and the A_1 CH_2 deformation frequency. They identify the latter with the Raman band at 1359 cm^{-1} , which here is interpreted as a combination band.

Interpretation. On the basis of the fundamental frequencies listed in Table 21, it has been possible to give a satisfactory interpretation of all but a few of the observed infrared and Raman bands. The following rules for determining the species of binary combination bands were used:

*Use of the value 1027 cm^{-1} , recently obtained by R. L. Arnett and B. L. Crawford, Jr. (Technical Report issued 1 March 1949 in connection with Contract #Sori-147, T.O.2), for the twisting frequency for ethylene gives the higher value 735 cm^{-1} . However, in view of the nature of the other assumptions, this does not materially weaken the argument.

$$A_1 \cdot A_1 = A_2 \cdot A_2 = B_1 \cdot B_1 = B_2 \cdot B_2 = A_1,$$

$$A_1 \cdot A_2 = B_1 \cdot B_2 = A_2,$$

$$A_1 \cdot B_1 = A_2 \cdot B_2 = B_1,$$

$$A_1 \cdot B_2 = A_2 \cdot B_1 = B_2.$$

The interpretation of the infrared bands is given in the third column of Table 19, the interpretation of the Raman bands in the third column of Table 20.

Discussion. Of the 64 infrared-active binary combination (sum or overtone) bands that can be formed from the 12 fundamentals, about two-thirds have been accounted for in the observed spectrum, although several such bands coincide or overlap. Several binary combination bands are masked by fundamentals or lie outside the spectral range investigated. Seven of the binary combinations that could not be identified in the spectrum are in the region beyond 3000 cm^{-1} where the dispersion is low and where bands are crowded together. Only one binary combination band, the overtone $2 \times 550 \text{ cm}^{-1}$, is conspicuously absent.

Six bands are interpreted as binary difference bands. For every one of these, the corresponding sum band appears to be present with about the intensity to be expected from the Boltzmann factor for the excited initial level of the difference band. However, because of overlapping of bands, no accurate test of the intensity relations could be made. A dozen or so of the weakest infrared bands are interpreted as ternary sum or difference bands. Because of the large number of possible combinations of this kind, the assignment of these bands must be regarded as tentative. For some bands more than one interpretation is given in Table 19. However, not all of the cases where alternative assignments are possible have been indicated.

TABLE 21
Fundamental Vibration Frequencies of $\text{CF}_2\text{:CH}_2$

Symmetry Species	Approximate Character *	Infrared (Gas)		Raman (Gas)	
		Wave Number	Description	Wave Number	Description
A_1	C=C Stretching	1728	vs Type A	1728.5	s sh
A_1	CH Stretching	3060	m Type A	3058.3	s sh
A_1	CF Stretching	926	vs Type A	925.3	vs sh
A_1	CH_2 Deformation	1414	m Type A	1405	w vd
A_1	CF_2 Deformation	550	m Type A		
B_2	CH_2 Wagging	803	vs Type C	799	vw vd
B_2	CF_2 Wagging	611	w	615	vw vd
A_2	Twisting			590	vw vd
B_1	CH Stretching	3103	m	3099.8	m
B_1	CF Stretching	1302	vs Type B		
B_1	CH_2 Rocking	955	s Type B		
B_1	CF_2 Rocking	438†	w Type B	440	vw vd

* The terms in this column have only rough meaning, especially for vibrations involving the CF_2 group.

† Observed by Dr. E.K. Plyler, National Bureau of Standards.

The agreement between the calculated and observed frequencies for combination bands is very good, the most conspicuous exceptions being the bands at 1048 and 1522 cm^{-1} .

The peculiar contours of the fundamental bands at 803 and 1728 cm^{-1} have already been pointed out. The A_1 fundamental at 925 cm^{-1} apparently has a weak second zero branch at 923 cm^{-1} . It seems too strong to arise from molecules containing a C_{13} atom but may belong to an upper-stage band. The high intensities of the overtone bands at 1218 and 1611 cm^{-1} are surprising but may result from their proximity to the A_1 fundamentals at 1414 and 1728 cm^{-1} .

With the exception of the Raman bands at 3085 and 3112 cm^{-1} , which are believed to be caused by a photochemical reaction product, all of the observed Raman bands have been satisfactorily interpreted.

The assignment of fundamentals for $\text{CH}_2=\text{CF}_2$ may be compared with that of Kilpatrick and Pitzer (31) for isobutene and with that of Thompson and Torkington (34) for vinylidene chloride. The latter workers also give a partial assignment for vinylidene bromide. The results for these $\text{CH}_2=\text{CX}_2$ molecules are shown in Figure 21. Although it will be noted that vibrations of the same species do not cross in these correlations, there are several unexpected features.

As mentioned previously, the C=C stretching frequency (A_1) for $\text{CH}_2=\text{CF}_2$ is definitely higher than might be expected, and the CH_2 wagging frequency of Species B_2 is correspondingly lower. The CH_2 deformation (A_1) is quite constant throughout this series while the CX_2 deformation and the symmetrical C-X stretching frequencies (both A_1) decrease uniformly, as expected. It is clear that the B_1 vibration near 1100 cm^{-1} for the heavier molecules is due to a CH_2 rocking mode, since it is too high for a C-X valency vibration, and the B_1 vibration at 1302 cm^{-1} in $\text{CH}_2=\text{CF}_2$ is accordingly assigned to the CH_2 rocking mode in Figure 21. This is contrary to the previous description of this mode as a C-F valency vibration. Although in addition to consideration of intensity of absorption there are other reasons for believing that 1302 cm^{-1} involves a considerable amount of C-F stretching, it must be realized that these two B_1 frequencies at 955 and 1302 cm^{-1} are probably mixed and that neither can be described as a pure valency or pure rocking motion. It is also

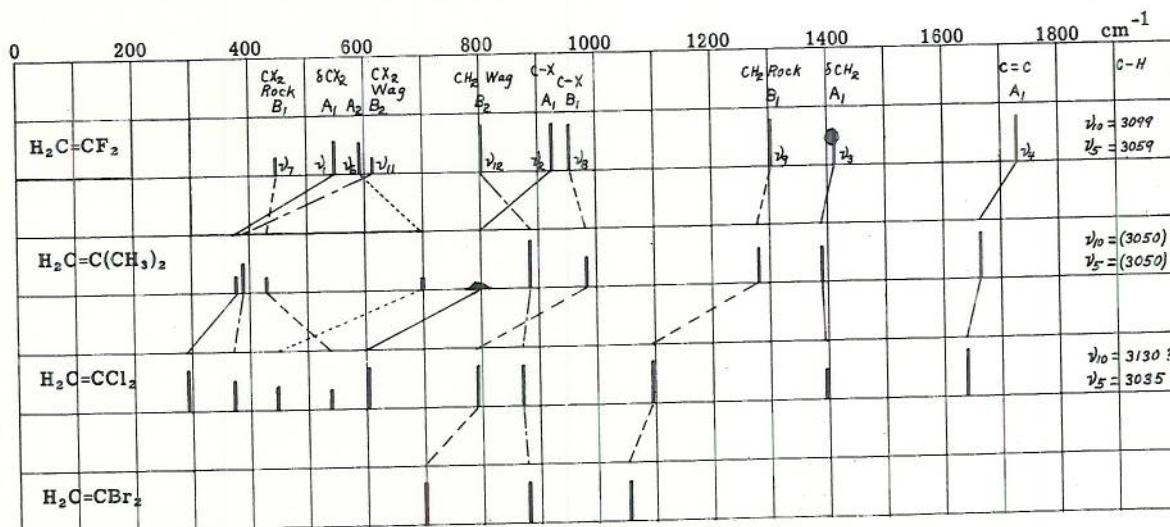


Figure 21 - Fundamental frequencies of $\text{H}_2\text{C}=\text{CX}_2$ molecules

surprising that the A_2 twisting frequency changes as it does in this group of molecules. However, it appears from the correlations that the assignments for the Raman bands at 450 and 540 cm^{-1} for $\text{CH}_2=\text{CCl}_2$ should be interchanged, in which case the correlations for both the twisting frequency and the CX_2 rocking frequency become satisfactory.

$\text{CF}_2=\text{CCl}_2$ (1, 1-Difluoro-2,2-dichloroethylene)

Previous Work. The Raman spectrum of liquid $\text{CF}_2=\text{CCl}_2$ has been studied by Hatcher and Yost (33). The infrared spectrum of the compound in the gaseous state has been investigated by Torkington and Thompson (20), who made an assignment of ten of the twelve fundamental vibration frequencies.

Experimental Results. The infrared absorption spectrum of gaseous 1,1-difluoro-2,2-dichloroethylene (Serial No. 325) from 2.5 to 22.6 microns is shown in Figure 32. The infrared absorption maxima at 668, 720, 2346, and 2355 cm^{-1} are caused by an admixture of carbon dioxide, and the resolved band in the region $2100\text{--}2200\text{ cm}^{-1}$ must be due to carbon monoxide. The wave numbers for the observed absorption maxima (or "shoulders") are given in the first column of Table 22. In the second column are indicated the relative intensities as well as the band contours in Badger and Zumwalt's notation.

The observed Raman shifts of liquid $\text{CF}_2=\text{CCl}_2$ are listed in the first column of Table 23. In the second column are given rough estimates of the relative intensities of the bands and, for some bands, information about exceptionally sharp or diffuse appearance. The measured depolarization ratios are listed in the third column.

The infrared spectrum, as observed in the present work, includes many bands not found by Torkington and Thompson, and the wave number measurements are considerably more accurate. The Raman shift of 883 cm^{-1} reported by Hatcher and Yost was not observed here. On the other hand, Table 23 contains four Raman bands, at 1313, 986, 187.8 and 167 cm^{-1} , not found by Hatcher and Yost. Except for the very faint band at 1966 cm^{-1} , which was observed by Hatcher and Yost at 1976 cm^{-1} , the agreement between the Raman shifts obtained in the present work and those reported by Hatcher and Yost is very good.

Molecular Structure. If it is assumed that the CF_2CCl_2 molecule has a planar structure of symmetry C_{2v} , the normal vibrations will divide themselves into species in the same manner as for CF_2CH_2 , i.e., $5A_1 + 1A_2 + 4B_1 + 2B_2$, and the rules for finding the species of combination bands will also be the same.

Assuming the dimensions for the $\text{CF}_2=\text{CCl}_2$ molecule to be: C=C distance = 1.27 \AA , C-F distance = 1.32 \AA , C-Cl distance = 1.7 \AA , and F-C-F angle = Cl-C-Cl angle = 110° , the moments of inertia obtained are:

$$I_A = 298 \times 10^{-40} \text{ g cm}^2,$$

$$I_B = 392 \times 10^{-40} \text{ g cm}^2,$$

$$I_C = 690 \times 10^{-40} \text{ g cm}^2.$$

From these values, Badger and Zumwalt's parameters are found to be $\rho = 0.74$ and $S = 0.16$. Using Badger and Zumwalt's curves for $\rho = 3/4$ and $S = 0$, the values 5.8, 2.7, and 9.7 cm^{-1} are obtained for the separation $\nu - \nu_0$ of the rotational branches from the band center for Type A, Type B, and Type C bands, respectively.

Wave 1

459

556

564

573

~ 617

622

~ 629

635

640

~ 647

758

805

838

881

884

887

986

996

1027

1037

1037

~ 1057

1051

1061

1121

1137

1131

117

121

122

125

128

132

133

142

* Frequencies

TABLE 22
Infrared Spectrum of $\text{CF}_2=\text{CCl}_2$ (Gas)

Wave Number	Description	Interpretation*	Wave Number	Description	Interpretation*
459 cm^{-1}	vw	B_1 Fundamental	1477	m	$459 + 1032 = 1491 (B_1)$
556			1485	m	
564	s Type C	B_2 Fundamental	1543	w	$1749 - (188) = 1561 (B_1)?$
573			1575	vvw	$2 \times 564 + 459 = 1587 (B_1)?$
~617			1585	vvw	$264 + 1032 = 1596 (B_2)?$
622	m Type A	A_1 Fundamental	1627		
~629			1636	vw Type B?	$640 + 993 = 1633 (B_1)$
635			1745		
640	s Type A	A_1 Fundamental	1749	vs Type A	A_1 Fundamental
~647			1752		
758	vvw	$1749 - 993 = 756 (B_1)?$	1798	vvw	$459 + 1327 = 1786 (A_1)$
805	vw	$993 - (188) = 805 (A_1);$ $(188) + 622 = 810 (B_1)$	1878	vvw	$(188) + 640 + 1032 = 1860 (B_1)?$
838	vvw	$1032 - (188) = 844 (B_1)$	1894	vvw	$2 \times 459 + 993 = 1911 (B_1)?$
881	m sh	$(258) + 622 = 880 (B_2)$	1936	vw	$(188) + 1749 = 1937 (B_1);$ $622 + 1327 = 1949 (B_1)$
884	m	$(434) + 459 = 893 (B_1)$	1978	m	$2 \times 993 = 1986 (A_1);$ $640 + 1327 = 1967 (B_1)$
887	m		1998	vvw	$(258) + 1749 = 2007 (B_2)$
989	vs Type B	B_1 Fundamental	2058	m	$2 \times 1032 = 2064 (A_1)$
996			2175	m	$(434) + 1749 = 2183 (A_1)$
1027			2296	vvw	$564 + 1749 = 2313 (B_2)$
1032	vs Type A	A_1 Fundamental	2375	vvw	$622 + 1749 = 2371 (A_1)$
1037			2441	vvw	$(258) + (434) + 1749 = 2441 (B_2)$
~1051			2500	vvw	$(188) + 993 + 1327 = 2508 (B_1)$
1056	vw Type A?	$(434) + 622 = 1056 (A_1)$	2563	vvw	$258 + 564 + 1749 = 2571 (A_1)$
1060			2636	s	$2 \times 1327 = 2654 (A_1)$
1125			2732	w	$993 + 1749 = 2742 (B_1)$
1131	s Type A	$2 \times 564 = 1128 (A_1)$	2770	s	$1032 + 1749 = 2781 (A_1)$
1136			2841	m	$(188) + 2 \times 1327 = 2842 (B_1);$ $459 + 640 + 1749 = 2848 (B_1)$
1171	s Type C?	$564 + 622 = 1186 (B_2);$ $(188) + 993 = 1181 (A_1)$	3062	m	$1327 + 1749 = 3076 (B_1)$
1214	m Type B	$(188) + 1032 = 1220 (B_1)$	3470	w	$2 \times 1749 = 3498 (A_1)$
1221			3620	w	$2 \times 1327 + 993 = 3629 (B_1)$
1250	vvw	$2 \times 622 = 1244 (A_1)$			
1281	w	$2 \times 640 = 1280 (A_1);$ $(258) + 1032 = 1290 (B_2)$			
1323	vs Type B	B_1 Fundamental			
1330					
1427	m	$(434) + 993 = 1427 (B_1)$			

* Frequencies observed as fundamentals only in the Raman spectrum of liquid $\text{CF}_2=\text{CCl}_2$ are enclosed in parentheses, since they may differ somewhat from the corresponding frequencies for the gas.

TABLE 23
Raman Spectrum of $\text{CF}_2=\text{CCl}_2$ (Liquid)

Wave Number	Description	Depolarization	Interpretation
167* cm^{-1}	vvw		A_2 Fundamental
187.8	w	0.88	B_1 Fundamental
258	vs	0.86	B_2 Fundamental
433.8	vs sh	0.07	A_1 Fundamental
454	w d	0.8	B_1 Fundamental
560.8	vs	0.83	B_2 Fundamental
623.0	s sh	0.12	A_1 Fundamental
646	w d	0.20	A_1 Fundamental
986	vw	~ 1	B_1 Fundamental
1027.6	m sh	0.35	A_1 Fundamental
1121.8	w sh	0.11	$2 \times 560.8 = 1121.6$ (A_1)
1313	vvw		B_1 Fundamental
1738.8	s sh	0.27	A_1 Fundamental
1966	vvw		$2 \times 986 = 1972$ (A_1)

* This faint band may be spurious, or it may be interpreted as $258 - 188 = 170$ (A_2).

Assignment of Fundamentals. Seven of the observed Raman bands, namely, 433.8, 623.0, 646, 1027.6, 1121.8, 1738.8, and 1966 cm^{-1} , are definitely polarized. The weak band 1121.8 cm^{-1} and the very faint band 1966 cm^{-1} are undoubtedly overtones, $2 \times 560.8 = 1121.6$ and $2 \times 986 = 1972$, respectively. The very strong Raman band at 433.8 cm^{-1} , which lies outside the range covered by the infrared measurements, must be a fundamental of species A_1 . The frequencies 1027 and 1738 cm^{-1} occur, with small shifts because of the change in the state of aggregation, as intense Type A bands in the infrared spectrum. They must also be interpreted as A_1 fundamentals. The contours of the two partly overlapping infrared bands at 622 and 640 cm^{-1} are not quite typical of Type A bands, perhaps in part because of the superposition of two A_1 combination bands, $188 + 434 = 622$ and $188 + 459 = 647$ cm^{-1} . However, the intensities of the bands in question are so high that the bands must be interpreted as fundamentals, and, since the corresponding Raman bands are polarized, they must belong to species A_1 . Thus, all of the five totally symmetrical fundamentals are accounted for.

The strong infrared band at 564 cm^{-1} is definitely of Type C, and its counterpart in the Raman spectrum, 560.8 cm^{-1} , is very strong and depolarized. There can be no doubt that these bands represent one of the two B_2 fundamentals. Another Raman band at 258 cm^{-1} is strikingly similar to 560.8 in appearance and intensity and is also depolarized. It is undoubtedly the other B_2 fundamental.

The very intense Type B infrared band at 1327 cm^{-1} must be a fundamental of species B_1 . The corresponding Raman band for liquid $\text{CF}_2:\text{CCl}_2$, at 1313 cm^{-1} , is so weak that its polarization could not be ascertained. Another very strong infrared band, at 993 cm^{-1} , appears rather definitely to be of Type B. Its counterpart in the Raman spectrum of the liquid is depolarized. It must also be a B_1 fundamental. Although the depolarization ratio for the weak and diffuse Raman band at 454 cm^{-1} is not measured with great accuracy, the band is fairly certainly depolarized. The corresponding band in the infrared, at 459 cm^{-1} , has not clearly defined contour. Nevertheless, it appears rather certain that these bands represent a B_1 fundamental. The depolarized Raman band at 187.8 cm^{-1} must be the last B_1 fundamental.

Sym
Spec

A_1
 A_1
 A_1
 A_1
 B_2
 B_2
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 B_1
 B_1
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* Onl

There remains only the A_2 fundamental. A rough estimate, based on the values of the twisting frequency C_2H_4 and $CF_2:CH_2$, indicates that this frequency should lie somewhere in the region between 110 and 150 cm^{-1} . Unfortunately, certain spurious light effects in the Lane-Wells Raman spectrograph make this region difficult to observe and throw some doubt upon the reality of the observed Raman band at 167 cm^{-1} . Until this doubt can be removed, and the region close to the exciting mercury line investigated, it is tentatively assumed that 167 cm^{-1} is the A_2 fundamental.

The infrared and Raman bands interpreted as fundamentals for $CF_2:CCl_2$ are listed in Table 24. The terms in the second column serve to indicate in a very rough manner the general nature of the vibrations but do not pretend to describe them with any accuracy.

As mentioned above, Torkington and Thompson (20), on the basis of Hatcher and Yost's Raman data and their own infrared observations, have made an assignment of ten of the fundamentals for $CF_2:CCl_2$. Two of their assignments, 648 cm^{-1} to B_2 and 255 cm^{-1} to A_1 , must be interchanged, since the former is strongly polarized and the latter depolarized. They interpreted the Raman band at 883 cm^{-1} , which was not observed in the present work, as a B_1 fundamental. If this Raman band should be real, it must be very faint; hence it would be more natural to interpret it as a combination band, $434 + 454 = 888\text{ cm}^{-1}$. Torkington and Thompson left unassigned one of the B_1 fundamentals as well as the A_2 twisting frequency.

On the basis of the fundamental vibration frequencies listed in Table 24, it has been possible to interpret all of the observed infrared and Raman bands. The interpretation of the infrared bands is given in the third column of Table 22 and that of the Raman bands in the third column of Table 23. In the former table, frequencies observed only as fundamentals in the Raman spectrum of liquid $CF_2=CCl_2$ are enclosed in parentheses, since these frequencies may be expected to differ somewhat from the corresponding frequencies for the gas.

Discussion. The interpretation of the two Raman bands not regarded as fundamentals is entirely satisfactory. The majority of the infrared bands are also interpreted

TABLE 24
Fundamental Vibration Frequencies of $CF_2=CCl_2$

Symmetry Species	Approximate Character *	Infrared (Gas)		Raman (Liquid)		Depolarization
		Wave Number	Description	Wave Number	Description	
A_1	C=C Stretching	1749 cm^{-1}	vs Type A	1738.8 cm^{-1}	s sh	0.27
A_1	CF Stretching	1032	vs Type A	1027.6	m sh	0.35
A_1	CCl Stretching	640	s	646	w d	0.20
A_1	CF_2 Deformation	622	m Type A	623.0	s sh	0.12
A_1	CCl_2 Deformation			433.8	vs sh	0.07
B_2	CF_2 Wagging	564	s Type C	560.8	vs	0.83
B_2	CCl_2 Wagging			258	vs	0.86
A_2	Twisting			167	vw	
B_1	CF Stretching	1327	vs Type B	1313	vw	~1
B_1	CCl Stretching	993	vs Type B	986	w d	0.8
B_1	CF_2 Rocking	459	vw	454	w	0.88
B_1	CCl_2 Rocking			187.8	w	

*Only very rough meaning can be attached to the terms used in this column.

satisfactorily. However, for many of the bands, especially at high wave numbers, alternative interpretations are possible. Except in cases where two assignments are about equally plausible, the alternatives are not listed in the table. Only about half of the possible binary combination bands have been observed. A third of the missing combination bands may be masked by stronger bands; the others are apparently too weak for observation. Four bands have been interpreted as difference bands and a number as ternary combination bands.

For some bands the interpretation given is not quite satisfactory, and there seems to be some evidence for violations of the selection rules for the molecular symmetry C_{2v} . Thus, the infrared band at 1936 cm^{-1} is interpreted as a B_1 combination, although its contour more nearly resembles that of a B_2 or A_1 band. Although the band at 758 cm^{-1} is of very low intensity, its interpretation as a difference band originating in the rather high level, 993 cm^{-1} , is somewhat unsatisfactory. If the selection rules were disregarded, it could be interpreted as $1327 - 564 = 763\text{ (A}_2\text{)}$. The band at 1894 (or 1878) cm^{-1} could be interpreted as the corresponding sum band.

The interpretation of the band at 1543 cm^{-1} as the difference band, $1749 - (188) = 1561\text{ (B}_1\text{)}$, is not very satisfactory, both because of the rather large difference between the calculated and observed frequency and because of the low intensity of the corresponding sum band. If the selection rule forbidding bands of species A_2 in infrared absorption is disregarded, it could be interpreted as $564 + 993 = 1557\text{ (A}_2\text{)}$. The faint absorption maxima at 1250 and 1585 cm^{-1} could be interpreted as $(258) + 993 = 1251\text{ (A}_2\text{)}$ and $(258) + 1327 = 1585\text{ (A}_2\text{)}$, respectively.

The evidence for a violation of the selection rules is hardly conclusive. If it should be substantiated by further investigation, it would be necessary to drop the assumption that the $\text{CF}_2=\text{CCl}_2$ molecule has a planar structure. However, the fact that both of the B_2 fundamentals give depolarized Raman bands would indicate that any deviation from planar structure is small.

$\text{CF}_2=\text{CF}_2$ (Tetrafluoroethylene)

Previous Work. The infrared spectrum of tetrafluoroethylene has been studied by Torkington and Thompson (20) but the Raman spectrum has apparently not been investigated previously. If this molecule has the same symmetry as ethylene, only five of the twelve fundamentals and none of the first overtones are active in infrared absorption. Hence, Torkington and Thompson were unable to assign with any certainty more than two or three of the fundamentals.

Experimental Results. Two samples of tetrafluoroethylene were investigated. The infrared absorption of the first sample (Serial No. 300) is shown in Figure 32. The Raman spectrum for the vapor state and polarization measurements were also made with this sample. However, the infrared spectrum did not agree well with that shown by Torkington and Thompson; some of the bands had about the same intensity, others were several-fold weaker, and a few were definitely stronger. Because of this, and because of difficulties encountered in the interpretation of the spectra, it became evident that the first sample (Serial No. 300) and also the sample studied by Torkington and Thompson were impure.

Through the courtesy of Dr. C. F. Hammer of the Plastics Department, E. I. du Pont de Nemours and Company, it was learned that the absorption bands near 700 , 960 , and 1800 cm^{-1} in the spectrum of C_2F_4 were due to CHF_3 , cyclic C_4F_8 , and olefinic C_3F_6 impurity, respectively. Weaker absorptions near 1290 , 1240 , and 1160 and part of that at

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1035 cm^{-1} are also due to impurity. The shoulder at 782 cm^{-1} is probably caused by as little as 0.05 percent CF_3Cl .

It was also learned from Dr. Hammer's measurements on pure $\text{CF}_2=\text{CF}_2$ in a longer cell (1 meter) that other weak absorptions, particularly those near 640, 750, and 850 and part of that near 950 and 1040 cm^{-1} are not foreign to $\text{CF}_2=\text{CF}_2$. Additional measurements on a purified sample (Serial No. 394) supplied by Dr. Hammer later showed that the absorption band observed at 510 cm^{-1} was also due to an impurity, undoubtedly CHF_3 , and that a weak Raman band at 1225 cm^{-1} had a similar origin.

In Table 25 the positions of the observed infrared absorption maxima and "shoulders" are listed, those due to impurities being omitted. Included are data obtained by Dr. E. K. Plyler at the National Bureau of Standards from measurements in the region 22 to 37.6 microns with a KRS-5 prism. The intensity and description of the bands are given in the second column.

A print of the observed Raman spectrum of gaseous C_2F_4 (Serial No. 394) and a microphotometer record of the original film are shown in Figure 22. In order to get as complete a spectrum as possible, the sample was exposed for 190 hours at a pressure of about seven atmospheres in the apparatus used for polarization measurements with all but a few baffles removed. The observed Raman shifts are listed in the first column of Table 26. In the second column are given rough estimates of the intensities of the bands and an indication of unusual sharpness or diffuseness. In the third column are given results of polarization measurements made on the impure sample (Serial No. 300), but because of the extreme weakness of the Raman bands, the polarization data are mostly qualitative.

Molecular Structure. The interpretation of the infrared and Raman spectra of tetrafluoroethylene has proved to be a very difficult problem, partly as a result of the presence of impurity bands in the spectrum of the first sample and of the fact that two of the infrared-active fundamentals lie beyond 22 microns. However, the main difficulties seem to have arisen from the peculiar structure and properties of the C_2F_4 molecule. There is some reason to believe that this molecule does not have a planar structure of symmetry V_h , as has ethylene, but has a chair form of symmetry C_{2h} . Neither a thorough study of the vibration spectra nor various normal coordinate treatments have revealed the molecular symmetry with certainty. It is therefore assumed that the C_2F_4 molecule has the symmetry V_h , but the possibility that the molecule is bent so as to have the symmetry C_{2h} is also considered.

From the electron diffraction data of Brockway and Livingston (18), C-C distance = 1.27Å, C-F distance = 1.32Å, and FCF angle = 110° , the moments of inertia are: 147, 261, and 408×10^{-40} g cm^2 . The axis of the smallest moment of inertia is the line through the two carbon atoms. Recent work by Drs. Jerome and Isabella Karle at NRL, however, has shown that these previous electron diffraction results are incorrect. Preliminary results from their work indicate that the $\text{CF}_2=\text{CF}_2$ molecule is planar, or very nearly so, having the dimensions C-C distance = 1.31Å, and the FCF angle = $112 \frac{2}{3}^\circ$. These data give for the three moments of inertia the values 150, 256, and 406×10^{-40} g cm^2 .

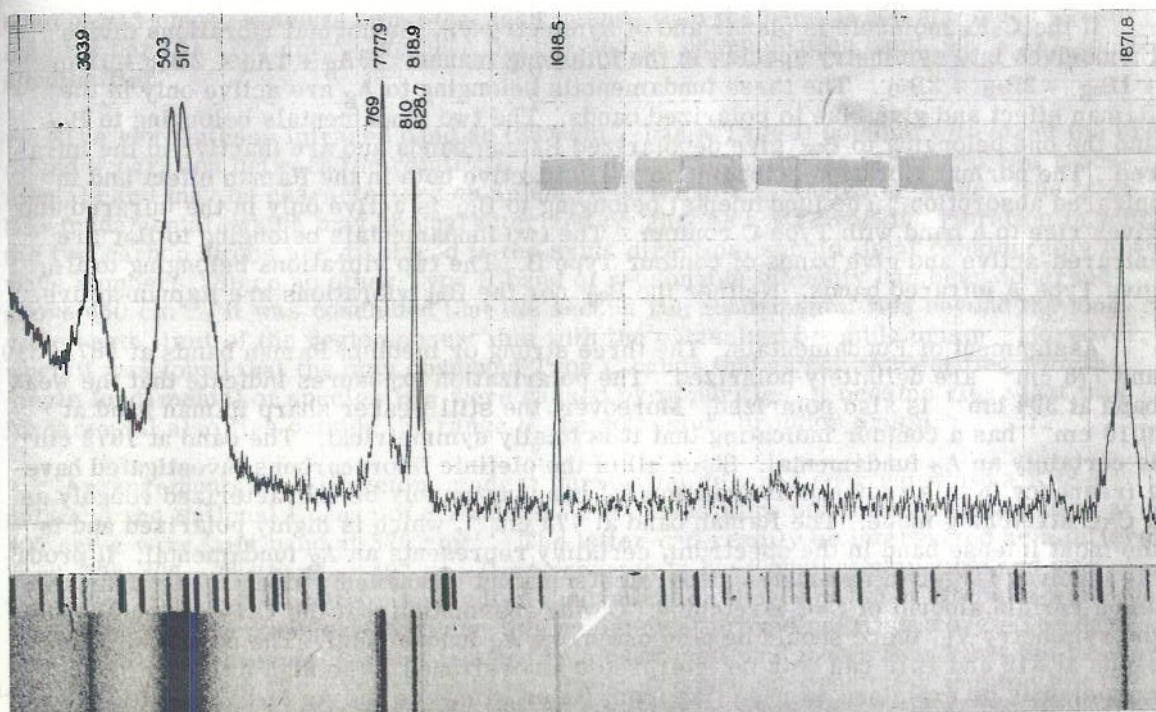
From these moments of inertia the Badger-Zumwalt parameters are found to be $\rho = 1.07$ and $S = -0.31$. From Badger and Zumwalt's curves for $\rho = 5/4$ and $S = -1/2$, the approximate values 7.1, 5.7, and 6.5 cm^{-1} are found for the separation $\nu - \nu_0$ of the rotational branches from the band center for Types A, B, and C bands respectively.

TABLE 25
Infrared Spectrum of Tetrafluoroethylene (Gas)

Wave Number	Description	Interpretation†	Wave Number	Description	Interpretation†
370* cm ⁻¹		778 - 407 (B _{1u})	1696	vw sh	517 + 1186 = 1703 (B _{1u})
407*	s Type A or C	B _{1u} Fundamental	1729	s Type B?	394 + 1337 = 1731 (B _{2u})
549			1741		
558	s Type A	B _{3u} Fundamental	1885	m	
627	vvw	3 x 210 = 630 (B _{2u})	1888	m	558 + 1338 = 1896 (B _{2u})
644	vvw		1893	m	
566			1954	m	
660	vvw	1186 - 517 = 669 (B _{1u})	1959	m	
755	vvw		1962	m sh	778 + 1186 = 1964 (B _{3u})
			1969	m	
789	vw	1186 - 394 = 792 (B _{3u})	1997		
796	vw	394 + 407 = 801 (B _{1u})	2002	m Type A	2 x 407 + 1186 = 2000 (B _{3u})?
			2011		
855	vvw		2105	s Type B	778 + 1337 = 2115 (B _{2u})
862	vvw		2116		
871	vw		2147	m Type B	2 x 407 + 1337 = 2151 (B _{2u})?
879	vw	778 + 517 - 407 = 888 (B _{3u})?	2156		
886	vw				
907			2213	vvw	2 x 517 + 1186 = 2220 (B _{3u})
913	s Type A	407 + 517 = 924 (B _{3u})	2240	vvw	
921			2255	vw	2 x 1337 - 407 = 2267 (B _{1u})
953	vw	394 + 558 = 952 (B _{3u})	2261	w	
960	vw		2274	m sh	407 + 1872 = 2279 (B _{1u})
			2279	w	
982	w Type B	210 + 778 = 988 (B _{2u})	2287	vw	2 x 558 + 1186 = 2302 (B _{3u})
992	w				
1021	vw Type B	2 x 407 + 210 = 1024 (B _{2u})	2421	w	
1031			2427	m	558 + 1872 = 2430 (B _{3u})
			2434	w	
1065	vvw Type C?	517 + 558 = 1075 (B _{1u}); 503 + 558 = 1061 (B _{2u})	2498	vvw	394 + 778 + 1337 = 2509 (B _{2u})
			2523	m Type B?	1186 + 1338 = 2524 (B _{2u})
1100	vvw Type B?		2534		
1107	vvw		2588		210 + 517 + 1872 = 2599 (B _{3u})
1181			2648	vw	
1186	vs Type A	B _{3u} Fundamental	2672	m	1337 + 1338 = 2675 (B _{3u})
1195			2680	vw	
1261	vvw	2 x 517 + 210 = 1244 (B _{2u})??	2723	vvw	2 x 778 + 1186 = 2742 (B _{3u})
1332	vs Type B	B _{2u} Fundamental	2762	vvw	2 x 1186 + 407 = 2779 (B _{1u})
1342			2880	vvw	2 x 778 + 1337 = 2893 (B _{2u})
1460	vw d	1872 - 407 = 1465 (B _{1u})?	2924	vvw	2 x 1186 + 558 = 2930 (B _{3u})
1524	m	2 x 558 + 407 = 1523 (B _{1u})?	2976	vvw	1338 + 1872 - 210 = 3000 (B _{3u})
1550	m	210 + 1338 = 1548 (B _{3u})?	3058	m	1186 + 1872 = 3058 (B _{3u})
1656	vvw	1872 - 210 = 1662 (B _{2u})	3205	m	1337 + 1872 = 3209 (B _{2u})
1671	vvw	3 x 558 = 1674 (B _{3u})			
1680	vvw	503 + 1186 = 1689 (B _{2u})			

*Observed by Dr. E.E. Plyler of the National Bureau of Standards.

†Assuming molecular symmetry V_h .

Figure 22 - Raman spectrum of gaseous $\text{CF}_2=\text{CF}_2$ TABLE 26
Raman Spectrum of Tetrafluoroethylene (Gas)

Wave Number	Description	Depolarization	Interpretation*
394 cm^{-1}	w	p?	A_g Fundamental
503	m d	0.88	B_{1g} Fundamental
517	m d	0.84	B_{2g} Fundamental
769.4	vw sh		$788 + \nu_x - \nu_x (\text{A}_g);$ $1186 - 407 = 779 (\text{B}_{2g})$
777.9	s sh	< 0.2	A_g Fundamental
809.7	vw sh		$2 \times 394 = 788 (\text{A}_g)$
818.9	m sh	< 0.4	$2 \times 407 = 814 (\text{A}_g)$
828.7	vw sh		$2 \times 407 + \nu_x - \nu_x (\text{A}_g);$ $1338 - 517 = 821 (\text{B}_{3g})$
1018.5	w sh?		$2 \times 517 = 1034 (\text{A}_g);$ $503 + 517 = 1020 (\text{B}_{3g})$
1340	vw vd		B_{1g} Fundamental
1872	m	p	A_g Fundamental

*Assuming molecular symmetry V_h .

If the C_2F_4 molecule is planar and of symmetry V_h , the normal vibrations divide themselves into symmetry species in the following manner: $3A_g + 1A_u + 2B_{1g} + 1B_{1u} + 1B_{2g} + 2B_{2u} + 2B_{3u}$. The three fundamentals belonging to A_g are active only in the Raman effect and give rise to polarized bands. The two fundamentals belonging to B_{1g} and the one belonging to B_{2g} give depolarized Raman bands and are inactive in the infrared. The normal vibration belonging to A_u is inactive both in the Raman effect and in infrared absorption. The fundamental belonging to B_{1u} is active only in the infrared and gives rise to a band with Type C contour. The two fundamentals belonging to B_{2u} are infrared-active and give bands of contour Type B. The two vibrations belonging to B_{3u} give Type A infrared bands. Neither the B_{2u} nor the B_{3u} vibrations are Raman-active.

Assignment of Fundamentals. The three strong or medium Raman bands at 1872, 819, and 778 cm^{-1} are definitely polarized. The polarization exposures indicate that the weak band at 394 cm^{-1} is also polarized. Moreover, the still weaker sharp Raman band at 1019 cm^{-1} has a contour indicating that it is totally symmetrical. The band at 1872 cm^{-1} is certainly an A_g fundamental. Since all of the olefinic fluorocarbons investigated have a frequency in this region, this fundamental can presumably be characterized roughly as a C=C stretching mode. The Raman band at 778 cm^{-1} , which is highly polarized and is the most intense band in the spectrum, certainly represents an A_g fundamental. It probably involves largely a symmetrical CF stretching but undoubtedly also CF_2 deformation and a certain amount of C=C stretching. On the assumption that the C_2F_4 molecule has the symmetry V_h , there should be only one more A_g fundamental. The polarized Raman bands at 819 and 1019 can both be interpreted as overtones. The high intensity of the former may be explained as resulting from its proximity to the A_g fundamental at 778 cm^{-1} . Thus, the third A_g fundamental must undoubtedly be identified with the rather weak Raman band at 394 cm^{-1} . It may be designated roughly as a symmetrical CF_2 deformation mode.

There are three fundamentals that should give depolarized Raman bands, but only two such bands, lying close together at 503 and 517 cm^{-1} , have been definitely observed. They must be associated roughly with in-plane rocking and out-of-plane wagging motions in which the two carbon atoms, moving out of phase with each other, have greater amplitude than does the fluorine atom. Since the out-of-plane motions have somewhat higher frequencies than the corresponding in-plane motions in CF_2CH_2 and $CF_2:CCl_2$, the Raman band at 517 cm^{-1} is identified with the single B_{2g} fundamental and the band at 503 cm^{-1} with the lower of the two B_{1g} fundamentals.

The other B_{1g} fundamental, which may be characterized roughly as an unsymmetrical CF stretching vibration, would be expected to lie in the region from 1100 to 1400 cm^{-1} . It was first identified with a weak band at 1225 cm^{-1} . However, when the second sample of C_2F_4 became available, this band was found to have been caused by an impurity. An attempt was therefore made to determine the high B_{1g} fundamental from the five binary infrared combination bands in which it should occur. Four of these bands were identified with a high degree of certainty (the fifth being masked by a fundamental) and the frequency 1338 cm^{-1} was determined. Afterwards, when a 190-hour exposure was made with the pure sample of C_2F_4 , a very weak and extremely diffuse Raman band with maximum at $1340 \pm 10\text{ cm}^{-1}$ was observed. There can be no doubt that it represents the high B_{1g} fundamental. Its low intensity may be an indication of the highly ionic character of the CF bonds in C_2F_4 .

The two fundamentals of species B_{3u} should give rise to Type A infrared absorption bands. As may be seen from Figure 32, three strong bands of this contour type have been observed. Those at 558 and 1186 cm^{-1} are undoubtedly B_{3u} fundamentals. The former may be characterized roughly as a CF_2 deformation and the other as a symmetrical CF stretching mode in which the motions in the two CF_2 groups are out of phase. The Type A

band at 913 cm^{-1} , which is somewhat less intense than the band at 558 and much weaker than the band at 1186 cm^{-1} , has been interpreted as a combination band, $407 + 517$, of species B_{3u} .

The very intense infrared band at 1337 cm^{-1} has a Type B contour with about the predicted separation between the rotational branches. It must be one of the two B_{2u} fundamentals and may be characterized as an unsymmetrical CF stretching mode. The other B_{2u} fundamental, which may be characterized roughly as a CF_2 rocking vibration in which the two carbon atoms are displaced in the same direction, should lie at considerably lower wave numbers. Since no other Type B band of reasonable intensity had been observed above 450 cm^{-1} , it was concluded that the second B_{2u} fundamental lies beyond the long wavelength limit of the region observable with the potassium bromide prism. Moreover, when it was found that the only observed Type C bands that might be identified with the single fundamental of species B_{1u} were caused by impurities, it became clear that this fundamental also lies outside the range of the potassium bromide prism.

Arrangements were therefore made to survey the infrared spectrum with a KRS-5 prism at the National Bureau of Standards. Two bands were observed, a strong band at 407 and a very faint band at 370 cm^{-1} . The latter can readily be interpreted as a difference band, $778-407$. The band at 407 was first reported to have doublet structure and was therefore interpreted as the missing B_{2u} fundamental. However, when attempts were made to identify certain combination bands, this assignment proved unsatisfactory. The data obtained at the Bureau of Standards were then examined, and it was found that the band at 407 cm^{-1} definitely has a PQR structure. Thus, although the resolution was too low to differentiate between Type A and Type C contours, it is clear that 407 cm^{-1} must be the B_{1u} rather than the B_{2u} fundamental. The latter then must lie below 266 cm^{-1} , the smallest wave number reached by the KRS-5 instrument. Attempts to determine it from infrared combination bands have led to two possible values, 210 cm^{-1} or 245 cm^{-1} . The evidence is somewhat less strong for the higher value, and the lower value, 210 cm^{-1} , has therefore been adopted.

The single fundamental of species A_u , which represents a torsional oscillation, is inactive both in the infrared and in the Raman effect. Attempts to determine it by identifying the three binary sum bands that involve it and are active in the infrared have proved inconclusive.

The eleven fundamental frequencies that have been assigned are listed in Table 27. On the basis of these fundamentals it has been possible to interpret practically all of the infrared and Raman bands. The interpretation of the infrared bands is given in the third column of Table 25, and the interpretation of the Raman bands appears in the third column of Table 26.

Discussion. Of the 26 binary sum bands that are infrared active, not counting those involving the twisting frequency, 18 have been observed. Two are masked by fundamentals, two overlap, and five are apparently too weak for observation. Five infrared bands are interpreted as binary difference bands and eighteen as ternary combination bands. Three or four faint infrared bands, which may involve the unknown twisting frequency or be caused by impurities, are left unassigned.

For the majority of the infrared bands the interpretation given in Table 25 is satisfactory. However, the interpretation of some of the bands is not quite convincing. Thus, the bands at 879 , 1524 , 2002 , and 2151 cm^{-1} have greater intensity than expected of ternary combination bands. The infra-bands at 1460 and 1550 cm^{-1} have abnormal contours, and for a few bands the difference between the calculated and the observed frequency is rather large.

TABLE 27
Fundamental Vibration Frequencies of Tetrafluorethylene*

Species	Characterization †	Wave Number
Ag	C=C Stretching	1872 cm ⁻¹
Ag	CF Stretching	777.9
Ag	CF ₂ Deformation	394
B _{1g}	CF Stretching	1338
B _{1g}	CF ₂ Rocking	503
B _{2g}	CF Wagging	517
A _u	Twisting	---
B _{1u}	CF ₂ Wagging	407
B _{2u}	CF Stretching	1337
B _{2u}	CF ₂ Rocking	210
B _{3u}	CF Stretching	1186
B _{3u}	CF ₂ Deformation	558

*Assuming molecular symmetry V_h .

†Only very rough meaning should be attached to the terms listed in this column.

The interpretation given of the five Raman bands not taken to be fundamentals also suffers from certain difficulties and ambiguities. The band at 819.9 cm⁻¹, interpreted as an overtone, has abnormally high intensity which may be caused by its proximity to the totally symmetrical fundamental at 778 cm⁻¹. The sharpness and rather high intensity of the band at 1018.5 cm⁻¹ make its interpretation as the overtone of 517 cm⁻¹ seem more plausible than its interpretation as 503 + 517 = 1020 (B_{3g}), despite the greater difference between calculated and observed frequencies. The interpretation of the two very sharp faint bands at 769.4 and 828.9 cm⁻¹ as upper-stage bands seems somewhat more plausible than their interpretation as difference bands. The rather large difference between 809.7 and 2 x 394 may be a result of coupling with the Ag fundamental, 778 cm⁻¹.

Because of the peculiarities indicated, and because of difficulties experienced in the normal coordinate treatment, the possibility that the C₂F₄ molecule has a nonplanar structure has been considered. Since no coincidences occur between infrared and Raman frequencies (except for the B_{1g} and B_{2u} fundamentals at 1338 cm⁻¹), the C₂F₄ molecule must have a symmetry center, and the only alternative structure that need be considered is the "chair" form of symmetry C_{2h}. With this symmetry, the even, wagging fundamental becomes totally symmetrical, and the twisting fundamental and four additional binary combination frequencies become active in the infrared.

Thus, it is now possible to interpret the medium Raman band at 818.9 cm⁻¹ as a fourth totally symmetrical fundamental associated with an even, wagging motion of the molecule. Its depolarization ratio, however, is smaller than one would expect if the shape of the molecule deviates only moderately from the planar form. If this assignment is made, either the two intensity maxima at 503 and 517 cm⁻¹ in the Raman spectrum must be interpreted as a single B_g fundamental of frequency about 510 cm⁻¹; or one of them must be explained as an upper-stage band, as a combination band involving the unknown twisting fundamental, or otherwise.

With this change in the assignment of two of the fundamentals, a few significant changes in the interpretation of the infrared absorption bands can be made. The strong band at

TABLE 28
Fundamental Frequencies of $X_2C=CX_2$ Molecules

Vibration		$C_2H_4^*$	$C_2D_4^*$	C_2F_4	$C_2(CH_3)_4^\dagger$	$C_2Cl_4^\ddagger$	$C_2Br_4^\ddagger$
ν_1	Ag	3019	2251	778	691	447	267
ν_2	Ag	1623	1515	1872	1676	1571	?
ν_3	Ag	1342	981	394	(240, 411)?	237	163 or 181
ν_4	Au	1027	726	-	?	135	(133)?
ν_5	B _{1g}	3272	2304	1338	1024 or 1060	512	1024?
ν_6	B _{1g}	1236	(1009)	503	506	347	211
ν_7	B _{1u}	949	720	407	600 (est.)	185	527
ν_8	B _{2g}	943	780	517	?	215	468?
ν_9	B _{2u}	3105	2345	1337	1151	913	843
ν_{10}	B _{2u}	810	(586)	(210)	(406)?	332	(363)?
ν_{11}	B _{3u}	2989	2200	1186	893	782	763
ν_{12}	B _{3u}	1443	1078	558	(475)?	387	?

* Assignment of R. L. Arnett and B. L. Crawford, University of Minnesota Report dated 3/1/49 for ONR Contract N5-ori-147, T.O.2. See also D. H. Rank, E. R. Shull and D. W. E. Axford, Penn. State College Report dated 6/4/49 for ONR Contract N6-ori-269.

† J. Guy and J. Lecomte, Bulletin de la Société Chimique de France, 14, 977 (1947).

‡ P. Torkington, Trans. Far. Soc. 45, 445 (1949).

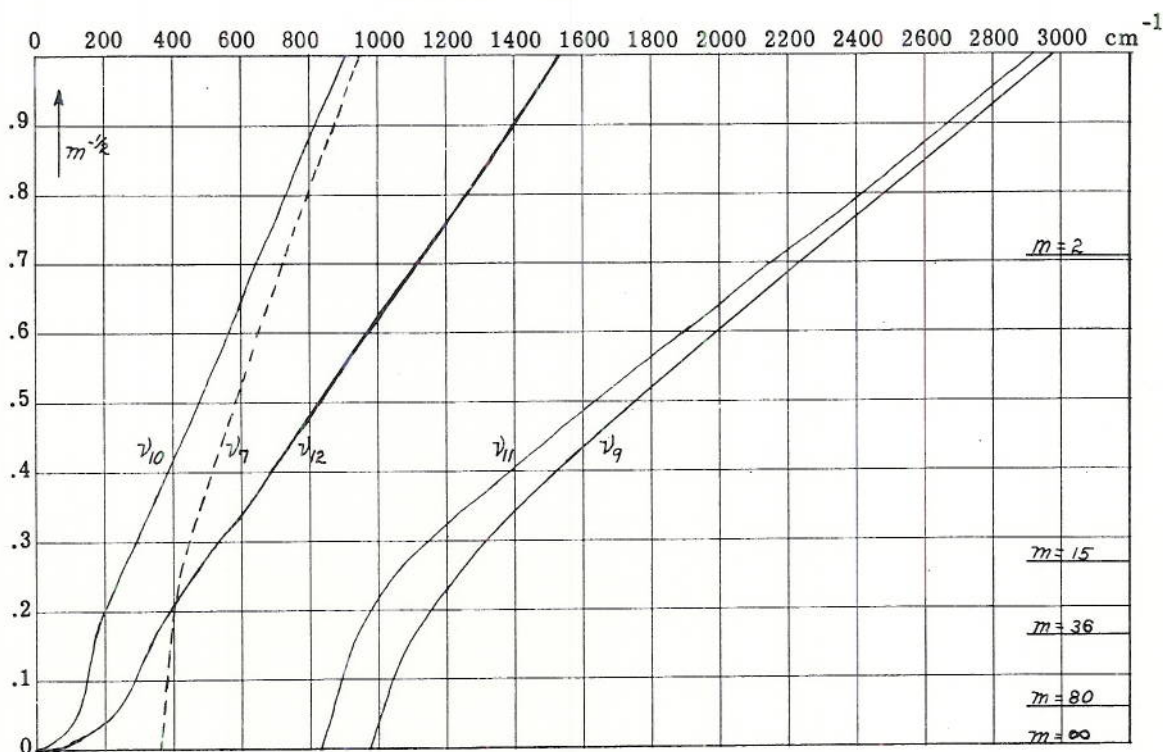


Figure 23 - Variation of infrared-active fundamentals of $X_2C=CX_2$ with mass X

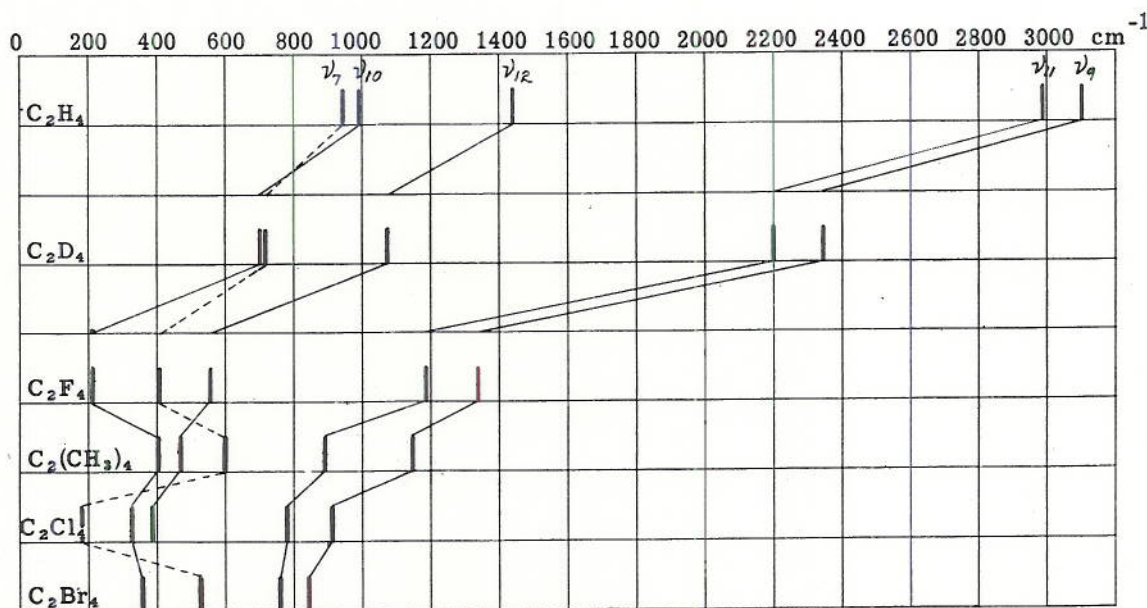


Figure 24 - Infrared-active fundamentals of $X_2C=CX_2$ molecules

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913 cm^{-1} must be interpreted as $407 + 510 = 917$ (A_u). The very weak Type B band at 1026 cm^{-1} , and the two medium bands at 2002 and 2151 cm^{-1} which were interpreted as ternary combination bands, can now be interpreted as the binary combination bands: $210 + 819 = 1024$ (A_u), $819 + 1186 = 2005$ (B_u), and $819 + 1337 = 2156$ (A_u), respectively. The latter two bands, as well as $407 + 510$, are among the four new infrared-active bands. Unfortunately, the fourth of these bands, $407 + 1338 = 1745$ (A_u), overlaps with $394 + 1337 = 1731$ (A_u); and the band, $407 + 819 = 1226$ (B_u), is masked by the B_u fundamental at 1186 cm^{-1} . In the Raman spectrum the faint sharp band at 809.7 cm^{-1} can now be interpreted as $2 \times 407 = 814$ (A_g) and the weak band at 1018.5 cm^{-1} as $2 \times 510 = 1020$ (A_g).

All in all, the assumption that the C_2F_4 molecule has the symmetry C_{2h} leads to a somewhat more satisfactory interpretation of the observed infrared and Raman spectra. However, the present evidence in favor of a chair form for the C_2F_4 molecule can hardly be regarded as conclusive. Should further work establish the chair form, this may perhaps be explained as a result of the removal of the double-bond electrons from between the carbon atoms because of the high electronegativity of the fluorine atoms.

The fundamental frequencies of various $X_2C=CX_2$ molecules, including $CF_2=CF_2$, are listed for comparison in Table 28. Kohlrausch (5, p. 116) has given frequency formulas for these molecules, assuming V_h symmetry and the usual valence force field. He also presents curves showing how the six Raman-active fundamentals vary as a function only of the mass of X and shows that the assigned Raman-active fundamentals for all molecules except $CF_2=CF_2$ fall along similar smooth curves. The present assignment of these fundamentals for $CF_2=CF_2$ is in good agreement with these previous data, except that the valency frequencies are somewhat high. Using the formulas and force constants of Kohlrausch ($f_{C=C} = 8.94$, $f_{C-X} = 4.85$, $g = 0.375 \times 10^5$ dyne/cm), the variation of the five infrared-active fundamentals as a function of the mass of X has also been calculated, as shown in Figure 23. The assigned frequencies are shown for comparison in Figure 24. There is little doubt about the identification of the stretching frequencies ν_9 and ν_{11} in this series of molecules. The assignments for ν_7 , ν_{10} , and ν_{12} seem to be satisfactory for $CH_2=CH_2$, $CD_2=CD_2$, and $CF_2=CF_2$; but for C_2Br_4 , $C_2(CH_3)_4$, and possibly C_2Cl_4 , some revision is undoubtedly required.

$CF_2=CFCl$ (Trifluorochloroethylene)

Experimental Results. The infrared absorption spectrum of gaseous $CF_2=CFCl$ (Serial No. 379) from 2 to 22.5 microns is shown in Figure 32. The wave numbers for the observed absorption maxima are listed in the first column of Table 29. In the second column, relative intensities and exceptional sharpness of the absorption maxima are indicated.

The Raman spectrum was obtained of the compound in the liquid state at a temperature somewhat above room temperature. Because of the low symmetry of the $CF_2=CFCl$ molecule and the presence of a fairly strong continuous background, no polarization measurements were made. The observed Raman frequencies are listed in the first column of Table 30. In the second column the relative intensities of the bands are indicated, and for a couple of bands information is given about exceptional sharp or diffuse appearance.

Molecular Structure. If it is assumed that the $CF_2=CFCl$ molecule has a planar structure of symmetry C_s , the twelve normal vibrations divide themselves into nine fundamentals of species A' and three of species A'' . The latter represent out-of-plane motions and should give Type C infrared bands and depolarized Raman bands. Because of the lack of symmetry in the plane of the molecule, the infrared bands corresponding to in-the-plane motions of species A' will not have typical contours. The majority of the bands may be expected to approximate Type A bands in appearance, while a few may have very nearly Type B contour. Electron diffraction data for the $CF_2=CFCl$ molecule are not yet available.

RESULTS AND DISCUSSION

 TABLE 29
 Infrared Spectrum of CF_3CFCl (Gas)

Wave Number	Description	Interpretation	Wave Number	Description	Interpretation
~457 cm^{-1}	s		1387	m	$2 \times 691 = 1382$ (A')
463	s sh	A' Fundamental	1401	m	$340 + 1058 = 1398$ (A''); $180 + 1217 = 1397$ (A'')
~469	s				
~512	s		~1430	vvw	$691 + 739 = 1430$ (A'); $215 + 1217 = 1432$ (A')
517	s sh	A' Fundamental			
~524	s		1517	m	$463 + 1058 = 1521$ (A'); $180 + 1336 = 1516$ (A'')
538	s sh	A'' Fundamental			
543	s		1550	vw	$340 + 1217 = 1557$ (A''); $215 + 1336 = 1551$ (A')
592	vvw		1605	vw	$538 + 1058 = 1596$ (A''); $3 \times 538 = 1614$ (A'')
598	vvw	$1058 - 463 = 595$ (A')			
603	vvw		1667	w	
639	vvw		1672	w	$340 + 1336 = 1676$ (A'')
645	vvw	$180 + 463 = 643$ (A'')	1677	w	$463 + 1217 = 1680$ (A')
685	s				
691	s sh	A' Fundamental	1690	vvw	$463 + 538 + 691 = 1692$ (A'')
697	s		1742	vw	$691 + 1058 = 1749$ (A'); $517 + 1217 = 1734$ (A')
711	vw	$1058 - 340 = 718$ (A''); $180 + 538 = 718$ (A')	1755	vw	$538 + 1217 = 1755$ (A'')
~735	w				
739	m sh	A' Fundamental	1797	vs	
746	m		1802	vs sh	A' Fundamental
751	m sh	$215 + 538 = 753$ (A'')	1806	s	
803	vvw sh	$340 + 463 = 803$ (A'')			
807	vvw		1843	vvw	
~811	vvw		1849	vvw	$517 + 1336 = 1853$ (A')
820	vvw sh	$1336 - 517 = 819$ (A')			
828	vvw		1880	vvw	$538 + 1336 = 1874$ (A'')
849	vvw	$1058 - 215 = 843$ (A')	1908	w	$691 + 1217 = 1908$ (A')
851	vvw		1916	vw	
855	vw	$340 + 517 = 857$ (A'')			
862	w		1951	vvw	$739 + 1217 = 1956$ (A')
870	vvw	$340 + 538 = 878$ (A'); $180 + 691 = 871$ (A'')	1960	vvw	
			1978	vvw	
			1989	vw	$180 + 1802 = 1982$ (A'')
~887	vvw				
901	m		2016	w	$215 + 1802 = 2017$ (A')
906	m sh	$215 + 691 = 906$ (A')	2025	w	$691 + 1336 = 2027$ (A')
~910	m	$180 + 739 = 919$ (A'')			
914	m		2077	vvw	$739 + 1336 = 2075$ (A')
925	vvw	$2 \times 463 = 926$ (A')			
929	vvw		2111	vvw	
965	w		2119	w	$2 \times 1058 = 2116$ (A')
972	w sh	$463 + 517 = 980$ (A')	2131	w	
978	w		2137	w	$340 + 1802 = 2142$ (A'')
997	vvw	$1336 - 340 = 996$ (A'')	2161	w sh	$2 \times 739 + 691 = 2169$ (A')
1004	vvw	$463 + 538 = 1001$ (A'')			
~1030	vvw	$340 + 691 = 1031$ (A''); $2 \times 517 = 1034$ (A')	2261	vvw	$463 + 1802 = 2265$ (A')
1052	vs		2311	vw	$517 + 1802 = 2319$ (A')
1058	vs sh	A' Fundamental	2334	vvw	$538 + 1802 = 2340$ (A'')
1065	vs		2393	m	$1058 + 1336 = 2394$ (A')
~1074	s		2413	m	$2 \times 1217 = 2434$ (A')
1081	vs sh	$2 \times 538 = 1076$ (A'); $340 + 739 = 1079$ (A'')	2481	w sh	$691 + 1802 = 2493$ (A')
1087	vs		2539	vw	$739 + 1802 = 2541$ (A')
1116	vw	$1336 - 215 = 1121$ (A')			
1147	s		2657	m sh	$2 \times 1336 = 2672$ (A')
1153	s sh	$463 + 691 = 1154$ (A')	2713	vvw	$215 + 691 + 1802 = 2708$
1159	s				
1212	vs	A' Fundamental	2861	m sh	$1058 + 1802 = 2860$ (A')
1221	vs		2946	vvw	$463 + 691 + 1802 = 2956$ (A')
1252	vvw	$517 + 739 = 1256$ (A')	3008	w	$1217 + 1802 = 3019$ (A')
1276	vvw	$538 + 739 = 1277$ (A''); $215 + 1058 = 1273$ (A')	3121	w	$1336 + 1802 = 3138$ (A')
1292	vw	$2 \times 538 + 215 = 1291$ (A')	3172	vvw	$3 \times 1058 = 3174$ (A')
1332	vs	A' Fundamental	3340	vvw	$2 \times 1058 + 1217 = 3333$ (A'')
1340	vs		3620	vvw	$2 \times 1802 = 3604$ (A')

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TABLE 30
Raman Spectrum of $\text{CF}_2=\text{CFCl}$ (Liquid)

Wave Number	Description	Interpretation
340 cm^{-1}	m	A'' Fundamental
462.3	s	A' Fundamental
537	vs d	A'' Fundamental
690.4	vs sh	A' Fundamental
748	w	A' Fundamental
1054	vw	A' Fundamental
1078	w	$2 \times 538 = 1076$ (A')
1225	vvw	A' Fundamental
1323	vvw	A' Fundamental
1380	vvw	$2 \times 691 = 1382$ (A')
1794	s	A' Fundamental
2099	vw	$2 \times 1058 = 2116$ (A')

Assignment of Fundamentals. The strong infrared band at 538 cm^{-1} seems definitely to have a Type C contour. Its frequency lies between those found for the high wagging fundamentals for C_2F_4 and $\text{CF}_2=\text{CCl}_2$. There can be no doubt, therefore, that it represents the highest of the three A'' fundamentals. The next lower A'' fundamental may be expected to lie between the values 407 and 258 cm^{-1} found for the lower wagging frequency for C_2F_4 and $\text{CF}_2=\text{CCl}_2$ respectively. It must undoubtedly be identified with the medium Raman band observed at 340 cm^{-1} in liquid $\text{CF}_2=\text{CFCl}$. The third A'' fundamental is essentially a torsional oscillation of one end of the molecule with respect to the other. It lies outside the range of the infrared observations and has not been observed in the Raman effect. Attempts to determine the twisting frequency from combination bands have led to a value of 180 cm^{-1} , but the evidence cannot be regarded as conclusive.

The very intense infrared band at 1802 cm^{-1} in gaseous $\text{CF}_2:\text{CFCl}$ and the strong Raman band at 1794 cm^{-1} in the liquid must represent the highest A' fundamental. It may be characterized roughly as a C=C stretching mode. The two very intense infrared bands at 1336 and 1217 cm^{-1} , both of which have Type B contour, and the very faint Raman bands at 1323 and 1225 cm^{-1} must represent A' fundamentals involving primarily CF stretching of such a nature that the two fluorine atoms in the CF_2 group move in opposite phase. Either the very strong infrared band at 1058 or the somewhat weaker band at 1081 cm^{-1} must represent an A' fundamental involving CF stretching in which the two fluorine atoms in the CF_2 group move in phase.

In the Raman effect, a very weak band is observed at 1054 and a weak band at 1078 cm^{-1} . The band at 1058 cm^{-1} could be interpreted as a combination band, $517 + 538 = 1055$ (A'').

However, because of its high intensity and lack of the prominent Q branch characteristic of Type C bands, this interpretation is not plausible. The band at 1081 cm^{-1} can be interpreted as an overtone, $2 \times 538 = 1076\text{ (A')}$, which is enhanced (and shifted somewhat) by an A' fundamental at 1058 cm^{-1} . The relative intensities of the two bands in the Raman effect does not weaken this interpretation; for, fundamentals corresponding to CF stretching are usually found to be very weak in the Raman effect, whereas the overtone of the high wagging frequency has been observed with rather high intensity in all of the fluorinated ethylenes. For these reasons the band at 1058 cm^{-1} , rather than that at 1081 cm^{-1} , is interpreted as the A' fundamental.

The next lower A' fundamental must be either 906 or 739 cm^{-1} . Since the former appears too high to be identified with a motion involving primarily CF_2 deformation, the latter has been chosen. The strong infrared band at 691 , and the very intense Raman band at 690.4 cm^{-1} in liquid $\text{CF}_2=\text{CFCl}$, must also represent an A fundamental. The motion probably involves primarily C-Cl stretching. The next two A fundamentals are undoubtedly represented by the strong infrared bands at 517 and 463 cm^{-1} . The former probably involves primarily a deformation of the CFCl group and the latter, which is observed also in the Raman effect, a rocking of the CF_2 group.

The last A' fundamental, which may be thought of as a rocking of the CF_2 and CFCl groups in which the two carbon atoms are displaced roughly in the same direction, lies outside the range of the infrared measurements. It was not observed in the Raman effect. From the values of the lowest rocking frequencies in C_2F_4 and $\text{CF}_2=\text{CCl}_2$, it can be expected to lie in the neighborhood of 200 cm^{-1} . If the medium infrared band at 906 cm^{-1} is interpreted as a combination band of 691 with the lowest A fundamental, the value 215 cm^{-1} is obtained for the latter. This frequency explains a pair of faint infrared bands that had not previously been interpreted and gives alternative interpretations of several other bands. It has therefore been tentatively adopted. The fundamentals assigned are listed in Table 31.

Discussion. On the basis of these fundamentals it has been possible to interpret all but a few of the observed infrared bands and all of the Raman bands. The interpretation is given in the third columns of Tables 29 and 30. The interpretation of the three Raman bands not regarded as fundamentals is satisfactory. Of the 78 binary combination (sum or overtone) bands that can be formed from the twelve fundamentals, about four-fifths have been observed in the infrared spectrum, although some of them overlap. Of the remaining bands, about a dozen are masked by fundamentals, and three lie outside the range investigated. Only one binary combination band, $517 + 1058$, seems definitely to be absent. Six very faint infrared bands have been interpreted as binary difference bands, and seven very weak bands have been interpreted as ternary combination bands. For a number of bands, especially at high frequencies, more than one interpretation is possible. Alternative interpretations have been given in Table 29 only for bands ascribed to binary combinations and only when two interpretations appear about equally plausible.

The high intensity of the overtone band at 1081 cm^{-1} has already been discussed. The abnormally high intensity of the binary combination band at 1153 cm^{-1} may also be a result of its proximity to the A' fundamental at 1058 cm^{-1} . Except for a few bands, such as those at 2657 and 2481 cm^{-1} , the agreement between the calculated and the observed wave numbers is very close. The interpretation given of the infrared spectrum appears to be entirely satisfactory for all but a few of the bands. The only conspicuous exception is the weak band at 2161 cm^{-1} , which is interpreted as a ternary combination band of species A', although its contour definitely indicates that it belongs to species A". If higher than ternary combinations are neglected, the only possibility of interpreting this band as a band of species A" is $691 + 1802 - 340 = 2153\text{ (A")}$. But this may be ruled out, since

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TABLE 31
Fundamental Vibration Frequencies of $\text{CF}_2=\text{CFCl}$

Symmetry Species	Infrared (Gas)		Raman (Liquid)	
	Wave Number	Description	Wave Number	Description
A'	1802	vs	1794	s
A'	1336	vs	1323	vvw
A'	1217	vs	1225	vvw
A'	1058	vs	1054	vw
A'	739	m	748	w
A'	691	s	690.4	vs sh
A'	517	s	---	
A'	463	s	462.3	s
A'	215*		---	
A''	538	s	537	vs d
A''	---		340	m
A''	180†		---	

*Inferred from combination bands.

†Uncertain. Inferred from combination bands.

the corresponding sum band has not been observed. It is possible that the band at 2161 cm^{-1} is caused by an impurity.

The fundamental vibration frequencies of $\text{CF}_2=\text{CFCl}$ may be compared with those of $\text{CF}_2=\text{CH}_2$, $\text{CF}_2=\text{CF}_2$, and $\text{CF}_2=\text{CCl}_2$, as shown in Figure 25 where the frequencies are correlated according to the nature of the vibrational motion. In Table 32 these fundamentals are correlated according to species. Both sets of correlations appear to be satisfactory, except for the third and fourth A_1 fundamentals of $\text{CF}_2=\text{CCl}_2$ and the corresponding frequencies for $\text{CF}_2=\text{CFCl}$ given in Table 32. It appears that the vibration motions associated with the fundamentals 640 and 622 cm^{-1} for $\text{CF}_2=\text{CCl}_2$ and the fundamentals 739 and 691 cm^{-1} for $\text{CF}_2=\text{CFCl}$ should be interchanged in Table 32. This will also improve the correlations of Figure 25, and, since the fundamentals are of the same species, the interchange is permitted.

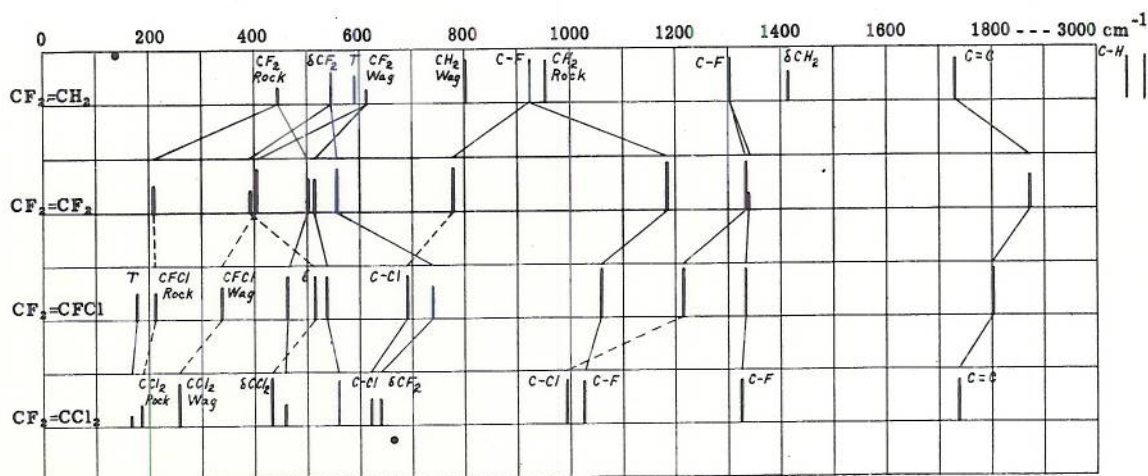


Figure 25 - Fundamental vibration frequencies of $\text{CF}_2=\text{CH}_2$, $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CFCF}$ and $\text{CF}_2=\text{CCl}_2$

TABLE 32
The Series $\text{CF}_2=\text{CH}_2$, $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CFCF}$, $\text{CF}_2=\text{CCl}_2$

$\text{CF}_2=\text{CH}_2$			\rightarrow	$\text{CF}_2=\text{CF}_2$			\rightarrow	$\text{CF}_2=\text{CFCF}$			\rightarrow	$\text{CF}_2=\text{CCl}_2$		
A_1	C-H	(3060)	\rightarrow	A_g	C=C	(1872)	\rightarrow	A'	C=C	(1802)	\rightarrow	A_1	C=C	(1749)
A_1	C=C	(1728)	\rightarrow	B_{3u}	C-F	(1186)	\rightarrow	A'	C-F	(1058)	\rightarrow	A_1	C-F	(1032)
A_1	δCH_2	(1414)	\rightarrow	A_g	C-F	(778)	\rightarrow	A'	δCF_2	(739)	\rightarrow	A_1	δCF_2	(646)
A_1	C-F	(926)	\rightarrow	B_{3u}	δCF_2	(558)	\rightarrow	A'	C-Cl	(691)	\rightarrow	A_1	C-Cl	(622)
A_1	δCF_2	(550)	\rightarrow	A_g	δCF_2	(394)	\rightarrow	A'	δCFCF	(517)	\rightarrow	A_1	δCCl_2	(434)
A_2	T	(590)	\rightarrow	A_u	T	(?)	\rightarrow	A''	T	(180?)	\rightarrow	A_2	T	(167)
B_1	C-H	(3098)	\rightarrow	B_{1g}	C-F	(1337)	\rightarrow	A'	C-F	(1336)	\rightarrow	B_1	C-F	(1327)
B_1	C-F	(1302)	\rightarrow	B_{2u}	C-F	(1338)	\rightarrow	A'	C-F	(1217)	\rightarrow	B_1	C-Cl	(993)
B_1	CH_2 Rock	(955)	\rightarrow	B_{1g}	CF_2 Rock	(503)	\rightarrow	A'	CF_2 Rock	(463)	\rightarrow	B_1	CF_2 Rock	(459)
B_1	CF_2 Rock	(447)	\rightarrow	B_{2u}	CF_2 Rock	(210)	\rightarrow	A'	CFCF Rock	(215)	\rightarrow	B_1	CCl_2 Rock	(187)
B_2	CH_2 Wag	(803)	\rightarrow	B_{2g}	CF_2 Wag	(517)	\rightarrow	A''	CF_2 Wag	(538)	\rightarrow	B_2	CF_2 Wag	(564)
B_2	CF_2 Wag	(611)	\rightarrow	B_{1u}	CF_2 Wag	(407)	\rightarrow	A''	CFCF Wag	(340)	\rightarrow	B_2	CCl_2 Wag	(258)

$\text{CF}_2=\text{CF}-\text{CF}_3$ (Hexafluoropropene)

Previous Work. When tetrafluoroethylene polymer is subjected to pyrolysis a compound of composition C_3F_6 is formed. This was first believed to be cyclic but was later

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shown to be hexafluoropropene (35, 36, 37). Edgell (36) has investigated the Raman spectrum of the compound in the liquid state and has made a tentative assignment of all but one of the twenty-one fundamentals. He lists seven infrared absorption maxima for C_3F_6 . Young and Murray (35) show a rather poor infrared spectrum for the range 4 to 15 μ .

Experimental Results. The infrared spectrum of gaseous C_3F_6 (Serial No. 327) from 2 to 23 μ is shown in Figure 34. This sample contained a small amount of C_3F_8 impurity as evidenced by the absorption at 731 and 1263 cm^{-1} (compare spectra, Figure 34). A later sample (Serial No. 358) showed no absorption at 731 cm^{-1} , the spectrum in this region consisting only of two weak Type A or Type C bands with centers at 720 and 739 cm^{-1} . The later sample, however, was evidently not completely fluorinated, as indicated by several weak C-H absorption bands near 2950 cm^{-1} ; and because of other impurity absorptions in the region from 870 to 980 cm^{-1} , the spectrum is not shown. It is possible that some of the absorption in the region 900 to 1000 cm^{-1} in the spectrum shown is also due to impurity. The positions of the observed maxima are listed in the first column of Table 33.

The Raman spectrum of the purer sample (Serial No. 327) was obtained for the vapor state at a pressure of about five atmospheres and a few degrees above room temperature. The observed shifts are listed in the first column of Table 34. Attempts to obtain Raman spectra of the compound in the liquid state at room temperature failed because of polymerization of the sample during irradiation. White needle-shaped particles were formed which scattered the light so strongly as to mask the Raman spectrum. For comparison, the Raman shifts observed by Edgell (36) for liquid $CF_2=CF-CF_3$ at low temperature are listed, together with his intensity estimates, in the second column of Table 34.

Molecular Structure. The hexafluoropropene molecule will at most have a single symmetry element—the plane through the three carbon atoms. If this symmetry, C_s , is assumed, the twenty-one normal vibrations divide themselves into fourteen of species A' (symmetrical with respect to the plane) and seven of species A'' (antisymmetrical with respect to the plane). Fundamentals of both species and all combinations are active both in the infrared and in the Raman effect. Bands of species A' are polarized in the Raman effect. Infrared bands of species A'' should have Type C contours.

Assignment of Fundamentals. On the basis of the infrared and Raman data for gaseous C_3F_6 given here and Edgell's data for the liquid, it is not difficult to assign most of the fundamental vibration frequencies with considerable certainty. However, a complete assignment of fundamentals and the determination of the vibration pattern for each normal mode are hardly possible until reliable force constants and molecular dimensions have become available and a normal coordinate treatment has been carried out. The present effort is limited to making a tentative assignment of fundamentals on the basis of the spectral data and the previous work on CF_3-CF_3 (17) and $CF_2=CFCl$.

The very strong infrared band at 1797 cm^{-1} , which corresponds to the band at 1802 cm^{-1} in $CF_2=CFCl$, must represent the highest A' fundamental. It may be characterized roughly as a C=C stretching mode, although it is quite possible that CF stretching is strongly involved. The intense infrared bands at 1399, 1336, 1211, 1179, and 1037 cm^{-1} must all be fundamentals involving CF stretching. The somewhat weaker band at 1122 cm^{-1} , which has not been observed in the Raman effect, is probably also a fundamental, although it could be interpreted as a combination or overtone band, e.g., $359 + 767 = 1126$ or $2 \times 559 = 1118$. From its contour the band at 1179 is judged to belong to species A'' . It must involve an unsymmetrical CF stretching of the CF_3 group. The frequency at 1122 cm^{-1} undoubtedly involves the same type of motion of the CF_3 group, except for a rotation (of 120 degrees about the axis of this group) which makes the vibration belong to species A' . The fundamental at 1399 cm^{-1} undoubtedly involves a symmetrical CF stretching of the CF_3 group.

RESULTS AND DISCUSSION

 TABLE 33
 Infrared Spectrum of Hexafluoropropene (Gas)

Wave Number	Description	Interpretation	Wave Number	Description	Interpretation
~ 457 cm ⁻¹	s	213 + 248 = 461 (A'')	1541	m	359 + 1179 = 1538 (A'); 2 x 767 = 1534 (A')
462	s	A' Fundamental	1580	m	462 + 1122 = 1584 (A'); 248 + 1336 = 1584 (A'')
488	w	2 x 248 = 496 (A')	1635	w	513 + 1122 = 1635 (A'); 462 + 1179 = 1641 (A'')
~ 508			1687	w	655 + 1037 = 1692 (A'); 513 + 1179 = 1692 (A''); 359 + 1336 = 1695 (A'')
513	s	A' Fundamental	~ 1727	w	513 + 1211 = 1724 (A'); 559 + 1179 = 1738 (A'')
~ 517			1797	vs	A' Fundamental
559	m	A'' Fundamental	1868	m	655 + 1211 = 1866 (A'); 462 + 1399 = 1861 (A'')
~ 566	w		1941	w	767 + 1179 = 1945 (A'')
602	w		1980	m	767 + 1211 = 1978 (A')
609	w	A' Fundamental	~ 2047	w	655 + 1399 = 2054 (A'); 248 + 1797 = 2045 (A'')
651			2099	w	767 + 1336 = 2103 (A')
655	vs	A' Fundamental	2157	m	359 + 1797 = 2156 (A''); 767 + 1399 = 2166 (A''); 1037 + 1122 = 2159 (A')
659			2210	m	1037 + 1179 = 2216 (A'')
~ 684	m	173 + 513 = 686 (A')	2250	m	1037 + 1211 = 2248 (A'); 462 + 1797 = 2259 (A'); 2 x 1122 = 2244 (A')
706	m	A' Fundamental	2345	m	559 + 1797 = 2356 (A'')
711	m	248 + 462 = 710 (A'')	2364	s	2 x 1179 = 2358 (A'); 1037 + 1336 = 2374 (A')
720	vw	2 x 359 = 718 (A')	2398	w	1179 + 1211 = 2390 (A''); 606 + 1797 = 2403 (A')
726	w		2444	m	1037 + 1399 = 2436 (A'); 655 + 1797 = 2452 (A')
731	w	C ₃ F ₈ impurity	2512	vw	1179 + 1336 = 2515 (A'')
~ 736	w		2560	m	767 + 1797 = 2564 (A')
739	w	84 + 655 = 739 (A'')	2606	m	1211 + 1399 = 2610 (A')
762			2661	s	2 x 1336 = 2672 (A')
767	vs	A' Fundamental	2723	w	1336 + 1399 = 2735 (A')
772			2792	m	2 x 1399 = 2798 (A')
829	vw	173 + 655 = 828 (A'); 359 + 462 = 821 (A'')	2829	m	1037 + 1797 = 2834 (A')
~ 868	vw	213 + 655 = 868 (A'); 359 + 513 = 872 (A'')	2907	vw	1122 + 1797 = 2919 (A')
~ 904	w	248 + 655 = 903 (A'')	3008	m	1211 + 1797 = 3008 (A')
914	w		3122	m	1336 + 1797 = 3133 (A')
919	w	359 + 559 = 918 (A'); 2 x 462 = 924 (A')	3185	w	1399 + 1797 = 3196 (A')
963	m	359 + 606 = 965 (A'')			
1037	vs	A' Fundamental			
1041	s				
1122	s	A' Fundamental			
1179	vs	A'' Fundamental			
1211	vs	A' Fundamental			
1255	m	213 + 1037 = 1250 (A')			
1263	m	C ₃ F ₈ Impurity			
1299	w	2 x 655 = 1310 (A'); 84 + 1211 = 1295 (A''); 173 + 1122 = 1295 (A')			
1333	vs	A' Fundamental			
1340	vs				
1399	vs	A' Fundamental			
1464	m	248 + 1211 = 1459 (A'')			
1477	m	359 + 1122 = 1481 (A''); 140 + 1336 = 1476 (A'')			

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TABLE 34
Raman Spectrum of Hexafluoropropene

Gaseous		Liquid *		Interpretation
Wave Number	Description	Wave Number	Description	
---		84 cm ⁻¹	w	A'' Fundamental
---		140	m	A' Fundamental
---		173	w	A'' Fundamental
---		213	w	A' Fundamental
---		248	w	A'' Fundamental
---		306	vw	140 + 173 = 313 (A'')
359 cm ⁻¹	m	360	s	A'' Fundamental
369	w	---		Upper Stage, or 513 - 140 = 373 (A'')
---		453	vw	A' Fundamental
509	w d	511	m	A' Fundamental
561	m	560	s	A'' Fundamental
---		607	s	A' Fundamental
655	m d	648	s	A' Fundamental
---		714	w	A' Fundamental
767.2	vs sh	764	s	A' Fundamental
777	vw	---		Upper Stage, or 173 + 606 = 779 (A')
---		1020	w	A' Fundamental
1181	w d	1156	m	A'' Fundamental
1215	w d	1208	m	A' Fundamental
1333	m	1330	m	A' Fundamental
1397	m d	1386	m	A' Fundamental
1795	vs	1790	s	A' Fundamental

* Data for liquid C₃F₆ at low temperature taken from W.F. Edgell, JACS 70, 2816 (1948).

The fundamentals at 1336 and 1211 cm⁻¹, which agree closely with frequencies observed in CF₂=CFCl, must represent unsymmetrical and the frequency 1037 cm⁻¹ symmetrical CF stretching of the CF₂=CF group. All of these fundamentals belong to A'.

The very strong infrared band at 767 cm⁻¹ and the intense sharp Raman band at 767.2 cm⁻¹ must represent an A' fundamental involving primarily C-C stretching. The bands at 655 and 513 cm⁻¹ undoubtedly correspond to the bands at 691 and 517 cm⁻¹ in CF₂=CFCl and represent A' fundamentals involving CF₂ and CFCF₃ deformation. The frequencies 706 and 606 cm⁻¹ are probably A' fundamentals involving unsymmetrical and symmetrical CF₃ deformation. They are the least certain of the fundamentals assigned and could be interpreted as overtones: 248 + 462 = 710 and 248 + 359 = 607 or 140 + 462 = 602 cm⁻¹. While there is considerable infrared absorption between 600 and 750 cm⁻¹, where the A'' fundamental involving unsymmetrical CF₃ deformation is expected to occur, no plausible assignment could be made.

The strong infrared band at 462 cm⁻¹ must undoubtedly correspond to the frequency 463 cm⁻¹ in CF₂=CFCl and is therefore identified with an A' fundamental involving CF₂ rocking. The Raman band at 213 cm⁻¹, observed by Edgell in liquid hexafluoropropene,

must be an A' fundamental involving CF-CF₃ rocking. The Raman band at 173 cm⁻¹ probably represents the lowest A' fundamental, consisting largely of CF₃ rocking.

From its contour and spectral position, the infrared band at 559 cm⁻¹ has been assigned as an A' fundamental involving primarily CF₂ wagging with the two carbon atoms moving out of phase. The Raman band at 359 cm⁻¹ has been identified as an A'' fundamental involving wagging of the CF₂ and CFCF₃ groups in which the two carbon atoms are displaced in the same direction. The weak Raman band at 248 probably represents an A'' wagging of the CF₃ group and the Raman band at 140 cm⁻¹ a CF₂ twisting mode, also of species A''. Finally, the low Raman frequency at 84 cm⁻¹, observed by Edgell in the liquid, probably represents CF₃ twisting of species A''. All of the twenty fundamentals assigned are listed in Table 35.

Discussion. Except for differences that may be ascribed to the different states of aggregations, all but one of the frequencies assigned as fundamentals agree with those assigned by Edgell. However, there is little agreement between his and the present choice of species and characterization of the vibrations. The present choice was based largely upon the close agreement between certain of the observed frequencies for CF₂=CF-CF₃ and the fundamentals of CF₂=CFCl (Tables 31 and 35).

TABLE 35
Tentative Assignment of Fundamental Vibration
Frequencies for Hexafluoropropene *

Species	Characterization†	Infrared (Gas)	Raman (Gas)	Raman (Liquid)‡
A'	C=C Stretching	1797 vs	1795 vs	1790 s
A'	Symm. CF ₃ Stretching	1399 vs	1397 m d	1386 m
A'	Unsymm. CF ₂ Stretching	1336 vs	1333 m	1330 m
A'	Unsymm. CF ₂ Stretching	1211 vs	1215 w d	1208 m
A'	Unsymm. CF ₃ Stretching	1122 s	----	----
A'	Symm. CF ₂ Stretching	1037 vs	----	1020 w
A'	C-C Stretching	767 vs	767.2 vs sh	764 s
A'	Unsymm. CF ₃ Deformation	706 m	----	714 w
A'	CF ₂ Deformation	655 vs	655 m d	648 s
A'	Symm. CF ₃ Deformation	606 w	----	607 m
A'	CF-CF ₃ Deformation	513 s	509 w d	511 m
A'	CF ₂ Rocking	462 s	----	453 vw
A'	CF-CF ₃ Rocking	----	----	213 w
A'	CF ₃ Rocking	----	----	173 m
A''	Unsymm. CF ₃ Stretching	1179 vs	1181 w d	1156 m
A''	Unsymm. CF ₃ Deformation	----	----	----
A''	CF ₂ Wagging	559	561 m	560 s
A''	CF-CF ₃ Wagging	----	359 m	360 s
A''	CF ₃ Wagging	----	----	248 w
A''	CF ₂ Twisting	----	----	140 w
A''	CF ₃ Twisting	----	----	84 w

* Assumed molecular symmetry: C₃.

† Only very rough meaning should be attached to the terms in this column.

‡ Data for liquid C₃F₆ at low temperature taken from W.F. Edgell, JACS 70, 2816 (1948).

On the basis of these fundamentals it has been possible to interpret satisfactorily all of the infrared bands observed. In fact, for most of the bands lying between 1500 and 2500 cm^{-1} , more than one interpretation can be given. It has not been necessary to consider difference bands or ternary combination bands, and no use has been made of the uncertain fundamental at 706 cm^{-1} . The interpretation of the infrared bands is given in the third column of Table 33.

Only three of the Raman bands observed by Edgell or in the present work have not been interpreted as fundamentals. The faint band at 306 cm^{-1} in the Raman spectrum of liquid hexafluoropropene could be interpreted as a difference band, $767 - 462 = 305$. However, since the spectrum of the liquid was obtained at low temperature, this interpretation is not plausible. In the third column of Table 34 this band has therefore been interpreted as a combination band, $140 + 173 = 313$. The weak bands at 369 and 777 are most likely upper-stage bands corresponding to the strong fundamentals at 359 and 767 cm^{-1} respectively. As indicated in the table, however, the former may be interpreted as a difference band and the latter as a combination band.

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FLUORINATED ETHANES

 $\text{CF}_3\text{-CH}_3$ (Methyl Fluoroform)

Previous Work. The Raman spectrum of methyl fluoroform in the liquid state at -75°C has been investigated by Hatcher and Yost (33). Some corrections to their data were given by Russell, Golding, and Yost (38). The infrared spectrum of $\text{CF}_3\text{-CH}_3$ has been studied by Thompson and Temple (39). Attempts at the assignment of fundamentals have been made by Kohlrausch (5, page 173); by Russell, Golding, and Yost (38); by Thompson and Temple (39); and by Herzberg.* There is wide divergence between the assignments proposed by the different workers, and none of them has attempted to determine the twisting frequency. Recently, Daily, Minden, and Shulman (40) have derived a value for the twisting frequency from the relative intensities at different temperatures of certain microwave absorption lines.

Experimental Results. The infrared spectrum of gaseous $\text{CF}_3\text{-CH}_3$ (Serial No. 298) is shown in Figure 33. Some evidence of impurity absorption was found, as will be mentioned later. The positions of the infrared absorption maxima are listed in the first column of Table 36, and the intensity and appearance of the bands are indicated in the second column. Corresponding data for the Raman shifts observed for the gas are given in Table 37. No polarization measurements were made.

TABLE 37
Raman Spectrum of $\text{CF}_3\text{-CH}_3$ (Gas)

Wave Number	Description	Interpretation
365 cm^{-1}	vw d	E Fundamental
541	vw d	E Fundamental
602	w sh	A_1 Fundamental
830.3	s sh	A_1 Fundamental
966	vw d	E Fundamental
1232	vvw d	E Fundamental
1277	vvw d	A_1 Fundamental
~ 1450	w vd	E Fundamental
2796.4	w	$2 \times 1408 = 2816 (A_1)$
2833	vw	$1408 + 1433 = 2851 (E)?$
2891	vw d	$2 \times 1443 = 2886 (A_1 + E)$
2965	vw d	
2974.6	vs sh	A_1 Fundamental
3022	w d	
3034.7	m	E Fundamental
3049	w d	

* G. Herzberg, private communication to J. Rud Nielsen.

TABLE 36
Infrared Spectrum of $\text{CF}_3\text{-CH}_3$ (Gas)

Wave Number	Description	Interpretation	Wave Number	Description	Interpretation	Wave Number	Description	Interpretation
~410 cm^{-1}	vw	830 - 365 = 465 (E); or $\text{CH}_2\text{-CHF}_2$ Impurity						
~530	w	E Fundamental	1155	w	C_2F_6 Impurity	2183	m	365 + 541 + 1280 = 2186 (A_1 + A_2 + E)
541	m	[180 + 365 = 545 (E)]	1172	w	$830 + 2 \times 180 = 1190$ (A_1)?	2187	m	966 + 1233 = 2199 (A_1 + A_2 + E)
546	m		1186	vs	$2 \times 602 = 1204$ (A_1); 365 + 830 = 1195 (E)	2215	m	3035 - 830 = 2205 (E)?
560	m		1233	vs	E Fundamental	2231	m	830 + 1408 = 2238 (A_1)
594	s	[966 - 365 = 601 (A_1 + A_2 + E)]	1267	vs	A_1 Fundamental	2242	m	966 + 1280 = 2246 (E)
600	s	A_1 Fundamental	1280	sh	A_1 Fundamental	2251	m	365 + 602 + 1280 = 2247 (E)
602	s	[966 - 2 x 180 = 606 (E)]	1282			2273	w	830 + 1443 = 2273 (E)
605	s		1333	vw	365 + 966 = 1331 (A_1 + A_2 + E)	2286	w	$2 \times 1443 - 602 = 2284$ (A_1 + E)
616	s		1397	s		2369	vw	
678	vw	1280 - 602 = 678 (A_1) or Impurity	1408	s	A_1 Fundamental	2376	w	966 + 1408 = 2374 (E); 2975 - 602 = 2373 (A_1)
686	vw	1233 - 541 = 692 (A_1 + A_2 + E) or Impurity	1422	s	E Fundamental	2385	vw	
724	vw	180 + 541 = 721 (E); 365 + 2 x 180 = 725 (E)	1443	s		2406	vw	966 + 1443 = 2409 (A_1)
732	vw	$2 \times 365 = 730$ (A_1 + E) or C_2F_6 Impurity	1456	sh		2415	vw	2975 - 541 = 2434 (E); 3035 - 602 = 2433 (E)
737	vw	1280 - 541 = 739 (E)	1504	w	541 + 966 = 1507 (A_1 + A_2 + E)	2431	w	$2 \times 1408 - 365 = 2447$ (E)
743	vw		1522	w	830 + 1233 - 541 = 1522 (A_1 + A_2 + E)	2460	w	$2 \times 1233 = 2466$ (A_1 + E)
746	vw		1570	vw	602 + 966 = 1568 (E)	2509	m	1233 + 1280 = 2513 (E)
749	vw		1592	w	$1233 + 2 \times 180 = 1593$ (E)	2542	vw	$2 \times 1280 = 2560$ (A_1)
754	vw		1603	w	365 + 1233 = 1598 (A_1 + A_2 + E)	2615	vw	2975 - 2 x 180 = 2615 (A_1); 2975 - 365 = 2610 (E)
762	vw		1647	w	365 + 1280 = 1645 (E); $2 \times 180 + 1280 = 1640$ (A_1)	2630	vw	1233 + 1408 = 2641 (E)
780	vw	966 - 180 = 786 (E) or C_2F_6 Impurity	1678	vw	$2 \times 830 = 1660$ (A_1)?	2681	w	1233 + 1443 = 2676 (A_1 + A_2 + E)
818	s	A_1 Fundamental	1892	m	830 + 966 = 1798 (E); $3 \times 602 = 1806$ (A_1)	2684	vw	1280 + 1408 = 2688 (A_1)
831	s	[1443 - 602 = 841 (E)]	1898	sh	365 + 1443 = 1808 (A_1 + A_2 + E);	2714	vw	602 + 830 + 1280 = 2712 (A_1)
838	s		1938	m	541 + 1280 = 1821 (E)	2725	vw	1280 + 1443 = 2723 (E)
842	s		1962	sh	602 + 1280 = 1882 (A_1)	2784	vw	
869	vw	$\text{CH}_2\text{-CHF}_2$ Impurity	1974	sh	$2 \times 966 = 1932$ (A_1 + E); 541 + 1408 = 1949 (E)	2794	vw	$2 \times 1408 = 2816$ (A_1)
911	m	365 + 541 = 906 (A_1 + A_2 + E);	1997	vw	541 + 1443 = 1984 (A_1 + A_2 + E)?	2807	vw	
918	w	541 + 2 x 180 = 901 (E)	2002	sh	$180 + 541 + 1280 = 2001$ (E)?	2833	vw	602 + 830 + 1408 = 2840 (A_1)
965	vs	1280 - 365 = 915 (E); 1280 - 2 x 180 = 920 (A_1)	2006	vw	$2 \times 365 + 1280 = 2010$ (A_1 + E)?	2849	vw	1408 + 1443 = 2851 (E)
967	vs		2015	sh	602 + 1408 = 2010 (A_1)	2860	vw	3035 - 180 = 2855 (E)
973	vs	[365 + 602 = 967 (E); 602 + 2 x 180 = 982 (A_1)]	2061	sh	$830 + 1233 = 2063$ (E)	2874	vw	602 + 830 + 1443 = 2875 (E)
1005	m	E Fundamental	2106	w		2882	vw	$2 \times 1443 = 2886$ (A_1 + E)
1008	m	C_2F_6 Impurity	2117	sh		2897	vw	$3 \times 966 = 2898$ (A_1 + A_2 + E)
1015	m	602 + 1233 - 830 = 1005 (E)	2137	vw		2910	vw	365 + 2 x 1280 = 2925 (E)
1029	m	541 + 1443 - 966 = 1018 (A_1 + A_2 + E)				2967	vw	
1034	m	602 + 966 - 541 = 1027 (A_1 + A_2 + E)				2976	vw	A_1 Fundamental
1070	w	1408 - 365 = 1043 (E); 1408 - 2 x 180 = 1048 (A_1)				3036	sh	
1082	m	1443 - 365 = 1078 (A_1 + A_2 + E)				3049	s	E Fundamental
1086	m	$2 \times 541 = 1082$ (A_1 + E); 1443 - 2 x 180 = 1083 (E)				3143	vw	541 + 2975 - 365 = 3151 (A_1 + A_2 + E)
1089	w	$180 + 365 + 541 = 1086$ (A_1 + A_2 + E)				3234	vw	$180 + 3035 = 3215$ (E)
1135	vw	$3 \times 365 = 1095$ (A_1 + A_2 + E)				3240	vw	
		541 + 602 = 1143 (E); 966 + 180 = 1146 (E);				3336	vw	2975 + 2 x 180 = 3335 (A_1); 365 + 2975 = 3340 (E)
		or $\text{CH}_2\text{-CHF}_2$ Impurity				3397	vw	365 + 3035 = 3400 (A_1 + A_2 + E)

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Molecular Structure. The electron diffraction work of Brockway and Livingston (18) has given the following data:

$$\text{C-C distance} = 1.45 \pm 0.05 \text{ \AA},$$

$$\text{C-F distance} = 1.33 \pm 0.03 \text{ \AA},$$

$$\text{FCF angle} = 108\frac{1}{2} \pm 2^\circ.$$

Assuming a C-H distance of 1.09 \AA and tetrahedral angles for the methyl group, the following moments of inertia were calculated:

$$I_A = I_B = 153.2 \times 10^{-40}, I_C = 151.3 \times 10^{-40} \text{ g cm}^2.$$

Thus, the molecule is very nearly spherical, and the parallel and perpendicular bands will have essentially the same contour.

The $\text{CF}_3\text{-CH}_3$ molecule undoubtedly has the symmetry C_{3v} , the fluorine atoms being either "eclipsed" or "staggered" with respect to the hydrogen atoms, probably the latter. The normal vibrations, in either case, divide themselves into symmetry species in the following manner: $5A_1 + 1A_2 + 6E$. The vibrations of the totally symmetrical species A_1 and the doubly degenerate species E are active both in infrared absorption and in the Raman effect. The torsional oscillation of species A_2 , on the other hand, is inactive both in the infrared and in the Raman effect. The pertinent rules for determining the species of combination bands and overtones are:

$$A_1 \cdot A_1 = A_2 \cdot A_2 = A_1,$$

$$A_1 \cdot A_2 = A_2,$$

$$A_1 \cdot E = A_2 \cdot E = E,$$

$$E \cdot E = A_1 + A_2 + E,$$

$$(E)^2 = A_1 + E,$$

$$(E)^3 = A_1 + A_2 + E.$$

Here $E \cdot E$ refers to a combination band of two different frequencies of species E , whereas $(E)^2$ refers to an overtone of a frequency of species E .

Assignment of Fundamentals. Since the mass of the methyl group is not much smaller than that of a fluorine atom, the problem of assigning the fundamentals for $\text{CF}_3\text{-CH}_3$ may be attacked conveniently by taking the vibration spectrum of CF_4 as a starting point. This spectrum consists of a doubly degenerate frequency at 437 cm^{-1} , a triply degenerate at 635 , a totally-symmetrical at 904 , and a triply degenerate frequency around 1265 cm^{-1} (5). Considering the correlation between the vibrations of CF_4 and X-CF_3 molecules as shown in Figure 9, it is concluded that the "skeletal vibrations" of $\text{CF}_3\text{-CH}_3$ must consist of a doubly degenerate fundamental around 400 cm^{-1} , a fundamental frequency of species E and another of species A_1 around 600 cm^{-1} , an A_1 fundamental in the neighborhood of 900 cm^{-1} , and an E and an A_1 fundamental near 1250 cm^{-1} .

The Raman band at 365 cm^{-1} , which has the diffuse appearance typical of doubly degenerate bands, must be the lowest E fundamental. It may be characterized roughly as a bending of the $\text{CH}_3\text{-C}$ bond.

According to Kahovec and Wagner (41), of the next two fundamentals the totally symmetrical is the lower for both ClCF_3 and Cl_3CF , but in neither case is the difference in frequency great (Figures 8 and 9). For $\text{CCl}_3\text{-CH}_3$, Wagner (12), on the basis of a valence force model and considering the methyl group as a mass point, calculated almost equal values for these two frequencies but found from polarization measurements that the E fundamental lies somewhat lower than the A_1 fundamental. In the case of $\text{CF}_3\text{-CH}_3$, the frequencies in question must be 541 and 602 cm^{-1} , both of which have high intensity in the infrared. The Raman band at 541 cm^{-1} is diffuse, whereas the Raman band at 602 cm^{-1} is sharp and more intense. Thus, there can be no doubt that 541 cm^{-1} is an E and 602 cm^{-1} an A_1 fundamental. These skeletal fundamentals may be designated roughly as CF_3 deformation frequencies.

The frequency at 830 cm^{-1} , which is observed as an intense infrared absorption band and as a strong and sharp Raman band, must be the skeletal frequency of species A_1 corresponding to the totally symmetrical vibration of CF_4 . It may be designated very roughly as a C-C stretching frequency.

The two very intense bands at 1233 and 1280 cm^{-1} must represent the remaining two skeletal fundamentals. According to Kahovec and Wagner, the E fundamental lies lower than the A_1 fundamental for Cl_3CF , whereas the A_1 fundamental is the lower for ClCF_3 (Figures 8 and 9). For $\text{CF}_3\text{-CF}_3$ the average value of the highest frequencies belonging to species A_{1g} and A_{2u} is higher than the average value of the corresponding frequencies belonging to E_g and E_u (17). The infrared band at 1280 cm^{-1} has a typical PQR-structure, while the stronger band at 1233 cm^{-1} has less regular appearance and resembles the E fundamental at 541 cm^{-1} as well as the perpendicular band at 1250 cm^{-1} in $\text{CF}_3\text{-CF}_3$. In the Raman spectrum of gaseous $\text{CF}_3\text{-CH}_3$ both bands are very faint. However, the band of lower frequency is diffuse, whereas the other band appears to be sharp. For these reasons it seems fairly certain that the band at 1232 cm^{-1} is an E fundamental and the band at 1280 cm^{-1} an A_1 fundamental. Both of these fundamentals may very roughly be characterized as C-F stretching modes.

To these "skeletal" vibrations must be added an A_1 and an E C-H stretching frequency near 3000 cm^{-1} , an A_1 and an E CH_3 deformation frequency in the region 1400 - 1460, a doubly degenerate CH_3 rocking frequency near 1000 cm^{-1} , and finally a low twisting frequency of species A_2 . The order of these frequencies follows uniquely from Wagner's work on molecules of form XCH_3 (10) or from Figure 5.

Thus, the very strong infrared band at 966 cm^{-1} is evidently the CH_3 rocking frequency of species E. It is observed as a very weak diffuse band in the Raman effect. The two strong infrared bands at 1408 and 1443 must be the A_1 and E CH_3 deformation frequencies, respectively. The former of these bands was not observed in the Raman effect, as is commonly the case for compounds containing methyl groups. The E fundamental was observed as a very diffuse band with a maximum near 1450 cm^{-1} .

The band at 2975 cm^{-1} , which is very strong and sharp in the Raman effect, must be the CH stretching frequency of species A_1 . The band at 3035 cm^{-1} must be the corresponding fundamental of species E.

There remains the twisting frequency of species A_2 which is inactive in both the infrared and the Raman effect. To assign this fundamental, as many as possible of the infrared bands not taken to be fundamentals were first interpreted as binary combination bands involving the eleven fundamental frequencies just assigned. Attempts were then made to interpret the stronger of the remaining bands as combination bands involving the unknown A_2 fundamental. This procedure was not entirely conclusive. However, assumption that

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the twisting frequency has a value of about 180 cm^{-1} permitted the interpretation of considerably more bands than any of several other assumptions tested. Hence, the value of 180 cm^{-1} was tentatively assigned to the A_2 fundamental. Recently, Daily, Minden, and Shulman (40), on the basis of intensity measurements at different temperatures in the microwave spectrum of $\text{CF}_3\text{-CH}_3$, have obtained a frequency, $165 \pm 25\text{ cm}^{-1}$, which they interpret as the twisting frequency. This is in good agreement with the value adopted here.

The assigned fundamental vibration frequencies for $\text{CF}_3\text{-CH}_3$ are listed in Table 38. The characterization of the various vibration modes given in the second column is fairly meaningful for the vibrations involving primarily the atoms of the CH_3 group. For the "skeletal" vibrations, on the other hand, they have only very rough meaning.

On the basis of these fundamentals it has been possible to interpret all of the Raman bands and all but half a dozen of the 120 infrared absorption maxima observed. The interpretations of the bands are given in the third column of Tables 36 and 37.

Discussion. The assignment of fundamentals given here differs greatly from those made by Russell, Golding, and Yost and by Thompson and Temple. The former workers assign the Raman bands at 368 and 968 cm^{-1} to A_1 and at 1279 cm^{-1} to E. Assuming that a Raman band, here ascribed to excitation by the mercury line 4047 A , is caused by Hg 4358 A , they obtained a fundamental, 1025 cm^{-1} , which they assigned to species E. Lacking the frequency 1233 cm^{-1} , which had not been observed in the Raman effect by Hatcher and Yost, they assigned six fundamentals to A_1 and five to E, rather than the opposite. Thompson and Temple assign 541 to A_1 and 606 to E and assign both 1412 and 1450 to E. They take 1135 cm^{-1} , which was undoubtedly due to an impurity in their sample, to be an A_1 fundamental. The assignment of fundamentals given here agrees with Herzberg's, except for an interchange of 1233 and 1280 cm^{-1} . For the reasons stated above, the lower frequency was here assigned to E and the higher to A_1 . The disagreement with Herzberg could be settled by polarization measurements. However, because of the very low intensity of the Raman bands at 1233 and 1280 cm^{-1} and their proximity to 2975 and 3035 cm^{-1} excited by the 4047 A mercury line, such measurements would be extremely difficult,

TABLE 38
Fundamental Vibration Frequencies of $\text{CF}_3\text{-CH}_3$

Species	Approximate Character*	Wave Number
A_1	CH Stretching	2975 cm^{-1}
A_1	CH_3 Deformation	1408
A_1	CF Stretching	1280
A_1	C-C Stretching	830
A_1	CF_3 Deformation	602
A_2	Twisting	180
E	CH Stretching	3035
E	CH_3 Deformation	1443
E	CF Stretching	1233
E	CH_3 Rocking	966
E	CF_3 Deformation	541
E	CF_3 Rocking	365

* The designations in this column have only very rough meaning, especially for vibrations involving the CF_3 group.

especially with gaseous $\text{CF}_3\text{-CH}_3$. Since this was the only problem requiring polarization measurements, no such measurements were made. Kohlrausch's assignment of nine of the fundamentals is confirmed by the present work.

It may be noted that the "skeletal" frequencies assigned here correlate very nicely with the fundamentals of other $\text{X}\cdot\text{CF}_3$ molecules in Figure 9 and that the "methyl" frequencies also correlate well with those for the methyl halides in Figure 5. The only serious uncertainty in the present assignment of fundamentals is the value of A_2 twisting frequency which is based on the interpretation of a number of very weak bands, some perhaps caused by impurities. The fact that 2×180 is very nearly equal to 365, the wave number of the lowest E fundamental, increases somewhat the uncertainty in the interpretation of several of the combination bands involving the A_2 fundamental.

Some of the intense infrared bands interpreted as fundamentals have extra zero branches or abnormal contours. In some cases this seems to be caused by overlapping combination bands. These are given in brackets in Table 36. The interpretation of the infrared bands given in this table is, on the whole, very satisfactory. Except for bands that are masked by stronger bands or that lie outside the range of observation, all binary sum bands have been observed, as well as a number of binary difference bands. In several cases two interpretations are equally plausible. Except for the bands at 1172 and 1660 cm^{-1} , the calculated frequencies agree closely with the observed. A number of bands, mostly of very low intensity are interpreted as ternary combination bands. Because of the large number of such active combinations, there are many cases, especially at high wave numbers, in which one or more alternative interpretations can be made. No attempts have been made to indicate all such alternatives in the table.

It has not been possible to find plausible interpretations for all of the faint absorption maxima around 750 cm^{-1} . They are probably caused by impurities. In particular, the sharp band at 732 cm^{-1} and weaker maxima or shoulders at 780 , 1008 , 1155 , 1200 , and 1205 , and near 1350 cm^{-1} , all correspond to positions of strong $\text{CF}_3\text{-CF}_2\text{-CF}_3$ absorption and undoubtedly are due to a small amount of this compound (b.p. = -38° vs. -47.5°C for $\text{CH}_3\text{-CF}_3$). Likewise, the very weak band at 869 cm^{-1} and weak absorptions at 1135 and near 470 cm^{-1} probably are caused by a small amount of $\text{CH}_3\text{-CHF}_2$ impurity (b.p. = -24.7°C). The bands at 678 and 686 cm^{-1} , considerably weaker than those observed by Thompson and Temple in this region, are probably due to impurity, although they can be interpreted satisfactorily as difference bands. The absorption maximum at 1997 cm^{-1} has been left unassigned, and the assignments of some of the neighboring maxima are not very plausible. Since similar absorption maxima occur at these places in $\text{CF}_2=\text{CH}_2$, and in part in C_2F_4 , they too are probably caused by impurities.

The interpretation of the Raman spectrum given in Table 37 is entirely satisfactory. The maxima at 2965 , 3022 , and 3049 cm^{-1} evidently represent rotational branches of the fundamentals at 2975 and 3035 cm^{-1} .

$\text{CH}_3\text{-CCl}_3$ (Methyl Chloroform)

Methyl chloroform, although containing no fluorine, is of interest in connection with the assignment of fundamentals of $\text{CH}_3\text{-CF}_3$, $\text{CF}_3\text{-CCl}_3$, and other molecules, and for correlation of group frequencies. The Raman spectrum has been investigated by several workers, but no infrared data has been published. Wagner (12; also 5, p. 173) has assigned all of the twelve fundamentals, except for the torsion frequency, on the basis of Raman data which included polarization measurements. His assignment is listed in the last column of Table 39. It appears from considerations similar to those used in the case of $\text{CH}_3\text{-CF}_3$,

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TABLE 39
Fundamental Vibration Frequencies of $\text{CH}_3\text{-CCl}_3^*$

Species	Description	Infrared (Gas)	Raman (Liquid) †
A ₁	C-H Stretching	2953 m, sh	2938 (12, p)
A ₁	CH ₃ Deformation	1387 s, sh	1378 ($\frac{1}{2}$)
A ₁	C-C Stretching	1088 vs	1068 (4, p); 1082 (4, p)
A ₁	C-Cl Stretching	526 s, sh	522 (5, p)
A ₁	C-Cl ₃ Deformation	(342)‡	342 (12, p)
A ₂	Torsion	—	—
E	C-H Stretching	3016 s, sh	3002 (8b, dp)
E	CH ₃ Deformation	1458 s, sh	1420 (3, dp); 1444 (4, dp)
E	CH ₃ Rocking	?	1179 ($\frac{1}{2}$)
E	C-Cl Stretching	726 vs, b	713 (8, dp)
E	CCl ₃ Deformation	(308)†	308 (0)
E	CCl ₃ Rocking	(240)†	240 (8, dp)

* For a slightly different assignment and a discussion of thermodynamic properties see T. R. Rubin, B. H. Leredahl, and D. M. Yost, *J.A.C.S.* **66**, 279 (1944)

† Assignment of Wagner (12).

‡ This assignment is confirmed by W. L. Hyde, *J. Chem. Phys.* **16**, 744 (1948), who observed a very strong infrared band in the vapor at 343 cm^{-1} .

i.e., from the fundamentals for X-CCl_3 molecules (Figure 8) and the methyl halides (Figure 5), that the magnitudes of the assigned fundamentals must be essentially correct.

The infrared spectrum of gaseous $\text{CH}_3\text{-CCl}_3$ (Serial No. 365) is shown in Figure 33. The solid curve was obtained with a 69-cm cell instead of the 10-cm cell because of the low vapor pressure of this compound at room temperature. New Raman data have not yet been obtained.

Seven of the fundamentals assigned by Wagner are easily identified as strong infrared bands; their positions are listed in Table 39. Three of the remaining fundamentals, and the unknown twisting frequency, are beyond the range of the infrared measurements. The last fundamental, which may be described roughly as a CH_3 rocking motion, was assigned by Wagner to a very weak Raman band at 1179, but this assignment is not confirmed by the infrared data.

The positions of the observed infrared maxima are listed in the first column of Table 40. Using the seven fundamentals observed in the infrared and the Raman frequencies 240, 308, and 342 cm^{-1} , good interpretations are obtained for many of the observed bands, as indicated in the last column of Table 40. Only binary combinations have been used. The values enclosed in parentheses involve Raman frequencies obtained for the liquid and probably do not correspond exactly to the vapor-phase frequencies. Since each of these ten fundamentals, including the Raman frequencies 240, 308, and 342 cm^{-1} , are observed in from 3 to 8 sum bands and in one or more difference bands there can be no doubt that they are correct.

The Raman frequency 1179 cm^{-1} , if present in the infrared spectrum, must correspond to the very weak band at 1167 cm^{-1} . Neither of these frequencies is useful in accounting for any of the observed combination bands, however, and it appears probable

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TABLE 40
Infrared Spectrum of $\text{CH}_3\text{-CCl}_3$ (Gas)

Wave Number	Description	Interpretation	Wave Number	Description	Interpretation
456 cm^{-1}			1287	vw sh	
481	vvw	$2 \times (240) = (480) A_1 + A_2 + E$	1294	vw sh	
~ 485	vvw	$726 - (240) = (486) A_1 + E$	1300	vw sh	
494	vvw		1321	vw	
517			1379		
521			1387	s sh	A_1 Fundamental
526	s sh	A_1 Fundamental	1397		
534			1431	s sh	$(342) + 1088 = (1430) A_1$
549	m sh	$(240) + (308) = (548) A_1 + E$	1449		
556			1458	s sh	E Fundamental; $2 \times 726 = 1452 A_1 + A_2 + E$
565	m sh	$1088 - 526 = 562 A_1 ?$	1468		
576	vw	$(342) + (240) = 582 E$	1543	w sh	
590	vw		1567	w	
~ 615	vvw	$2 \times (308) + (616) A_1 + A_2 + E$	1597	w	
630	vw		1730	w	$(342) + 1387 = (1729) A_1$
639	vw		1800	w sh	$526 + 1387 = 1913 A_1$
689	m sh	$2 \times (342) = (684) A_1$	1910	w	
~ 726	vvs b	E Fundamental	~ 2040	vvw	
~ 748	w	$1088 - (342) = (746) A_1$	~ 2110	vw	$726 + 1387 = 2113 E$
759	w sh		2140	w sh	
763	m sh		2455	w sh	$1088 + 1387 = 2475 A_1$
767	m sh	$(240) + 526 = (766) E$	2530	vw	
774			2680	vw	$3016 - (342) = (2674) E$
778			~ 2770	vvw	$2 \times 1387 = 2774 A_1$; $3016 - (240) = 2776 A_1 + E$; $1387 + 1458 = 2845 E$;
783	m sh	$1088 - (308) = (780) E ?$	2831	sh	
798	m		2874	w sh	
806	m		2893	w sh	
~ 818	w		2946	m sh	
845			2953	m sh	A_1 Fundamental
850	m sh	$1088 - (240) = 848 E ?$	2962	m sh	
854			3016	s sh	E Fundamental
864		$1387 - 526 = 861 A_1$	3100	w sh	
867	m sh	$(342) + 526 = (868) A_1$	3180	vw	$(240) + 2953 = (3193) E$
871	m sh		3247	w sh	$(308) + 2953 = (3261) E$; $(240) + 3016 = (3256) A_1 + E$; $(342) + 2953 = (3295) A_1$; $(342) + 3016 = (3358) E$; $526 + 3016 = 3542 E$; $726 + 2953 = 3679 E$; $726 + 3016 = 3742 A_1 + E$
~ 878			3292	w sh	
~ 898	vw b		3352	w sh	
936	m	$1458 - 526 = 932 E ?$	3560	vw	
945	m		3660	vw	
~ 962	w	$(240) + 726 = (966) A_1 + E$	3760	vw	
971	w		3860	vw	
998	w sh		4050	w sh	$1088 + 2953 = 4041 A_1$
1010	m sh		4120	w sh	
1015	m sh		4410	w sh	$1387 + 3016 = 4403 E$; $1458 + 2953 = 4411 E$; $1458 + 3016 = 4474 A_1 + E$
1074	s sh	$2 \times 526 = 1052 A_1$	4460	w sh	
1088	vs	A_1 Fundamental	~ 4720	vw	
1095	vs				
1161					
1167	vw sh	$1458 - (308) = 1150 A_1 + E ?$			
1170					
1230					
1241	m				
~ 1250		$526 + 726 = 1252 E$			

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because of the low intensity that they are due to impurity. In the region from 800 to 1300 cm^{-1} , where this fundamental must occur, there remain infrared bands of medium intensity near 1241, 1010, and 940 cm^{-1} which are not satisfactorily accounted for. If 1241 cm^{-1} is chosen as the methyl rocking fundamental, then 1010 and 940 cm^{-1} could be explained as $1241 - (240) = (1001) \text{ cm}^{-1}$ and $1241 - (308) = (933) \text{ cm}^{-1}$, respectively, except that the intensities are much too great. The corresponding sum frequency $1241 + (308) = (1549) \text{ cm}^{-1}$ could be the observed band at 1543 cm^{-1} , and $1241 + (240) = (1481)$ may be masked by 1458 cm^{-1} . Other combinations of 1241 cm^{-1} , e.g., $1241 + (342) = (1583)$ and $1241 - (342) = (899)$, might also be used to account for some of the observed bands. However, the evidence is not conclusive, and it is believed that the Raman spectrum of pure $\text{CH}_3\text{-CCl}_3$ should be re-examined before making a final choice.

No evidence of the low torsional frequency has been noted in the infrared spectrum. The infrared frequency 1431 cm^{-1} is probably $(342) + 1088 = (1430) \text{ A}_1$ in resonance with 1458 A_1 , as suggested by Kohlrausch. The maximum at 1074 cm^{-1} could be explained as $(342) + 726 = (1068) \text{ E}$ or $1387 - (308) = (1079) \text{ E}$, but it undoubtedly corresponds to the Raman band at 1068 cm^{-1} , which is polarized, and must therefore be interpreted as $2 \times 526 = 1052 \text{ cm}^{-1} (\text{A}_1)$ in resonance with the 1088 A_1 fundamental.

$\text{CF}_3\text{-CCl}_3$, $\text{CH}_3\text{-CHF}_2$, $\text{CF}_2\text{Cl-CF}_2\text{Cl}$, and $\text{CF}_2\text{Cl-CFCl}_2$

The infrared spectra of gaseous $\text{CF}_3\text{-CCl}_3$ (Serial No. 366), $\text{CH}_3\text{-CHF}_2$ (Serial No. 371), and $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ (Serial No. 329) are shown in Figure 33. The spectrum of another sample of $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ (Serial No. 368) was essentially identical with that shown. The spectrum of liquid $\text{CF}_2\text{Cl-CFCl}_2$ (Serial No. 330) has also been obtained and is shown in Figure 34. The positions of the observed absorption maxima are listed in the tables facing the spectral figures. None of these samples have been studied previously in the infrared.

Glockler and Sage (42) have observed 13 bands in the Raman spectrum of liquid $\text{CF}_3\text{-CCl}_3$ and conclude that the molecule has symmetry C_{3v} . They have observed 23 bands for liquid $\text{CF}_2\text{Cl-CF}_2\text{Cl}$, which at room temperature presumably consists of two rotational isomers, a trans isomer of symmetry C_{2h} and another of symmetry C_2 obtained by 120° rotation of one end group relative to the other. For liquid $\text{CF}_2\text{Cl-CFCl}_2$ they observe 24 bands, a fact which is interpreted as evidence of two rotational isomers of symmetry C_{1h} and C_1 . These same authors also present Raman data for $\text{CCl}_3\text{-CHFCl}$ (18 lines, one isomer, C_1), for $\text{CF}_2\text{Br-CF}_2\text{Br}$ (22 lines, two isomers, C_{2h} and C_2), for $\text{CF}_2\text{Cl-CF}_2\text{H}$ (21 bands, two isomers, C_{1h} and C_1), and for $\text{CF}_2\text{Cl-CHFCl}$ and $\text{CF}_2\text{Br-CFClBr}$ (28 bands, three isomers, all C_1). Twenty-two Raman frequencies for liquid $\text{CFCl}_2\text{-CFCl}_2$ have also been reported (43). No Raman data for $\text{CH}_3\text{-CHF}_2$ have been reported, but the related molecules, $\text{CH}_3\text{-CHCl}_2$, $\text{CH}_3\text{-CHBr}_2$, and $\text{CH}_3\text{-CHI}_2$, have been studied in the Raman effect by Kahovec and Wagner (44) and in the infrared by Emschwiller and Lecomte (45).

Raman data for these and other fluorinated ethanes listed in Table 18 have not yet been determined in the course of the present investigation but will be reported later together with assignment of fundamentals (insofar as possible) and correlation with results for other related molecules, particularly the 1,1-dihalogenated ethanes.

FLUORINATED PROPANES

A sample of C_3F_6 (Serial No. 327), originally thought to be completely fluorinated cyclopropane, was quickly identified as a propene and has already been discussed under Ethylenes. Cyclopropane has apparently not yet been fluorinated. Of the three propane derivatives available, namely $CF_3-CF_2-CF_3$, $CF_3-CFH-CF_3$, and $CF_3-CH_2-CH_3$, only the first has been studied. One sample of $CF_3-CF_2-CF_3$ (Serial No. 328) showed appreciable infrared absorption in the region of 3000 cm^{-1} and at 930, 908, 868, and 803 cm^{-1} which was not present in the spectrum of the other sample and apparently resulted from hydrogen-containing impurities. The other sample (Serial No. 326) is believed to be of high purity; its infrared spectrum is shown in Figure 34 for the vapor. The Raman shifts have also been measured for the gas, and the results are listed in Table 41. Polarization measurements were not made. It is intended to make additional Raman exposures for the liquid state and also to obtain spectral data for other fluorinated propanes before attempting to interpret the spectra of any of these compounds. However, correlation of the spectra of C_3F_8 with those for other saturated fluorocarbons is discussed in the section on Applications.

TABLE 41
Raman Spectrum of $CF_3-CF_2-CF_3$ (Gas)

Wave Number	Description
315	s
346	m d
381	w d
454	vvw
544	vw d
621	vw d
663.8	w sh
723	vvw sh
779.6	vs sh
1150	vvw
1209	vw d
1262	vw d
1349	vw d
1368.1	w

FLUORINATED BUTANES

Samples of completely fluorinated n-butane and iso-butane have not yet been obtained for study. Three halogenated butanes and three halogenated butadienes (see Table 18) obtained from Prof. Miller are being studied, but the results are not yet complete. Only one fluorocarbon of this type, namely, the cyclic C_4F_8 compound, has been studied.

Cyclic C_4F_8 (Perfluorocyclobutane)

Previous Work. The Raman spectrum of perfluorocyclobutane has been studied by Edgell (46) who also reported four infrared absorption maxima observed in the du Pont Laboratories and made an assignment of fundamentals.

Experimental Results. The infrared absorption spectrum of gaseous perfluorocyclobutane from 2.0 to 23 microns is shown in Figure 34. The wave numbers for the observed absorption maxima are given in the first column of Table 42. In the second column the relative intensities are indicated. The infrared spectrum from 21 to 25 microns was also obtained at the Bureau of Standards by Dr. Plyler. He found one band at 441 cm^{-1} .

The observed Raman shifts for gaseous and liquid perfluorocyclobutane are given in the first two columns of Table 43. In the third column are given rough estimates of the relative intensities of the bands and, for some bands, information about exceptionally sharp or diffuse appearance. The measured depolarization ratios are listed in the fourth column.

The Raman spectrum, as observed in the present work, agrees well with that reported by Edgell, except that more than twice as many bands were found here. Two of the shifts reported by Edgell have been observed as pairs of bands. Thus, in place of his value 267 cm^{-1} , 258 and 273 cm^{-1} have been observed; in place of his 651 cm^{-1} , 642.9 and 659.5 cm^{-1} have been observed.

Molecular Structure. In view of the lack of coincidences among the infrared and Raman frequencies, this C_4F_8 molecule is evidently centro-symmetric and its symmetry has been taken to be D_{4h} . The fundamentals divide themselves in the following manner: $3A_{1g} + 1A_{1u} + 1A_{2g} + 2A_{2u} + 2B_{1g} + 3B_{1u} + 3B_{2g} + 1B_{2u} + 3E_g + 4E_u$. The species A_{1g} , B_{1g} , B_{2g} , and E_g are Raman-active, A_{1g} giving polarized and the other species depolarized bands. The species A_{2u} and E_u are infrared-active, whereas A_{1u} , A_{2g} , B_{1u} , and B_{2u} are forbidden in both spectra. The rules for determining the species of binary combination bands are:

$$E_u^2 = E_g^2 = A_{1g} + B_{1g} + B_{2g}$$

$$B_1 \cdot B_2 = A_2$$

$$E_u \cdot E_u = E_g \cdot E_g = A_{1g} + A_{2g} + B_{1g} + B_{2g}$$

$$A_2 \cdot B_2 = B_1$$

$$E_g \cdot E_u = A_{1u} + A_{2u} + B_{1u} + B_{2u}$$

$$A_2 \cdot B_1 = B_2$$

$$A_{1g}^2 = A_{1u}^2 = A_{2g}^2 = A_{2u}^2 = B_{1g}^2 = B_{1u}^2 = B_{2g}^2 = B_{2u}^2 = A_{1g}$$

$$A_1 \cdot E = A_2 \cdot E = B_1 \cdot E = B_2 \cdot E = E,$$

together with the g,u rule: $g \cdot g = u \cdot u = g$, $g \cdot u = u$.

The infrared bands, as observed here, are not easily distinguishable by their contours. This is not too surprising since the two moments of inertia are large and do not differ greatly. Thus, assuming the molecular dimensions C-C = 1.53 Å, C-F = 1.36 Å, C-C-C angle = 90° , and FCF angle = 112° , the moments of inertia $I_A = I_B = 796$ and $I_C = 951 \times 10^{-40}$ g cm² are obtained. Because of the uninformative contours of the infrared bands, and because six fundamentals are completely inactive and only three others are identified by polarization measurements of the Raman lines, it has been impossible to interpret the spectra of this compound solely on the basis of the experimental results. Recourse was therefore made to normal coordinate calculations (see Appendix). Using the results of these calculations, together with considerations of the intensity of the observed bands and of their usefulness in binary sums to explain infrared bands, it has been possible to determine most of the fundamentals with confidence.

Assignment of Fundamentals. Five Raman bands have been observed to be definitely polarized. Of these, the two weakest are readily explained as overtones, so that the three A_{1g} fundamentals 1431, 699, and 358 cm⁻¹ are known with certainty. The assignments for the other Raman-active species, B_{1g} , B_{2g} , and E_g , depend largely on the normal coordinate calculations discussed later. These assignments are given in Table 44.

There should be six infrared-active fundamentals, and six very intense infrared absorption bands are observed. They are 1340, 1292, 1239, 963, 569, and 441 cm⁻¹. However, these cannot all be fundamentals. The calculated frequencies belonging to E_u are 1399, 935, 544, and 277 cm⁻¹, and those for A_{2u} are 1239 and 278 cm⁻¹. It seems evident that 963 and 569 must belong to E_u and that the lowest E_u band and the lower A_{2u} band must lie below the observed frequency range. The calculations are too inaccurate to decide how to assign 1340, 1292, and 1239 cm⁻¹, only two of which can be fundamentals. However, the band at 1340 cm⁻¹ can be definitely assigned to E_u on the basis of activity of binary sums. Thus, E_u frequencies can combine with each of the four Raman-active species to give infrared-active combination bands, whereas A_{2u} frequencies, combining with B_{2g} and with B_{1g} frequencies, give inactive combination bands.

Now all of the frequencies obtained by adding 1340 cm⁻¹ to the B_{2g} and B_{1g} frequencies 1008, 660, 192, 1220, and 258 cm⁻¹ are observed as 2347 m, 1996 s, 1531 s, 2557 s, and 1600 w. The assignment of 1292 and 1239 cm⁻¹ is more difficult. For 1292 cm⁻¹, two sums with B_{2g} and B_{1g} frequencies, namely, $1292 + 1008 = 2300$ and $1292 + 1220 = 2512$ cm⁻¹ are observed as 2300 vw and 2508 s. For 1239 cm⁻¹, two such sums, $1008 + 1239 = 2247$ and $1239 + 1258 = 1497$ cm⁻¹, are observed as 2247 vw and 1502 s, but these are satisfactorily interpreted otherwise as $1285 + 963 = 2248$ and $1220 + (285) = 1505$ (E_u). Thus, the indication is that 1239 cm⁻¹ belongs to A_{2u} and 1292 cm⁻¹ belongs to E_u . Now, 1292 cm⁻¹ can be interpreted as an E_u combination band, 1008 (B_{2g}) + (285) (E_u) = 1293 cm⁻¹ (E_u), the intensity of which is presumably enhanced by its proximity to 1340 cm⁻¹.

The value of 285 cm⁻¹ for the lowest E_u fundamental—first suggested by its overtone, 570 vw, in the Raman spectrum—is amply verified by its usefulness in combinations. All combinations of 285 with Raman-active fundamentals appear in the infrared except two, both of which may be masked by nearby fundamentals. Thus, 285 cm⁻¹ plus the Raman frequencies yields 1716, 985, 644, 1505, 543, 1293, 945, 477, 1570, 724, and 558 cm⁻¹. All but three of these are observed as 1715 w, 983 s, 640 w, 1502 s, 1292 vvs, 464 s, 1572 m, and 725 w. The remaining three, 543, 945, and 558 cm⁻¹ are masked by the stronger bands at 963 and 560 cm⁻¹. The frequency 285 cm⁻¹ cannot belong to any of the other u species, because none of the other species can combine with all Raman-active species to give infrared-active combinations. The lower of the A_{2u} fundamental frequencies, for which 278 cm⁻¹ has been calculated, cannot be determined with complete certainty. The value of 338 cm⁻¹ is, on the basis of several infrared and Raman combination

TABLE 43
 Infrared Spectrum of Perfluorocyclobutane (Gas)

Wave Number	Description	Interpretation	Wave Number	Description	Interpretation	Wave Number	Description	Interpretation
437	m	1008 - 569 = 439 (E_u)	1030	w	(745) + (285) = 1030 (E_u)	1866	vw	1220 + 568 + (285) = 1863 (E_u)
442	m	273 + 173 = 446 (E_u)	1037	s	699 + (338) = 1037 (A_{u1})	1893	w	1285 + (613) = 1898 (E_u)
464	s	285 + 192 = 477 (E_u)	1042	s	(613) + 439 = 1052 (E_u)	1940	s	1239 + 699 = 1938 (A_{u1})
533	m	439 + (66) = 528 (E_u); 1239 - 699 = 540 (A_{u1})	1093	m	1008 + (86) = 1094 (A_{u1})	1971	m	1008 + 963 = 1971 (E_u)
569	vs	E_u Fundamental	1149	s	1340 - 192 = 1148 (E_u)	1996	s	1008 + 963 = 1971 (E_u)
598	w	439 + (173) = 612 (E_u)	1156	s	963 + 192 = 1155 (E_u)	2037	w	1431 + 569 = 2000 (E_u); 1340 + 699 = 2039 (E_u)
605	m	963 - 359 = 604 (E_u)	1180	w	(745) + 273 + 173 = 1191 (E_u); 699 + (205) + 192 = 1176 (E_u)	2135	vw	
611	w	(389) + 273 = 611 (E_u); 439 + (173) = 612 (E_u)	1223	m	963 + 268 = 1231 (E_u); 690 + 509 = 1229 (E_u)	2141	vw	
634	w	2 x 173 = (285) = 631 (E_u)	1239	vs	A_{u1} Fundamental	2180	s	1220 + 963 = 2183 (E_u)
640	w	359 + (285) = 644 (E_u)	1269	s	699 + 569 = 1268 (E_u); 660 + (613) = 1273 (A_{u1})	2247	vw	1265 + 963 = 2248 (A_{u1} + A_{u2} + B_{u1} + B_{u2})
650	w	1220 - 569 = 651 (E_u)	1292	vs	1008 + 285 = 1293 (E_u)	2300	vw	2 x 1008 + (285) = 2301 (E_u)
659	w	2 x 192 + (285) = 669 (E_u)	1304	w	(745) + 569 = 1314 (E_u)	2347	m	1340 + 1008 = 2348 (E_u)
682	vw	439 + (250) = 689 (E_u)	1340	vs	E_u Fundamental	2392	s	1431 + 963 = 2394 (E_u); (1385) + 1008 = 2393 (A_{u1})
725	w	439 + (285) = 724 (A_{u1} + A_{u2} + B_{u1} + B_{u2}); 1008 - (285) = 723 (E_u)	1403	s	963 + 439 = 1402 (A_{u1} + A_{u2} + B_{u1} + B_{u2})	2437	m	1431 + 569 + 439 = 2439; 1285 + 963 + 192 = 2440 (A_{u1} + A_{u2} + B_{u1} + B_{u2})
743	vw	660 + (66) = 746 (A_{u1})	1443	m	1285 + 173 = 1458 (E_u)	2508	s	1220 + 1008 + (285) = 2513 (E_u)
763	vw	569 + 192 = 761 (E_u)	1473	s	1220 + (250) = 1470 (A_{u1})	2557	s	1340 + 1220 = 2560 (E_u)
767	vw		1502	s	1220 + (285) = 1505 (E_u)	2625	m	1340 + 1285 = 2625 (A_{u1} + A_{u2} + B_{u1} + B_{u2})
774	vw	439 + (338) = 777 (E_u)	1531	s	1340 + 192 = 1532 (E_u)	2670	s	1431 + 1239 = 2670 (A_{u1}); (1385) + 1285 = 2670 (E_u)
797	vw	359 + 273 + (173) = 805 (A_{u1})	1572	m	1008 + 569 = 1577 (E_u); 1285 + (285) = 1570 (A_{u1} + A_{u2} + B_{u1} + B_{u2})	2718	m	1431 + 1008 + (285) = 2724 (E_u)
802	vw	(613) + 192 = 805 (A_{u1})	1600	w	1239 + 359 = 1598 (A_{u1}); 1340 + 258 = 1598 (E_u)	2766	m	1431 + 1340 = 2771 (E_u)
845	w	569 + 273 = 842 (A_{u1} + A_{u2} + B_{u1} + B_{u2})	1621	s	963 + 660 = 1623 (E_u); 1008 + (613) = 1621 (A_{u1})	2835	vw	1340 + 1220 + 273 = 2833 (A_{u1} + A_{u2} + B_{u1} + B_{u2})
850	w	3 x (285) = 855 (E_u)	1626	s	1008 + (613) = 1621 (A_{u1})	2889	vw	1220 + 963 + 699 = 2882 (E_u)
865	m	1431 - 569 = 862 (E_u)	1649	w	1285 + (386) = 1671 (E_u)	2903	vw	1285 + 963 + 660 = 2908 (A_{u1} + A_{u2} + B_{u1} + B_{u2})
870	w	439 + 258 + (173) = 870 (E_u)	1658	m	1008 + 359 + (285) = 1652 (E_u)	2976	vw	2 x 1008 + 963 = 2979 (E_u)
880	vw	(613) + 273 = 886 (E_u)	1680	vw	963 + 699 = 1662 (E_u); (1385) + 273 = 1658 (E_u)	3213	vw	1431 + 1239 = 3220 (E_u)
887	w	359 + (285) + 238 = 902 (E_u)	1715	w	1239 + 439 = 1678 (E_u)	3260	vw	2 x 1008 + 1239 = 3255 (A_{u1}); 1008 + 1285 + 963 = 3256 (A_{u1} + A_{u2} + B_{u1} + B_{u2})
905	vw	(745) + (173) = 918 (A_{u1}); 439 + (285) + 192 = 916 (A_{u1} + A_{u2} + B_{u1} + B_{u2})	1795	m	1431 + (285) = 1716 (E_u)	3356	vw	2 x 1008 + 1340 = 3356 (E_u)
963	vs	E_u Fundamental	1825	s	1220 + 569 = 1789 (E_u)	3390	vw	1431 + 1008 + 963 = 3402 (E_u)
983	s	699 + 285 = 984 (E_u)			(1385) + 439 = 1824 (E_u)			
1003	w	1285 - (285) = 1000 (A_{u1} + A_{u2} + B_{u1} + B_{u2})						
1010	w	439 + 569 = 1008 (A_{u1} + A_{u2} + B_{u1} + B_{u2})						

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TABLE 43
Raman Spectrum of Perfluorocyclobutane (Gas and Liquid)

Wave Number		Description	Polarization (Liquid)	Interpretation
Gas cm^{-1}	Liquid cm^{-1}			
	192	m d	dp*	E_g Fundamental
	258	s d	0.87	B_g Fundamental
	273	s d	0.87	E_g Fundamental
	347.0	s	p*	$2 \times 173 = 346 (A_{1g})$
358.2	360.6	vs sh	0.22	A_{1g} Fundamental
	384	m	0	$2 \times 192 = 384 (A_{1g})$
439	438	vs d	0.82	E_g Fundamental
	570	vw		$2 \times (285) = 570 (A_{1g} + B_{1g} + B_{2g})$
	603	w		$358 + 258 = 616 (B_{1g})$
	659.5	m sh	dp*	B_{2g} Fundamental
	675	w		$2 \times (338) = 676 (A_{1g})$
699.3	698.7	vvs	0.04	A_{1g} Fundamental
719.3	721.9	m sh	0.3	$2 \times 358.2 = 716.4 (A_{1g})$
	767	vww		$569 + (250) = 819 (E_g)$
	810	vww		$569 + (285) = 854 (E_g)$
	854	vww		$192 + 660 = 852 (A_{1g})$
				$699 + 273 = 972 (E_g)$
	972	w		B_{2g} Fundamental
1008	1006.5	s d	0.82	$963 + (86) = 1049 (E_g)$
	1051	vw		
	1117	vww		B_{1g} Fundamental
1220	1215.0	s	1†	E_g Fundamental
1285	1281	m d	0.9†	
	1337†	vw d		A_{1g} Fundamental
1431.3	1429.2	s sh	0.69†	$1285 + (745) = 1753 (E_g)$
	1747	vww		$2 \times 1008 = 2016 (A_{1g})$
	2020	vww		

* Cannot be measured accurately because of overlapping.

† Cannot be measured accurately because of uncertainty in background correction.

‡ May possibly be the very intense $1340 E_u$ due to violation of selection rules in the liquid.

TABLE 44
Fundamental Vibration Frequencies of Perfluorocyclobutane*

Active Vibrations					
Symmetry Species	Approximate Character†	Infrared (Gas)		Raman (Gas)	
		Wave Number	Description	Wave Number	Description
A_{1g}	CF Stretching			1431.3 cm^{-1}	s sh; $\rho = 0.69$
A_{1g}	Ring Stretching			699.3	vvs 0.04
A_{1g}	CF ₂ Deformation			358.2	vs sh 0.22
A_{2u}	CF Stretching	1239	vs		
A_{2u}	CF ₂ Rocking	338		1220	s -1
B_{1g}	CF Stretching			258†	s d 0.87
B_{1g}	CF ₂ Wagging			1008	s d 0.82
B_{2g}	CF Stretching			659.5†	m sh dp?
B_{2g}	CF ₂ Deformation			192†	m d dp?
B_{2g}	In-plane Ring Bending			1285	m 0.9
E_g	CF Stretching			439	vs d 0.82
E_g	CF ₂ Twisting			273†	s d dp
E_g	CF ₂ Twisting	1340	vs		
E_u	CF Stretching	962	vs		
E_u	Ring Stretching	569	vs		
E_u	CF ₂ Deformation	(285)			
E_u	CF ₂ Wagging				
Inactive Vibrations					
Symmetry Species	Approximate Character	Calculated Value			
A_{1u}	CF ₂ Twisting	(173)			
A_{2g}	CF ₂ Wagging	(745)			
B_{1u}	CF Stretching	(1385)			
B_{1u}	CF ₂ Rocking	(613)			
B_{1u}	Out-of-plane Ring Bending	(86)			
B_{2u}	CF ₂ Twisting	(250)			

* Fundamentals not observed directly are enclosed in parentheses.

† Only very rough meaning can be attached to the terms used in this column.

‡ Observed in the liquid only.

bands, the most probable, but it would be desirable to check this prediction of infrared-active bands at 285 and 338 cm^{-1} by observation of the spectrum out to 35 microns.

The inactive fundamentals assigned are listed at the end of Table 44. These have been evaluated by searching, near the computed values, for frequencies which would explain by combinations the strongest of the observed infrared bands not explainable by binary sums of the active fundamentals. All of the inactive frequencies are in satisfactory agreement with computed frequencies, but some of the values listed are based on only two or three observed combination bands, and hence are not known with great certainty.

Discussion. The interpretation of the infrared and Raman spectra is given in the last columns of Tables 42 and 43. Fundamentals not directly observed are written in parentheses. Of the 84 observed infrared bands, four are interpreted as fundamentals, 54 as binary sums, six as binary differences, 19 as ternary sums, and five weak or very weak bands are left unexplained. There have been considered only the ternary sums for which the sum of two of the fundamentals was observed in the infrared or in the Raman spectrum. Of the 26 observed Raman bands, 11 are interpreted as fundamentals, 12 as binary sums or first overtones, and three are left unexplained. One of the unexplained bands practically coincides with the very intense infrared band at 1340 cm^{-1} , is very weak, and is observed only for the liquid. Hence it is probably a result of violation of the selection rules. The other two are very, very weak and they, as well as the five unexplained infrared bands, may be caused by impurities.

The agreement between calculated and observed frequencies for binary combination bands is generally very good. Only a few differ by more than 5 cm^{-1} . The intensity relations between corresponding sum and difference bands is plausible in all cases, possibly with one exception. Both the band at 437 cm^{-1} , interpreted as 1008-569, and the corresponding sum band are listed as being of medium intensity. The intensity estimate for the 437 cm^{-1} band, however, is very unreliable, since the intensity maximum falls only 5 cm^{-1} from that of the sum band at 442 cm^{-1} , near the extreme transmission limit of potassium bromide optics.

The present assignment of observed fundamentals does not agree with that given by Edgell (46) except for two frequencies belonging to A_{1g} , one belonging to A_{2u} and one to E_u . The discrepancy is not surprising, since Edgell's experimental data included only eleven Raman bands and four infrared bands. His assignments were made largely on the basis of estimates of characteristic valence frequencies. Since all the atoms in perfluorocyclobutane have comparable masses, it is very difficult to characterize the normal modes in this manner and to estimate frequencies reliably.

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FLUORINATED PENTANES

Samples of cyclic C_5F_{10} , cyclic C_5F_9H , $n-C_5F_{12}$, and $iso-C_5F_{12}$ (Serial Nos. 354 through 357, Table 18), all highly purified, were obtained from Prof. Cady for spectral study. The infrared spectra of cyclic C_5F_{10} and $n-C_5F_{12}$ have been obtained for the gaseous state and are shown in Figure 35. The Raman shifts for these two compounds have been measured for the liquid using exposure times of 1, 5, and 20 hours. Polarizations of the Raman lines were also determined using an exposure time of 50 hours. The results are given in Tables 45 and 46. The Raman spectrum of $iso-C_5F_{12}$ has not yet been obtained, but the infrared spectrum has been obtained for both liquid and vapor as shown in Figure 35. No measurements have yet been made on cyclic C_5F_9H .

Although there are no previous infrared or Raman data on fluorinated pentanes with which to compare the present results, it may be noted that no Raman frequencies or infrared absorption of appreciable intensity has been found in the region of C-H stretching at 3000 cm^{-1} . Likewise, the spectral data in other regions indicate that these compounds are relatively free of impurities, except for the close-boiling C_5F_{12} isomers which may not be completely separated.

No attempt has been made to obtain a detailed interpretation of the spectra of these fluorocarbons, first because of the complexity of the skeletal vibrations and further because of the possibility of rotational isomers for both $n-C_5F_{12}$ and $iso-C_5F_{12}$ and the consequent necessity for determination of the temperature dependence of their spectra. The spectral data have been considered, however, in the correlations discussed under

TABLE 45
Raman Spectrum of Cyclic C_5F_{10} (Liquid)

Frequency Shift cm^{-1}	Description	Depolarization	Exciting Line
252	w d	0.7	e
295	m d	0.9	e
~342	m d	-	e
358	vs d	0.21	e, i, k
406	vs d	0.80	e, f, i, k
545	w d	0.5	e
606	w d	p	e
628	m d	0.68	e
682	vs	0.06	e, i, k
~693	vw	-	e
712	vw	p	e
990	vw d	-	e
1053	w d	0.7	e
1189	w d	0.8	e
1243	s d	0.86	f, e
1298	w d	-	e
1322	w d	0.20	e
1374	w d		

RESULTS AND DISCUSSION

TABLE 46
Raman Spectrum of $n\text{-C}_5\text{F}_{12}$ (Liquid)

Frequency Shift cm^{-1}	Description	Depolarization	Exciting Line
179	m	-	e
293	s	0.27	e, i, k
308	w	-	e
321	s d	0.84	e, f, i, k
354	w	-	e
367	w	-	e
384	s	0.44	e
537	m d	-	e
593	m d	} 0.9	e
612	m d		e
653	m	0.5	e
689	m sh	0.35	e
705	s sh	0.12	e, i, k
743	vw	p	e
762	vs	0.04	e, f, i, k
833	vvw	-	e
879	vvw	-	e
1020	vvw	-	e
1045	m sh	0.2	e
1129	vvw	-	e
1151	vvw	-	e
1186	vw d	~ 0.7	e
1219	m d	0.64	e
1267	vw d	0.7	e
1296	w d	0.8	e
1338	m	0.76	e
1356	m	0.62	e
1378	s	0.61	e

Applications. It may be mentioned here that the Raman bands for cyclic C_5F_{10} and $n\text{-C}_5\text{F}_{12}$ are predominately diffuse and fall into the three spectral regions 240-440, 520-770, and 1170-1430 cm^{-1} . It is suggested that the vibrations in these regions may be ascribed roughly to gross molecular deformations, to group deformations, and to valence stretching motions, respectively. For each compound more Raman bands have been observed for the fluorocarbon than for the corresponding hydrocarbon in spite of the weakness of Raman scattering for fluorocarbons. The infrared data do not extend to the lowest frequency region, but the observed bands fall into two regions on either side of a "window" at about 800 cm^{-1} . In the region 700-750 cm^{-1} a pair of intense bands observed for $n\text{-C}_5\text{F}_{12}$ (unequal intensity) are, with small shifts, also observed for $\text{iso-C}_5\text{F}_{12}$ (equal intensity) but are not found for cyclic C_5F_{10} , indicating that CF_3 groups must participate strongly in these vibrations.

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The infrared spectrum of liquid $n\text{-C}_7\text{F}_{16}$ is shown in Figure 35, and the Raman shifts, together with intensity and descriptive symbols for the bands, are listed in Table 47. The present infrared data are in fairly good agreement with those of Thompson and Temple (47) for the gas except for changes in position and intensity of some of the bands which could be caused by the different states of aggregation. Many more weak bands are observed for the liquid than were reported for the gas. In most cases this is undoubtedly due to differences in resolving power and the greater sharpness of the bands for the liquid state, but the possibility of weak impurity absorptions in the present data cannot be entirely excluded. On the other hand, no evidence of residual hydrogen in the sample was found in either the infrared or Raman spectra near 3000 cm^{-1} .

TABLE 47
Raman Frequencies of $n\text{-C}_7\text{F}_{16}$ (Liquid)

Frequency	Description
144.0 cm^{-1}	m
168.3	w
185	vvw d
295.7	m
307	m d
335	vvw
349	vvw
384.0	m
418	vvw d
536	vvw d
564.0	vvw sh
589	vvw d
607	vw d
643	vvw
680.6	vvw
701.8	vvw
718.8	m sh
734.1	vvvw sh
753.8	vs
783.4	vvvw sh
810	vvvw
895	vvvw
908.8	vvw
948	vvvw
1022	vvvw
1049	vvvw
1119	vvvw
1148	vvvw
1205	vw d
1233	vw d
1298	w d
1345	vw d
1362.0	w sh
1374.6	w sh

The infrared and Raman spectra of completely fluorinated ethylcyclopentane, methylcyclohexane, 1,2- and 1,4-dimethylcyclohexane, and 1,3,5-trimethylcyclohexane have also been obtained for the liquid state. The infrared results are shown in Figure 36 and the Raman data in Tables 48 through 52. For fluorinated methylcyclohexane, the agreement between the present infrared data and the spectrum for the vapor reported by Thompson and Temple (47) is about the same as in the case of $n\text{-C}_7\text{F}_{16}$ discussed above. No infrared data for the other compounds have been published.

TABLE 48
Raman Frequencies of
Perfluoroethylcyclopentane (Liquid)

Frequency	Description
159 cm^{-1}	vvw
169.8	vvw
179.5	vw
208	vw d
270.2	vw
309	w d
330.7	w
356.1	m
370.6	vw
400.0	w
424.4	vvw
464	vvw d
503	vvvw
538	vvw d
572.6*	vvw
583	vvvw d
605	vvw
633.4†	vvw sh
674.5	vs sh
685.8	vvw sh
734.0	s sh
813.4	vvw sh
868.3	vvvw
971	vvvw
1019.5	vvvw
1061	vvvw
1072	vvvw
1136.8	vvvw
1180	vvw b
1244	vw d
1277	vw d
1310	w d
1342	vw
1359	vw

* Seems too intense to be interpreted as 674.5 cm^{-1} excited by $\text{Hg } 4339\text{\AA}$.

† Too intense to be 734.0 excited by $\text{Hg } 4339\text{\AA}$.

TABLE 49
Raman Frequencies of
Perfluoromethylcyclohexane (Liquid)

Frequency	Description
179.2 cm^{-1}	vvw d
215.2	w
248	vvw
276.5	m
300	vw
306	vw
313.3	w sh
333	vs b
369.2	m
398.4	vvw sh
411.1	vvw sh
505.4	vw sh
547	vvw b
591.2	vw
601.3	vvw
630.5*	vvw
645	vvvw
687.3	vs sh
732.7	s sh
850	vvvw
868.6	vvvw
1028	vvvw
1063	vvvw
1139.2	vvw
1172.2	vvw
1187.3	vvw
1213.5	vvw
1230	vvvw
1245	vw
1270	w b
1303.4	w
1318	vw
1325	w
1341.9	m
2333	vvvw
2375	vvvw d

* Seems too intense to be 687.3 cm^{-1} excited by $\text{Hg } 4347\text{\AA}$ or 732.7 cm^{-1} excited by $\text{Hg } 4339\text{\AA}$.

TABLE 50
Raman Frequencies of
Perfluoro-o-dimethylcyclohexane (Liquid)

Frequency	Description
150 cm ⁻¹	vvw
175	vw d
189	vvw
218.5	m
277.5	m
293.0	s
301	m
312	m d
333.3	vs d
384.1	w sh
392.5	w
409	vvw
423.3	vvvw
435.1	vw sh
464.4	vvvw sh
481.5	vvvw
503.6	vw
537.7	vw
555.6	vw
578.2	vvw
599.6	vw
616.1*	vvw
636	vvw
672.6	s sh
685.0	w sh
724.4	s sh
732.3	m sh
748.0	s sh
848.0	vw sh
863.2	vvvw
912	vvvw
932	vvvw
1002	vvvw
1018	vvvw
1034	vvvw
1042	vvvw
1068	vvvw
1114.5	vvw
1136	vvvw d
1185	vvw d
1204	vvw d
1221†	vw d
1276	m vd
1306	w
1327	s d
2325	vvvw

* Seems too intense to be 672.6 cm⁻¹ excited by Hg 4347A.

† Seems too intense to be 1276 cm⁻¹ excited by Hg 4347A.

TABLE 51
Raman Frequencies of
Perfluoro-p-dimethylcyclohexane (Liquid)

Frequency	Description
159 cm ⁻¹	vvvw
178	w
188.9	vw
196.8	w
241	vvvw
258	vvvw
274.8	w
283	vw
306	w
313	vw
320	w
335.9	s d
371.3*	w
438.4	vvw sh
481.1	vvvw sh
503.2	vvvw
523.3	vvvw
544.6	vvw
549.4	vvw
583	vvvw
603.5	w
648.6	vw sh
666	vvw
677.5	s sh
729.2	vs sh
748.4	vw sh
844.0	vvvw sh
855	vvvw sh
865	vvvw sh
888.9	vvw
930	vvvw
950	vvvw
1018	vvvw
1063	vvvw
1081	vvvw
1123	vvvw
1141.4	vvw
1154.6	vvw
1177	vvw
1195.5	vvw
1233	vw
1248	vw
1280	m d
1297	m d
1347	w
1357	m

* Apparently a sharp band superposed upon a weaker diffuse band.

TABLE 52
Raman Frequencies of Perfluoro-1,3,5-trimethylcyclohexane (Liquid)

Frequency	Description	Frequency	Description
116 cm^{-1}	vvw	673.1 cm^{-1}	vs sh
173	vw	682.3	w sh
191	w	711.0	vvvw
204.0	m	722.9	vvvw
211.9	w	731.0	vvw sh
232.3	w sh	750.1	vs sh
280.0	s	827	vvvw
308.7	m	841.2	vvvw
319	w	860	vvvw
329.6	s	880	vvvw
339.7	w	914	vvvw
360.6	vw	1011	vvvw
386.6	vw	1021	vvvw
409.8	w d	1036.9	w sh
426.7	w sh	1046.8	vvw sh
444	vvvw	1123.2	vvw
460.3	vvvw	1139	vvvw
500.7	vvw	1152	vvvw
527.0	w	1177	vw
533.8	w	1190	w
549	w b	1202*	vvw
594	w	1250†	w d
605.5	vw	1279‡	w d
628	vvvw	1308	s vd
640	vvvw	1330.3	m sh
651.5	vw	2638	vvvw sh

* May be 1308 cm^{-1} excited by H γ 4339A.

† Seems too intense to be 1308 cm^{-1} excited by H γ 4347A.

‡ Seems too intense and diffuse to be 1330.6 cm^{-1} excited by 4347A.

As in the case of the fluorinated pentanes, the strongest Raman bands for these heavier fluorocarbons fall into three spectral regions centered around 330, 700, and 1300 cm^{-1} . Again, the bands for $n\text{-C}_7\text{F}_{16}$ are predominantly diffuse, whereas for the cyclic compounds there are several sharp bands. In the lowest frequency region, $n\text{-C}_7\text{F}_{16}$ has only three medium-intensity bands, 295, 307, and 384 cm^{-1} ; the cyclopentane derivative has a group of six bands extending from 270 to 400 cm^{-1} ; and the cyclohexane derivatives are characterized by a closely spaced group of bands ranging from 275 to 336 cm^{-1} with the most intense band lying between 329 and 336 cm^{-1} . In the next region, each of these compounds has at least two strong Raman bands and some weaker bands between 670 and 755 cm^{-1} . Because of the intensity and sharpness of these bands this region is probably the most useful for some analytical purposes. In this connection it may be remarked that a careful comparison of the spectra gave no indication that any of these compounds contained any of the others as contaminants. In the last spectral region, extending from 1200 to 1400 cm^{-1} , most of the bands are diffuse. In some cases this may be due to failure to resolve the many C-F stretching vibrations which occur in this region.

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The most striking feature of the infrared spectra of the compounds is the absence of bands in the 760 to 800 cm^{-1} region for all the cyclic compounds, but not for $n\text{-C}_7\text{F}_{16}$. Except for this "window," the region from 450 to 1400 cm^{-1} is practically filled with bands, many of which are very intense. Thompson and Temple (47), who obtained data for two compounds not investigated here [cyclic C_6F_{12} and $\text{CF}_3(\text{CF}-\text{CF}_3)_2\text{-CF}_2\text{CF}_3$], suggest that the strong band observed at 985 and 975 cm^{-1} for cyclic C_6F_{12} and C_7F_{14} , respectively, may be a characteristic vibration of the cyclohexane ring. This, however, is not borne out by the spectra of the di- and tri-substituted cyclohexane derivatives, and, in addition, the cyclopentane derivative also has a strong band at this position. Further correlation of the present spectral data will be discussed under Applications. None of these cyclic compounds showed any evidence of Raman bands in the region of 3000 cm^{-1} , nor were any infrared bands of appreciable intensity found in this region. These samples, therefore, contain very little, if any, residual hydrogen.

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FLUORINATED AROMATICS

The aromatic ring, being electronically unsaturated, has the property of transmitting electronic effects from one atom to another in the molecule and thus forms a basis for the study of interactions between polar or other groups not electronically neutral. The fluorinated aromatics are, therefore, of theoretical interest to the spectroscopist for much the same reasons that they are of interest to the chemist—because they permit the study of the effect of highly electronegative fluorine in molecules.

Previous Work

The Raman spectrum of fluorobenzene has been investigated by a number of workers (48-53). The Raman spectra of o-fluorotoluene and p-fluorotoluene have been investigated by Kohlrausch and Pongratz (49). Herz (54) has investigated the Raman spectra of twenty-three ortho derivatives, including o-fluorotoluene and o-fluorochlorotoluene. Herz, Kohlrausch, and Vogel (55) have studied the Raman spectra of a number of para derivatives including p-fluorotoluene.

The Raman spectrum of benzotrifluoride has been studied by Pendl and Radinger (56). Kohlrausch and Pongratz (57) have also investigated the Raman spectrum of m-difluorobenzene, and Kohlrausch and Ypsilanti (58) have investigated the Raman spectra of para-, bromo-, iodo-, hydroxy-, and aminofluorobenzene. Reitz and Ypsilanti (59) have studied p-methoxyfluorobenzene, and Reitz and Stockmair (60) have investigated the Raman spectrum of p-nitrofluorobenzene.

Thompson and Temple (47) have recently reported the infrared spectra of o-fluoro-, m-fluoro-, p-fluoro-, and 2,4-difluorotoluene; of benzotrifluoride; and of m-fluoro-, p-fluoro-, and 2,5-difluorobenzotrifluoride.

Experimental Results

A group of nine fluorinated aromatics were supplied by Dr. G. C. Finger of the Illinois State Geological Survey. The compounds consisted of three series of related molecules. The first series consisted of fluorobenzene and p-difluoro-, 1,2,4-trifluoro-, and 1,2,4,5-tetrafluorobenzene; the second of p-fluoro- and o-fluorotoluene; and the third of benzotrifluoride and m-fluoro- and 2,5-difluorobenzotrifluoride. The synthesis of some of these compounds has been described in the literature (61). The compounds had been carefully refined to constant physical properties and had been identified by chemical methods and precise elemental analysis. The samples appeared to be of very high purity.

In Figures 37 and 38 are given the infrared transmittance curves for the nine fluorinated aromatics in the liquid state. The positions for the absorption maxima are given opposite each figure. The spectrum of 1,2,4,5-tetrafluorobenzene has also been determined for the gaseous state, as shown in Figure 37.

The Raman spectra of the nine aromatic compounds have also been determined for the liquid state. Figure 26 shows the Raman spectrum of fluorobenzene for six exposures varying from two minutes and thirteen seconds to nine hours by factors of three. The iron arc comparison spectrum has been included as an aid in identifying the frequency

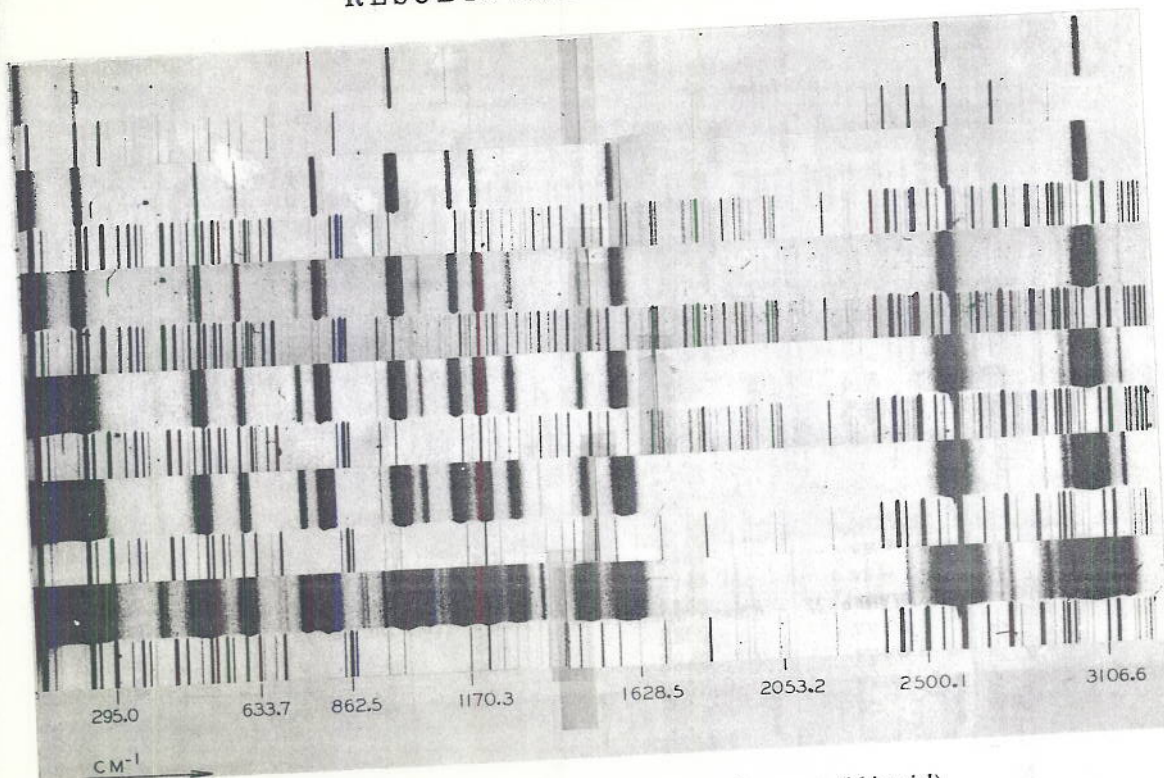


Figure 26 - Raman spectrum of fluorobenzene (liquid)

shifts. A similar set of exposures was made for each compound as well as a one-hour exposure with water in place of the NaNO_2 filter solution.

Figure 27 shows the Raman spectra obtained with twenty-minute exposures of benzene, fluorobenzene, p-difluorobenzene, 1,2,4-trifluorobenzene, and 1,2,4,5-tetrafluorobenzene. Figure 28 shows twenty-minute exposures of o-fluorotoluene and p-fluorotoluene. The spectrum of p-difluorobenzene has been included for comparison. In Figure 29 are shown the Raman spectra obtained with twenty-minute exposures of benzotrifluoride, m-fluorobenzotrifluoride and 2,5-difluorobenzotrifluoride.

In Tables 53 through 61 are given the Raman frequencies, relative intensities, and widths for the nine fluorinated aromatics. The values listed in column one in each of these tables were obtained from weighted averages of all the observed Raman bands corresponding to a particular frequency shift. The second column of each of the tables gives the relative intensities as obtained by careful microphotometry of the Stokesian bands corresponding to these frequencies. In the third column of these tables are given the widths of the Raman bands in cm^{-1} at one-half intensity. Raman frequencies which are questionable, unsymmetrical, or possibly double, are marked with an asterisk.

The Raman spectra of the nine fluorinated aromatics are believed to be reasonably complete. Kohlrausch (5, p. 380) lists thirty-two Raman frequencies for fluorobenzene, seven of which are given as questionable. In the present investigation forty-two Raman frequencies have been found in fluorobenzene, and the existence of four of the questionable frequencies given by Kohlrausch has been confirmed. In addition, Kohlrausch lists five frequencies for fluorobenzene, not designated as questionable, which are completely absent

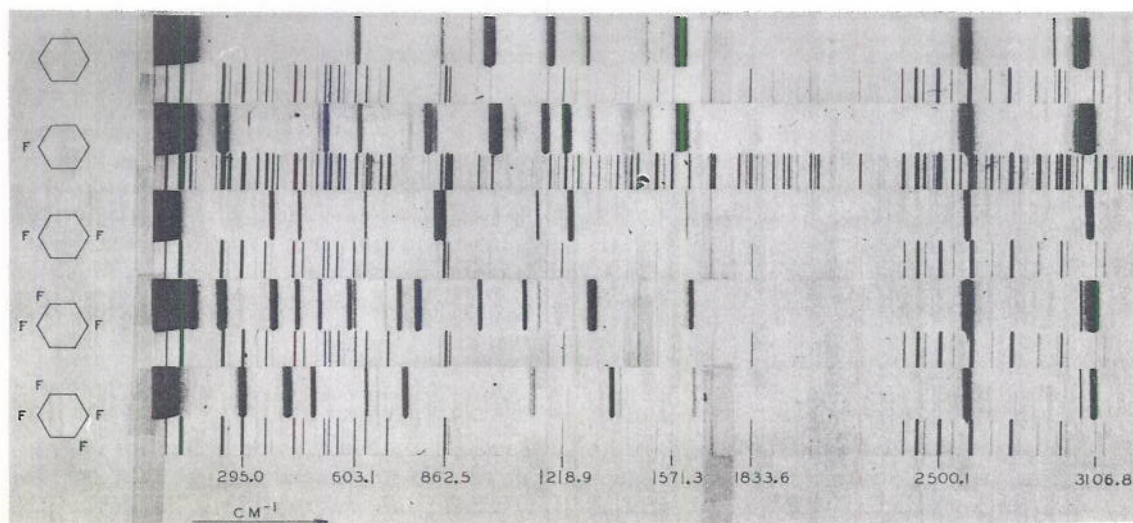


Figure 27 - Raman spectra of fluorinated benzenes

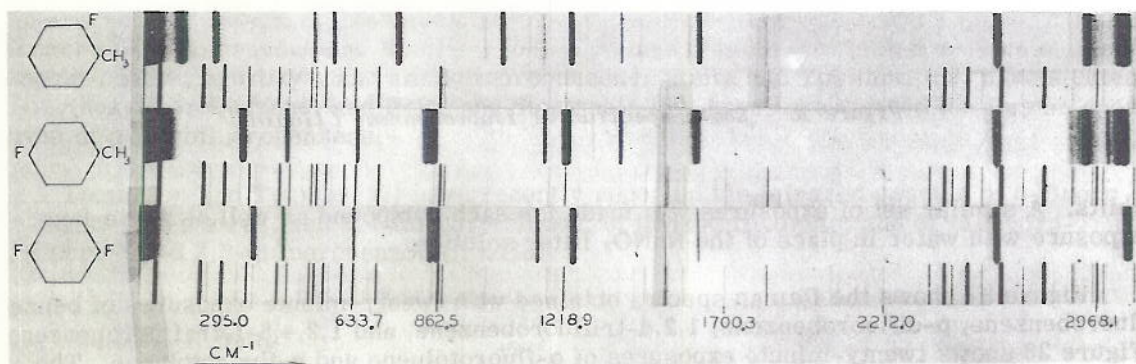


Figure 28 - Raman spectra of o- and p-fluorotoluene and p-difluorobenzene

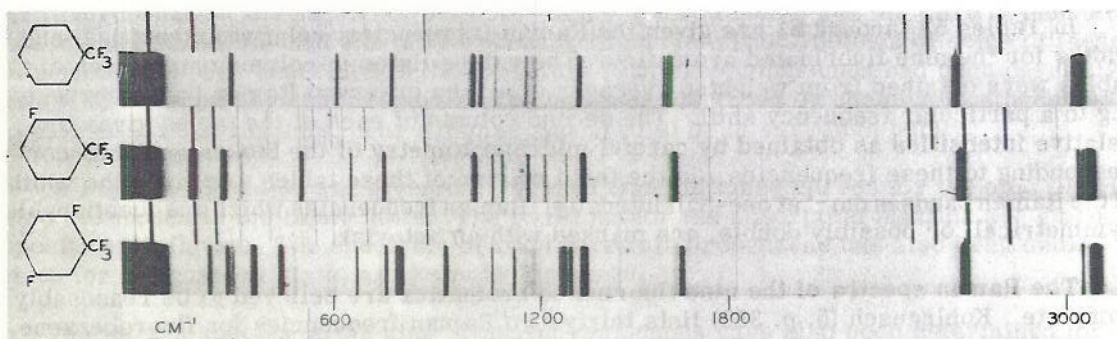


Figure 29 - Raman spectra of benzotrifluoride and m-fluoro- and 2,5-difluorobenzotrifluoride

TABLE 53
Raman Frequencies of Fluorobenzene

Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹	Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹
242	23	10	1602	6.2	21
277	w	d	1623	vw	
406.9	vw		1693	vvvw	
416	vw		1735	vvvw	
462.9	vw	sh	1789	vvvw	
499.2	0.88	10	1915	vvvw	
519.2	9.7	7.3	1960	vvvw	
612.6	4.5	7.8	2022	vvvw	
687.1	vvw		2117	vvvw	
754.4	0.96	19	2214	vvvw	
805.7	44	6.3	2313	vvvw	
829.1	0.88	6.6	2359	vvvw	
996.8	9.7	11	2443.0	vvvw	
1008.9	110	5.8	2491	vvw	
1021.0	8.8	7.2	2745.3	vvw	
1065.2	0.88	15	2846	vvvw	
1156.4	16	8.4	2869	vvvw	
1217.2	11	14	2948	vvvw	
1369	w	sh	2978.9	vvw	
*1457.1	vw	sh	3072.4	45	15
1495.7	1.8	15	3184.4	w	

TABLE 54
Raman Frequencies of p-Difluorobenzene

Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹	Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹
165	vw	d	1385.3	.26	9.4
239	vvvw		1414	vvvw	
270	vvvw		1473	vvvw	
316	vvw	sh	1605	vvw	
375.3	13	9.1	*1617	5.0	13
451.3	15	5.9	1668	vvvw	
507	vvvw		1691	vvvw	
578	vvvw		1849	vvvw	
635.3	6.5	7.1	*1885	vvvw	
692.4	0.97	7.9	2282	vvvw	
*740	vvw	d	*2296	vvvw	
758	vvw	d	2367	vvvw	
*800	0.36	14	2393	vvvw	
840.0	27	7.0	2420	vvvw	
858.5	24	7.4	2464	vvvw	
886.8	vvw		2492	vvvw	
1015	0.38	16	2899	vvw	
1070	vvw		2914	vvw	
1142.3	7.7	7.3	3005	w	sh
1245.0	29	11	3083.7	27	21
1285.1	0.58	13	3198	vvvw	
			3230	vvvw	

RESULTS AND DISCUSSION

TABLE 55
Raman Frequencies of 1,2,4-Trifluorobenzene

Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹	Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹
129.3	2.6	10	916	vw	
161.3	5.0	11	963.7	23	3.9
237.8	23	8.2	1003	vvw	
288.1	w		1064	vw	
341	w		1098.2	7.1	8.0
376.9	38	6.2	1142.6	1.5	7.7
400.9	w		1205	0.59	8.9
441.6	18	4.9	1231.6	vvw	
457	vw		*1250	0.61	7.4
503.5	14	4.3	1287.5	vw	
585.6	16	5.4	*1308	20	14
601	w		1375.5	0.18	6.8
618	vvw		1441.3	0.60	5.7
688.2	w		1455	vvw	
727.8	57	3.8	1517.9	0.48	12
780.6	100	4.9	*1628	4.4	11
808	vw		1708	vvw	
835.0	vw		1859	vvw	
859	vvw		3062	vw	
*908	vw		3094	25	19

TABLE 56
Raman Frequencies of 1,2,4,5-Tetrafluorobenzene

Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹	Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹
169	w		1164	vvw	
202.4	w	d	1196.2	0.28	14.4
279.8	w		1255	vvw	
294.6	19	6.4	*1272	vvw	
417.0	21	9.5	1335	0.47	11.6
487.3	35	3.6	1374.3	14	6.4
533	vvw		1402.1	0.64	6.5
591	vw	d	1521	vvw	
635.4	3.6	5.4	1574	vvw	
668.8	0.67	10.6	1610	vw	
747.9	140	2.8	1643	1.6	14.4
783	vvw		1677	vvw	d
832	0.33	14	1734	vvw	
871.0	vw		1782	vvw	
920	vw		1834	vvw	
963.7	vvw		1864	vvw	
1000	vvw		2316	vvw	
1026.6	vvw		2439	vvw	
1121	0.60	8.0	3097.2	18	13.2
1130	0.75	8.0			

TABLE 57
Raman Frequencies of p-Fluorotoluene

Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹	Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹
152	vw	d	1214.5	21	13
312.2	w		1221.4	38	13
340.6	22	9.1	1278	vvw	
425.4	vvw	d	1299	2.0	13
454.1	38	4.3	*1351	vvvw	d
502.3	0.42	12	1382.3	8.3	9.1
637.9	14	5.1	1404	vvw	
695.2	1.1	6.9	1433	vvvw	
728.4	0.90	5.2	1455	vw	d
740	vvvw		*1495	w	
825.0	38	9.8	1507.7	vw	
842.5	62	8.1	1601	6.6	11
908	vvvw		1614	3.0	11
929	vvvw	d	1858	vvvw	
1003	0.33	13	1906	vvvw	
1016.6	0.20	7.2	1940	vvvw	
1040	vvvw	d	2385	vvvw	
1061	vvvw	d	2416	vvvw	
*1099	0.31	13	2454	vvvw	
1157.3	11	7.0	2740	vw	
1178	vvw		2871	vw	
2928	20	19	3070.6	45	15
3009.7	5.0	21			

TABLE 58
Raman Frequencies of o-Fluorotoluene

Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹	Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹
186	9.2	13	*1281.2	0.51	8.6
*271.9	8.2	9.8	1382.3	3.3	7.5
426.8	0.24	8.2	1406	vw	
443	0.19	8.2	*1442	0.90	20
525.5	3.9	7.0	1490	vw	
535	vw		1589.0	1.1	12
576.6	9.3	6.4	1620	9.2	9.1
704	vw		*1674	vvvw	
715.1	vw		1702	vvvw	
*747.0	61	4.5	1813	vvvw	
841	vw		1866	vvw	
851	vw		1945	vvvw	
886.3	vvw		1981	vvvw	
*934.9	vvw		2369	vvvw	
953	vvvw		2415	vvw	
988	1.2	11	2451	vvw	
1038.0	22	6.1	2717	vvw	
1073.7	0.39	8.0	2743	vw	
1112.6	0.78	8.0	2930	14	19
*1155	1.6	12	2959	vw	
1324.3	23	7.1	2982	vw	
3069	20	20	3172	vvw	

RESULTS AND DISCUSSION

TABLE 59
Raman Frequencies of Benzotrifluoride

Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹	Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹
139	57	20	*1187	1.7	19
199	vvw		1239	vvvw	
235	vvvw		1324	15	7.5
321	vw		1365	vvvw	
339.0	17	6.1	1389	vvvw	
400	0.47	12	1427	vvvw	
485	vw	d	1458	vw	
583	vw	b	1593	3	9.6
618.0	8.5	5.8	1610	18	7.0
657.7	0.54	6.5	1662	vw	d
769.5	66	3.1	1687	vw	
800	0.18	13	1841	vvvw	
844	0.24	14	1940	vvvw	
*925	vw	d	1981	vvvw	
*972	vw	d	2204	vvvw	
991	w		2265	vvvw	
1003.5	220	3.2	2321	vvvw	
1027.2	21	4.0	2461	vw	d
1070.9	1.6	8.7	*2741	vw	
1127	vw	d	*2913	vw	
1161	2.2	13	2926	vw	
2952	vvvw		3076	39	20
2995	1.1	13	3183	0.36	15
3022	1.5	12	3218	0.45	14

TABLE 60
Raman Frequencies of m-Fluorobenzotrifluoride

Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹	Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹
134	110	11	1087.5	3.7	9.3
241	28	8.5	1144	vw	b
318	12	9.0	1163	3.3	10
365	2.7	11	1215	2.4	13
*447	0.50	8.2	1280.1	2.8	6.0
481	vvvw		1309	vw	d
*522.8	12	6.6	1332	21	7.9
588	vvvw		1395	vw	
633.7	0.58	9.2	1430	vw	
656	5.0	5.1	1457.2	0.55	9.1
697	vvvw		1494	0.53	11
746.9	29	2.5	1607	vw	
795	0.50	11	1622	11	9.5
*895	0.32	7.8	1662	vw	sh
*905	vw		1758	vvvw	d
*949	0.34		1806	vvvw	d
964	vvvw		1949	vvvw	d
994.6	vw	sh	2066	vvvw	
1005.5	190	2.2	2361	vvvw	
1028	vw		2439	vvvw	
1059.6	4.1	6.4	*2840	vvvw	
2903	vvvw	d	3088	30	19.0
2980	vw				

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TABLE 61
Raman Frequencies of 2,5-Difluorobenzotrifluoride

Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹	Frequency cm ⁻¹	Relative Intensity	Width cm ⁻¹
126	110	15	1049.8	4.3	5.8
*276	6.2	10	1115	3.8	9.8
321	6.1	11	1149	vw	b
334	vw		1172	vw	b
*387.2	10	8	1190	vw	
*392.2	9	8	1253	1.5	12
459.1	36	4.8	1264	10	12
498.0	1.1	10	1285.4	1.4	11
536	vvw		1323	17	11
587	0.70	14	1333	vw	
625.8	0.50	13	1410	vvw	
663.6	6.9	6.2	1440.4	0.90	12
729.9	1.0	11	1457	vvw	
745.5	34	5.7	1512	vvw	b
780	19	8.7	1617	vw	b
791	vw		1637	10	9.3
828.8	vvw		1717	vvw	d
891	vvw	b	2362	vvv	
914.1	20	5.3	2396	vvv	
939	vw	b	2730	vvv	
1005.7	vw	sh	2757	vvv	
3000	vvw		3095	26	19

in the present work. The infrared spectra of these fluorinated aromatics are also believed to be complete and accurate over the range from 450 to 3300 cm⁻¹. The curves for the fluorotoluenes and benzotrifluoride derivatives do not agree as well as would be expected with those given by Thompson and Temple; but this may be due to differences in the physical state of the samples, since it is not clear whether their curves are for the liquid or gas. Many more weak bands and a few stronger bands were observed in the present work and many of the frequencies listed differ by more than the experimental error.

It may be noted that nine weak infrared bands at 587, 604, 728, 781, 810, 963, 1100, 1144, and 1250 cm⁻¹ in the 1,2,4,5-tetrafluorobenzene spectrum have identical positions with intense bands of 1,2,4-trifluorobenzene. This could be caused by less than one percent 1,2,4-trifluorobenzene impurity in the tetrafluoro compound.

Basis for Spectral Interpretations

The determination of the fundamental frequencies of the benzene molecule has been the subject of a large number of investigations (3, p. 362). Several attempts have been made to calculate the benzene frequencies from an assumed potential function (62-68). In particular, Miller and Crawford (68) have calculated the frequencies of the out-of-plane vibrations with considerable success. But the most comprehensive study of the Raman and infrared spectra of benzene has been made by Ingold et al. (69). These authors have studied the Raman and infrared spectra of benzene and deuterobenzene and have made

frequency assignments which appear to be essentially correct. The Raman spectra of deuterated benzenes have also been studied by Redlich and Stricks (70), Klit and Langseth (71), and Langseth and Lord (72).

In a recent paper Mair and Hornig (73) have reported the infrared spectra of benzene in the crystalline state. They have confirmed the frequency assignments of Ingold et al. (69) except for the B_{2u} species. Of special interest is the fact that they have observed some frequencies which are inactive in benzene and which were formerly known only from the application of the Redlich-Teller product rule. The agreement is excellent.

The changes in the spectra of benzene with progressive halogen substitution have been investigated by Murray and Andrews (74) and by Dadiou, Kohlrausch, and Pongratz (75). Murray and Andrews have observed new bands not observed by Dadiou, Kohlrausch, and Pongratz and have confirmed most of their observations. In particular, Murray and Andrews note that the spectrum of fluorobenzene resembles that of the heavier monohalogenated benzenes but that it shows certain marked differences, especially in the region of 1200 cm^{-1} . They have also noted that several of the bands appearing in benzene as well as in the monohalogenated benzenes have in fluorobenzene higher values than in benzene itself, while the values for bands of the heavier derivatives are lower than those in benzene. They interpret this as indicating that the substitution of fluorine has the effect of increasing the force constants involved in certain vibrations.

In the present work the results of Ingold et al. (69) and of Langseth and Lord (72) on the deuterated benzenes have been used to estimate the frequency shifts to be expected for the fluorinated benzenes. In addition, use has been made of the frequency assignments of Dadiou, Kohlrausch, and Pongratz (75) and of Murray and Andrews (74) for fluorobenzene and p-fluorotoluene.

By far the most useful information is the knowledge of the selection rules for the various symmetry species. Though the data on the Raman spectrum of fluorobenzene obtained in the present work do not in all cases agree with the values given by Kohlrausch (5, p. 380), the polarization values given by him for a number of the bands have helped in making assignments for fluorobenzene. For 1,2,4,5-tetrafluorobenzene, whose infrared spectrum was obtained both in the liquid and gaseous state, the envelopes of the bands belonging to the various species may be determined by extrapolating from the values given by Badger and Zumwalt (29). This knowledge allows the assignment of fundamentals to proceed from benzene down through 1,2,4,5-tetrafluorobenzene, or vice versa.

The symmetry species, the number of vibrations belonging to each species, the selection rules for the Raman and infrared spectra, and the polarization of the Raman bands are given in Table 62 for benzene and for the four fluorinated benzenes. The translational and rotational null vibrations have been included in the number of vibrations belonging to each species.

In Figure 30 are reproduced schematically the fundamental modes of vibration into which the thirty degrees of internal freedom in benzene can be resolved. For convenience in discussing the frequencies, the fundamentals have been numbered according to Wilson (62). It must be kept in mind that the displacement patterns shown are specifically those for a structure of symmetry D_{6h} and that, as soon as the D_{6h} symmetry is destroyed by substitution, these modes change into others appropriate to the new symmetry. Thus, degenerate fundamentals will in general split up. Vibrations in benzene that can be considered as essentially carbon vibrations should show the least change, whereas those that are essentially hydrogen vibrations may be changed greatly.

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TABLE 62
Normal Vibrations of Benzene and Fluorinated Benzenes

Compound	Symmetry Species	Number of Vibrations	Selection Rules *		Polarization †
			Infrared	Raman	
C_6H_6 (Symmetry D_{6h})	A_{1g}	2	-	+	p
	A_{2g}	1 R_z	-	-	
	B_{2g}	2	-	-	
	E_{2g}	4	-	+	dp
	E_{1g}	1 R_x, R_y	-	-	dp
	A_{2u}	1 T_z	+	-	
	B_{1u}	2	-	-	
	B_{2u}	2	-	-	
	E_{2u}	2	-	-	
	E_{1u}	3 T_x, T_y	+	-	
C_6H_5F (Symmetry C_{2v})	A_1	11 T_y	+	+	p
	A_2	3 R_y	-	+	dp
	B_1	10 T_x, R_z	+	+	dp
	B_2	6 T_z, R_x	+	+	dp
p- $C_6H_4F_2$, p- $C_6H_2F_4$ (Symmetry V_h)	A_{1g}	6	-	+	p
	A_{1u}	2	-	-	
	B_{1g}	1 R_y	-	+	dp
	B_{1u}	5 T_y	+	-	
	B_{2g}	5 R_z	-	+	dp
	B_{2u}	3 T_z	+	-	
	B_{3g}	3 R_x	-	+	dp
	B_{3u}	5 T_x	+	-	
Unsym- $C_6H_3F_3$ (Symmetry C_s)	A'	21 T_x, T_y, R_z	+	+	p
	A''	9 T_z, R_x, R_y	+	+	dp

*Plus and minus signs indicate "active" and "inactive," respectively.

†p = polarized. dp = depolarized

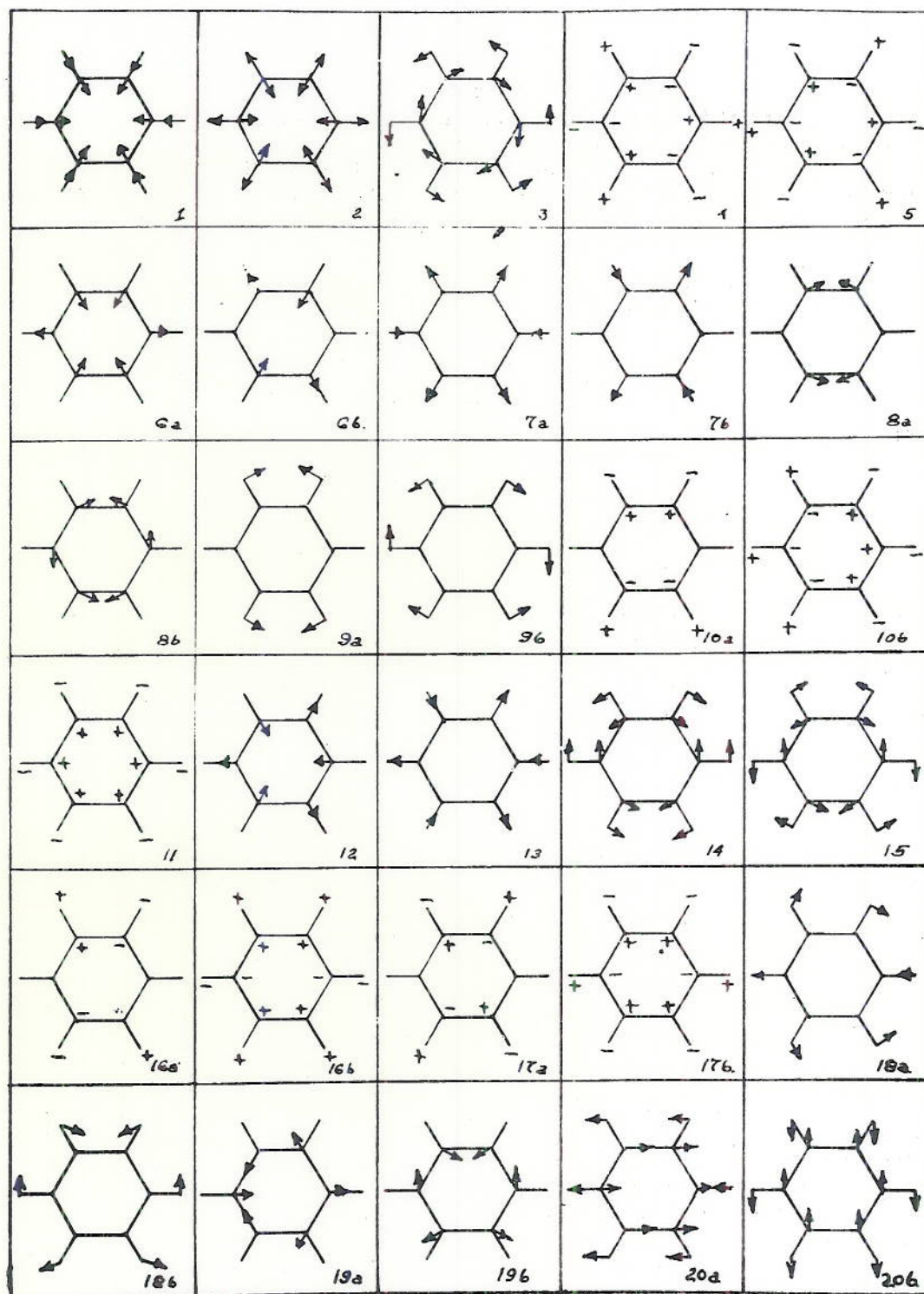


Figure 30 - Fundamental vibrations of benzene

The correlation between the symmetry species for the different molecular symmetry groups of interest are given in Table 63. The notation to be used for a given fundamental or pair of fundamentals is that given in the first column.

Assignment of Fundamentals for Fluorinated Benzenes

As an aid in following the assignments of the fundamentals for the fluorinated benzenes, Figure 31 shows graphically the positions and approximate intensities of all but the weak Raman or infrared bands. It also shows, as indicated by the arrows, the fundamentals corresponding to those of benzene that have been assigned for these compounds. The frequencies corresponding to the inactive fundamentals of benzene have been indicated by arrows extending downward to the base line. The infrared bands are indicated by dashed lines and the Raman bands by solid lines. If the same frequency occurs as a strong band in the infrared spectrum and as a medium band in the Raman effect, this is indicated by a line first dashed and then solid. If the intensity of a band in the Raman effect is high and the intensity in the infrared small, only the Raman band is indicated.

TABLE 63
Relations Between Symmetry Species of Group D_{6h}
and Its Sub-Groups

	D_{6h}	C_{2v}	V_h	C_s	C^*_{2v}
ν_1 (CC)	A_{1g}	A_1	A_{1g}	A'	A_1
ν_2 (CH)					
ν_3 ($H_{ }$)	A_{2g}	B_1	B_{2g}	A'	B_1
ν_4 (C_{\perp})	B_{2g}	B_2	B	A''	A
ν_5 (H_{\perp})					
ν_6 ($C_{ }$)	E_{2g}	A_1, B_1	A_{1g}, B_{2g}	$2A'$	A_1, B_1
ν_7 (CH)					
ν_8 (CC)					
ν_9 ($H_{ }$)					
ν_{10} (H_{\perp})	E_{1g}	A_2, B_2	B_{1g}, B_{3g}	$2A''$	B_2, A_2
ν_{11} (H_{\perp})	A_{2u}	B_2	B_{2u}	A''	B_2
ν_{12} ($C_{ }$)	B_{1u}	A_1	B_{1u}	A'	B_1
ν_{13} (CH)					
ν_{14} (CC)	B_{2u}	B_1	B_{3u}	A'	A_1
ν_{15} ($H_{ }$)					
ν_{16} (C_{\perp})	E_{2u}	A_2, B_2	A_{1u}, B_{2u}	$2A''$	A_2, B_2
ν_{17} (H_{\perp})					
ν_{18} ($H_{ }$)	E_{1u}	A_1, B_1	B_{1u}, B_{3u}	$2A'$	B_1, A_1
ν_{19} (CC)					
ν_{20} (CH)					

Table 64 gives in the first column the frequency designations of Wilson for the fundamentals of benzene, the frequency for these fundamentals in cm^{-1} , and the symmetry species for each fundamental. In columns 2, 3, 4, and 5 are given the frequencies of the bands which have been assigned to the corresponding fundamentals in the fluorinated benzenes and the symmetry species to which each belongs. Approximate frequency values and questionable assignments are indicated. Table 64 and Figure 31 show then the assignments which have been made and which are discussed in the following paragraphs.

The frequency shifts, as one goes from benzene to the fluorinated benzenes, will in general be toward lower frequencies, especially for the so-called H_{11} and H_{12} vibrations of benzene. It is convenient, therefore, to start the assignments at the high-frequency end of the spectra. Few contradictions or uncertainties will be encountered in the high-frequency region, but some ambiguity in the assignments may be expected for the lower frequency shifts. The fundamental frequencies to be assigned to the corresponding fundamentals of benzene must obey the selection rules given in Tables 62 and 63. In addition, the intensity of a band in the Raman or infrared spectrum may be expected to change only in a gradual manner as the degree of fluorine substitution increases. Thus, fundamentals that are only Raman-active in benzene will in general have only weak infrared bands associated with them in the fluorinated benzenes, and vice versa. The bands to be assigned to the fundamentals will further be required to have a similar pattern of frequency shifts as given in the previously discussed work on the deuterobenzenes (69, 72).

The degree of depolarization of the Raman bands of fluorobenzene, as given by Kohlrausch (5, p. 380), may be used in assigning the fundamentals of this compound, and the half-intensity width of the bands, which is usually a good indication of the polarization of a Raman band, will aid in assigning the fundamentals in the remaining compounds. Finally, the assignments of the fundamentals for each compound to the corresponding fundamentals of benzene must be consistent with the assignments of bands of higher frequency.

The fundamental ν_2 of benzene consists largely of symmetrical carbon-hydrogen stretching vibration. It is active in the Raman effect and has been assigned the value 3061.9 cm^{-1} . The ν_2 Raman band in fluorobenzene occurs at 3072.4 cm^{-1} . In p-difluorobenzene the frequency corresponding to ν_2 has again increased, occurring at 3083.7 cm^{-1} . In 1,2,4-trifluorobenzene it occurs at 3094 cm^{-1} , and in 1,2,4,5-tetrafluorobenzene it occurs at 3097.2 cm^{-1} . Except for the last compound, the increase is quite regular.

The remaining carbon-hydrogen stretching fundamentals of benzene which occur in this region are $\nu_7 = 3046.8 \text{ cm}^{-1}$, $\nu_{20} = 3063 \text{ cm}^{-1}$, and $\nu_{13} = 3071 \text{ cm}^{-1}$, the fundamentals ν_7 and ν_{20} being doubly degenerate. The dispersion in this region and the appearance of the infrared bands of the fluorinated benzenes are such that assignment of the bands to the corresponding fundamentals of benzene is difficult. Nevertheless, the fundamentals corresponding to ν_{13} and ν_{20} of benzene may be accounted for by strong infrared bands occurring around 1200 cm^{-1} and by a weak band around 3050 cm^{-1} in each of the fluorinated benzenes. In the Raman spectra of the fluorinated benzenes one of the fundamentals that corresponds to ν_7 of benzene is undoubtedly superimposed on the fundamental assigned to ν_2 . This is indicated by the diffuseness of the Raman band in each compound.

The benzene fundamental ν_8 has been assigned a value of 1596 cm^{-1} by Ingold et al. (69). There is little doubt that the medium Raman band occurring at 1602 cm^{-1} in fluorobenzene belongs to the fundamental of species A_1 . Since the corresponding band in benzene is depolarized, the rather high depolarization factor 0.77 given by Kohlrausch for this Raman band is to be expected. The very strong infrared band found at 1597 cm^{-1} may represent this same fundamental frequency. The corresponding band in p-difluorobenzene

TABLE 64
Assignment of Fundamentals for Fluorinated Benzenes

C_6H_6 cm^{-1}	C_6H_5F cm^{-1}	$p-C_6H_4F_2$ cm^{-1}	$1,2,4-C_6H_3F_3$ cm^{-1}	$p-C_6H_2F_4$ cm^{-1}
ν_1 992(A _{1g})	805.7(A ₁)	840.0(A _{1g})	780.6(A')	747.9(A _{1g})
ν_2 3061.9(A _{1g})	3072.4(A ₁)	3083.7(A _{1g})	3094(A')	3097.2(A _{1g})
ν_3 1326(A _{2g})				
ν_4 703(B _{2g})				
ν_5 995(B _{2g})		858.5(B _{3g})		
ν_6 606(E _{2g})	519.2(A ₁) 416(B ₁)	451.3(A _{1g}) 375.3(B _{2g})	441.6(A') 376.9(A')	417.0(A _{1g}) 294.6(B _{2g})
ν_7 3046.8(E _{2g})	1217.2(A ₁) ~3070(B ₁)	1245.0(A _{1g}) ~3080(B _{1g})	1308(A') ~3094(A')	1374.3(B _{1g}) ~3100(A _{1g})
ν_8 1596(E _{2g})	1602(A ₁)	1617(A _{1g})	1628(A')	1643(A _{1g})
ν_9 1178(E _{2g})	1156.4(A ₁) 612.6(B ₁)	1142.3(A _{1g}) 635.3(B _{2g})	1098.2(A') 688.2(A')	635.4(A _{1g}) 1121 or 1130(B _{2g})
ν_{10} 848.9(E _{1g})	829.1(A ₂)	800(B _{1g})	585.6(A'')	487.3(B _{1g})
ν_{11} 675(A _{2u})	499.2(B ₂)			
ν_{12} 1010(B _{1u})	1008.9(A ₁)	?1015(B _{1u})	963.7(A')	869(B _{1u})
ν_{13} 3071(B _{1u})	~3050(A ₁)	~3050(B _{1u})	~3050(A')	~1200(B _{1u})
ν_{14} 1310(B _{2u})				
ν_{15} 1150(B _{2u})				
ν_{16} 405(E _{2u})	242(B ₂)		161.3(A'')	
ν_{17} 975(E _{2u})	896(B ₂)	833(B _{2u})	727.8(A'')	461(B _{2u})
ν_{18} 1037(E _{1u})	1021.0(A ₁)	984(B _{1u})	854(A')	700(B _{1u})
ν_{19} 1485(E _{1u})	1457.1(A ₁) 1495.7(B ₁)	1437(B _{1u}) 1511(B _{3u})	1443(A') 1522(A')	1439(B _{1u}) 1534(B _{3u})
ν_{20} 3063(E _{1u})				

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of species A_{1g} occurs at 1617 cm^{-1} . The frequency continues to increase with fluorine substitution, occurring at 1628 (species A') and 1643 cm^{-1} (species A_{1g}) in 1,2,4-trifluoro- and 1,2,4,5-tetrafluorobenzene, respectively. The gradual increase in this symmetrical carbon-carbon stretching frequency is undoubtedly caused by the increase of the strength of the carbon-carbon bonds between carbons 2-3 and 5-6. This effect arises from the partial fixation of the "double bonds" in the benzene structure due to the allowed quinoidal resonance form. The assignment of the unsymmetrical fundamental arising from the degenerate fundamental ν_8 of benzene is uncertain.

The strong infrared band of benzene occurring at 1485 cm^{-1} (ν_{19}) is associated with a carbon-carbon stretching vibration. This fundamental should give rise to two frequencies in fluorobenzene active in both the Raman effect and the infrared, but since the corresponding frequency in benzene is active only in the latter, they should appear stronger in the infrared. The two bands occurring in the Raman spectrum of fluorobenzene at 1495.7 and 1457.1 cm^{-1} have been assigned to these fundamentals. The 1495.7 cm^{-1} band is diffuse and the weak band at 1457.1 cm^{-1} is quite sharp. Thus, the appearance of these two bands indicates the assignment of the totally symmetrical A_1 frequency to the lower value and the fundamental of species B_1 to the higher frequency. The infrared bands associated with these fundamental frequencies are those at 1499 cm^{-1} (strong) and at 1460 cm^{-1} (weak). In *p*-difluorobenzene the corresponding fundamentals should be active only in the infrared. Only two bands of any appreciable intensity occur in this region; they are found at 1511 cm^{-1} and 1437 cm^{-1} and have been assigned to the fundamentals of species B_{3u} and B_{1u} , respectively. In 1,2,4-trifluorobenzene both fundamentals are allowed in the Raman effect as well as in the infrared, but they should be stronger in the infrared, since the corresponding fundamental in benzene is Raman-inactive. The bands assigned to these two fundamentals occur in the infrared at 1522 cm^{-1} and 1443 cm^{-1} . There is another infrared band occurring in this region, but it is weaker than the two assigned and may be interpreted as an overtone. In the Raman spectrum two weak bands occur at 1517.9 (width 12 cm^{-1}) and 1441.3 (width 5.7 cm^{-1}). These Raman bands probably represent the same two fundamentals.

In 1,2,4,5-tetrafluorobenzene the two fundamentals should occur again only in the infrared spectrum. One band should be of type A with P, Q, and R branches of nearly equal intensity, and the other should be a type B band, i.e., a band having no Q branch. The band at 1534 cm^{-1} is not resolved but may be of type A. It is assigned to the B_{3u} fundamental. The strong band occurring at 1439 cm^{-1} is definitely of type B and is, therefore, assigned to the B_{1u} fundamental.

The degenerate carbon-hydrogen stretching vibration corresponding to ν_7 occurs in benzene at 3046.8 cm^{-1} and splits into two frequencies in the fluorinated benzenes. In fluorobenzene the fundamental of species A_1 , which is primarily a carbon-fluorine stretching vibration, occurs at 1217.2 cm^{-1} . Kohlrausch gives the depolarization factor for this band as 0.15, a value quite low for a band corresponding to a depolarized band in benzene. However, because of the position of this frequency in the remaining compounds, there appears to be little doubt about this assignment. In the infrared spectrum of fluorobenzene a strong band is found at 1220 cm^{-1} , whereas a weak band would be expected on the basis of the selection rules. It is not clear, therefore, whether this band belongs to the fundamental in question, especially since strong infrared bands occur in this region for the remainder of the compounds.

In 1,4-difluorobenzene this fundamental should be present only in the Raman effect and should be quite strong. Such a band occurs at 1245.0 cm^{-1} . The only other possibility appears to be a weaker band occurring at 1142.3 cm^{-1} , but this band may be given a more satisfactory interpretation. In 1,2,4-trifluorobenzene a band which may be associated

with this fundamental occurs at 1308 cm^{-1} in the Raman effect and at 1312 cm^{-1} in the infrared. In 1,2,4,5-tetrafluorobenzene a strong band occurs in the Raman spectrum at 1374.3 cm^{-1} with two weaker bands on each side. The strongest band must be assigned to the unsymmetrical carbon-fluorine stretching mode of species B_{2g} . The A_{1g} fundamental occurs in the 3100 cm^{-1} region.

At least one of the three strong infrared bands occurring at 1183, 1202, and 1212 cm^{-1} in the paradifluorobenzene corresponds to the degenerate benzene fundamental ν_{20} . As mentioned earlier, it is not certain whether the strong infrared band occurring in fluorobenzene at 1220 cm^{-1} represents one of the fundamental modes corresponding to ν_7 of benzene. It appears more probable that it is one of the fundamentals corresponding to ν_{20} , as are two of the bands occurring in the other derivatives. The three bands spread out in 1,2,4-trifluorobenzene, appearing at 1144, 1203, and 1250 cm^{-1} , and are strong in the infrared spectrum and weak in Raman effect. In 1,2,4,5-tetrafluorobenzene they occur only in the infrared, at 1164, 1222, and 1277 cm^{-1} , and have contour type A, type B, and probably type B, respectively. It appears that one of the type B bands should be assigned to the fundamental ν_{13} . The type A and the other type B band should be assigned to the fundamentals corresponding to ν_{20} , but the definite assignment of either ν_{13} or ν_{20} to one of the type B bands is uncertain.

The degenerate benzene fundamental ν_9 occurs at 1178 cm^{-1} and represents a bending of the hydrogen atoms in the plane of the ring. This frequency splits into two components in fluorobenzene. The fundamental of species A_1 , which should be represented by a polarized band, should suffer only a small frequency shift relative to benzene. The fundamental of species B_1 , which according to the data on deuterated benzenes should occur in the region from 600 to 750 cm^{-1} , should be depolarized in the Raman effect. The totally symmetrical mode has been identified with the strong Raman band having a depolarization factor 0.63 occurring in fluorobenzene at 1156.4 cm^{-1} , whereas the fundamental of species B_1 has been assigned to the depolarized band occurring at 612.6 cm^{-1} , which has a depolarization factor 0.92. In fluorobenzene these fundamentals should also occur in the infrared spectrum. There is a medium band at 1156 cm^{-1} but none has been found at 612 cm^{-1} . The interpretation of the asymmetrical mode, therefore, must be considered less satisfactory. Moreover, the lower frequency has an alternative interpretation as a band of species A_2 , which is forbidden in the infrared spectrum of fluorobenzene. In 1,4-difluorobenzene the fundamental of species A_{1g} occurs at 1142.3 cm^{-1} and in 1,2,4-trifluorobenzene the corresponding fundamental appears at 1098.2 cm^{-1} . In 1,2,4,5-tetrafluorobenzene this fundamental has changed from an $H_{||}$ vibration to an $F_{||}$ vibration, and it occurs at 635.4 cm^{-1} . It is significant in each case that these bands are sharp.

The unsymmetrical companion fundamental of species B_{2g} in 1,4-difluorobenzene may be assigned to the medium band occurring in the Raman effect at 635.3 cm^{-1} . A weak Raman band, which is probably this fundamental, occurs at 688.2 cm^{-1} in 1,2,4-trifluorobenzene. In 1,2,4,5-tetrafluorobenzene the corresponding fundamental should have approximately the same frequency as in benzene and may be represented by one of two Raman bands, 1121 or 1130 cm^{-1} .

The strong Raman band at 992 cm^{-1} in benzene represents the ring breathing fundamental ν_1 . This band is highly polarized, and the corresponding band should be strong and polarized in the monoderivative. The band at 805.7 cm^{-1} , with a depolarization factor 0.12, has been assigned to this fundamental in fluorobenzene. Langseth and Lord (72) have assigned the corresponding fundamentals which appear in the Raman spectra of the deuterated benzenes. Their work indicates a rather consistent decrease in frequency on going from fluorobenzene through the intermediate compounds to 1,2,4,5-tetrafluorobenzene. In 1,4-difluorobenzene this fundamental may be assigned to one of the strong

Raman bands, 840.0 or 858.5 cm^{-1} . Of these, 858.5 cm^{-1} has a weak infrared band associated with it and may be interpreted as the out-of-plane hydrogen bending fundamental corresponding to ν_5 . The lower band is, therefore, assigned to ν_1 . In 1,2,4-trifluorobenzene, the Raman band occurring at 780.6 cm^{-1} has been assigned to this fundamental. An alternative assignment would be the 727.8 cm^{-1} band. This band, however, may be assigned to one of the fundamentals of ν_{17} . In 1,2,4,5-tetrafluorobenzene there is a strong Raman band occurring at 747.9 cm^{-1} as well as a medium band at 635.4 cm^{-1} which has previously been assigned to the fundamental ν_9 , an $F_{||}$ vibration. The stronger band is assigned to ν_1 . The rather large frequency shifts indicated by this assignment for ν_1 in the fluorinated benzenes are surprising.

The benzene fundamental ν_{12} is largely a planar trigonal bending vibration. The frequency is known only indirectly but has been assigned the value of 1010 cm^{-1} by Ingold et al. (69). The highly polarized band which appears with considerable intensity at 1008.9 cm^{-1} in the Raman spectrum of fluorobenzene has been assigned to this fundamental. It should be somewhat infrared-active, but the two infrared bands occurring at 996 cm^{-1} and 1020 cm^{-1} would probably mask a weak band in this region. It is uncertain where this fundamental occurs in 1,4-difluorobenzene; however, it has been assigned to the weak infrared band at 1015 cm^{-1} . In 1,2,4-trifluorobenzene this fundamental has been identified with the 963.7 cm^{-1} band which occurs in both the Raman and the infrared spectrum. This fundamental occurs at 869 cm^{-1} in 1,2,4,5-tetrafluorobenzene as a very strong infrared band. There is a weak Raman band at 871.0 cm^{-1} which may be interpreted as a combination band. The contour of the infrared band of 1,2,4,5-tetrafluorobenzene appears to be a type B band which agrees with its assignment as ν_{12} of species B_{1u} .

The strong infrared band of benzene at 1037 cm^{-1} represents the ν_{18} fundamental. The vibration consists largely of an in-plane bending of the carbon-hydrogen bonds. In fluorobenzene the corresponding A_1 fundamental has shifted to 1020.0 cm^{-1} . The assignment in 1,4-difluorobenzene is less certain, but the B_{1u} fundamental is probably the weak band at 985 cm^{-1} in the infrared spectrum. In 1,2,4-trifluorobenzene there are two strong infrared bands at 809 cm^{-1} and 854 cm^{-1} , and the one of the higher frequency has been assigned to this fundamental. In 1,2,4,5-tetrafluorobenzene the infrared band corresponding to the ν_{18} fundamental of species B_{1u} should have a type B contour. It has been identified with the type B band which is observed at 700 cm^{-1} . Except possibly for 1,2,4-trifluorobenzene, these assignments appear to be quite satisfactory. The assignment of the other fundamental corresponding to ν_{18} cannot be made with certainty at this time.

The three Raman bands occurring at 996.8, 1008.9, and 1021.0 cm^{-1} in fluorobenzene have a composite depolarization factor of 0.07. It seems certain, therefore, that all three of these bands are of species A_1 . The two bands of higher frequency have been assigned satisfactorily to the fundamentals ν_{18} and ν_{12} . The lower band may be interpreted as an overtone ($2 \times 499.2 = 998.4$) of the fundamental ν_{11} and is enhanced by Fermi resonance.

Of particular interest in the remaining compounds is the absence of any but very weak bands in the region of 1000 cm^{-1} in the Raman and the infrared spectra of 1,4-difluorobenzene, 1,2,4-trifluorobenzene, and 1,2,4,5-tetrafluorobenzene.

The out-of-plane hydrogen frequency ν_{17} in benzene was formerly known only indirectly but had been assigned the value of 970 cm^{-1} by Ingold et al. (69). Recently, however, Mair and Hornig (73) have observed this fundamental at 975 cm^{-1} in the infrared spectrum of benzene in the solid state. This vibration splits into two fundamentals of species A_2 and B_2 . Of the nine out-of-plane fundamental vibrations of fluorobenzene three belong to species A_2 . Ingold et al. (69) have shown that only one, that which is symmetric to the center of symmetry in benzene, will be active in the Raman spectrum even though all are

allowed by the selection rules as given in Table 62. This effect arises because for all three of the fundamentals of species A_2 there is no motion of the fluorine atom, and it could be replaced with hydrogen without affecting these vibrations. The new symmetry (D_{6h}) which is thus introduced forbids the appearance of the fundamental of species A_2 corresponding to ν_{16} and ν_{17} (E_{2u}) but not the fundamental ν_{10} (E_{1g}). The B_2 fundamental is observed in the infrared at 896 cm^{-1} . In 1,4-difluorobenzene the corresponding infrared band occurs at 833 cm^{-1} . In 1,2,4-trifluorobenzene two strong bands occur both in the Raman and in the infrared spectrum at 780.6 and 727.8 cm^{-1} . The band of higher frequency is stronger and has already been assigned to ν_1 . Hence, the lower band is taken as a ν_{17} fundamental. In 1,2,4,5-tetrafluorobenzene only one strong infrared band, 461 cm^{-1} , occurs in the proper region; it has type C contour and therefore can definitely be assigned to one of the fundamentals corresponding to ν_{17} .

The out-of-plane vibration ν_{10} , of the hydrogen atoms, of benzene occurs at 848.9 cm^{-1} and is of species E_{1g} . It gives rise to two fundamentals in fluorobenzene of species A_2 and B_2 . Of these, the one of species A_2 should not differ appreciably in frequency from the benzene fundamental, since it does not involve motion of the fluorine atom. It has been identified with the Raman band at 829.1 cm^{-1} . In agreement with the selection rules for symmetry C_{2v} , it appears only in the Raman effect. In p-difluorobenzene the corresponding fundamental should still remain in this region, since the vibration does not involve any motion of the fluorine atoms. The Raman band at 800 cm^{-1} has been assigned to this fundamental. In 1,2,4-trifluorobenzene the frequency of this fundamental should lie considerably lower, since one of the fluorine atoms is now strongly involved in an out-of-plane vibration. The fundamental should be active in both the Raman effect and the infrared, but should appear particularly strong in the Raman spectrum. The Raman and infrared band at 585.6 cm^{-1} has been assigned to this fundamental. In 1,2,4,5-tetrafluorobenzene the strong Raman band at 487.3 cm^{-1} has been identified with the corresponding fundamental. This now represents an out-of-plane bending of the fluorine atoms. The other ν_{10} fundamental has not been assigned; it should occur at a considerably lower frequency.

The fundamental ν_6 in benzene consists essentially of a stretching and contraction of the carbon ring brought about almost entirely by the bending of the ring angles rather than by alteration of the bond lengths. The value of this degenerate fundamental is given by Ingold et al. (69) as 605.6 cm^{-1} . The corresponding A_1 fundamental in fluorobenzene occurs at 519.2 cm^{-1} , and the fundamental of species B_1 has been assigned to the weak Raman band, 416 cm^{-1} . In 1,4-difluorobenzene the fundamentals have been assigned to the Raman bands 451.3 cm^{-1} of species A_{1g} and 375.3 cm^{-1} of species B_{2g} . It is worth noting that these frequencies are considerably lower than might be expected. If these assignments are correct, then the character of the benzene ring must have been altered considerably by the fluorine substitution. In 1,2,4-trifluorobenzene these fundamentals have been identified with the Raman bands at 441.6 and 376.9 cm^{-1} . There is a weak infrared band associated with the former band. In 1,2,4,5-tetrafluorobenzene the A_g fundamental occurs at 417.0 cm^{-1} and the B_{2g} at 294.6 cm^{-1} .

The fundamental ν_{16} of benzene occurs at 405 cm^{-1} and corresponds to an out-of-plane bending motion of the carbon ring. Although this fundamental is inactive in both the Raman effect and the infrared, according to the selection rules, it has been observed by Plyler (76) in the infrared spectrum of liquid benzene. In fluorobenzene the corresponding B_2 fundamental occurs at a considerably lower frequency, whereas the A_2 fundamental should not be shifted much. Ingold et al. (69) have shown that the symmetrical species A_2 in the monoderivative should be inactive since this fundamental does not involve the motion of the fluorine atoms. This has been discussed in regard to one of the other out-of-plane bending fundamentals ν_{17} of species E_{2u} . The B_2 fundamental may be identified with the

Wave N
cm

75
99
106
162
169
173

178
191

196

202

211

221

231

235

244

249

274

294

297

318

106

130

132

139

153

162

165

167

169

171

177

187

196

198

202

207

208

211

212

217

222

226

230

TABLE 65
 Raman and Infrared Bands of Fluorobenzenes Interpreted as Combination or Overtone Bands

Wave Number cm ⁻¹	Description	Interpretation	Wave Number cm ⁻¹	Description	Interpretation
Fluorobenzene (Raman)			Fluorobenzene (Infrared)		
754.4	w	242 + 519 = 761 (B ₂)	2313	vvw	2 x 1156 = 2312 (A ₁)
996.8	s	2 x 499 = 998 (A ₁)	2351	vvw	896 + 1457 = 2353 (B ₂)
1065.2	w	829 + 242 = 1071 (B ₁)	2375	vvw	1156 + 1217 = 2373 (A ₁)
1623	vw	612 + 1009 = 1621 (B ₁)	2400	vvw	806 + 1602 = 2408 (A ₁)
1693	vvvw	806 + 896 = 1702 (B ₂)	2434	vvw	2 x 1217 = 2434 (A ₁)
1735	vvvw	242 + 1496 = 1738 (B ₂)	2484	vvvw	1021 + 1457 = 2478 (A ₁)
		519 + 1217 = 1736 (A ₁)	2503	vvvw	1021 + 1496 = 2517 (B ₁)
1789	vvvw	2 x 896 = 1792 (A ₁)	2649	vvw	1156 + 1496 = 2652 (B ₁)
1915	vvvw	416 + 1496 = 1922 (A ₁)	2713	vvvw	1217 + 1496 = 2713 (B ₁)
		896 + 1021 = 1917 (B ₂)	2747	vvvw	1156 + 1602 = 2758 (A ₁)
1960	vvvw	806 + 1156 = 1962 (A ₁)	2821	vvvw	1217 + 1602 = 2819 (A ₁)
		499 + 1457 = 1956 (B ₂)	2915	vvvw	2 x 1457 = 2914 (A ₁)
2022	vvvw	2 x 1009 = 2018 (A ₁)	3053	s	1602 + 1457 = 3059 (A ₁)
		806 + 1217 = 2023 (A ₁)	3193	vvw	2 x 1602 = 3204 (A ₁)
		416 + 1602 = 2018 (B ₂)	3317	vvvw	242 + 3072 = 3314 (B ₂)
2117	vvvw	519 + 1602 = 2121 (A ₁)	3480	vvvw	416 + 3072 = 3488 (B ₁)
		896 + 1217 = 2113 (B ₂)	4080	vvw	1009 + 3072 = 4081 (A ₁)
2214	vvvw	613 + 1602 = 2215 (B ₁)	4290	vvw	1717 + 3072 = 4290 (A ₁)
		1009 + 1217 = 2226 (A ₁)	4670	vvw	1602 + 3072 = 4674 (A ₁)
2313	vvvw	2 x 1156 = 2312 (A ₁)	p-Difluorobenzene (Raman)		
2359	vvvw	896 + 1457 = 2353 (B ₂)		w	451 + 840 = 1291 (A _{1g})
2443	vvvw	2 x 1217 = 2434 (A ₁)	1285.1		
2491	vvw	896 + 1602 = 2498 (B ₂)	1414	vvvw	635 + 800 = 1435 (B _{3g})
		1009 + 1496 = 2505 (B ₁)	1473	vvvw	635 + 840 = 1475 (B _{2g})
		1021 + 1457 = 2478 (A ₁)	1605	vvw	2 x 800 = 1600 (A _{1g})
2745.3	vvw	1156 + 1602 = 2758 (A ₁)	1668	vvvw	2 x 833 = 1666 (A _{1g})
2948	vvvw	1457 + 1496 = 2953 (B ₁)	1691	vvvw	451 + 1245 = 1696 (A _{1g})
2978.9	vvw	2 x 1496 = 2992 (A ₁)			840 + 859 = 1699 (B _{3g})
3184	w	2 x 1602 = 3204 (A ₁)	1849	vvvw	833 + 1015 = 1848 (B _{3g})
Fluorobenzene (Infrared)			2282	vvvw	2 x 1142 = 2284 (A _{1g})
1066	s	242 + 829 = 1071 (B ₁)	2393	vvvw	1142 + 1245 = 2387 (A _{1g})
1302	vw	806 + 499 = 1305 (B ₂)	2420	vvvw	984 + 1437 = 2421 (A _g)
1326	w	806 + 519 = 1325 (A ₁)	2464	vvvw	859 + 1617 = 2476 (B _{3g})
1397	vw	896 + 499 = 1395 (A ₁)			840 + 1617 = 2457 (A _{1g})
1531	w	519 + 1009 = 1528 (A ₁)	2492	vvvw	2 x 1245 = 2490 (A _{1g})
		1021 + 519 = 1540 (A ₁)			984 + 1511 = 2495 (B _{2g})
1624	vw	613 + 1009 = 1622 (B ₁)	3005	w	2 x 1511 = 3022 (A _{1g})
1652	vvw	2 x 829 = 1658 (A ₁)	3230	vvvw	2 x 1617 = 3234 (A _{1g})
1676	vvw	520 + 1156 = 1676 (A ₁)	p-Difluorobenzene (Infrared)		
1695	vvw	806 + 896 = 1702 (B ₂)	1350	vvvw	375 + 984 = 1359 (B _{3u})
1714	w	499 + 1217 = 1716 (B ₂)	1437	m	451 + 984 = 1435 (B _{1u})
1778	vw	613 + 1156 = 1769 (B ₁)	1634	m	800 + 833 = 1633 (B _{3u})
		2 x 896 = 1792 (A ₁)	1805	vvvw	375 + 1437 = 1812 (B _{3u})
1874	vvw	416 + 1457 = 1873 (B ₁)	1868	m	859 + 1015 = 1874 (B _{3u})
1962	vw	806 + 1156 = 1962 (A ₁)	1978	w	833 + 1142 = 1975 (B _{2u})
1984	vvw	519 + 1457 = 1976 (A ₁)	2056	w	635 + 1437 = 2072 (B _{3u})
2021	vw	806 + 1217 = 2023 (A ₁)	2125	vvvw	984 + 1142 = 2126 (B _{1u})
2070	vvw	613 + 1457 = 2070 (B ₁)	2151	vvw	1015 + 1142 = 2157 (B _{1u})
2085	vvw	499 + 1602 = 2101 (B ₂)			635 + 1511 = 2146 (B _{1u})
2113	vvw	896 + 1217 = 2113 (B ₂)	2228	w	984 + 1245 = 2229 (B _{1u})
2129	vvw	519 + 1602 = 2121 (A ₁)	2257	vvvw	1015 + 1245 = 2260 (B _{1u})
2175	vvw	1021 + 1156 = 2177 (A ₁)	2273	vvvw	840 + 1437 = 2277 (B _{1u})
2222	vw	1009 + 1217 = 2226 (A ₁)	2296	vvw	859 + 1437 = 2296 (B _{2u})
2261	vvw	806 + 1457 = 2263 (A ₁)			800 + 1511 = 2311 (B _{2u})
2302	vvw	806 + 1496 = 2302 (B ₁)	2345	vvw	840 + 1511 = 2351 (B _{3u})

TABLE 65 (Cont.)
Raman and Infrared Bands of Fluorobenzenes Interpreted as Combination or Overtone Bands

Wave Number cm ⁻¹	Description	Interpretation	Wave Number cm ⁻¹	Description	Interpretation
p-Difluorobenzene (Infrared)			1,2,4-Trifluorobenzene (Infrared)		
2444	vvw	833 + 1617 = 2450 (B _{2u})	2086	vw	781 + 1308 = 2089 (A')
2627	vvvw	1015 + 1617 = 2632 (B _{1u})	2102	vvvw	586 + 1522 = 2108 (A'')
2646	vvvw	1142 + 1511 = 2653 (B _{3u})	2132	vvvw	688 + 1443 = 2131 (A')
2687	vvvw	1245 + 1437 = 2682 (B _{1u})	2165	vvw	728 + 1443 = 2171 (A'')
2749	vvvw	1245 + 1511 = 2756 (B _{3u})			854 + 1308 = 2162 (A')
3064	vw	1437 + 1617 = 3054 (B _{1u})	2196	vvw	2 x 1098 = 2196 (A')
3124	vw	1511 + 1617 = 3128 (B _{3u})	2211	vvw	586 + 1628 = 2214 (A'')
3940	vvvw	833 + 3084 = 3917 (B _{2u})			688 + 1522 = 2210 (A')
4100	vvvw	1015 + 3084 = 4099 (B _{1u})	2235	vvvw	781 + 1443 = 2224 (A')
4500	vvvw	1437 + 3084 = 4521 (B _{1u})	2246	vw	728 + 1522 = 2250 (A'')
4590	vvvw	1511 + 3084 = 4595 (B _{3u})	2300	vw	781 + 1522 = 2303 (A')
					854 + 1443 = 2297 (A')
1,2,4-Trifluorobenzene (Raman)			2356	vvw	728 + 1628 = 2356 (A'')
601	w	161 + 442 = 603 (A'')	2404	vw	1098 + 1308 = 2406 (A')
1064	vw	377 + 688 = 1065 (A')			964 + 1443 = 2407 (A')
1231.6	vvw	377 + 854 = 1231 (A')			781 + 1628 = 2409 (A')
1250	w	161 + 1098 = 1259 (A'')	2480	vvw	854 + 1628 = 2482 (A')
1287.5	vw	442 + 854 = 1296 (A')			964 + 1522 = 2486 (A')
1375.5	w	2 x 688 = 1376 (A')	2537	vw	1098 + 1443 = 2541 (A')
1708	vvw	2 x 854 = 1708 (A')	2581	vvw	964 + 1628 = 2592 (A')
3062	vw	1443 + 1628 = 3071 (A')	2615	vvw	2 x 1308 = 2616 (A')
					1098 + 1522 = 2620 (A')
1,2,4-Trifluorobenzene (Infrared)			2726	vvw	1098 + 1628 = 2726 (A')
603	s	161 + 442 = 603 (A'')	2765	vvvw	1308 + 1443 = 2751 (A')
753	m	2 x 377 = 754 (A')	2822	vvw	1308 + 1522 = 2830 (A')
		161 + 586 = 747 (A')	2882	vvvw	2 x 1443 = 2886 (A')
1014	vvw	161 + 854 = 1015 (A'')	3914	vvw	1308 + 1628 = 2936 (A')
1059	vw	377 + 688 = 1065 (A')	3142	vvw	1522 + 1628 = 3150 (A')
1171	m	2 x 586 = 1172 (A')	3700	vvvw	586 + 3094 = 3680 (A'')
1250	vs	161 + 1098 = 1259 (A'')	3820	vvvw	728 + 3094 = 3822 (A'')
1287	m	442 + 854 = 1296 (A')	3880	vvvw	781 + 3094 = 3875 (A')
1376	w	2 x 688 = 1376 (A')	4050	vvvw	964 + 3094 = 4058 (A')
1406	m	442 + 964 = 1406 (A')	4220	vvvw	1098 + 3094 = 4192 (A')
1460	s	2 x 728 = 1456 (A')	4410	vvvw	1308 + 3094 = 4402 (A')
		688 + 781 = 1469 (A')	4520	vvvw	1443 + 3094 = 4537 (A')
		161 + 1308 = 1469 (A'')	4690	vvvw	1628 + 3094 = 4722 (A')
1550	m	586 + 964 = 1550 (A'')			
1575	w	728 + 854 = 1582 (A'')	1,2,4,5-Tetrafluorobenzene (Raman)		
1645	w	688 + 964 = 1652 (A')	591	vw	2 x 295 = 590 (A _{1g})
1685	vw	377 + 1308 = 1685 (A')	783	vvw	295 + 487 = 782 (B _{3g})
		586 + 1098 = 1684 (A'')	832	w	2 x 417 = 834 (A _{1g})
		161 + 1522 = 1683 (A'')	920	vw	2 x 461 = 922 (A _{1g})
1691	vw	728 + 964 = 1692 (A'')	1121	w	487 + 635 = 1122 (B _{1g})
1743	vw	781 + 964 = 1745 (A')	1164	vvw	417 + 748 = 1165 (A _{1g})
		442 + 1308 = 1750 (A')			461 + 700 = 1161 (A _{1g})
1788	vw	161 + 1628 = 1789 (A'')	1272	vvw	2 x 635 = 1270 (A _{1g})
		688 + 1098 = 1786 (A')	1335	w	461 + 869 = 1330 (A _{1g})
1826	w	728 + 1098 = 1826 (A'')			295 + 1130 = 1325 (A _{1g})
		377 + 1443 = 1820 (A')	1402.1	w	2 x 700 = 1400 (A _{1g})
1868	w	781 + 1098 = 1879 (A')	1574	vvw	700 + 869 = 1569 (A _{1g})
1893	vvw	586 + 1308 = 1894 (A')	1610	vw	487 + 1130 = 1617 (B _{3g})
		377 + 1522 = 1899 (A')	1734	vvw	2 x 869 = 1738 (A _{1g})
1926	vvw	2 x 964 = 1928 (A')	1782	vvw	417 + 1374 = 1791 (B _{1g})
1945	vvvw	854 + 1098 = 1952 (A')	1864	vvw	487 + 1374 = 1861 (A _{1g})
1961	vvvw	442 + 1522 = 1964 (A')	2316	vvw	869 + 1439 = 2308 (A _{1g})
2028	vw	586 + 1443 = 2029 (A'')			
		728 + 1308 = 2036 (A'')	1,2,4,5-Tetrafluorobenzene (Infrared)		
2061	vvw	964 + 1098 = 2062 (A')	755	w	295 + 461 = 756 (B _{3u})
		442 + 1628 = 2070 (A')	990	vw	295 + 700 = 995 (B _{3u})

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TABLE 65 (Cont.)
Raman and Infrared Bands of Fluorobenzenes Interpreted as Combination or Overtone Bands

Wave Number cm ⁻¹	Description	Interpretation	Wave Number cm ⁻¹	Description	Interpretation
1,2,4,5-Tetrafluorobenzene (Infrared)			1,2,4,5-Tetrafluorobenzene (Infrared)		
1100	w	461 + 635 = 1096 (B _{1u})	2105	vvvw	461 + 1643 = 2104 (B _{1u})
1121	m	417 + 700 = 1117 (B _{1u})	2165	vvvw	635 + 1534 = 2169 (B _{3u})
1277	s	417 + 869 = 1286 (B _{1u})	2182	vvvw	748 + 1439 = 2187 (B _{1u})
1339	m	635 + 700 = 1335 (B _{1u})	2279	vw	748 + 1534 = 2282 (B _{3u})
1451	w	700 + 748 = 1448 (B _{1u})	2340	w	700 + 1643 = 2343 (B _{1u})
1511	s	635 + 869 = 1504 (B _{1u})	2490	vw	869 + 1643 = 2512 (B _{1u})
1819	m	700 + 1130 = 1830 (B _{3u})	2564	vvw	1130 + 1439 = 2569 (B _{3u})
1830	w	295 + 1534 = 1829 (B _{1u})	2649	vw	1130 + 1534 = 2664 (B _{1u})
1857	vw	417 + 1439 = 1856 (B _{1u})	2918	w	1374 + 1534 = 2908 (B _{2u})
1950	vvw	417 + 1534 = 1951 (B _{3u})	3176	vw	1534 + 1643 = 3177 (B _{3u})
2020	vvvw	487 + 1534 = 2021 (B _{2u})	4520	vvvw	1439 + 3097 = 4536 (B _{1u})
2069	vvw	635 + 1439 = 2074 (B _{1u})			

Raman band occurring at 242 cm⁻¹. Assignment cannot be made for the corresponding fundamentals of p-difluorobenzene and 1,2,4,5-tetrafluorobenzene, since they are both forbidden in the Raman effect and since the infrared data do not extend to this region. In 1,2,4-trifluorobenzene the medium Raman band at 161.3 cm⁻¹ is probably one of the fundamentals, and the other fundamental may be either 288.1 cm⁻¹ or 341 cm⁻¹.

Although the assignment of fundamentals for the fluorinated benzenes discussed above is incomplete and somewhat tentative, it has been possible to give a satisfactory explanation of many of the observed infrared and Raman bands on the basis of the assigned fundamentals listed in Table 64. Those bands which have been interpreted as combinations or overtones are listed in Table 65.

Assignment of Fundamentals for Fluorotoluenes

In the interpretation of the fluorinated toluenes, the spectrum of toluene itself may be chosen as the initial basis for determination of the frequency shifts that occur when a fluorine atom is substituted into the ortho or para positions of the aromatic ring. However, since the assignments have been made for the fluorinated benzenes, and since the mass of the CH₃ group is not greatly different from that of a fluorine atom, the interpretation may be made much easier by considering the relation between the spectra of the fluorinated toluenes and the fluorinated benzenes. Except for the C-H stretching modes of the CH₃ group, lying in the region from 2900 to 3010 cm⁻¹, and the C-H bending modes, lying between 1360 and 1450 cm⁻¹, the spectra of p-difluorobenzene and p-fluorotoluene would be expected to be practically identical and this is found to be the case as may be seen from Figures 37 and 38.

To a first approximation p-fluorotoluene may then be considered as belonging to the symmetry group V_h. The number and species of the various modes of vibration for p-fluorotoluene will then be the same as those given in Table 62 for p-difluorobenzene. To these must be added the above-mentioned modes associated with the CH₃ group.

The molecule of o-fluorotoluene will similarly be taken as belonging to the symmetry group C_{2v} with a symmetry plane perpendicular to the plane of the molecule and to a line joining the fluorine atom and the CH₃ group. The symmetry species, the number of vibrations, and the selection and the polarization rules are given in Table 66.

TABLE 66
Normal Vibrations of o-C₆H₄FCH₃ (Symmetry C_{2v})

Symmetry Species	Number of Vibrations	Selection Rules		Polarization
		Infrared	Raman	
A ₁	T _x	+	+	p
A ₂	5 R _x	-	+	dp
B ₁	10 T _x R _z	+	+	dp
B ₂	4 T _z R _y	+	+	dp

The spectrum of o-fluorotoluene does not correspond to any of the fluorinated benzenes studied. However, a number of the bands would be expected to occur in similar positions, as in the spectrum of fluorobenzene. Langseth and Lord (72) have obtained the Raman spectrum of deuterobenzene and o-dideuterobenzene which are of symmetry C_{2v} and C_{2v} respectively. They assigned most of the fundamentals, and their results have been used in the present work to estimate the differences in frequency shifts between molecules of these two symmetry groups.

The selection rules given in Tables 62 and 66 are, of course, obeyed only approximately. Strictly speaking, all thirty fundamentals are allowed to appear in both the Raman effect and the infrared. However, the intensities of the bands may be used as an indication of whether or not the fundamentals are predominantly Raman- or infrared-active.

The infrared and Raman spectra of o-fluoro- and p-fluorotoluene along with the fluorinated benzenes are shown graphically in Figure 31. This figure shows the correlations of the fundamentals of these compounds that correspond to those of benzene. In addition, a summary of the assignments for the fluorinated toluenes is given in Table 67.

The rather strong Raman band occurring in p-fluorotoluene at 3070.6 cm⁻¹ and in o-fluorotoluene at 3069 cm⁻¹ may be associated with the symmetrical carbon-hydrogen stretching mode ν_2 in benzene. The infrared spectrum reveals a weak band occurring at 3069 cm⁻¹ for p-fluorotoluene and a medium band occurring at 3067 cm⁻¹ in o-fluorotoluene. These two bands probably correspond to the unsymmetrical stretching fundamental ν_{20} of species B_{3u} for p-fluorotoluene and of species A₁ for o-fluorotoluene. The high values of the half-intensity widths of many of the Raman bands occurring in this region in the spectrum of the fluorinated aromatics probably result because of the overlapping of ν_2 and one of the fundamentals corresponding to ν_{20} .

The unsymmetrical C-H stretching mode ν_{13} is inactive in benzene and is known only indirectly. It has been assigned the value of 3071 cm⁻¹ on the basis of Leberknight's (77) data of the infrared spectrum of gaseous benzene. The corresponding fundamental occurs at 3043 cm⁻¹ in the infrared spectrum of p-fluorotoluene and at 3045 cm⁻¹ in the infrared spectrum of o-fluorotoluene. These bands are observed in the infrared spectra. The failure to observe a weak Raman band at this frequency in o-fluorotoluene may be caused by the presence of the 5025.64 Å mercury line which corresponds to a shift of 3045.6 cm⁻¹.

In the frequency region from 2920 cm⁻¹ to 3010 cm⁻¹, there occur in both compounds at least one strong and several weak Raman bands and several weak infrared bands, all of which may be attributed to the stretching modes of the CH₃ group.

TABLE 67
Assignment of Fundamentals for Fluorinated Toluenes

	C_6H_6	$p-C_6H_4FCH_3$	$o-C_6H_4FCH_3$
ν_1	992(A_{1g})	825.0(A_{1g})	
ν_2	3061.9(A_{1g})	3070.6(A_{1g})	3069(A_1)
ν_3	1326(A_{2g})		
ν_4	703(B_{2g})		
ν_5	995(B_{2g})	842.5(B_{3g})	
ν_6	606(E_{2g})	?454.1(A_{1g}) ?340.6(B_{2g})	?426.8(A_1) ?271.9(B_1)
ν_7	3046.8(E_{2g})	1214.5(A_{1g})	1234.3(A_1)
ν_8	1596(E_{2g})	1614(A_{1g}) 1601(B_{2g})	1620(A_1) 1589.0(B_1)
ν_9	1178(E_{2g})	1157.3(A_{1g}) 637.9(B_{2g})	1038.0(A_1) 704(B_1)
ν_{10}	848.9(E_{1g})		
ν_{11}	675(A_{2u})	?502.3(B_{2u})	?525.5(B_2)
ν_{12}	1010(B_{1u})	929(B_{1u})	
ν_{13}	3071(B_{1u})	3043(B_{1u})	3045(B_1)
ν_{14}	1310(B_{2u})		
ν_{15}	1150(B_{2u})		
ν_{16}	405(E_{2u})	?152(B_{2u})	?186(B_2)
ν_{17}	975(E_{2u})	817(B_{2u})	754(B_2)
ν_{18}	1037(E_{1u})	1016.6(B_{1u})	839(B_1)
ν_{19}	1485(E_{1u})	1513(B_{3u})	1499(B_1) 1460 or 1471(A_1)
ν_{20}	3063(E_{1u})	~ 3070(B_{3u}) 1221(B_{1u})	~ 3070(A_1) 1188(B_1)

The benzene fundamental ν_8 which is inactive in the infrared spectrum has been assigned the value of 1596 cm^{-1} . This fundamental gives rise to two frequencies in the fluorinated toluenes, one a symmetrical carbon-carbon stretching mode involving not the motion of the para constituents but only the carbon atoms on opposite sides of the ring. As in the case of the fluorinated benzenes, the frequency of this mode should increase, since the substitution of the fluorine atom causes a "partial fixation of the double bonds." The Raman band at 1614 cm^{-1} in p-fluorotoluene corresponds to this fundamental ν_8 of species A_{1g} , and the Raman band at 1601 cm^{-1} corresponds to the other fundamental of species B_{2g} . The corresponding fundamentals occur in o-fluorotoluene at 1620 and 1589.0 cm^{-1} , respectively.

The infrared-active carbon-carbon stretching frequency corresponding to the fundamental ν_{19} of benzene occurs at 1485 cm^{-1} . This fundamental, as in the fluorinated benzenes, splits into two components which remain in the region from 1440 to 1540 cm^{-1} . In the case of the fluorinated benzenes the lower frequency has been assigned to the symmetrical carbon-carbon stretching mode. In p-fluorotoluene the medium infrared band occurring at 1513 cm^{-1} may be assigned to the fundamental of species B_{3u} , whereas the position of the fundamental of species B_{1u} is uncertain. In o-fluorotoluene the fundamental of species B_1 corresponds to the observed infrared band at 1499 cm^{-1} , and one of the two weak infrared bands occurring at 1460 and 1471 cm^{-1} is probably to be interpreted as the fundamental $\nu_{19}(A_1)$. In the region from 1370 to 1460 cm^{-1} there occur in both compounds several weak infrared and Raman bands ascribable to the C-H bending modes of the CH_3 group.

In p-fluorotoluene there appear two strong Raman bands at 1214.5 cm^{-1} and 1221.4 cm^{-1} and a strong infrared band at 1224 cm^{-1} . The lower Raman frequency in p-fluorotoluene must be interpreted as the symmetrical stretching frequency corresponding to ν_7 . The Raman band occurring at 1221 cm^{-1} and the infrared band at 1224 cm^{-1} probably both originate in the degenerate benzene fundamental ν_{20} and are of species B_{1u} . In benzene, ν_{20} primarily involves alternate stretching and compression of the bonds in the para positions. The corresponding fundamentals in p-difluorobenzene occur at 1245 cm^{-1} , and one of the bands at 1184 and 1212 cm^{-1} belongs to species B_{1u} arising from ν_{20} . As mentioned earlier, the selection rules are obeyed only approximately for this molecule, and the fundamentals which involve stretching or bending of the carbon-hydrogen bonds of the CH_3 group or of carbon-fluorine bonds should show greater violations of the selection rules than do the fundamentals involving C-C ring vibrations. In the Raman and infrared spectra of o-fluorotoluene this ν_7 fundamental appears with high intensity at 1234.3 and 1236 cm^{-1} respectively. The stretching frequency corresponding to the other fundamental of ν_{20} may be correlated with the strong infrared band at 1188 cm^{-1} .

The degenerate in-the-plane hydrogen bending fundamental ν_9 occurs in benzene at 1178 cm^{-1} . As in the case of the fluorinated benzenes, this frequency splits. In the para compound the symmetrical mode, A_{1g} , should occur at approximately the same frequency as in benzene; but the unsymmetrical mode, B_{2g} , should appear somewhere in the region from 600 to 650 cm^{-1} .

The symmetrical ν_9 fundamental appears at 1157.3 cm^{-1} in both the Raman and the infrared spectrum of p-fluorotoluene. The unsymmetrical mode has been assigned to the Raman and infrared bands occurring at 637.9 cm^{-1} . These frequencies correspond quite closely to those for p-difluorobenzene. The assignment of these fundamentals is less certain for o-fluorotoluene, but they are probably to be identified with the bands at 1038.0 and 704 cm^{-1} . The fundamental of species B_{1u} in p-fluorotoluene may be identified with a weak sharp Raman band at 1016.6 cm^{-1} which corresponds to a weak infrared band at

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1017 cm^{-1} . The mode of species B_1 in the ortho derivative would be expected to occur at a lower frequency and has been assigned to the strong infrared band at 839 cm^{-1} .

The Raman and infrared spectra of the fluorinated toluenes have a number of weak bands in the 1000 cm^{-1} region, in contrast to those of 1,4-difluorobenzene, 1,2,4-trifluorobenzene, and 1,2,4,5-tetrafluorobenzene. However, most of these bands can easily be explained as overtones.

The position of the symmetrical trigonal breathing frequency ν_{12} in the fluorotoluenes is uncertain, though in p-fluorotoluene it is probably represented by the infrared band appearing at 929 cm^{-1} .

The symmetrical breathing frequency ν_1 of benzene occurs at 992 cm^{-1} . As in the case of p-difluorobenzene, this frequency is much lower (825.0 cm^{-1}) in p-fluorotoluene than in benzene. As in p-difluorobenzene, the Raman band is accompanied by a strong band on the long-wavelength side which also appears weakly in the infrared spectrum. This band probably corresponds to the inactive benzene fundamental ν_5 associated with the symmetrical out-of-plane bending of the carbon-hydrogen bonds. The frequency of the band that may correspond to ν_5 is 842.5 cm^{-1} in p-fluorotoluene and 858.5 cm^{-1} in p-difluorobenzene.

The out-of-plane hydrogen bending mode ν_{17} is degenerate and inactive in benzene. Thompson and Temple (47) have correlated with this fundamental the strong infrared band occurring in p-fluorotoluene and o-fluorotoluene at 817 and 754 cm^{-1} respectively. Since A_{1u} vibrations are inactive in both the Raman effect and the infrared for para derivatives, this vibration must belong to species B_{2u} in p-fluorotoluene. Though both are allowed in o-fluorotoluene, the fundamental of species A_2 in this compound cannot be assigned with certainty. The fundamental of species B_2 is correlated with the 754 cm^{-1} infrared band.

The fundamentals occurring in the lower frequency range cannot be assigned without ambiguity. In the case of p-fluorotoluene the bands occurring in the Raman effect at 502.3, 454.1, and 340.6 cm^{-1} are probably to be ascribed to ν_{11} and to the two frequencies contributed by the degenerate fundamental ν_6 . The band occurring at 152 cm^{-1} probably belongs to one of the fundamentals corresponding to ν_{16} , an out-of-plane motion of the carbon atoms. The bands that may be assigned to the corresponding fundamentals of o-fluorotoluene are probably $\nu_{11} = 525.5 \text{ cm}^{-1}$, $\nu_6 = 426.8$ and 271.9 cm^{-1} , and $\nu_{16} = 186 \text{ cm}^{-1}$, though these values are more uncertain than for p-fluorotoluene.

The observed bands which can be explained satisfactorily as combinations or overtones of the fundamentals proposed in the present assignment are listed in Table 68.

Assignment of Fundamentals for Benzotrifluorides

The Raman and infrared spectra of benzotrifluoride, m-fluorobenzotrifluoride and 2,5-difluorobenzotrifluoride are very complex. Benzotrifluoride may be considered as belonging to the symmetry group C_{2v} , whereas the other two compounds may to the same approximation be regarded as having a symmetry plane and belonging to the symmetry group C_s . The selection rules for these compounds are obviously of little help. Consequently, assignments for these compounds are not as complete as are those for the other fluorinated aromatics, and they are not included in Figure 31. The proposed assignments are summarized, however, in Table 69.

The predominantly Raman-active C-H stretching fundamental ν_2 in benzotrifluoride is observed at 3076 cm^{-1} , which is near the frequency 3072.4 cm^{-1} observed in fluorobenzene.

TABLE 68
Raman and Infrared Bands of Fluorotoluenes Interpreted as Combination or Overtone Bands

Wave Number cm ⁻¹	Description	Interpretation	Wave Number cm ⁻¹	Description	Interpretation
p-Fluorotoluene (Raman)			o-Fluorotoluene (Raman)		
908	vvvw	2 x 454 = 908 (A ₁ g)	1281.2	w	526 + 754 = 1280 (A ₁)
1003	w	2 x 502 = 1004 (A ₁ g)	1406.1	vw	2 x 704 = 1408 (A ₁)
1099	w	454 + 638 = 1092 (B ₂ g)	1674	vvvw	2 x 839 = 1678 (A ₁)
1178	vvw	341 + 843 = 1184 (B ₁ g)	1702	vvvw	526 + 1188 = 1714 (A ₂)
1278	vvw	454 + 825 = 1279 (A ₁ g)	1813	vvvw	186 + 1620 = 1806 (B ₂)
		2 x 638 = 1276 (A ₁ g)	1866	vvw	839 + 1038 = 1877 (B ₁)
1299	m	454 + 843 = 1297 (B ₃ g)			272 + 1589 = 1861 (A ₁)
1433	vvvw	502 + 929 = 1431 (B ₂ g)	1945	vvvw	754 + 1188 = 1942 (A ₂)
1455	vw	638 + 825 = 1463 (B ₂ g)	1981	vvvw	526 + 1460 = 1986 (B ₂)
1495	w	341 + 1157 = 1498 (B ₂ g)	2369	vvvw	2 x 1188 = 2376 (A ₁)
1507.7	vw	502 + 1017 = 1519 (B ₃ g)			754 + 1620 = 2374 (B ₂)
1858	vvvw	2 x 929 = 1858 (A ₁ g)	2415	vvw	839 + 1589 = 2428 (A ₁)
		638 + 1215 = 1853 (B ₂ g)	2451	vvw	839 + 1620 = 2459 (B ₁)
1940	vvvw	341 + 1601 = 1942 (B ₃ g)	2959	vw	1460 + 1499 = 2959 (B ₁)
		929 + 1017 = 1946 (A ₁ g)			
2416	vvvw	2 x 1215 = 2430 (A ₁ g)	o-Fluorotoluene (Infrared)		
		825 + 1601 = 2426 (B ₁ g)	935	m	186 + 754 = 940 (A ₁)
2454	vvvw	843 + 1614 = 2457 (B ₃ g)	~ 977	w	272 + 704 = 976 (A ₁)
2740	vw	1221 + 1513 = 2734 (B ₂ g)	1172	w	427 + 754 = 1181 (B ₂)
			1267	w	427 + 839 = 1266 (B ₁)
p-Fluorotoluene (Infrared)			1282	vw	526 + 754 = 1280 (A ₁)
956	vw	454 + 502 = 956 (B ₂ u)	1299	w	272 + 1038 = 1310 (B ₁)
1280	vw	454 + 817 = 1271 (B ₂ u)	1471	s	427 + 1038 = 1465 (A ₁)
1300	w	152 + 1157 = 1309 (B ₂ u)	1499	s	2 x 754 = 1508 (A ₁)
1321	vw	502 + 825 = 1327 (B ₂ u)	1637	vvw	186 + 1460 = 1646 (B ₂)
1383	m	454 + 929 = 1383 (B ₁ u)	1678	vw	2 x 839 = 1678 (A ₁)
1458	m	454 + 1017 = 1471 (B ₁ u)	~ 1724	vvw	272 + 1460 = 1732 (B ₁)
1709	vvvw	502 + 1215 = 1717 (B ₂ u)	1742	vvw	704 + 1038 = 1742 (B ₁)
1746	vvvw	825 + 929 = 1754 (B ₁ u)	1784	w	754 + 1038 = 1792 (B ₂)
		152 + 1601 = 1753 (B ₃ u)	~ 1866	vw	839 + 1038 = 1877 (B ₁)
1766	vvw	152 + 1614 = 1766 (B ₂ u)			272 + 1589 = 1861 (A ₁)
		843 + 929 = 1772 (B ₂ u)	1904	w	272 + 1620 = 1892 (B ₁)
2034	vvvw	817 + 1215 = 2032 (B ₂ u)	1979	vw	526 + 1460 = 1986 (B ₂)
2054	vw	843 + 1221 = 2064 (B ₂ u)	2024	vvw	839 + 1188 = 2027 (A ₁)
2109	vvvw	502 + 1601 = 2103 (B ₃ u)			427 + 1589 = 2016 (B ₁)
2140	vvvw	929 + 1215 = 2144 (B ₁ u)	2070	vw	2 x 1038 = 2076 (A ₁)
2173	vvvw	1017 + 1157 = 2174 (B ₁ u)	2146	vvvw	526 + 1620 = 2146 (B ₂)
2236	vvvw	1017 + 1215 = 2232 (B ₁ u)	2222	vvvw	1038 + 1188 = 2226 (B ₁)
2335	vvw	825 + 1513 = 2338 (B ₃ u)			754 + 1460 = 2214 (B ₂)
2379	vvw	1157 + 1221 = 2378 (B ₁ u)	2317	vvw	704 + 1620 = 2324 (B ₁)
2442	vw	1215 + 1221 = 2436 (B ₁ u)	~ 2338	vvw	839 + 1499 = 2338 (A ₁)
		817 + 1614 = 2431 (B ₂ u)			704 + 1620 = 2324 (B ₁)
2525	vvvw	1017 + 1513 = 2530 (B ₂ u)	2372	vvvw	2 x 1188 = 2376 (A ₁)
2665	vvw	1157 + 1513 = 2670 (B ₃ u)			754 + 1620 = 2374 (B ₂)
3111	vw	1513 + 1601 = 3114 (B ₂ u)	2420	vw	839 + 1589 = 2428 (A ₁)
3700	vvvw	638 + 3043 = 3681 (B ₃ u)	2461	vw	839 + 1620 = 2459 (B ₁)
3890	vvvw	817 + 3071 = 3888 (B ₂ u)	2528	vvvw	1038 + 1499 = 2537 (B ₁)
4080	vvw	1017 + 3071 = 4088 (B ₁ u)	2664	vvvw	1038 + 1620 = 2658 (A ₁)
4310	vvw	1221 + 3071 = 4292 (B ₁ u)	2681	vvw	1188 + 1499 = 2687 (A ₁)
4650	vvw	1614 + 3043 = 4657 (B ₁ u)	2770	w	1188 + 1589 = 2777 (A ₁)
			2990	w	2 x 1499 = 2998 (A ₁)
o-Fluorotoluene (Raman)			3203	vvvw	1589 + 1620 = 3209 (B ₁)
715.1	vw	186 + 526 = 712 (A ₁)	3500	vvvw	427 + 3069 = 3496 (A ₁)
851	vw	2 x 427 = 854 (A ₁)	3620	vvvw	526 + 3069 = 3595 (B ₂)
886.3	vvw	186 + 704 = 890 (A ₂)	3910	vvvw	839 + 3069 = 3908 (B ₁)
934.9	vvw	186 + 754 = 940 (A ₁)	4080	vvvw	1038 + 3045 = 4083 (B ₁)
953	vvvw	427 + 526 = 953 (B ₂)	4260	vvvw	1188 + 3069 = 4257 (B ₁)
1112.6	w	272 + 839 = 1111 (A ₁)	4630	vvvw	1589 + 3045 = 4634 (A ₁)

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TABLE 69
Assignment of Fundamentals for
Benzotrifluoride and Fluorinated Benzotrifluorides

		C_6H_6	$C_6H_5CF_3$	$m-C_6H_4FCF_3$	$2,3,5-C_6H_3F_2CF_3$
30 (A_1)	ν_1	992 (A_{1g})	769.5 (A_1)	746.9 (A')	745.5 (A')
714 (A_2)	ν_2	3061.9 (A_{1g})	3076 (A_1)	3088 (A')	3095 (A')
306 (B_2)	ν_3	1326 (A_{2g})			
377 (B_1)	ν_4	703 (B_{2g})			
361 (A_1)	ν_5	995 (B_{2g})			
342 (A_2)	ν_6	606 (E_{2g})			
386 (B_2)	ν_7	3046.8 (E_{2g})		1280.1 (A')	1264 (A')
3 (A_1)	ν_8	1596 (E_{2g})	1610 (A_1) 1593 (B_1)	1622 (A') ?1607 (A')	1637 (A') 1617 (A')
174 (B_2)	ν_9	1178 (E_{2g})			
128 (A_1)	ν_{10}	848.9 (E_{1g})			
159 (B_1)	ν_{11}	675 (A_{2u})			
1959 (B_1)	ν_{12}	1010 (B_{1u})	1003.5 (A_1)	1005.5 (A')	914.1 (A')
1 (A_1)	ν_{13}	3071 (B_{1u})			
1 (A_1)	ν_{14}	1310 (B_{2u})			
11 (B_2)	ν_{15}	1150 (B_{2u})			
16 (B_1)	ν_{16}	405 (E_{2u})	139 (B_2)	134 (A'')	126 (A'')
10 (A_1)	ν_{17}	975 (E_{2u})			
10 (B_1)	ν_{18}	1037 (E_{1u})			
65 (A_1)	ν_{19}	1485 (E_{1u})	1431 (A_1) 1460 (B_1)	1458 (A') 1496 (A')	1443 (A') 1506 (A')
46 (B_2)	ν_{20}	3063 (E_{1u})			

The corresponding fundamental occurs at 3088 cm^{-1} in *m*-fluorobenzotrifluoride and at 3095 cm^{-1} in 2,5-difluorobenzotrifluoride. In each case a medium infrared band is found at the same frequency. Benzotrifluoride also has a medium infrared band occurring at 3051 cm^{-1} and two weak Raman bands at 3022 and 2995 cm^{-1} . In *m*-fluoro- and 2,5-difluorobenzotrifluoride only a few very weak Raman and infrared bands are observed in this region, other than the strong band that has been assigned to ν_2 .

In the region of 1600 cm^{-1} in benzene occurs the carbon-carbon stretching frequency ν_8 . One of the fundamentals in benzotrifluoride is identified, because of its sharpness, with a band of medium intensity at 1610 cm^{-1} of species A_1 . A band at lower frequency, 1593 cm^{-1} , has been assigned to the fundamental of species B_1 . In *m*-fluorobenzotrifluoride the fundamental corresponding to the fundamental of species A_1 in benzotrifluoride occurs at 1622 cm^{-1} , and in 2,5-difluorobenzotrifluoride it is found at 1637 cm^{-1} . The assignment of the other fundamental is less certain in these two compounds, but it probably occurs at 1607 and 1617 cm^{-1} respectively.

The carbon-carbon stretching mode corresponding to ν_{19} of benzene splits into two fundamentals in the benzotrifluorides. The fundamental of species B_1 in benzotrifluoride occurs at 1460 cm^{-1} and appears strong in the infrared but very weak in the Raman spectrum. The symmetrical mode of species A_1 occurs weakly in the infrared at 1431 cm^{-1} and very weakly in the Raman effect at 1427 cm^{-1} . The corresponding bands in m-fluorobenzotrifluoride are found at 1496 and 1458 cm^{-1} in the infrared spectrum. Two infrared bands at 1506 and 1443 cm^{-1} in 2,5-difluorobenzotrifluoride may be assigned to the two fundamentals corresponding to ν_{19} in benzene.

The strong infrared band and the medium Raman band occurring at 1326 and 1324 cm^{-1} in benzotrifluoride are probably associated with a C-F stretching vibration of the CF_3 group. Bands occur both in the Raman and infrared spectra of m-fluorobenzotrifluoride and 2,5-difluorobenzotrifluoride at 1332 and 1323 cm^{-1} , respectively, and there appears some doubt whether these bands should be ascribed to fundamentals involving the CF_3 group or to vibrations corresponding to the benzene fundamental ν_7 . The Raman and infrared band occurring at 1280.1 cm^{-1} , however, probably corresponds to the fundamental ν_7 in the case of m-fluorobenzotrifluoride, and the Raman and infrared band at 1264 cm^{-1} may correspond to this fundamental in 2,5-difluorobenzotrifluoride.

In the region from 1050 to 1180 cm^{-1} there occur several strong infrared bands and weak Raman bands. These are, undoubtedly, associated with carbon-fluorine stretching of the CF_3 group, since no comparable set of bands occur in the fluorinated benzenes.

A very strong and sharp Raman band and a weak infrared band are found in benzotrifluoride at 1003.5 cm^{-1} and in m-fluorobenzotrifluoride at 1005.5 cm^{-1} . This frequency has been associated by Sponer (78) with the symmetrical breathing mode, ν_1 , of benzene. However, Ingold et al. (69) and Lord and Langseth (72) have shown from their results on deuterated benzenes that this frequency decreases, whereas the value of ν_{12} , the trigonal breathing frequency of the aromatic ring, remains practically the same for the mono and ortho derivatives. These bands are therefore assigned here to the fundamental corresponding to ν_{12} in benzene. This fundamental should, according to the work on deuterated benzenes, occur at a lower frequency in 2,5-difluorobenzotrifluorides. It has been assigned to the only Raman and infrared band of any appreciable intensity occurring in this region, namely, 914.1 cm^{-1} , which is intermediate between the values, 963.7 and 868 cm^{-1} , assigned to this fundamental in 1,2,4-trifluorobenzene and 1,2,4,5-tetrafluorobenzene, respectively.

The symmetrical breathing frequency corresponding to the fundamental ν_1 of benzene appears as a strong band in both the Raman and the infrared spectra in each of the benzotrifluorides. It occurs in benzotrifluoride at 769.5 cm^{-1} , in m-fluorobenzotrifluoride at 746.9 cm^{-1} , and in 2,5-difluorobenzotrifluoride at 745.5 cm^{-1} . The Raman bands are quite sharp in each case.

Very few correlations or assignments may be made below this region. However, in each of the three compounds the Raman spectrum shows an intense diffuse band around 130 cm^{-1} which is undoubtedly caused by the out-of-plane bending of the carbon atoms of the benzene ring and corresponds to the benzene fundamental ν_{16} . The bands lying between 240 and 340 cm^{-1} probably account for the parallel carbon vibrations corresponding to ν_6 .

MISCE

Ti
here w
R=CH₃
perflu
of periTi
tetrafl
in regi
connec
spectr
molec

MISCELLANEOUS FLUORINATED COMPOUNDS

The infrared spectra of a few additional samples have been obtained and are included here without interpretation. The spectra of four ethers of the type $R-O-CF_2-CHFCl$, with $R=CH_3$, C_2H_5 , $n-C_3H_7$, and $n-C_4H_9$, are shown in Figure 39 together with the spectrum of perfluorodibutyl ether, presumably $(CF_3-CF_2-CF_2-CF_2)_2O$. Figure 40 shows the spectrum of perfluorotributylamine.

The spectrum obtained with two different thicknesses of teflon sheet, a polymer of tetrafluoroethylene, is shown in Figure 40, but thinner sheet is needed to locate the maxima in regions of strong absorption. Some of the bands in this spectrum will be mentioned in connection with the correlations for CF_2 group vibrations. In Figure 40 is also shown the spectrum of solid fluorothene sheet, a polymer of $CF_2=CFCl$. Fluorothene G is a lower molecular weight polymer of $CF_2=CFCl$ and is similar but softer than fluorothene W (24).

CH ₂ =CF ₂			CF ₂ =CF ₂			CF ₂ =CCl ₂			CF ₂ =CFCI		
$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$
2.11	4740	5.409	1849	ca. 3.120	ca.3205	ca. 3.120	ca.3205	ca. 3.120	ca.3205	ca. 3.120	ca.3205
2.22	4500	5.542	1804	ca. 3.270	ca.3058	ca. 3.270	ca.3058	ca. 3.270	ca.3058	ca. 3.270	ca.3058
2.28	4390	5.744	1741	ca. 3.360	2876	ca. 3.360	2876	ca. 3.360	2876	ca. 3.360	2876
2.43	4120	5.770	1733	ca. 3.420	2824	ca. 3.420	2824	ca. 3.420	2824	ca. 3.420	2824
2.48	4030	5.770	1733	ca. 3.472	2880	ca. 3.472	2880	ca. 3.472	2880	ca. 3.472	2880
2.887	3464	5.786	1728	ca. 3.620	ca.2762	ca. 3.620	ca.2762	ca. 3.620	ca.2762	ca. 3.620	ca.2762
2.896	3463	5.802	1724	ca. 3.673	2723	ca. 3.673	2723	ca. 3.673	2723	ca. 3.673	2723
3.165	3160	5.814	1720	ca. 3.732	2680	ca. 3.732	2680	ca. 3.732	2680	ca. 3.732	2680
3.178	3147	5.814	1720	ca. 3.742	2672	ca. 3.742	2672	ca. 3.742	2672	ca. 3.742	2672
3.216	3109	6.207	1611	ca. 3.776	2638	ca. 3.776	2638	ca. 3.776	2638	ca. 3.776	2638
3.228	3098	6.244	ca.1602	ca. 3.824	2584	ca. 3.824	2584	ca. 3.824	2584	ca. 3.824	2584
3.255	3072	6.57	1522	ca. 3.874	2534	ca. 3.874	2534	ca. 3.874	2534	ca. 3.874	2534
3.268	3060	6.70	1493	ca. 3.944	2498	ca. 3.944	2498	ca. 3.944	2498	ca. 3.944	2498
3.280	3049	7.02	1414	ca. 4.004	2434	ca. 4.004	2434	ca. 4.004	2434	ca. 4.004	2434
3.414	2824	7.27	1376	ca. 4.120	2427	ca. 4.120	2427	ca. 4.120	2427	ca. 4.120	2427
3.516	2817	7.35	1361	ca. 4.130	2421	ca. 4.130	2421	ca. 4.130	2421	ca. 4.130	2421
3.550	2770	7.61	1314	ca. 4.373	2287	ca. 4.373	2287	ca. 4.373	2287	ca. 4.373	2287
3.614	2767	7.66	1305	ca. 4.397	2274	ca. 4.397	2274	ca. 4.397	2274	ca. 4.397	2274
3.692	2709	7.70	1299	ca. 4.422	2261	ca. 4.422	2261	ca. 4.422	2261	ca. 4.422	2261
3.758	2681	7.73	1294	ca. 4.434	2255	ca. 4.434	2255	ca. 4.434	2255	ca. 4.434	2255
3.837	2606	8.21	1218	ca. 4.518	2213	ca. 4.518	2213	ca. 4.518	2213	ca. 4.518	2213
3.856	2593	8.28	1208	ca. 4.538	2156	ca. 4.538	2156	ca. 4.538	2156	ca. 4.538	2156
ca. 3.870	ca.2584	8.55	1156	ca. 4.558	2147	ca. 4.558	2147	ca. 4.558	2147	ca. 4.558	2147
3.948	2533	8.65	1150	ca. 4.578	2116	ca. 4.578	2116	ca. 4.578	2116	ca. 4.578	2116
4.054	2487	9.54	1048	ca. 4.733	2011	ca. 4.733	2011	ca. 4.733	2011	ca. 4.733	2011
4.123	2425	10.30	952	ca. 4.955	2002	ca. 4.955	2002	ca. 4.955	2002	ca. 4.955	2002
4.266	2344	10.64	940	ca. 5.007	1997	ca. 5.007	1997	ca. 5.007	1997	ca. 5.007	1997
4.290	2331	10.80	926	ca. 5.078	1969	ca. 5.078	1969	ca. 5.078	1969	ca. 5.078	1969
4.313	2319	10.83	923	ca. 5.096	1962	ca. 5.096	1962	ca. 5.096	1962	ca. 5.096	1962
4.366	2280	11.57	864	ca. 5.118	1954	ca. 5.118	1954	ca. 5.118	1954	ca. 5.118	1954
4.377	2263	12.16	822	ca. 5.283	1883	ca. 5.283	1883	ca. 5.283	1883	ca. 5.283	1883
4.418	2263	12.35	810	ca. 5.304	1885	ca. 5.304	1885	ca. 5.304	1885	ca. 5.304	1885
4.442	2251	12.46	803	ca. 5.380	ca.1792	ca. 5.380	ca.1792	ca. 5.380	ca.1792	ca. 5.380	ca.1792
4.476	2234	12.55	797	ca. 5.744	ca.1741	ca. 5.744	ca.1741	ca. 5.744	ca.1741	ca. 5.744	ca.1741
4.500	2222	12.76	784	ca. 5.785	ca.1729	ca. 5.785	ca.1729	ca. 5.785	ca.1729	ca. 5.785	ca.1729
4.512	2216	12.87	784	ca. 5.896	1696	ca. 5.896	1696	ca. 5.896	1696	ca. 5.896	1696
4.528	2208	12.76	784	ca. 5.970	ca.1675	ca. 5.970	ca.1675	ca. 5.970	ca.1675	ca. 5.970	ca.1675
4.600	2174	13.35	743	ca. 6.037	ca.1656	ca. 6.037	ca.1656	ca. 6.037	ca.1656	ca. 6.037	ca.1656
4.640	2155	13.45	743	ca. 6.20	1613	ca. 6.20	1613	ca. 6.20	1613	ca. 6.20	1613
4.889	2045	13.60	735	ca. 6.45	1550	ca. 6.45	1550	ca. 6.45	1550	ca. 6.45	1550
4.942	2023	14.12	690	ca. 6.56	1524	ca. 6.56	1524	ca. 6.56	1524	ca. 6.56	1524
4.989	2004	14.12	690	ca. 6.85	ca.1460	ca. 6.85	ca.1460	ca. 6.85	ca.1460	ca. 6.85	ca.1460
5.001	2000	15.87	630	ca. 6.95	1342	ca. 6.95	1342	ca. 6.95	1342	ca. 6.95	1342
5.010	1996	16.37	611	ca. 7.45	1332	ca. 7.45	1332	ca. 7.45	1332	ca. 7.45	1332
5.048	1981	16.87	593	ca. 7.51	1281	ca. 7.51	1281	ca. 7.51	1281	ca. 7.51	1281
5.206	1921	ca.17.75	ca. 563	ca. 8.37	1195	ca. 8.37	1195	ca. 8.37	1195	ca. 8.37	1195
5.227	1913	ca.18.19	ca. 550	ca. 8.43	1186	ca. 8.43	1186	ca. 8.43	1186	ca. 8.43	1186
5.238	1909	ca.18.54	ca. 539								
5.274	1896	ca.22.22	ca. 450								
5.328	1877										
5.368	1863										

Note: Absorption at 960 and 1209 cm⁻¹ due to cyclic C₂F₂ impurity.

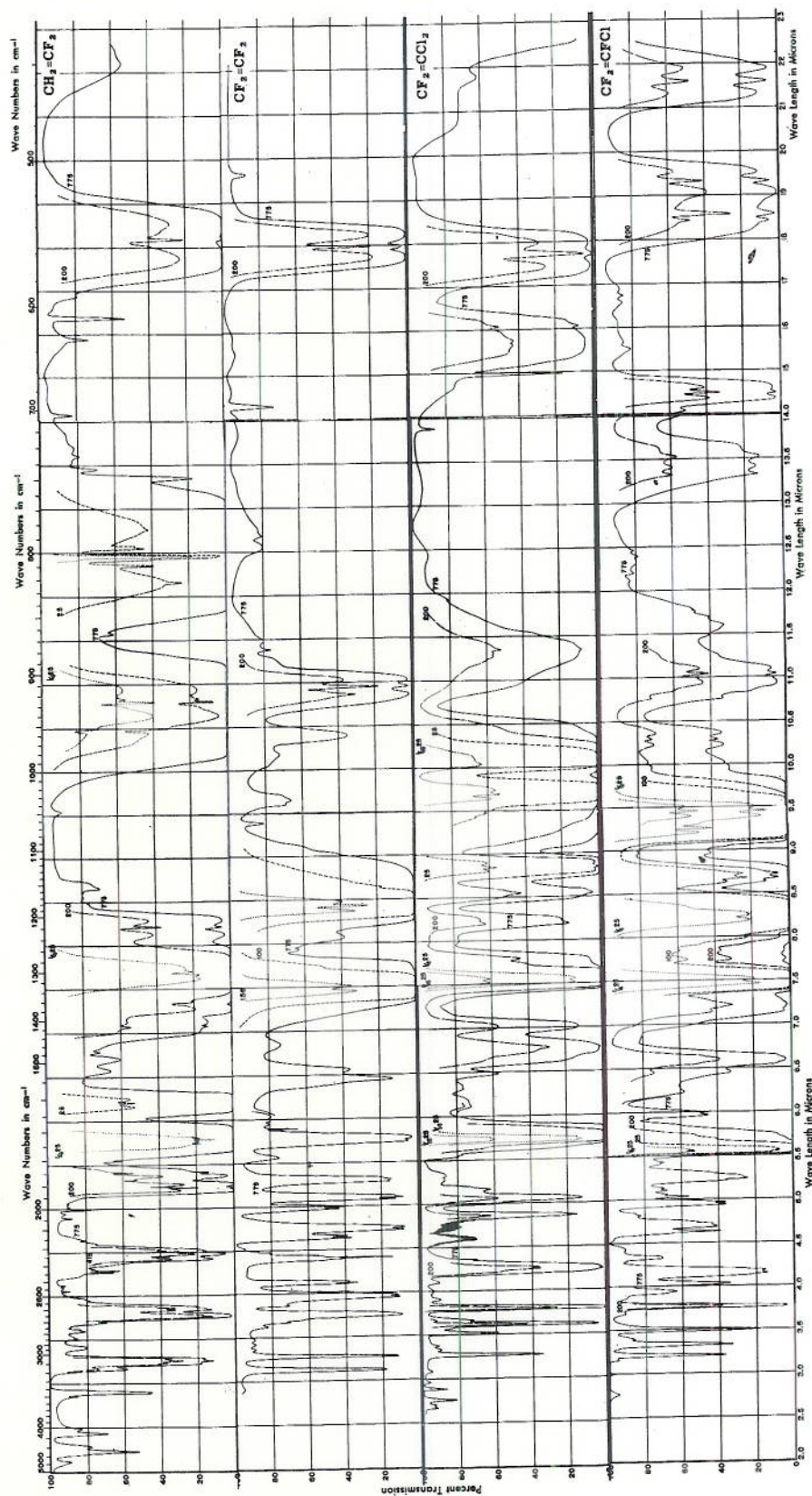


Figure 32 - $\text{CH}_2=\text{CF}_2$, $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CCl}_2$ and $\text{CF}_2=\text{CFCl}$

CH ₃ -CF ₃			CH ₃ -CHF ₂			CF ₃ -CCl ₃			CH ₃ -CCl ₃			CF ₃ Cl-CF ₂ Cl			
$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$
2.944	3397	5.96	1678	ca. 2.870	ca. 3484	6.85	1460	ca. 2.77	ca. 3610	ca. 2.12	ca. 4720	10.58	945	3.958	2527
2.998	3336	6.07	1647	ca. 2.936	3406	7.02	1425	ca. 2.98	3360	2.24	4460	10.68	936	4.068	2458
3.078	3249	6.24	1603	ca. 3.095	3231	7.07	1414	ca. 3.35	ca. 2990	2.27	4410	11.13	896	4.155	2407
3.092	3234	6.28	1592	ca. 3.110	3215	7.13	1403	ca. 4.03	2480	2.43	4120	11.48	871	4.232	2363
3.162	3143	6.37	1552	ca. 3.126	3199	7.29	1372	ca. 4.08	2450	2.47	4050	11.53	867	4.312	2319
3.280	3049	6.57	1504	ca. 3.223	ca. 3103	7.91	ca. 1264	ca. 4.23	2365	2.59	3860	11.58	864	4.419	2263
3.284	3046	6.65	1456	ca. 3.300	3030	7.97	1255	ca. 4.54	2185	2.66	3760	11.71	854	4.476	2234
3.306	3025	6.93	1443	ca. 3.314	3018	8.00	1250	ca. 4.74	2110	2.73	3660	11.77	850	ca. 4.538	ca. 2204
3.346	2987	7.03	1432	ca. 3.332	3001	8.54	1171	ca. 4.74	2110	2.81	3560	11.83	845	ca. 4.712	ca. 2122
3.358	2978	7.10	1408	ca. 3.357	2979	8.58	1166	ca. 4.92	2075	2.83	3352	12.40	806	ca. 4.905	ca. 2039
3.370	2967	7.16	1397	ca. 3.375	2963	8.76	1142	ca. 5.18	1930	3.080	3247	12.53	798	ca. 5.100	ca. 1961
3.436	2810	7.50	1333	ca. 3.446	2902	9.33	1072	ca. 5.18	1930	3.080	3247	12.53	798	ca. 5.279	ca. 1894
3.452	2807	7.74	1292	ca. 3.464	2887	9.33	1072	ca. 5.52	1810	3.145	3160	12.77	783	ca. 5.378	ca. 1859
3.470	2802	7.81	1280	ca. 3.476	2871	9.60	1042	ca. 5.80	1785	3.316	3016	12.86	778	ca. 5.417	ca. 1846
3.480	2874	7.89	1283	ca. 3.562	2807	9.60	1042	ca. 6.06	1650	3.316	3016	12.92	774	ca. 5.572	ca. 1795
3.497	2860	8.11	1233	ca. 3.627	2757	10.59	944	ca. 6.06	1650	3.386	2943	13.03	767	ca. 5.761	ca. 1738
3.511	2949	8.43	1186	ca. 3.644	2744	10.59	944	ca. 6.17	1595	3.386	2943	13.10	759	ca. 5.775	ca. 1732
3.530	2939	8.53	1172	ca. 3.688	2711	11.43	873	ca. 6.35	1575	3.457	2893	13.17	753	ca. 5.964	ca. 1677
3.579	2794	9.18	1089	ca. 3.715	2692	11.46	873	ca. 6.60	1515	3.480	2874	13.45	739	ca. 6.042	ca. 1655
3.582	2807	9.21	1088	ca. 3.854	2595	11.52	868	ca. 6.80	1471	3.532	2831	14.51	699	ca. 6.070	ca. 1647
3.670	2725	9.24	1082	ca. 3.870	2584	11.52	868	ca. 6.99	1431	3.532	2831	14.51	699	ca. 6.110	ca. 1637
3.684	2714	9.67	1034	ca. 3.924	2548	12.73	ca. 786	ca. 7.05	1418	3.73	2680	15.86	630	ca. 6.185	ca. 1617
3.712	2694	9.72	1029	ca. 4.010	ca. 2494	13.70	730	ca. 7.11	1406	3.85	2530	16.96	576	ca. 6.43	ca. 1555
3.730	2681	9.85	1015	ca. 4.186	2369	13.88	720	ca. 7.14	1401	4.07	2455	17.36	566	ca. 6.64	ca. 1506
3.834	2542	9.92	1008	ca. 4.228	2365	13.93	718	ca. 7.47	1339	4.30	2300	17.90	549	ca. 6.77	ca. 1477
3.986	2509	9.95	1005	ca. 4.255	2350	17.04	ca. 587	ca. 7.83	1277	4.90	ca. 2040	18.23	556	ca. 6.93	ca. 1443
4.065	2460	10.28	973	ca. 4.259	2326	17.52	ca. 577	ca. 7.97	ca. 1255	5.52	1800	18.73	534	ca. 7.34	ca. 1362
4.080	2451	10.34	967	ca. 4.387	2279	17.95	ca. 557	ca. 8.15	1227	5.78	1750	19.01	ca. 526	ca. 7.54	ca. 1326
4.140	2415	10.36	965	ca. 4.417	2264	ca. 20.68	ca. 484	ca. 8.40	1189	6.25	1597	ca. 19.01	ca. 526	ca. 7.85	ca. 1274
4.157	2406	10.88	911	ca. 4.478	2233	21.10	ca. 474	ca. 8.76	1145	6.38	1597	ca. 19.21	ca. 521	ca. 8.11	ca. 1233
4.208	2376	11.51	869	ca. 4.726	2116	21.26	ca. 470	ca. 9.21	1086	6.48	1543	ca. 19.36	ca. 517	ca. 8.14	ca. 1229
4.221	2369	ca. 11.87	ca. 842	ca. 4.802	ca. 2082	ca. 21.48	ca. 466	ca. 9.54	1037	6.81	1468	20.24	494	ca. 8.37	ca. 1195
4.221	2369	ca. 11.87	ca. 842	ca. 4.802	ca. 2082	ca. 21.48	ca. 466	ca. 9.54	1037	6.81	1468	20.24	494	ca. 8.37	ca. 1195
4.300	2286	11.94	838	ca. 4.830	ca. 2070	ca. 21.60	ca. 459	ca. 9.69	1032	6.86	1468	20.78	481	ca. 8.45	ca. 1186
4.400	2273	12.04	831	ca. 4.990	ca. 2004	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 8.77	ca. 1140
4.442	2251	ca. 12.22	ca. 818	ca. 5.158	ca. 1939	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 8.77	ca. 1140
4.460	2242	12.82	780	ca. 5.278	ca. 1895	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 9.00	ca. 1111
4.483	2231	ca. 13.12	ca. 762	ca. 5.290	ca. 1890	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 9.50	ca. 1053
ca. 4.515	ca. 2215	ca. 13.27	ca. 754	ca. 5.316	ca. 1881	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 9.97	ca. 1003
ca. 4.552	ca. 2197	ca. 13.36	ca. 749	ca. 5.327	ca. 1877	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 10.12	ca. 988
ca. 4.590	ca. 2183	ca. 13.40	ca. 746	ca. 5.349	ca. 1870	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 10.19	ca. 981
4.680	2137	13.45	743	ca. 5.450	ca. 1835	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 10.55	ca. 948
4.724	2117	13.56	737	ca. 5.488	ca. 1832	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 10.78	ca. 943
4.749	2106	13.66	732	ca. 5.497	ca. 1819	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 10.84	ca. 923
4.778	2093	ca. 14.57	ca. 686	ca. 5.538	ca. 1808	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 10.84	ca. 923
4.853	2061	14.74	678	ca. 5.532	ca. 1790	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 11.26	ca. 888
4.902	2015	ca. 16.24	ca. 616	ca. 5.768	ca. 1734	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 11.33	ca. 883
4.986	2006	16.52	605	ca. 5.883	ca. 1700	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 11.51	ca. 860
4.994	2002	16.54	603	ca. 5.963	ca. 1676	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 11.57	ca. 864
5.008	1997	ca. 16.64	601	ca. 6.028	ca. 1659	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 11.77	ca. 850
5.020	1992	ca. 17.88	ca. 559	ca. 6.17	ca. 1621	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 11.85	ca. 849
5.16	1835	18.37	544	ca. 6.54	ca. 1529	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 11.85	ca. 849
5.31	1863	18.37	541	ca. 6.54	ca. 1529	ca. 21.60	ca. 459	ca. 9.69	1032	6.90	1448	ca. 21.94	ca. 456	ca. 12.96	772
5.53	1808	18.48		ca. 6.58	1520			10.30	971	10.30	971	13.60	735	13.12	762
														13.51	740
														13.60	735



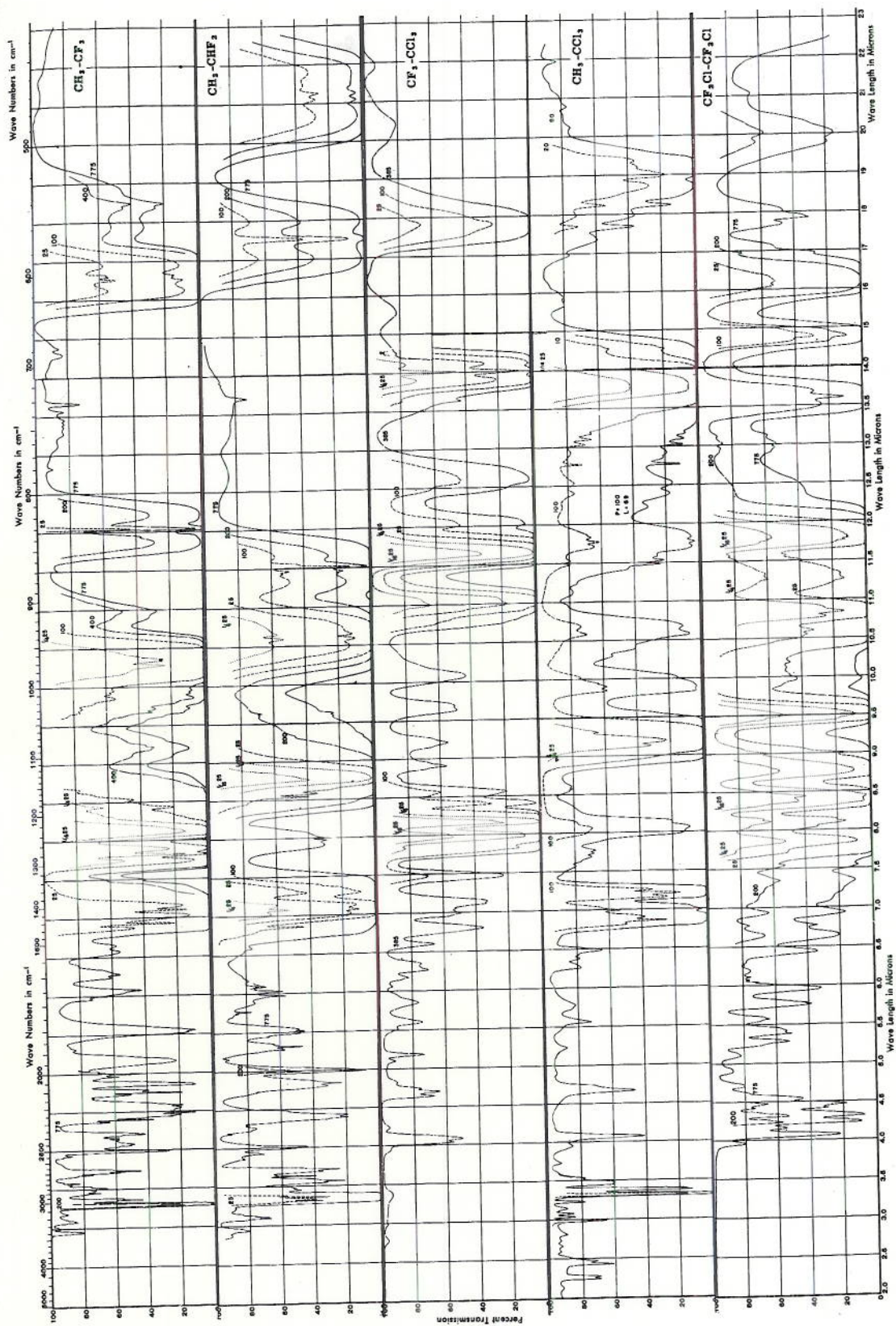


Figure 33 - CH₃-CF₃, CH₃-CHF₂, CF₃-CCl₃, CH₃-CCl₃ and CF₃Cl-CF₂Cl

CF ₃ Cl-CFCl ₃		CF ₃ -CF ₂ -CF ₃		CF ₃ -CF ₂ -CF ₃		CYCLIC C ₆ F ₆	
$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$
ca. 2.92	ca. 3420	3.140	3185	ca. 14.07	ca. 711	ca. 11.83	ca. 845
ca. 3.07	ca. 3260	3.203	3122	ca. 14.16	ca. 706	ca. 12.47	ca. 802
ca. 4.20	ca. 2360	3.325	3008	ca. 14.62	ca. 684	ca. 12.54	ca. 797
4.31	2320	3.440	2907	15.17	659	ca. 12.92	ca. 774
4.51	2215	3.535	2829	15.27	655	ca. 3.360	ca. 2976
4.63	2160	3.582	2772	15.37	651	13.04	767
4.72	2120	3.672	2723	ca. 16.42	ca. 609	ca. 13.80	ca. 725
4.95	2020	3.758	2661	ca. 16.61	ca. 602	ca. 14.87	ca. 682
5.22	1915	3.838	2606	ca. 17.66	ca. 566	ca. 3.540	ca. 2825
5.39	1855	3.906	2560	ca. 17.88	ca. 559	3.615	2766
5.49	1820	3.981	2512	ca. 18.33	ca. 517	ca. 15.78	ca. 850
5.67	1765	4.092	2444	ca. 19.50	ca. 513	ca. 15.36	ca. 834
5.82	1720	4.170	2398	20.48	488	ca. 16.36	ca. 611
5.89	1700	4.231	2364	21.66	462	3.746	2670
6.11	1637	4.285	2345	ca. 21.87	ca. 457	3.810	2625
6.38	1567	4.444	2250			3.911	2557
6.55	1527	4.525	2210			4.104	2437
6.71	1490	4.636	2157			4.180	2392
6.86	1458	ca. 4.764	ca. 2099			4.260	2347
7.07	1414	ca. 4.885	ca. 2047			ca. 4.348	ca. 2300
7.26	1377	5.050	1980			4.587	2180
7.45	1342	5.152	1941			4.870	2141
8.01	1248	ca. 5.332	ca. 1868			4.884	2135
8.27	1209	5.564	1797			5.010	1996
8.54	1171	ca. 5.782	ca. 1727			ca. 5.074	ca. 1971
9.02	1109	6.118	1635			5.153	1930
9.57	1045	6.33	1580			5.254	1893
9.68	1033	6.49	1541			5.353	1863
10.30	971	6.77	1477			ca. 5.480	ca. 1825
ca. 10.82	ca. 924	7.83	1384			ca. 5.572	ca. 1795
ca. 11.09	ca. 902	7.15	1399			ca. 5.832	ca. 1715
ca. 11.29	ca. 886	7.46	1340			6.030	1658
11.45	873	7.50	1333			6.083	1649
852		7.70	1290			6.150	1625
ca. 12.41	ca. 806	7.92	1263			6.188	1621
ca. 12.67	ca. 789	8.26	1211			6.25	1600
ca. 13.41	ca. 746	8.48	1179			6.36	1572
ca. 13.63	ca. 744	8.91	1122			6.53	1531
14.31		9.61	1041			6.66	1502
15.31	633	9.64	1037			6.79	1473
16.31	633	10.38	963			6.93	1443
17.82	581	10.88	919			7.13	1403
18.80	532	10.94	914			7.46	1340
19.63	509	ca. 11.06	ca. 904			7.74	1292
ca. 21.67	ca. 461	ca. 12.06	ca. 829			7.88	1269
ca. 22.52	ca. 444	12.96	772			8.07	1249
		13.04	767			8.65	1156
		13.12	762			8.70	1149
		13.54	739			9.15	1093
		ca. 13.59	ca. 736			9.60	1042
		13.63	731			9.64	1037
		13.78	726			10.17	983
		13.88	720			10.38	963
						ca. 11.15	ca. 897
						11.56	865

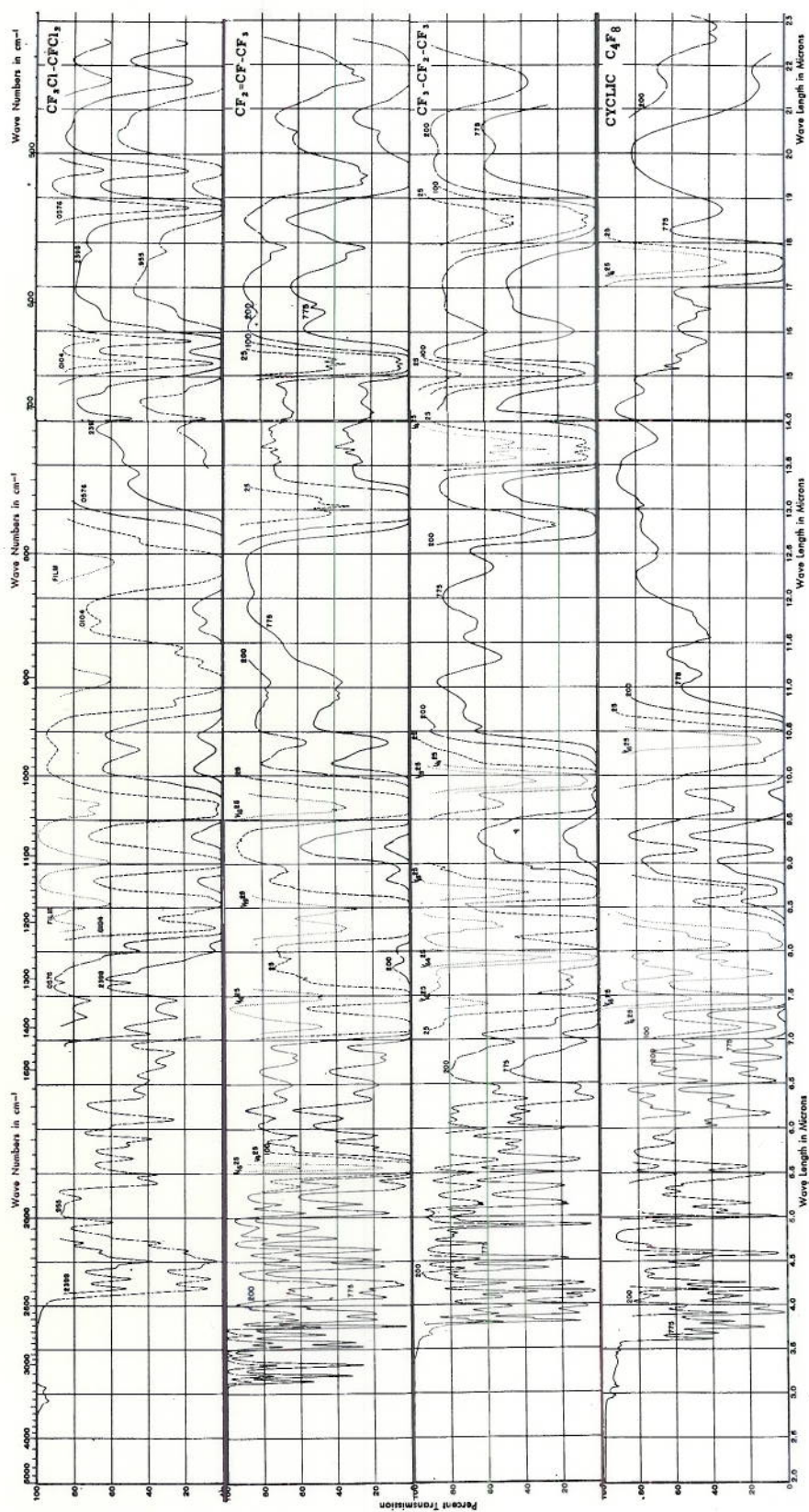


Figure 34 - $\text{CF}_2\text{Cl-CFCl}_2$, $\text{CF}_2=\text{CF-CF}_3$, $\text{CF}_2=\text{CF-CF}_2\text{-CF}_3$ and cyclic C_4F_8 .

CYCLIC C ₆ F ₆			n-C ₆ F ₁₂			ISO-C ₆ F ₁₂ (GAS)			ISO-C ₆ F ₁₂ (LIQUID)			n-C ₆ F ₁₈			
$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$
ca. 3.852	ca. 2596	3.794	2636	13.81	724	ca. 3.300	ca. 3030	13.73	728	ca. 2.76	ca. 3620	2.77	3610	ca. 17.40	ca. 575
ca. 3.985	ca. 2522	3.855	2594	ca. 14.45	ca. 692	ca. 3.360	ca. 2976	ca. 14.95	ca. 669	ca. 3.07	ca. 3260	3.04	2805	ca. 17.63	ca. 567
ca. 4.030	ca. 2481	3.880	2577	15.63	640	ca. 3.460	ca. 2874	15.40	649	ca. 3.35	ca. 2990	3.34	2490	ca. 18.88	ca. 530
ca. 4.108	ca. 2434	ca. 4.040	ca. 2475	ca. 16.37	611	ca. 3.508	2851	ca. 16.04	ca. 623	3.87	2585	4.02	2445	ca. 19.46	ca. 514
ca. 4.130	ca. 2421	ca. 4.094	ca. 2443	ca. 16.88	ca. 592	ca. 3.600	ca. 2778	ca. 16.70	ca. 599	4.09	2445	4.20	2380	ca. 21.12	ca. 473
ca. 4.196	ca. 2383	ca. 4.155	ca. 2407	18.83	531	ca. 3.862	2589	ca. 18.63	ca. 537	4.20	2380	4.40	2250	ca. 21.12	ca. 473
ca. 4.228	ca. 2366	4.218	2371	21.86	457	ca. 3.926	ca. 2547	ca. 19.72	ca. 507	4.44	2250	4.44	2250	ca. 21.68	ca. 461
ca. 4.322	ca. 2314	ca. 4.290	ca. 2331			ca. 3.985	ca. 2509	ca. 20.37	ca. 491	4.52	2210	4.52	2210		
ca. 4.466	ca. 2239	ca. 4.436	ca. 2280			ca. 4.030	ca. 2481	ca. 22.55	ca. 442	4.58	2185	4.59	2180		
ca. 4.512	ca. 2216	ca. 4.482	2261			ca. 4.082	ca. 2450			4.64	2155	4.64	2155		
ca. 4.588	2180	4.470	2237			ca. 4.122	2426			4.67	2140	4.77	2095		
ca. 4.740	ca. 2110	4.526	2205			ca. 4.185	ca. 2389			4.80	2085	4.97	2010		
ca. 4.974	ca. 2010	4.720	2119			ca. 4.246	2355			5.02	1990	5.05	1980		
ca. 5.103	1960	4.832	2070			4.330	2309			5.14	1945	5.42	1845		
ca. 5.190	ca. 1927	4.932	2017			4.435	2255			5.20	1925	5.66	1765		
ca. 5.340	ca. 1873	ca. 4.880	ca. 2049			4.513	2216			5.31	1885	5.93	1685		
ca. 5.544	ca. 1804	4.958	2017			4.530	2208			ca. 5.51	ca. 1815	6.32	1601		
ca. 5.770	ca. 1733	5.090	1976			4.580	2183			ca. 5.64	ca. 1775	6.46	ca. 1577		
ca. 5.976	ca. 1673	5.393	1963			4.666	2143			5.83	1715	6.56	ca. 1548		
ca. 6.118	ca. 1618	5.508	1920			4.744	2096			5.92	1690	6.74	ca. 1484		
ca. 6.46	ca. 1548	5.824	1893			4.794	2086			6.14	1629	6.96	ca. 1437		
ca. 6.72	ca. 1488	5.388	1856			4.867	2055			6.31	1585	7.44	ca. 1344		
ca. 6.87	1456	ca. 5.448	ca. 1836			4.922	2032			ca. 6.44	ca. 1553	7.68	1302		
7.29	1372	ca. 5.567	ca. 1763			4.959	2000			ca. 6.70	ca. 1493	8.06	ca. 1241		
7.51	1332	ca. 5.672	ca. 1731			ca. 5.043	ca. 1983			ca. 6.88	1453	8.16	ca. 1225		
7.72	1295	ca. 5.776	ca. 1701			5.117	1954			6.97	1435	8.44	1185		
8.13	1230	ca. 5.910	ca. 1692			5.180	1931			7.36	1355	8.66	ca. 1155		
ca. 8.79	ca. 1138	ca. 6.012	ca. 1663			5.244	1907			ca. 7.94	ca. 1335	8.77	1140		
9.53	1049	ca. 6.11	ca. 1637			5.288	1891			ca. 8.14	ca. 1259	8.94	ca. 1119		
10.10	990	ca. 6.22	1608			ca. 5.495	ca. 1820			ca. 8.40	1176	9.12	1096		
ca. 11.22	ca. 891	ca. 6.38	ca. 1567			ca. 5.636	ca. 1774			ca. 8.64	ca. 1157	9.45	1058		
11.34	882	ca. 6.48	1543			ca. 5.822	ca. 1718			9.08	1101	9.53	1049		
ca. 12.07	829	ca. 6.60	ca. 1515			ca. 5.916	ca. 1690			9.13	1095	9.71	1030		
ca. 12.65	ca. 791	6.81	1468			6.15	1626			9.38	1066	10.13	987		
ca. 13.18	ca. 759	7.05	1418			6.31	1585			10.12	988	10.27	974		
ca. 13.58	ca. 736	7.47	1359			6.43	1555			10.66	938	10.53	950		
ca. 14.18	ca. 705	7.76	1289			6.69	1495			11.16	896	11.17	936		
ca. 16.30	ca. 613	8.20	1220			6.87	1456			12.02	832	11.57	882		
ca. 18.26	ca. 548	8.68	1152			7.38	1355			ca. 12.47	ca. 802	11.72	853		
ca. 20.10	ca. 498	8.81	1135			7.74	1292			13.04	767	11.79	845		
		8.81	1135			7.88	1269			13.55	738	12.32	812		
		9.05	1104			8.00	1250			ca. 13.75	ca. 727	12.49	801		
		ca. 9.36	ca. 1068			8.09	1236			ca. 14.96	ca. 668	12.75	784		
		9.56	1046			8.47	1181			15.41	649	12.85	778		
		10.10	990			8.62	1160			16.06	623	12.85	778		
		ca. 10.76	ca. 929			9.06	1104			16.78	596	13.30	752		
		11.14	898			9.36	1068			18.07	553	13.45	743		
		11.35	881			10.09	991			ca. 18.68	ca. 535	13.63	734		
		ca. 11.99	ca. 834			10.64	940			ca. 19.72	507	13.89	720		
		ca. 13.14	ca. 761			11.13	898			21.85	491	14.03	713		
		13.50	741			11.92	834			ca. 22.65	ca. 442	14.15	707		
		13.55	738			13.02	768					ca. 14.62	ca. 684		
		13.78	726			13.54	739					15.07	664		
						ca. 13.64	ca. 733					15.53	644		
												ca. 16.90	ca. 592		



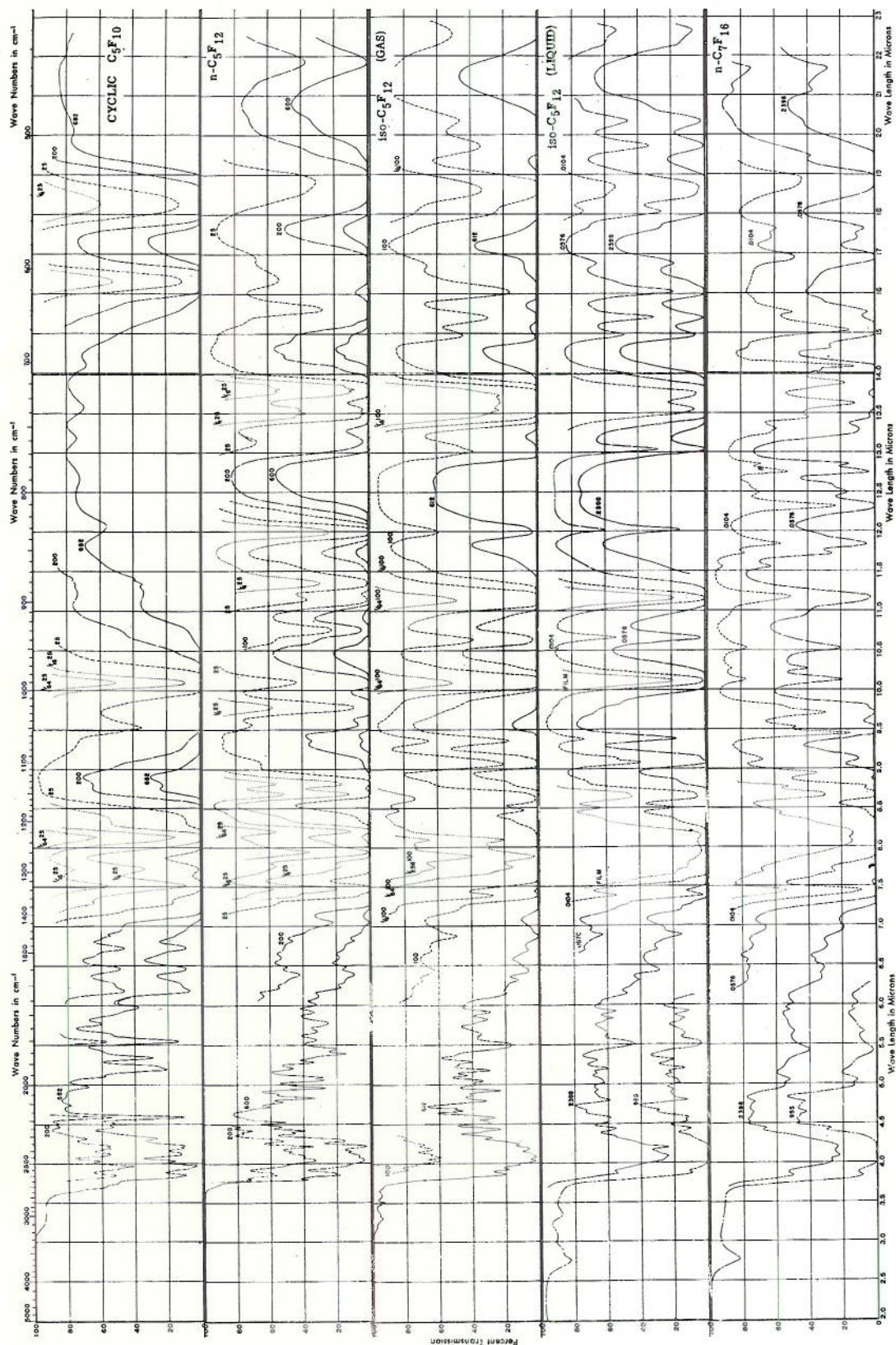


Figure 35 - Cyclic C_5F_{10} , $n\text{-C}_5\text{F}_{12}$ (gas), $\text{iso-C}_5\text{F}_{12}$ (liquid) and $n\text{-C}_7\text{F}_{16}$

$\text{C}_2\text{F}_5-\text{CF}_2-\text{CF}_2$		$\text{CF}_3-\text{CF}_2-\text{CF}_2-\text{CF}_3$		$\text{CF}_3-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_3$		$\text{CF}_3-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_3$		$\text{CF}_3-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_3$	
$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$
2.74	3650	ca. 2.78	ca. 3600	ca. 2.76	ca. 3620	2.77	3610	2.77	3610
2.83	3530	3.99	2505	ca. 3.38	ca. 2960	4.02	2480	3.37	2970
ca. 3.42	ca. 2920	4.10	2440	3.84	2605	4.17	2400	3.37	2970
ca. 3.916	ca. 2554	4.20	2380	3.94	2400	4.49	2225	4.51	2215
4.024	2485	4.33	2310	ca. 4.12	ca. 2425	4.67	2140	4.62	2165
ca. 4.078	ca. 2462	4.44	2250	4.31	2320	4.77	2095	4.78	2090
ca. 4.202	ca. 2380	4.51	2215	4.43	2255	4.83	2070	ca. 4.88	ca. 2050
4.244	2366	4.65	2150	4.46	2240	4.92	2035	5.05	1980
4.304	2315	4.86	2080	4.52	2210	4.99	2005	5.20	1925
4.404	2211	4.97	2010	4.63	2160	5.11	1955	5.40	1850
ca. 4.444	ca. 2250	5.02	1990	4.79	2090	5.21	1920	5.47	1830
ca. 4.835	ca. 2157	5.11	1955	4.83	2070	5.33	1875	5.55	1800
ca. 4.896	2042	5.26	1900	4.91	2035	5.43	1840	5.62	1780
5.098	1982	5.34	1875	ca. 5.07	ca. 1970	5.53	1810	5.80	1725
ca. 5.140	ca. 1946	5.38	1860	5.20	1925	5.63	1775	ca. 6.33	ca. 1580
ca. 5.240	ca. 1908	5.52	1810	5.34	1875	5.82	1720	6.61	1513
ca. 5.335	ca. 1874	5.59	1790	5.45	1845	6.00	1667	ca. 7.02	ca. 1425
ca. 5.480	ca. 1825	5.83	1715	5.53	1800	6.08	1645	7.55	1307
5.520	1812	5.88	1700	5.60	1785	6.24	1587	7.80	1282
5.602	1765	5.98	1670	5.68	1700	6.30	1567	7.99	1252
5.750	1745	6.08	1645	5.82	1661	6.38	1507	8.16	1225
5.845	1711	6.24	1603	6.11	1637	6.46	1485	8.31	1203
6.06	1650	6.38	1567	6.20	1625	6.53	1455	8.50	1176
ca. 6.27	ca. 1595	6.56	1524	6.38	1507	6.66	1430	8.57	1153
6.44	1553	ca. 6.56	ca. 1524	6.53	1464	6.77	1395	8.65	1143
6.90	1449	6.83	1464	6.84	1462	6.89	1425	8.85	1125
7.43	1346	6.96	1437	7.15	1358	7.03	1405	9.05	1095
7.65	1307	7.07	1414	7.29	1372	7.17	1371	9.24	1077
ca. 7.88	ca. 1269	7.44	1344	7.70	1299	7.29	1326	9.40	1050
8.13	1230	7.54	1325	7.91	1264	7.52	1330	9.60	1030
ca. 8.50	ca. 1176	7.58	1319	8.04	1244	7.66	1305	10.00	1000
8.79	ca. 1138	7.97	1304	8.33	1200	7.87	1271	10.53	950
9.31	1074	8.52	1176	8.54	1171	8.03	1245	10.88	936
9.82	1018	8.82	1138	8.77	1140	8.29	1206	11.10	910
10.30	971	9.02	1109	9.02	1109	8.46	1182	11.34	882
ca. 11.01	ca. 908	9.27	1079	9.27	1079	8.63	1159	11.59	858
11.49	870	9.41	1063	9.41	1063	8.80	1136	11.89	841
11.80	847	9.55	1045	9.55	1045	8.96	1110	12.09	827
12.29	814	9.77	1018	9.77	1018	9.01	1100	13.36	749
13.64	733	10.28	973	10.28	973	9.21	1086	13.45	743
14.35	687	10.72	933	10.72	933	9.41	1063	13.60	735
14.83	674	11.01	908	11.01	908	9.58	1045	13.85	722
15.45	647	11.51	866	11.51	866	9.76	1025	14.07	711
15.69	637	11.75	851	11.75	851	9.82	1018	14.60	685
16.24	616	12.20	820	12.20	820	10.38	963	15.34	652
ca. 17.08	ca. 585	12.66	792	12.66	792	10.94	914	15.58	642
ca. 17.33	ca. 577	13.06	765	13.06	765	11.49	873	ca. 15.83	ca. 628
ca. 18.48	ca. 541	13.51	735	13.51	735	11.93	838	16.50	606
ca. 18.66	ca. 536	13.75	725	13.75	725	12.13	824	17.08	585
ca. 19.74	ca. 507	14.15	699	14.15	699	12.40	806	17.47	572
21.31	489	14.54	688	14.54	688	12.66	773	18.33	546
		ca. 14.86	ca. 673	14.07	711	13.66	732	18.71	534



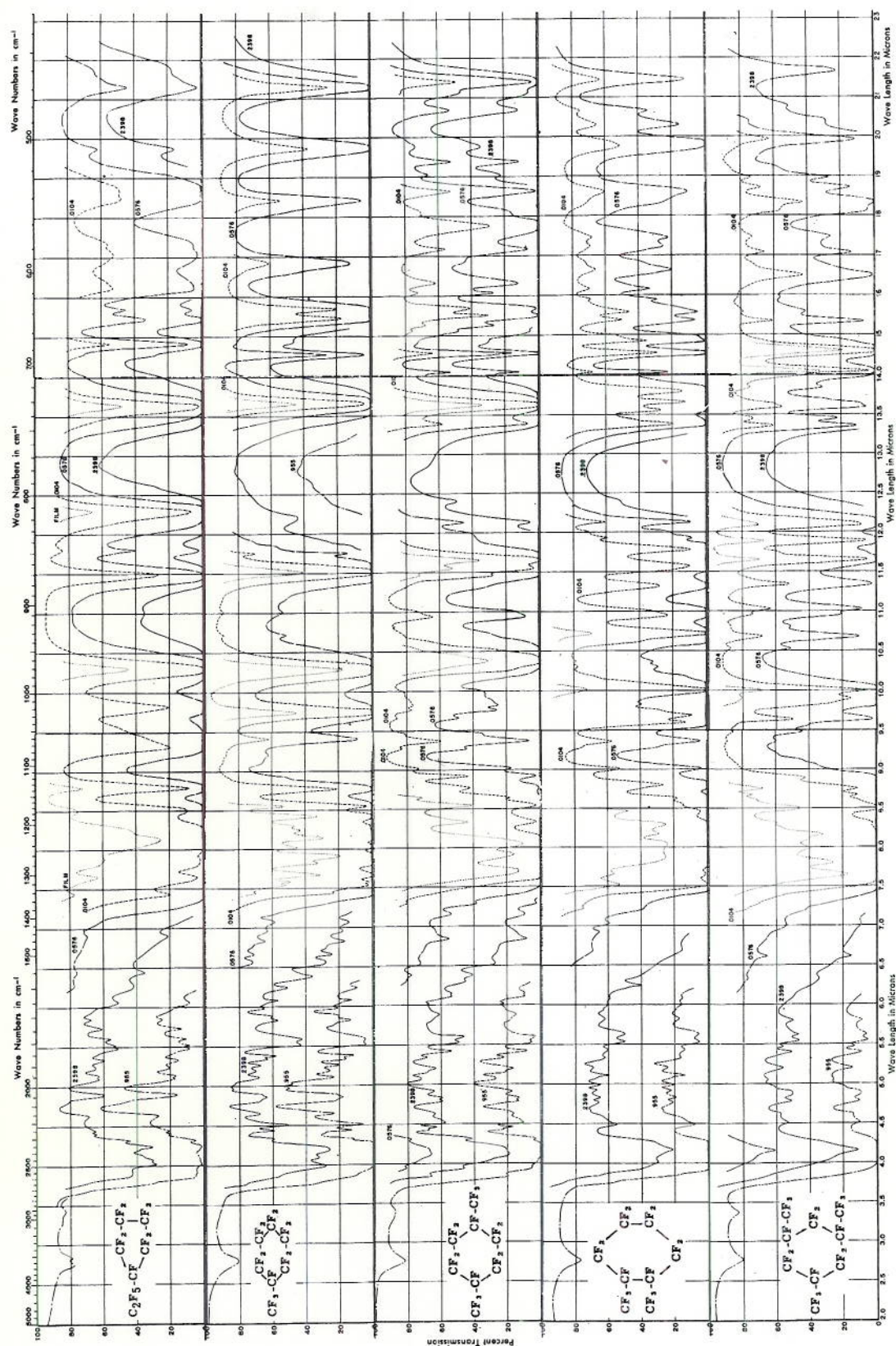


Figure 36 - Completely fluorinated ethylcyclopentane, methylcyclohexane, 1,4-dimethylcyclohexane, 1,2-dimethylcyclohexane and 1,3,5-trimethylcyclohexane

FLUOROBENZENE			p-DIFLUOROBENZENE			1,2,4-TRIFLUOROBENZENE			1,2,4,5-TETRAFLUOROBENZENE (LIQUID)			1,2,4,5-TETRAFLUOROBENZENE (GAS)			
$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$
2.14	4670	6.67	1499	2.13	4690	7.63	1311	2.13	4690	5.935	1685	2.13	4690	6.138	1629
2.33	4290	6.85	1460	2.18	4590	ca. 8.25	ca. 1212	2.21	4520	6.090	1645	2.21	4520	6.246	1601
2.45	4080	7.16	1397	2.22	4500	8.32	1202	2.27	4410	6.137	1629	2.27	4410	6.52	1594
2.57	3990	7.54	1326	2.32	4310	8.45	1183	2.32	4310	6.198	1613	2.32	4310	6.82	1511
2.69	3720	7.68	1302	2.44	4100	8.74	1144	2.37	4260	6.31	1585	2.37	4260	6.89	1451
2.87	3480	7.75	1290	2.54	3940	8.95	1117	2.47	4050	6.35	1575	2.47	4050	7.05	1439
2.985	3373	8.20	1220	2.61	3830	9.22	1085	2.62	3760	6.45	1565	2.62	3760	7.26	1377
3.015	3317	8.65	1156	2.69	3720	9.88	1012	2.70	3690	6.45	1565	2.70	3690	7.47	1359
3.132	3193	9.05	1105	2.82	3550	10.15	985	2.78	3580	6.45	1565	2.78	3580	7.65	1348
3.239	3087	9.38	1066	2.92	3436	10.61	943	2.78	3580	6.53	1543	2.78	3580	7.83	1327
3.275	3063	9.80	1020	3.201	3124	10.78	928	3.183	3142	7.11	1406	3.183	3142	8.00	1250
3.275	3063	10.04	996	3.238	3068	11.31	884	3.238	3068	7.20	1389	3.238	3068	8.23	1228
3.384	2955	10.20	980	3.324	3064	11.66	858	3.324	3064	7.27	1376	3.324	3068	8.42	1188
3.431	2915	11.16	896	3.420	3028	12.00	833	3.420	3028	7.32	1376	3.420	3068	8.59	1164
3.458	2892	11.43	875	3.451	2994	12.41	806	3.451	2994	7.37	1367	3.451	2994	8.74	1144
3.473	2879	12.03	831	3.451	2968	13.57	697	3.451	2968	7.47	1287	3.451	2968	8.84	1131
3.545	2821	12.41	806	3.555	2813	14.56	687	3.555	2813	7.53	1287	3.555	2813	9.09	1100
3.596	2781	13.29	752	3.590	2760	14.73	636	3.590	2760	7.53	1287	3.590	2760	9.24	1082
3.640	2747	14.59	685	3.638	2742	15.82	510	3.638	2742	7.72	1268	3.638	2742	9.43	1063
3.666	2713	15.32	653	3.674	2722			3.674	2722	7.72	1268	3.674	2722	9.72	1039
3.775	2649	16.26	615	3.721	2687			3.721	2687	7.72	1268	3.721	2687	9.72	1039
3.824	2615	19.23	520	3.780	2646			3.780	2646	7.72	1268	3.780	2646	9.72	1039
3.877	2579	19.86	501	3.807	2627			3.807	2627	7.72	1268	3.807	2627	9.72	1039
ca. 3.928	ca. 2546			3.915	2554			3.915	2554	7.72	1268	3.915	2554	9.72	1039
3.980	2513			3.957	2527			3.957	2527	7.72	1268	3.957	2527	9.72	1039
3.986	2503			4.030	2481			4.030	2481	7.72	1268	4.030	2481	9.72	1039
4.026	2484			4.092	2444			4.092	2444	7.72	1268	4.092	2444	9.72	1039
ca. 4.094	ca. 2443			4.126	2424			4.126	2424	7.72	1268	4.126	2424	9.72	1039
ca. 4.108	ca. 2434			4.228	2305			4.228	2305	7.72	1268	4.228	2305	9.72	1039
4.166	2400			4.265	2345			4.265	2345	7.72	1268	4.265	2345	9.72	1039
4.210	2375			4.356	2296			4.356	2296	7.72	1268	4.356	2296	9.72	1039
4.254	2351			4.399	2273			4.399	2273	7.72	1268	4.399	2273	9.72	1039
4.323	2313			4.430	2257			4.430	2257	7.72	1268	4.430	2257	9.72	1039
4.344	2302			4.488	2228			4.488	2228	7.72	1268	4.488	2228	9.72	1039
4.422	2261			ca. 4.805	2172			ca. 4.805	2172	7.72	1268	ca. 4.805	2172	9.72	1039
4.500	2222			ca. 4.850	2151			ca. 4.850	2151	7.72	1268	ca. 4.850	2151	9.72	1039
4.597	2175			ca. 4.902	2096			ca. 4.902	2096	7.72	1268	ca. 4.902	2096	9.72	1039
4.696	2128			4.980	2049			4.980	2049	7.72	1268	4.980	2049	9.72	1039
4.733	2113			4.948	2021			4.948	2021	7.72	1268	4.948	2021	9.72	1039
4.796	2065			5.055	1978			5.055	1978	7.72	1268	5.055	1978	9.72	1039
4.830	2070			ca. 5.154	1940			ca. 5.154	1940	7.72	1268	ca. 5.154	1940	9.72	1039
4.848	2061			5.210	1919			5.210	1919	7.72	1268	5.210	1919	9.72	1039
ca. 5.040	ca. 1894			5.354	1868			5.354	1868	7.72	1268	5.354	1868	9.72	1039
5.098	1862			5.540	1805			5.540	1805	7.72	1268	5.540	1805	9.72	1039
5.138	1839			5.736	1737			5.736	1737	7.72	1268	5.736	1737	9.72	1039
5.332	1855			5.970	1704			5.970	1704	7.72	1268	5.970	1704	9.72	1039
5.825	1778			6.12	1634			6.12	1634	7.72	1268	6.12	1634	9.72	1039
5.835	1714			6.25	1600			6.25	1600	7.72	1268	6.25	1600	9.72	1039
5.888	1695			6.62	1511			6.62	1511	7.72	1268	6.62	1511	9.72	1039
5.968	1678			6.96	1437			6.96	1437	7.72	1268	6.96	1437	9.72	1039
6.055	ca. 1652			7.07	1414			7.07	1414	7.72	1268	7.07	1414	9.72	1039
6.158	1624			7.28	1374			7.28	1374	7.72	1268	7.28	1374	9.72	1039
6.263	1597			7.41	1350			7.41	1350	7.72	1268	7.41	1350	9.72	1039
6.53	1531									7.72	1268			9.72	1039

Wave Numbers in cm^{-1} Wave Numbers in cm^{-1}

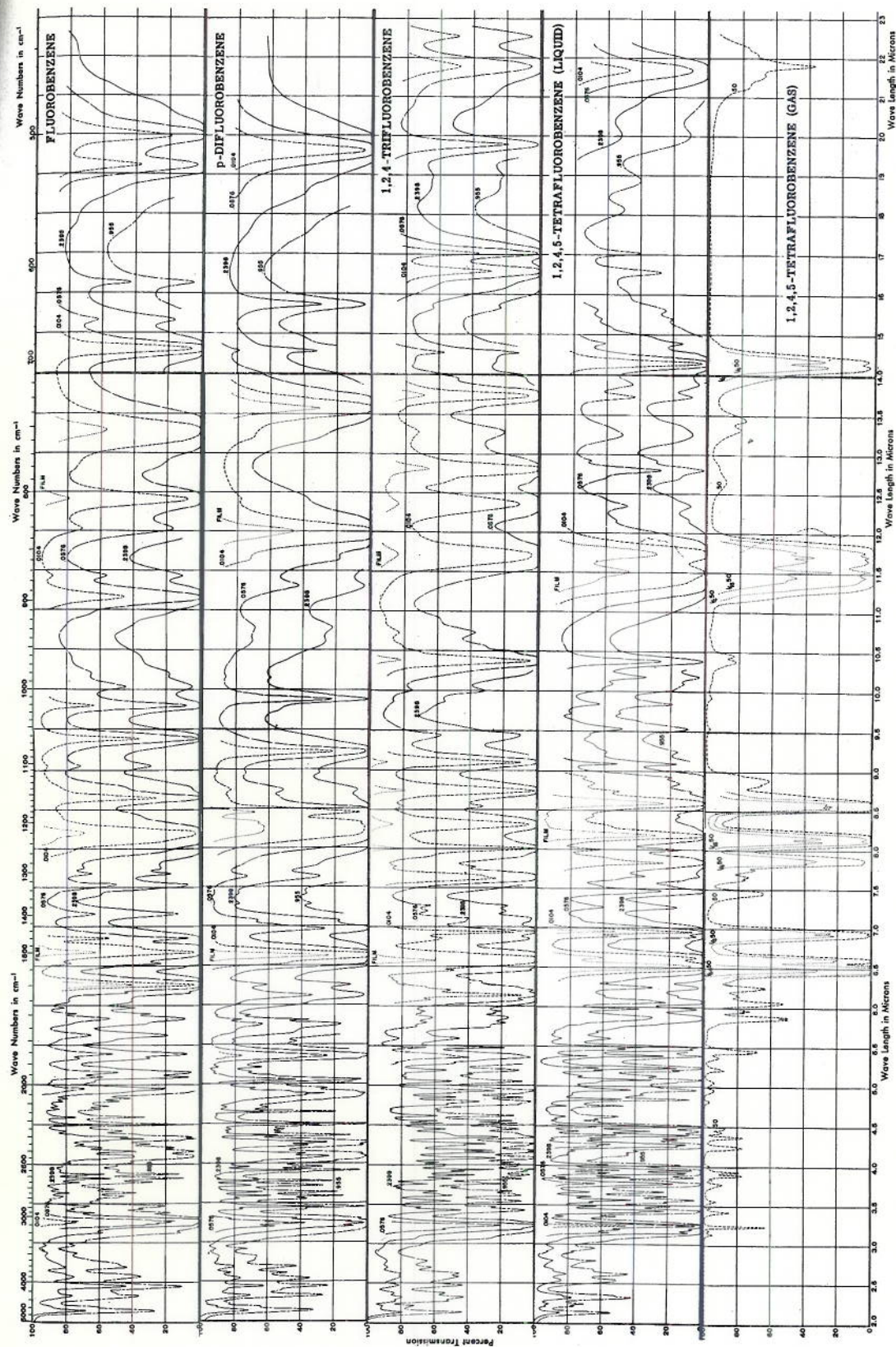


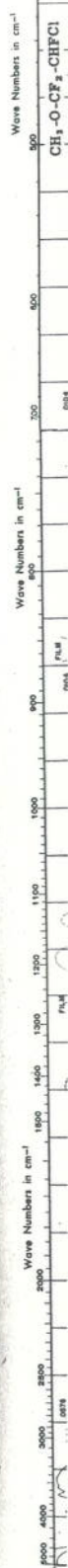
Figure 37 - Fluorobenzene, *p*-difluorobenzene, 1,2,4-trifluorobenzene, 1,2,4,5-tetrafluorobenzene (liquid) and 1,2,4,5-tetrafluorobenzene (gas)

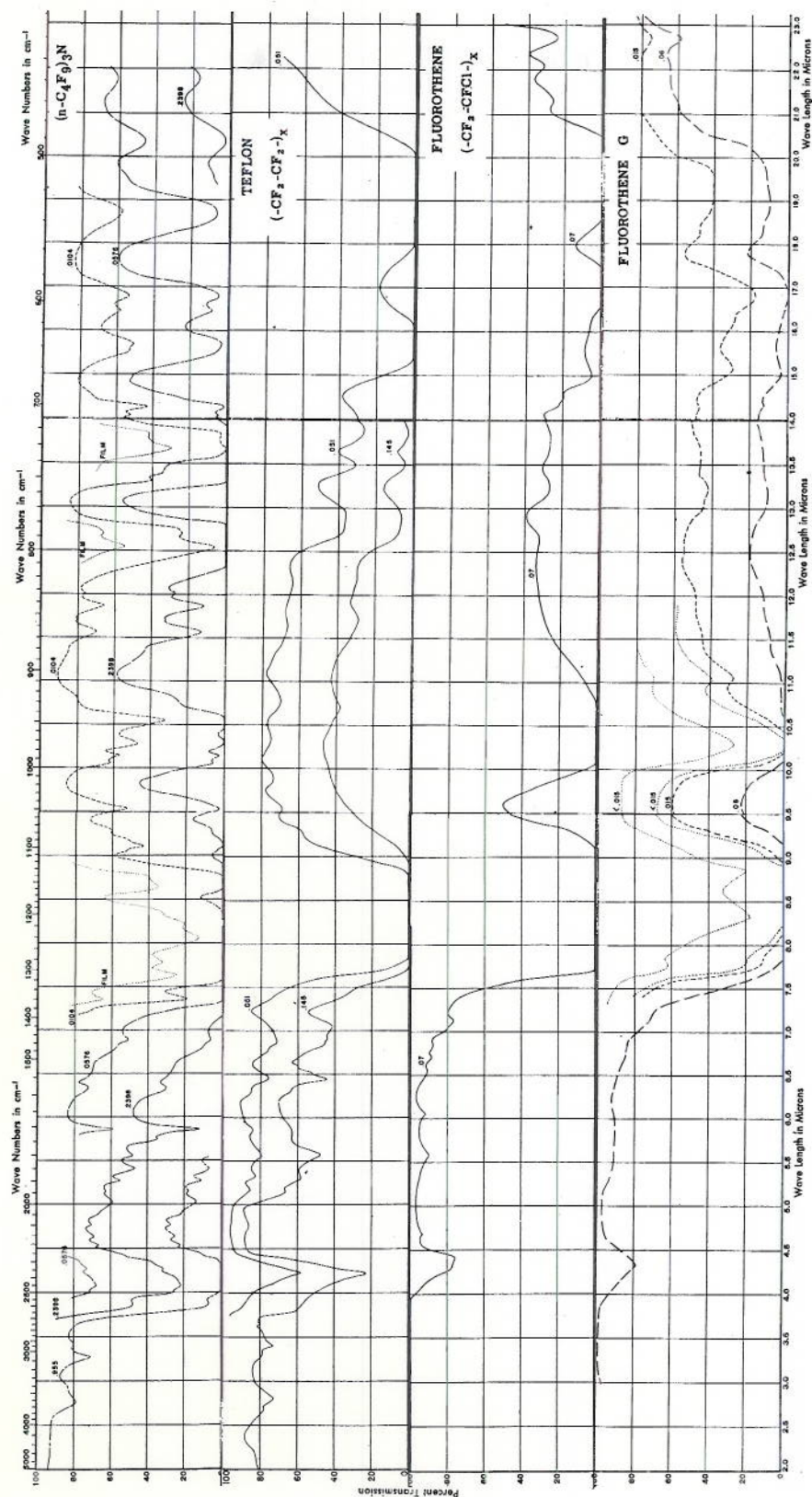
BENZOTRIFLUORIDE			m-FLUOROBENZOTRIFLUORIDE			2,5-DIFLUOROBENZOTRIFLUORIDE			o-FLUOROTOLUENE			p-FLUOROTOLUENE			
$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$
2.14	4670	6.99	1431	2.14	4670	6.86	1458	2.14	4670	7.91	1264	2.02	4950	6.28	1592
2.27	4410	7.08	1412	2.20	4550	6.98	1433	2.19	4570	7.97	1255	2.15	4650	6.67	1499
2.45	4080	7.19	1391	2.27	4410	7.13	1403	2.34	4270	8.29	1206	2.32	4310	6.80	1471
2.60	3850	7.32	1366	2.33	4290	7.50	1333	2.42	4130	8.34	1199	2.35	4260	6.85	1460
2.67	3750	7.54	1326	2.45	4080	7.80	1282	2.51	3980	8.40	1190	2.39	4180	7.23	1393
2.71	3690	7.83	1277	2.51	3980	8.01	1248	2.59	3860	8.70	1149	2.45	4080	7.55	1325
2.98	3404	8.04	1244	2.63	3800	8.24	1214	2.68	3730	8.96	1116	2.56	3910	7.70	1299
ca. 2.98	ca. 3356	8.50	1176	2.69	3720	8.52	1174	2.80	3570	9.53	1049	2.76	3820	7.80	1282
ca. 3.065	ca. 3263	8.84	1157	2.76	3620	8.81	1135	2.87	3460	9.94	1006	2.86	3500	7.89	1267
3.112	3213	9.37	1127	2.966	3372	9.20	1087	3.184	3141	10.59	944	2.946	3394	8.09	1236
3.146	3179	9.85	1070	3.108	3218	9.45	1058	3.230	3096	10.94	914	3.122	3203	8.42	1168
3.208	3117	9.74	1027	3.239	3087	9.94	1006	3.258	2968	11.30	885	3.260	3067	8.55	1142
3.226	3100	9.97	1003	3.354	2982	10.06	994	3.361	2908	12.07	829	3.284	3005	8.72	1114
3.250	3077	10.07	993	3.386	2953	10.24	977	3.447	2818	12.63	779	3.343	2944	9.31	1074
3.278	3051	10.29	972	3.419	2925	10.48	950	3.448	2800	13.42	730	3.408	2854	9.63	1038
3.382	2957	10.81	925	3.446	2885	11.19	884	3.562	2751	13.42	698	3.408	2854	9.63	1038
3.410	2933	11.11	900	3.544	2822	11.54	842	3.670	2725	15.04	665	3.468	2887	10.10	985
3.458	2884	11.94	845	3.594	2762	11.99	834	3.720	2698	15.07	658	3.610	2770	10.10	985
3.541	2824	12.23	818	3.651	2700	12.61	793	3.781	2645	17.02	588	3.645	2743	11.27	839
3.560	2793	12.98	770	3.696	2735	13.08	766	3.825	2612	18.67	536	3.754	2584	11.92	807
3.653	2651	14.07	707	3.853	2608	13.40	746	3.925	2548	20.00	500	3.851	2597	12.39	764
3.702	2584	14.83	674	3.762	2658	14.34	697	3.966	2521	21.23	471	3.890	2571	14.20	704
3.828	2512	16.78	597	3.815	2621	15.24	656	4.092	2415	ca. 21.70	ca. 461	3.956	2528	15.73	636
3.856	2503	20.52	487	3.953	2592	15.75	635	4.222	2369			3.982	2511	17.33	577
				3.958	2543	16.84	594	4.402	2245			4.064	2461	18.66	536
				3.992	2569			4.434	2231			4.132	2420	19.00	526
				3.990	2613	19.10	524	4.476	ca. 2285			4.180	2392	ca. 19.60	ca. 510
ca. 3.999	ca. 2501			4.013	2492	ca. 20.78	ca. 481	4.324	2313			4.215	2372	ca. 19.00	ca. 510
ca. 4.072	ca. 2456			4.128	2442	21.90	457	4.376	ca. 2285			4.278	ca. 2338	ca. 22.52	ca. 444
4.176	2395			4.186	2389	22.23	450	4.480	ca. 2232			4.436	2317		
4.200	2381			4.224	2367			4.572	ca. 2187			4.412	2297	4.317	2316
4.257	2349			4.254	2351			4.618	ca. 2165			4.412	2297	4.432	2256
4.296	2328			4.292	2330			4.754	2103			4.430	2257	4.472	2236
4.419	2263			4.434	2255			4.841	2068			4.458	2243	4.602	2173
ca. 4.448	ca. 2248			4.500	2222			4.902	2040			4.476	2224	ca. 4.673	ca. 2100
4.559	2193			4.540	2203			4.924	2031			4.500	2202	4.782	2054
4.634	2158			4.660	2146			4.979	2008			4.566	2190	4.868	2054
4.680	2137			4.755	2103			5.008	1998			4.600	2146	4.916	2034
4.778	2093			4.818	2076			5.098	ca. 1962			4.715	2128	5.048	1981
4.874	2052			4.880	2058			5.123	1950			4.750	2103	5.130	1949
4.980	2016			4.939	2025			5.280	1890			4.850	2074	5.314	1882
5.045	1982			5.050	1990			5.380	1859			4.935	2033	5.662	1766
5.094	1963			5.122	1952			5.460	1832			5.053	1979	5.728	1746
5.224	1914			5.218	1916			5.570	1795			5.140	1946	5.759	1736
5.274	1896			5.236	1910			5.636	1786			5.252	1904	6.193	1615
5.440	1838			5.456	1833			5.896	1718			5.360	ca. 1866	6.560	1709
5.510	1815			5.532	1808			6.037	1666			ca.	ca. 1821	6.193	1615
5.558	1787			5.580	ca. 1781			6.108	1637			5.517	1813	6.238	1602
5.738	1723			5.888	1698			6.186	1617			5.605	1784	6.280	1593
5.780	1707			5.978	1673			6.34	1577			5.740	1742	6.61	1513
6.013	1663			6.178	1621			6.64	1506			ca. 5.800	ca. 1724	6.86	1458
6.205	1612			6.232	1605			6.93	1443			5.914	1691	6.97	1435
6.48	1543			6.532	1531			7.21	1387			5.958	1678	7.23	1383
6.85	1460			6.88	1497			7.55	1325			6.110	1637	7.57	1321
				6.95	1460			7.77	1287			6.170	1621	7.69	1300



Figure 38 - Benzotrifluoride, *m*-fluorobenzotrifluoride, 2,5-difluorobenzotrifluoride, *o*-fluorotoluene and *p*-fluorotoluene

CH ₃ -O-CF ₃ -CHFCI			C ₂ H ₅ -O-CF ₃ -CHFCI			n-C ₃ H ₇ -O-CF ₃ -CHFCI			n-C ₄ H ₉ -O-CF ₃ -CHFCI			C ₆ F ₅ -O-C ₄ F ₉			
$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$	$\lambda(\mu)$	$\nu(\text{Cm}^{-1})$
2.23	4480	21.80	459	2.25	4440	2.30	4350	2.30	4350	2.82	3550	2.82	3550	2.82	3550
2.33	4290	ca.22.21	ca. 450	2.29	4370	2.34	4270	2.34	4270	3.16	3160	3.16	3160	3.16	3160
2.38	4200			2.33	4290	2.45	4080	2.45	4080	ca. 3.34	ca.2990	ca. 3.34	ca.2990	ca. 3.34	ca.2990
2.43	4120			2.44	4100	2.61	3830	2.61	3830	3.83	2610	3.83	2610	3.83	2610
2.62	3820			2.62	3820	2.69	3720	2.69	3720	ca. 4.04	ca.2475	ca. 4.04	ca.2475	ca. 4.04	ca.2475
2.68	3730			2.68	3730	2.76	3620	2.76	3620	4.18	2390	4.18	2390	4.18	2390
2.76	3620			2.76	3620	2.84	3520	2.84	3520	4.27	2340	4.27	2340	4.27	2340
2.83	3530			2.83	3530	2.89	3410	2.89	3410	4.56	2115	4.56	2115	4.56	2115
3.12	3019			3.325	3008	3.354	2982	3.354	2982	4.73	2080	4.73	2080	4.73	2080
3.360	2976			3.394	2946	3.390	2950	3.390	2950	5.13	1950	5.13	1950	5.13	1950
3.417	ca.2927			3.416	2927	3.428	2917	3.428	2917	5.32	1880	5.32	1880	5.32	1880
3.478	2875			3.470	2882	3.460	2880	3.460	2880	5.46	1830	5.46	1830	5.46	1830
3.65	2740			3.63	2610	3.71	2695	3.71	2695	5.64	ca.1775	5.64	ca.1775	5.64	ca.1775
3.74	2675			3.83	2545	3.85	2595	3.85	2595	5.81	1720	5.81	1720	5.81	1720
3.82	2620			4.09	2445	4.01	2495	4.01	2495	6.31	1585	6.31	1585	6.31	1585
3.95	2530			4.39	2185	4.14	2415	4.14	2415	6.46	1548	6.46	1548	6.46	1548
4.06	2465			4.73	2115	4.41	2270	4.41	2270	7.24	1381	7.24	1381	7.24	1381
4.20	ca.2380			4.93	2030	4.62	2165	4.62	2165	7.41	1350	7.41	1350	7.41	1350
4.31	2320			ca. 5.16	ca.1940	4.84	ca.2065	4.84	ca.2065	7.57	1321	7.57	1321	7.57	1321
4.47	2235			ca. 5.36	ca.1865	5.20	1925	5.20	1925	8.12	ca.1232	8.12	ca.1232	8.12	ca.1232
4.61	ca.2170			ca. 5.46	1830	5.48	ca.1825	5.48	ca.1825	8.69	1151	8.69	1151	8.69	1151
4.77	2095			ca. 5.56	ca.1800	5.67	1765	5.67	1765	9.07	1103	9.07	1103	9.07	1103
4.86	ca.2060			5.74	1740	5.81	1720	5.81	1720	9.43	1060	9.43	1060	9.43	1060
5.11	1955			6.09	1642	6.04	1656	6.04	1656	10.09	991	10.09	991	10.09	991
5.33	1875			6.20	1613	6.20	1613	6.20	1613	10.46	956	10.46	956	10.46	956
5.54	ca.1805			6.72	1488	6.76	1479	6.76	1479	10.67	937	10.67	937	10.67	937
5.82	1725			6.89	1451	6.80	1471	6.80	1471	10.91	917	10.91	917	10.91	917
ca. 5.90	ca.1695			7.24	1381	7.08	1412	7.08	1412	ca.11.20	ca. 893	ca.11.20	ca. 893	ca.11.20	ca. 893
6.21	1610			7.33	1364	7.18	1393	7.18	1393	11.63	880	11.63	880	11.63	880
ca. 6.50	ca.1538			7.70	1300	7.22	1385	7.22	1385	11.88	842	11.88	842	11.88	842
6.85	1460			8.01	1248	7.31	1368	7.31	1368	12.21	819	12.21	819	12.21	819
7.61	1314			ca. 8.21	ca.1218	7.62	1312	7.62	1312	12.46	803	12.46	803	12.46	803
7.67	1304			8.66	1155	7.72	1295	7.72	1295	12.86	778	12.86	778	12.86	778
7.73	1294			9.21	1086	8.04	1244	8.04	1244	13.01	769	13.01	769	13.01	769
ca. 7.99	ca.1252			ca. 9.74	ca.1027	8.25	1212	8.25	1212	13.38	747	13.38	747	13.38	747
ca. 8.12	ca.1232			ca. 10.64	ca. 940	9.18	1089	9.18	1089	ca.14.05	ca. 712	ca.14.05	ca. 712	ca.14.05	ca. 712
ca. 8.62	ca. 1160			10.89	918	9.39	1065	9.39	1065	ca.15.36	ca. 651	ca.15.36	ca. 651	ca.15.36	ca. 651
9.17	1091			11.12	895	10.21	979	10.21	979	ca.16.90	ca. 592	ca.16.90	ca. 592	ca.16.90	ca. 592
9.76	1025			11.79	848	10.44	958	10.44	958	ca.17.85	ca. 566	ca.17.85	ca. 566	ca.17.85	ca. 566
10.02	998			12.43	805	10.93	915	10.93	915	ca.20.48	ca. 488	ca.20.48	ca. 488	ca.20.48	ca. 488
10.68	888			13.63	734	11.04	ca. 893	11.04	ca. 893	ca.21.67	ca. 461	ca.21.67	ca. 461	ca.21.67	ca. 461
11.93	838			14.53	688	ca.11.04	ca. 906	ca.11.04	ca. 906						
12.46	803			ca.17.47	ca. 572	ca.12.40	ca. 805	ca.12.40	ca. 805						
12.69	788			ca.18.90	ca. 532	13.05	760	13.05	760						
ca.13.32	751			ca.22.12	ca. 452	13.15	769	13.15	769						
13.68	720					13.69	730	13.69	730						
14.27	701					14.32	698	14.32	698						
14.83	674					14.62	684	14.62	684						
17.47	572					17.40	575	17.40	575						
17.90	559					18.74	534	18.74	534						
18.47	541					ca.22.10	ca. 452	ca.22.10	ca. 452						
18.96	527														
19.94	502														
ca.20.80	ca. 481														



Figure 40 - $(\text{C}_4\text{F}_9)_3\text{N}$, Teflon, Fluorothene and Fluorothene G

APPLICATIONS

The relationship between results of spectral studies and chemical problems, or the conversion of spectroscopic information into chemical information, has been discussed in detail in several good reference works (79). In keeping with the purpose of the spectral studies here reported, we may now discuss some of the ways in which the results can be used in the solution of chemical problems.

ANALYSIS

Compound Identification

From the spectral data so far accumulated it is apparent that identification of a pure compound, the simplest sort of analysis, can be accomplished by means of either the infrared or the Raman spectrum. In either case, marked spectral differences are observed for similar compounds, e.g., for the completely fluorinated pentane isomers. It is to be expected however, that small differences in molecular weight of polymeric materials will not be reflected in the spectra. Even here the situation is superior to that for polymeric hydrocarbons because the vibrations involving fluorine atoms do not "pile up" in as narrow spectral ranges as do the vibrations involving hydrogen in hydrocarbons.

Determination of Purity

As in the case of other classes of compounds, the infrared or Raman spectrum may be used as a criterion of purity in fluorocarbons. The Raman spectrum may be superior to the infrared since (1) the Raman spectrum is weak and composed of relatively few bands whereas the infrared is strong and filled with many bands, so that the Raman spectrum has comparatively more "free" spectral regions in which to observe impurity absorption; and (2) "fluorescence" of fluorocarbons under Raman source radiation is very small indeed, a fact making possible the long exposures required to detect small concentrations in the Raman effect. It is undoubtedly true, however, that in some cases, particularly when the impurities show intense absorption and weak scattering, the infrared method will be superior. For example, impurity in the sample of $\text{CF}_3\text{-CH}_3$ studied here was detected by infrared absorption but not by the Raman effect. With either technique a high degree of purity will be assured when constant spectral properties are obtained upon successive purification steps. The minimum detectable concentration of impurities in fluorinated hydrocarbons ranges from about 1 ppm upwards, depending upon the particular impurities present and the compound being analyzed.

The determination of residual hydrogen in fluorocarbons is important in chemistry, and L. L. Burger (80) has outlined three different methods. One method, that of neutron scattering, is based upon the fact that the cross-section of hydrogen for capture of slow neutrons is about ten times that for either carbon or fluorine. It thus measures the hydrogen-to-fluorine ratio, presumably for any type of structure. A fluorescence method is based upon the fact that the fluorescence of fluorinated lube oils containing hydrogen decreases with decreasing amounts of that element. It is a rough method good for comparison of samples with like history. A specific refraction method can be used only when the composition (identity) of the pure material is known so that atomic refractions

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can be used to calculate calibration data. This method has been applied to C_7F_{16} by Grosse (81).

Although the question has not yet been investigated, it appears probable that residual hydrogen in fluorocarbons can be detected as easily by spectral methods as by any other. Thus, residual hydrogen in one sample of C_3F_8 investigated here was readily detected by infrared absorption. However, most of the fluorocarbons studied were exceptionally free of absorption or scattering in the region of C-H stretching frequencies around 3000 to 3100 cm^{-1} , indicating that little or no residual hydrogen was present. Raman bands in this region would positively indicate residual hydrogen since triply excited vibrational states (combination frequencies), which are the only type that could be observed for fluorocarbons, are too weak to detect. In the infrared the intensity of such combination bands, like the fundamentals, is much greater so that weak absorption in the C-H region does not always indicate the presence of residual hydrogen.

Qualitative and Quantitative Analysis of Mixtures

Since the spectra of different fluorinated compounds show pronounced differences, they can be used to identify individual compounds, or to identify the components in a mixture and to determine their concentrations. On the basis of analytical work with hydrocarbons, and from general considerations of the spectral differences for fluorocarbons as compared to those for hydrocarbons, it should generally be feasible to analyze by either infrared or Raman methods mixtures of from four to twelve components with an uncertainty of a few tenths to a few percent respectively. The reference spectra in this report are suitable for determining whether this can be done in any particular instance, for selecting the best analytical wavelengths to be used, and for estimating the expected accuracy.

Unfortunately, the calibration data cannot be taken directly from these spectra, first because impurity absorptions are present in some cases and secondly because, if accurate results are to be obtained, calibration measurements should be made on the same instrument as that used in the analysis. For the majority of complex molecules, the frequencies which appear to be most useful for analytical purposes fall in the range from 500 to 800 cm^{-1} . The bands in this region are strong and sharp in the Raman effect, and in both the infrared and Raman spectra marked spectral differences are observed invariably. In many cases, however, useful analytical bands are found in the broader spectral region from about 1400 cm^{-1} to 500 cm^{-1} or beyond.

Benning et al. (82) describe a procedure for the detection of as little as 1 ppm of water in several of the "Freon" refrigerants not containing hydrogen. The water absorption band at 2.76 μ is measured using a 4-inch high-pressure absorption cell filled with the liquid refrigerant.

In the spectrum of C_2F_4 (Figure 32) the weak absorption at 783 cm^{-1} is caused by about 0.05 percent $ClCF_3$ impurity. By using a longer absorption cell (one meter) the minimum detectable concentration of $ClCF_3$, HCF_3 , and other common impurities in C_2F_4 ranges from about 0.001 to 0.01 volume percent.* As mentioned previously (page 99) several prominent bands in the infrared spectrum of liquid 1,2,4,5-tetrafluorobenzene (Figure 37) are probably caused by about one percent 1,2,4-trifluorobenzene impurity.

*According to Dr. C. F. Hammer, Plastics Department, E. I. du Pont de Nemours & Company, Inc.

MOLECULAR STRUCTURE

The present discussion is not concerned with the precise determination of bond lengths and angles as required to specify the "arrangement in space" for the atoms of a molecule; instead it is concerned with the "configuration" of molecules (i.e., whether they have cyclic, straight-chain, or branched-chain structures), with the position of substituents on ring structures, and with the identity of the smaller molecular groups in the molecule. In general the discussion deals with those spectral methods and results of most use to the chemist in determining the "molecular structure" of an unknown reaction product.

The main objective has been to determine whether there exist "characteristic" group frequencies useful for identification of molecular groups in fluorocarbons and fluorinated hydrocarbons. The review of previous work on methane derivatives (see Introduction) indicated the existence of useful relationships of this sort and the spectral regions in which they would occur. The results of the correlation of C-F stretching frequencies for methane derivatives are summarized graphically in the upper portion of Figure 41.

The Olefinic $\text{CF}_2=\text{C}$ Group

Before considering the paraffinic fluorocarbons, where the methane correlations would be expected to be of most use, it is advantageous to correlate the data for ethylene derivatives, since for these compounds the fundamental frequencies have been assigned and some knowledge is available of the vibrational motions associated with the fundamentals. In the absence of this knowledge, erroneous correlations may result. For example, in the infrared spectra of the first three ethylenes examined, $\text{CH}_2=\text{CF}_2$, $\text{CF}_2=\text{CF}_2$, and $\text{CF}_2=\text{CCl}_2$, strong bands of nearly identical shape were observed at 550, 555, and 565 cm^{-1} respectively (Figure 32). This band was assigned to the CF_2 deformation fundamental in $\text{CF}_2=\text{CH}_2$, and it was assumed (a) that it had a similar explanation in the case of the other molecules and (b) that a similar band would be observed in this narrow spectral region for all compounds containing the olefinic $\text{CF}_2=\text{C}$ group. On this basis the compound C_3F_6 (Figure 34), which does not have a strong band in this spectral region, would be interpreted as being cyclic, whereas it is actually olefinic; and the compound C_4F_8 , which does have the expected band (Figure 34), would be interpreted as olefinic, whereas it is in fact cyclic. The correlation is obviously not valid, and the fallacy was found in connection with the assignment of fundamental frequencies when it became evident that the band in question is due to a CF_2 deformation motion in $\text{CH}_2=\text{CF}_2$ and $\text{CF}_2=\text{CF}_2$ but to an out-of-plane wagging of the CF_2 group in $\text{CF}_2=\text{CCl}_2$.

The olefinic $\text{CF}_2=\text{C}$ group is most readily identified by the strong infrared and Raman bands in the region from 1725 to about 1800 cm^{-1} where other saturated fluorocarbons do not have strong bands. These bands are due to valency vibrations (stretching) of the C=C bond. For vinyl type hydrocarbons and for substituted ethylene molecules which do not contain the olefinic CF_2 group, the corresponding frequency occurs near 1640 cm^{-1} . As pointed out by Torkington and Thompson (20), this frequency is enhanced by about 100 cm^{-1} when two fluorine atoms are attached to an olefinic carbon, as in $\text{CH}_2=\text{CF}_2$ (1728 cm^{-1}) and $\text{CF}_2=\text{CCl}_2$ (1749 cm^{-1}). Substitution of a third fluorine about the double bond enhances this frequency by another 50 cm^{-1} , as in $\text{CF}_2=\text{CFCl}$ (1802 cm^{-1}) and in $\text{CF}_2=\text{CF}-\text{CF}_3$ (1797 cm^{-1}). In $\text{CF}_2=\text{CF}_2$ the stretching frequency is still higher (1972 cm^{-1}) but is forbidden in the infrared because of symmetry considerations, and the band is unusually weak in the Raman spectrum.

The C-F stretching vibrations associated with the olefinic CF_2 group are spread over a large spectral range extending from about 925 cm^{-1} to 1340 cm^{-1} . However, each of

the five compounds studied has an intense infrared absorption (a type "B" band for the gas) in the upper portion of this region, from 1300-1340 cm^{-1} . Although there is some doubt as to the vibrational motion associated with this band in the case of $\text{CH}_2=\text{CF}_2$ (see page 43), it may be characterized roughly as an asymmetric C-F stretching of the olefinic CF_2 group in the other molecules. It appears, then, that this strong band may also be useful for identification of the $\text{CF}_2=\text{C}$ group in unknown samples.

Although the CF_2 deformation frequency of this olefinic group might be expected to show little variation throughout a series of molecules, it actually occurs in a spectral range extending from about 500 to 650 cm^{-1} , according to the assignments. The in-plane motion of the CF_2 group (rocking) and the out-of-plane motion (wagging) would be expected to be even more dependent upon the substituents on the opposite end of the double bond. None of the bending frequencies are very useful, therefore, for identification of this olefinic grouping. It may be of some importance to note that each of the olefins studied has a strong band in the region 500 to 565 cm^{-1} , but it must be emphasized that this correlation may not be reliable because the bands in this region do not always correspond to the same vibration. In addition, most other fluorocarbons also have bands in this region, so that the correlation cannot be of much value. However, it has been included in the regions of "characteristic" infrared absorption of the $\text{CF}_2=\text{C}$ group summarized in Figure 41.

CF_3 and CF_2 Groups in Saturated Molecules

According to the results for methane derivatives (Figure 41), it might be expected that for fluorocarbons (which contain no hydrogen) a lone C-F bond, i.e., a carbon atom with only one fluorine substituent, would be identified by a vibration frequency near 1070 cm^{-1} , a $>\text{CF}_2$ group by a pair of frequencies near 1080 and 1145 cm^{-1} , and a $-\text{CF}_3$ group

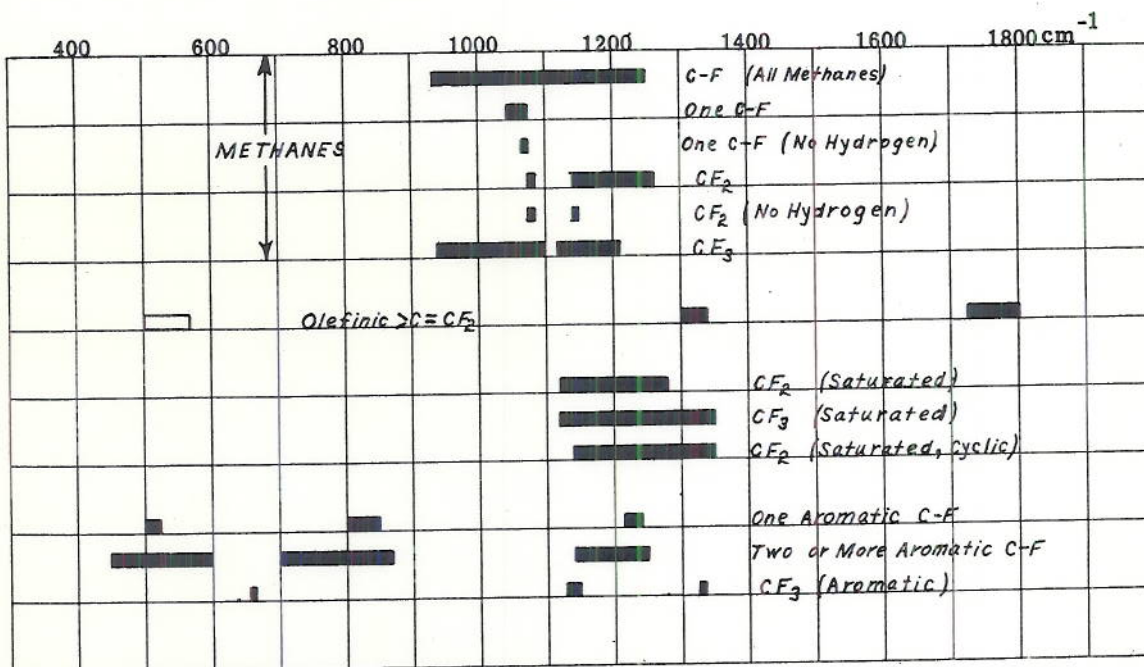


Figure 41 - Characteristic infrared absorption of fluorinated hydrocarbons

by a pair near 1100 and 1210 cm^{-1} . Since those spectral positions are rather closely spaced, and since each "position" actually corresponds to a "region" of at least 10 cm^{-1} , it is clear that, unless those correlations for methanes are preserved exactly, it will be very difficult, if not impossible, to arrive at useful correlations for these groups in the spectra of large complicated molecules.

$\text{CF}_2\text{H}-\text{CH}_3$ may be considered as a methane molecule composed of a CF_2 group with hydrogen and methyl substituents. Accordingly, one C-F valency vibration should appear between 1075 and 1085 cm^{-1} and another in the region from 1140 to 1260 cm^{-1} , presumably nearer 1260 cm^{-1} . Since this molecule possesses only a plane of symmetry, all frequencies should be active in infrared absorption, and these C-F valency vibrations should produce strong infrared bands. However, the spectrum (Figure 33) shows only one strong band instead of two, and it appears at 1040 cm^{-1} rather than in the 1075 to 1085 cm^{-1} region or at 1260 cm^{-1} . Thus the correlations for methane molecules are not adhered to closely in this favorable case. $\text{CF}_2\text{Cl}-\text{CFCl}_2$ and $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ also have no strong absorption near 1080 cm^{-1} but have strong bands at 1120 and 1160 cm^{-1} and at 1140 and 1190 cm^{-1} , respectively, which are undoubtedly closely associated with C-F stretching motions. It appears, therefore, that the strong bands associated with stretching motions of the CF_2 group are not confined to narrow spectral regions but occur anywhere from about 1120 cm^{-1} to about 1200 cm^{-1} or perhaps 1280 cm^{-1} .

Similarly, the molecule CF_3-CH_3 —which approximates a methane derivative if the methyl group is considered as a point mass—would be expected to have C-F stretching frequencies at 1100 and 1210 cm^{-1} , whereas these vibrations have been assigned the values 1232 and 1280 cm^{-1} . CF_3CCl_3 has corresponding intense bands at 1225 and 1255 cm^{-1} . Thus it appears that in larger molecules the CF_3 group is associated with strong infrared absorption in the region from 1200 to 1300 cm^{-1} rather than in the regions indicated for the methane derivatives.

The fluorocarbons C_3F_8 , $n-\text{C}_5\text{F}_{12}$, and $n-\text{C}_7\text{F}_{16}$ each have two CF_3 groups and 1, 3, and 5 CF_2 groups, respectively. On the basis of the previous results, strong infrared bands in the region of 1100 to 1200 cm^{-1} due to CF_2 and from 1200 to 1300 cm^{-1} due to CF_3 would be expected for these compounds. Actually, strong bands are observed not only throughout this region but from about 1000 cm^{-1} to 1350 cm^{-1} (Figures 34, 35). If the intensity of the stronger bands in this region can be taken as an indication that C-F stretching motions are involved, as is probable, then the fact that these vibrations spread out over a wider frequency interval in the larger molecules indicates there is considerable interaction between the vibrating groups. The concept of "characteristic" group frequencies for CF_3 and CF_2 groups is therefore a very poor approximation at best. This, of course, could have been predicted at the outset on the basis of general considerations, for it is obvious, because of the masses of the atoms involved, that the vibratory motion of the carbon atoms will be of great importance; and since these are bonded to other carbons in addition to the fluorines, only larger groups composed of at least two or more carbon atoms can be expected to possess "characteristic" group frequencies.

It is nevertheless important to obtain whatever relationships exist between absorption and the molecular structures CF_3 and CF_2 , even though the relationships are not precise. To this end it may be noted that the normal fluorocarbons all have an infrared band in the higher frequency range from 1340 to 1350 cm^{-1} and Raman bands in the region 1340 to 1380 cm^{-1} which appear to have the intensity behavior to be expected of CF_3 vibrations. Since in other cases the range for CF_3 frequencies extends to values higher than that for CF_2 frequencies, it is fairly certain that these higher frequencies in the range 1340 to 1380 cm^{-1} are associated mainly with C-F stretching motions in CF_3 groups. It may be noted that a "characteristic" olefinic CF_2 frequency falls in the adjoining lower region from 1300 to 1340 cm^{-1} . That CF_3 frequencies should be higher than those for the

olefinic CF_2 group is surprising but may be explained as an exaltation due to neighboring CF_2 groups. In fact this effect explains the trend toward higher frequencies which is observed for the various groups as they occur in progressively fluorine-enriched environments. As mentioned previously, the olefinic $\text{C}=\text{C}$ frequency increases about 50 cm^{-1} per attached fluorine under certain conditions. Likewise, the upper limit of CF_3 frequencies in $\text{CF}_3\text{-CX}_2$ -groups increases from about 1300 cm^{-1} to about 1350 cm^{-1} when X becomes fluorine. Also, a CF_2 group has frequencies at about 1145 cm^{-1} in the absence of other fluorine atoms (as in methane derivatives and in $\text{CF}_2\text{H-CH}_3$). This frequency increases to 1170 cm^{-1} and to 1190 cm^{-1} as the CF_2 group is attached to a carbon with one and two fluorine substituents, respectively (as in $\text{CF}_2\text{Cl-CFCl}_2$ and $\text{CF}_2\text{Cl-CF}_2\text{Cl}$), and it apparently increases again to values as high as 1250 or 1260 cm^{-1} on going to the n-fluorocarbons where each CF_2 group is attached to other CF_2 or CF_3 groups. Similarly, in $\text{CF}_3\text{-CF=CF}_2$, bonding of the CF_3 group to a fluorinated olefinic carbon apparently causes the uppermost CF_3 frequency to shift from around 1350 cm^{-1} to about 1400 cm^{-1} , the band at 1337 cm^{-1} being correlated with the olefinic CF_2 group as mentioned previously.

It appears, therefore, that for saturated fluorocarbons, where the CF_3 and CF_2 groups are attached only to other CF_3 or CF_2 groups, the C-F valency vibrations of the CF_2 group appear in the range from about 1120 to 1280 cm^{-1} . This overlaps the range for CF_3 groups which extends from about 1120 to 1350 cm^{-1} . It is not clear at present whether the lower frequencies in the 1000 to 1100 cm^{-1} range should be considered as CF_2 or CF_3 vibrations or as C-C vibrations which interact with C-F.

These conclusions are substantiated in part by the spectrum of Teflon which is composed essentially of CF_2 groups and absorbs strongly only in the region from 1140 to 1270 cm^{-1} (Figure 40). Also, according to the present correlations, the weak absorption shoulders at 1350 and 1080 cm^{-1} in Teflon could be caused by a few CF_3 groups.

All of the cyclic fluorocarbons studied also have strong infrared bands extending throughout the region of CF_2 frequencies from about 1140 to 1300 cm^{-1} and on into the region of CF_3 frequencies to about 1350 cm^{-1} . While bands in the higher region would be expected for those molecules which have CF_3 groups attached to the ring, they are also found for the four- and five-membered unsubstituted rings, perhaps because of steric effects and greater interaction of the CF_2 groups in small rings. It does not appear possible, therefore, to tell, by means of the absorption in this region, anything about the identity or position of the substituents on the ring for fluorocarbons of this type. The Raman frequencies in this region appear to be equally uninformative.

It does not appear likely that correlations for CF_2 or CF_3 groups can be found at lower frequencies, since in general the lower deformation vibrations are less "characteristic" than valency vibrations. But since from the spectral assignment the CF_2 deformation frequencies for cyclic C_4F_8 are known to occur at 358 , 569 , and 660 cm^{-1} , it is of interest, if possible, to trace these frequencies in the spectra of other cyclic compounds. Cyclic C_5F_{10} has a polarized Raman band at 358 cm^{-1} , and perfluoroethylcyclopentane has a strong sharp band at 356 cm^{-1} . These undoubtedly correspond to the polarized band at 358 cm^{-1} in cyclic C_4F_8 and are therefore CF_2 deformation frequencies. The other CF_2 deformation frequencies of C_4F_8 are not found for the two five-membered ring compounds, but, for the latter, coincidences are observed near 540 , 610 , and 680 cm^{-1} . For the six-membered ring compounds there appears to be a "characteristic" Raman band between 330 and 340 cm^{-1} corresponding to the CF_2 deformation frequency at 360 cm^{-1} for the five-membered ring compounds. The six-membered ring compounds also have a strong infrared and Raman band in the region from 680 to 690 cm^{-1} and another near 735 cm^{-1} . The latter position is identical with one observed for perfluoroethylcyclopentane and may be related to the CF_3 group substituent common to all these compounds.

The open-chain fluorocarbons, particularly the larger ones, also have bands distributed throughout the lower frequency region. No definite correlations have been made in this spectral range, but it may be noted that all compounds having CF_2 groups have strong infrared bands in the regions from 500 to 550 cm^{-1} and from 640 to 675 cm^{-1} , and that these regions correspond closely to regions of strong absorption of Teflon.

Although the correlations discussed for CF_2 and CF_3 groups are tentative and of such general nature that they can be of only limited value, they are summarized in Figure 41 for comparison with those for other structural groups.

Fluorinated Aromatics

In view of the correlation results for saturated molecules, it is somewhat surprising to find that several very useful correlations exist for the aromatic compounds.

Identity of the Ring. The study of hydrocarbons has shown (83) that there are at least fourteen absorption bands related to vibrations of the benzene ring (rather than the substituents) in mono-substituted alkyl benzenes. The average positions of these bands and an indication of their variability in position are listed in the first column of Table 70. These bands are rather easily identified in the spectra of fluorobenzene and benzonitrile, and their positions are also listed in Table 70. It will be noticed that in many cases these "characteristic" bands fall outside the position range given for hydrocarbons, and this may be taken as an indication that the ring substituents tend to modify the binding forces of the aromatic ring. The valence vibrations of the ring hydrogens, as indicated by the bands near 3000 cm^{-1} , are relatively unchanged in fluorobenzene but are raised

TABLE 70
Characteristic Absorption Bands of Mono-Substituted Benzenes

Hydrocarbons* cm^{-1}	Barnes cm^{-1}	Thompson cm^{-1}	Fluorobenzene cm^{-1}	Benzotrifluoride cm^{-1}
3068 \pm 10 s	3000-3100	3000-3100	3067 s	3077 ms
3030 \pm 10 s			3053 s	3051 ms
1940 \pm 5 m			1939 m	1963 m
1867 \pm 5 m			1855 m	1896 m
1800 \pm 5 m			1778 m	1815 m
1777 \pm 5 w	1740-1950		-	1767 m
1750 \pm 5 m			1714 m	1743 w
1605 \pm 3 ms			1597 vs	1612 s
1540 \pm 3 w	1580-1610	1580-1620	1499 vs	1460 s
	1485-1510	1485-1525	1070 vs	1066 s
	1070-1100		1020 s	1027 s
1030 \pm 1 ms			752 vs	770 vs
(a) 760 \pm 1 vs				
(b) 741 \pm 5 vs				
697 \pm 1 vs	680-725	705-750	685 vs	694 vs
622-625 w			623 w	ca. 622 vw

* Correlations from NRL Report C-3274.

(a) For $\text{C}_6\text{H}_5\text{-CH}$ and $\text{C}_6\text{H}_5\text{-C}$ structures.

(b) For $\text{C}_6\text{H}_5\text{-CH}_2$ structure.

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slightly in benzotrifluoride. The band at 1496 cm^{-1} is also unaffected by the single fluorine substituent but is lowered by CF_3 substitution. The group of bands in the 2000 to 1700 cm^{-1} region are combination frequencies, and some are raised and some are lowered by the fluorine substituents. The remaining bands are more closely associated with vibrations of the carbon ring, and the frequency shifts are not easily interpreted. Of these bands, the one near 750 cm^{-1} has been found most sensitive to the structure of the substituent in the case of alkyl benzenes. It appears at 760 cm^{-1} when the ring is attached to a secondary carbon and at 740 cm^{-1} when attached to a tertiary or quaternary carbon. Attachment of the ring to fluorine, as in fluorobenzene, produces a band at an intermediate position (752 cm^{-1}). In benzotrifluoride, however, where the ring is attached to a quaternary carbon, the band appears at 770 cm^{-1} , i.e., close to the $760 \pm 1\text{ cm}^{-1}$ range for analogous hydrocarbons. The correlations of Barnes et al. (1) and of Thompson (2) for the phenyl group have also been included in Table 70. Presumably they apply to all monosubstituted benzenes, including the fluorine derivatives, but it will be observed that the bands for fluorobenzene and for benzotrifluoride do not fall within the ranges given by these correlations.

The di-, tri-, and tetra-substituted benzenes also have characteristic absorption bands, although these are not as well-known as those for the phenyl group. In the first column of Table 71 are listed some of the bands common to the various isomeric xylenes and ethyltoluenes. In the second and third columns are listed the correlations of Barnes and Thompson for various aromatic structures; these presumably are independent of the substituents and apply to other compounds as well as to hydrocarbons. In the remaining columns the positions of the absorption bands are listed for the various fluorinated aromatics.

In most instances the fluorinated compounds exhibit bands which may be identified with the characteristic hydrocarbon bands, but it is noted again that the hydrocarbon correlations, and also some of those given by Barnes and Thompson, must be broadened before they can be applied rigidly to fluorinated aromatics. However, these compounds do follow previous correlations rather closely, and, for these di-substituted compounds at least, the various position isomers would have been identified correctly by the use of known correlation rules. This is of some importance, for it indicates it will be possible by means of infrared spectral correlations to identify the position (and sometimes the number) of the substituents in other fluorinated aromatics.

It may be noted that all except the first of the correlations for tri- and tetra-substituted benzenes listed in Table 71 also appear in the correlations for other aromatic structures and are characteristic of aromatic compounds in general. Identification of the position isomers of tri- and tetra-substituted aromatics must at present, be based upon a single band and is therefore very uncertain. The mono- and di-substituted rings, however, have several characteristic bands and may therefore be identified with greater certainty.

It is undoubtedly true that correlations of Raman bands could also be used either independently or in conjunction with infrared correlations for the identification of aromatic compounds and determination of the number and position of substituents. A few interesting points may be mentioned. First, the C-H stretching Raman band (or superposition of two bands) of the fluorinated benzenes appears higher than the corresponding frequency 3062 cm^{-1} in benzene. The increase from that of benzene is quite regular for the first three fluorinated benzenes and somewhat less for 1,2,4,5-tetrafluorobenzene. The increases are 10.5 cm^{-1} for fluorobenzene, 21.8 cm^{-1} for p-difluorobenzene, 32.1 cm^{-1} for 1,2,4-trifluorobenzene, and 35.1 cm^{-1} in the case of 1,2,4,5-tetrafluorobenzene. Thus, this band may be used to obtain an indication of the number of fluorine substituents.

APPLICATIONS

 TABLE 71
 Characteristic Absorptions of Various Aromatic Groupings

Previous Data			Present Results	
Smith*	Barnes	Thompson		
1,4-Substituted Benzenes				
			Para-fluoro- toluene	Para-difluoro- benzene
794-820 vvs	800-840	808-832	817 vs	833 vs
1012 s	-	-	1017 s	1012 ms
1040-1065 s	-	-	-	-
1120 s	1100-1120	1095-1125	1099 s	1085 s
1210-1220 m	1185-1210	1180-1225	1181 m	1183 vs
1520 vs	-	1485-1525	1513 vs	1511 vs
1630-1650 ms	-	1580-1620	1603, 1615 s	1634 m
ca. 1800 m	-	-	1882 ms	1805 w
ca. 1890 ms	-	-	3043 s	3064 m
ca. 3030 s	-	3000-3100	-	-
1,3-Substituted Benzenes				
			Meta-fluoro- benzotrifluoride	
690-700 vs	-	-	697 vs	
-	720-760	-	746 s	
770-782 vs	-	770-790	793 vs	
1040-1065 s	-	-	1058 vs	
ca. 1096 s	-	-	1087 s	
ca. 1156 m	1140-1160	1135-1175	ca. 1135 vs	
1170 ms	-	-	1174 vs	
ca. 1495 vs	-	1485-1525	1497 s	
1590 s	-	1580-1620	-	
1615 vs	-	-	1605 s	
1770 m	-	-	ca. 1770 m	
1860 m	-	-	1880 m	
1930 m	-	-	1952 m	
ca. 3030 s	-	3000-3100	3087	
1,2-Substituted Benzenes				
			Ortho-fluoro- toluene	
740-758 vs	755-800	740-760	754 vs	
ca. 935 m	-	-	935 m	
1040-1065 s	-	-	1038 s	
ca. 1125 ms	1090-1110	1082-1115	1114 s	
1495 vs	-	1485-1525	1499 vs	
1585 m	-	1580-1620	1592 s	
1605 s	-	-	1734 m	
1795 m	-	-	1821 mw	
1830 mw	-	-	1896 mw	
1865 w	-	-	1904 m	
1900 ms	-	-	1946 m	
1945 m	-	-	3045	
3030-3040 s	-	3000-3100	-	
1,2,4-Substituted Benzenes				
			1,2,4-trifluoro- benzene	2,5-difluoro- benzotrifluoride
	795-830	800-825	809 s	829 s
	-	1485-1525	1522 vs	1506 vs
	-	1580-1620	1629 vs	1637 s
	-	3000-3100	3098 ms	3096 ms
1,2,4,5-Substituted Benzenes				
			1,2,4,5-tetra- fluorobenzene	
		860-880	873 vs	
		1485-1520	1511, 1534 vs	
		1580-1620	1601, 1650 m	
		3000-3100	3088 s	

* For hydrocarbons only (xylenes and ethyl toluenes), NAL Report C-3274.

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In the fluorinated toluenes there occurs a medium band near 2930 cm^{-1} , and in p-fluorotoluene there is a weaker band at 3009.7 cm^{-1} which is associated with the C-H stretching of the CH_3 group. There also appears a strong Raman band at 3070.6 cm^{-1} in p-fluorotoluene and at 3069 cm^{-1} in o-fluorotoluene. The position of the latter bands, together with the frequency 3072.4 cm^{-1} for fluorobenzene, indicates that a Raman band may be expected in the range 3069 to 3073 cm^{-1} when a single fluorine is substituted on an aromatic nucleus.

In benzotrifluoride there is a Raman band at 3076 cm^{-1} , which is only slightly higher than the frequency on fluorobenzene (3072.4 cm^{-1}). In m-fluorobenzotrifluoride the band occurs at 3088 cm^{-1} , which again is only slightly higher than the corresponding band in p-difluorobenzene (3083.7 cm^{-1}). In 2,5-difluorobenzotrifluoride the band occurs at 3095 cm^{-1} , a value comparable to the corresponding band in 1,2,4-trifluorobenzene (3097 cm^{-1}). These correlations indicate that, insofar as the C-H stretching vibrations are concerned, the addition of a CF_3 group is comparable to the substitution of a fluorine directly onto the aromatic ring.

The frequency of the Raman band in the region of 1600 cm^{-1} is also enhanced by an amount roughly proportional to the number of fluorine substituents, as shown by the series: benzene (1596), fluorobenzene (1602), p-difluorobenzene (1617), 1,2,4-trifluorobenzene (1628), 1,2,4,5-tetrafluorobenzene (1643 cm^{-1}). The two fluorotoluenes and the three benzotrifluorides each have two bands in this region, that at higher frequency being the more intense, except for p-fluorotoluene. Again the frequency of the stronger band increases roughly with the number of F and CF_3 substituents, except for o-fluorotoluene (1620 cm^{-1}), as shown by the sequence: p-fluorotoluene (1601), benzotrifluoride (1610), m-fluorobenzotrifluoride (1622), 2,5-difluorobenzotrifluoride (1637 cm^{-1}).

Identity of the Substituents. Returning again to the infrared spectra, the results so far obtained for fluorinated aromatics indicate that it is also possible to identify the substituent. Having recognized that the compound is aromatic (by the above correlations), the presence of fluorine in the substituents is indicated first by the unusually great intensity of many of the absorption bands and also by the fact that the "characteristic" ring absorptions deviate slightly from their positions for hydrocarbons.

With regard to the identification of fluorine atoms and CF_3 groups as substituents, the infrared spectra of fluorinated benzenes and toluenes (i.e., compounds not containing CF_3 groups) may be considered first. In the 500 to 2000 cm^{-1} region the spectra of fluorobenzene and toluene are very similar, except that corresponding bands occur at slightly different positions and are frequently stronger for fluorobenzene. The main spectral differences are the appearance in fluorobenzene of strong absorption bands at 501 , 806 , and 1220 cm^{-1} which have no analog in toluene. That at 1220 cm^{-1} is undoubtedly due largely to stretching of the C-F bond. In the fluorotoluenes the C-F stretching frequency is only slightly higher, appearing at 1224 and 1236 cm^{-1} for the para and ortho compounds respectively. In the lower frequency range the spectra of these fluorotoluenes are very similar to those of the corresponding ethyltoluenes. The bands at 842 and 503 cm^{-1} for the para isomer and at 839 and 526 cm^{-1} for the ortho isomer are stronger than those for the hydrocarbons, however, and are apparently related to the presence of the fluorine substituent. These correlations indicate that when a single fluorine atom is attached directly to an aromatic ring intense absorption bands may be expected in the fairly narrow regions 1215 - 1240 , 800 - 850 , and 500 - 525 cm^{-1} .

Comparison of the spectra of p-difluorobenzene and of p-xylene shows that C-F stretching vibrations appear at about 1212 cm^{-1} in the difluoro compound and that the very strong band at 737 cm^{-1} and the strong band at 510 cm^{-1} are probably related to the fluorine

substituents. Both 1,2,4-trimethylbenzene and 1,2,4-trifluorobenzene have a group of five uniformly spaced bands in the 1100-1300 cm^{-1} region. These bands are at least five times more intense in the fluorinated compound, and all of them may involve C-F stretching motions; but those at 1144, 1203, and 1250 probably correspond most nearly to C-F stretching. Absorptions at 728 and 781 cm^{-1} and 587 and 603 cm^{-1} are also considerably stronger than for the hydrocarbon, apparently as a result of fluorine substitution. In 1,2,4,5-tetrafluorobenzene the intense absorptions at 1164 and 1222 cm^{-1} are undoubtedly due to C-F stretching. Strong bands are also observed at 700, 854, and 867 cm^{-1} and at 459 cm^{-1} .

These results indicate that when two or more fluorines are attached directly to an aromatic ring intense absorption bands will appear in the regions 1140-1250, 700-870, and 450-600 cm^{-1} , these regions being considerably broader than those for compounds containing a single fluorine substituent. As will be seen shortly, in the presence of a CF_3 group substituent the characteristic bands for a single fluorine substituent also fall in these broader regions rather than in the narrow regions indicated previously.

Considering now the benzotrifluoride series, each of the three compounds having a CF_3 group attached to the ring have strong bands of nearly equal intensity in each of the narrow regions 1325-1333, 1127-1149, and 658-665 cm^{-1} . Since the corresponding hydrocarbons have no characteristic absorption in these regions, these bands may be confidently assigned to CF_3 vibrations. The two higher frequencies are C-F stretching vibrations, that near 1330 cm^{-1} probably being the symmetric mode and that near 1130 cm^{-1} the doubly-degenerate asymmetric mode. The one near 660 cm^{-1} is then one of the deformation modes due to bending of the C-F bonds. These three regions of CF_3 absorptions are not overlapped by the regions for C-F (aromatic) absorption discussed above, and may therefore be used to identify a CF_3 group substituent, even in the presence of other fluorine substituents.

Two of these compounds have, in addition to the CF_3 group, fluorine atoms substituted directly on the ring. Meta-fluorobenzotrifluoride, which has a single C-F (aromatic) bond, does not have characteristic bands in the narrow regions found for other mono-fluorinated aromatics. It does, however, have strong bands in the broader regions suggested for the more completely fluorinated benzenes. This indicates that, in attempting to predict the spectral absorption of fluorine attached to the ring, the CF_3 group is to be treated not as an alkyl group but rather as another fluorine atom. 2, 5-Difluorobenzotrifluoride also has, in addition to the characteristic CF_3 vibrations, strong bands which fall in the broader spectral regions assigned to characteristic vibrations of compounds having two or more fluorine substituents.

These correlations for the identification of fluorine and CF_3 substituents in fluorinated aromatics are shown graphically in Figure 41. When used in conjunction with knowledge of the number and position of the substituents (as obtained from the characteristic ring frequencies), these correlations would allow the development of considerable structural detail for an unknown fluorinated aromatic. However, the correlations at present are based on only a few compounds and should be used with due caution until additional compounds can be studied. For example, it is not yet known whether the correlations for a CF_3 group are modified when two or more such groups are present (as in pure $\text{CF}_3\text{-C}_6\text{H}_4\text{-CF}_3$), or whether the correlations are completely preserved in the presence of chlorine or other substituents.

As in the case of the infrared absorption, some of the bands in the Raman spectra of fluorinated aromatics also appear to be associated with the presence of fluorine or CF_3 group substituents. For compounds with a single fluorine substituent, Raman bands associated with C-F stretching motions are observed in the region 1214-1234 cm^{-1} , as

in the infrared. In the case of compounds containing two or more fluorine substituents, however, the strongest Raman bands in this region occur in the range $1245\text{--}1375\text{ cm}^{-1}$, whereas the strongest infrared bands occur from about $1140\text{ to }1250\text{ cm}^{-1}$. Compounds having a CF_3 group all have sharp Raman bands in the region from about $1325\text{ to }1335\text{ cm}^{-1}$, where characteristic infrared bands also occur. All of the fluorinated aromatics have strong sharp Raman bands in the region $725\text{--}825\text{ cm}^{-1}$. All of the benzotrifluorides also have a Raman band in the region $125\text{--}140\text{ cm}^{-1}$, which is not accessible to the infrared. These bands are undoubtedly due to an out-of-plane wagging motion of the CF_3 and should be useful in identifying this substituent since Raman bands have not been found below 200 cm^{-1} in other fluorinated benzenes. In general, however, the Raman correlations do not appear to be as useful as those in the infrared for the identification of fluorine and CF_3 substituents because the Raman bands associated with C-F stretching, unlike those in the infrared, are not very intense.

THERMODYNAMIC PROPERTIES

In Table 72 are listed the values of the heat capacity of the gas at one atmosphere, the entropy, the Gibbs free energy function, and the heat content function which have been calculated for those molecules for which a complete assignment of fundamental vibrational frequencies has been made. The equations given by Herzberg (3, Chapter V) and the tables of Hougen and Watson (84) were used in these calculations. Each function is evaluated at temperatures of 600, 400, and 298°K and at the boiling point for each compound except $\text{CF}_2=\text{CCl}_2$ which boils just below room temperature. The contributions of translation plus rotation and of vibration (including torsion) and the total are listed for each temperature. In addition, the contribution of the torsional motion is listed separately, since the frequency of this vibration is less certain. For $\text{CF}_2=\text{CF}_2$, this frequency was unassigned and the contribution of the torsional motion is lacking in both the vibrational and total values given.

For $\text{CF}_2=\text{CH}_2$, the microwave values for the moments of inertia and a symmetry number of two were used. For $\text{CF}_2=\text{CCl}_2$, the moments of inertia were calculated from assumed molecular dimensions (see page 44) and may not be very accurate. A symmetry number of four and moments of inertia calculated from satisfactory electron diffraction data were used for $\text{CF}_2=\text{CF}_2$, but in this case the results obtained are incomplete because of the missing torsional frequency. For $\text{CF}_2=\text{CFCl}$, a symmetry number of unity was used, and the product of the three moments of inertia was calculated by the formula of Hirschfelder (85) using the assumed molecular dimensions C-C distance = C-F distance = 1.32\AA , C-Cl distance = 1.70\AA , and FCF angle = FCCl angle = 110° . A symmetry number of three and the moments of inertia from electron diffraction data (see page 71) were used for CF_3-CH_3 .

The symmetry number for cyclic C_4F_8 is eight. The moments of inertia were calculated from assumed dimensions (page 80), and the entropy and free-energy values are somewhat uncertain for this reason.

Calorimetric data for comparison with the values calculated from spectral data are not available for any of the olefins. For cyclic C_4F_8 , Edgall (46) refers to a calorimetric value of 37.4 cal/mole/deg for C_p at 42°C and atmospheric pressure. A slightly higher value of $37.7 \pm 1.13\text{ cal/mole/deg}$ has been referred to by Mr. E. Young of Kinetic Chemicals, Inc. (private communication) but even this value is low compared to the value $39.26\text{ cal/mole/deg}$ calculated from the present spectroscopic data. This may be due to errors in the present assignment, since two of the frequencies calculated for the unobserved fundamentals are very low.

APPLICATIONS

TABLE 72
Calculated Thermodynamic Functions for
 $\text{CF}_2=\text{CH}_2$, $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CFCl}$, $\text{CF}_2=\text{CCl}_2$, CF_3-CH_3 , and Cyclic C_4F_8

T Deg. K		C_p° Cal/Deg/Mole	S° Cal/Deg/Mole	$\frac{F_o-H_o^\circ}{T}$ Cal/Deg/Mole	$\frac{H_o-H_o^\circ}{T}$ Cal/Deg/Mole
<u>$\text{CF}_2=\text{CH}_2$</u>					
216	Trans. + Rot.	7.95	58.13	50.18	7.95
	Vib.	3.53	1.16	.25	.91
	Tor.	(.67)	(.20)	(.04)	(.16)
	Total	11.48	59.29	50.43	8.86
298	Tran. + Rot.	7.95	60.77	52.82	7.95
	Vib.	6.41	2.79	.71	2.08
	Tor.	(1.10)	(.47)	(.12)	(.35)
	Total	14.35	63.56	53.53	10.03
400	Tran. + Rot.	7.95	63.07	55.12	7.95
	Vib.	9.41	5.07	1.52	3.55
	Tor.	(1.42)	(.82)	(.25)	(.53)
	Total	17.36	68.14	56.64	11.50
600	Tran. + Rot.	7.95	66.26	58.31	7.95
	Vib.	13.48	9.55	3.50	6.04
	Tor.	(1.72)	(1.47)	(.56)	(.91)
	Total	21.43	75.81	61.81	13.99
<u>$\text{CF}_2=\text{CF}_2$ (incomplete)</u>					
222	Tran. + Rot.	7.95	61.02	53.07	7.95
	Vib. - Tor.	6.94	3.66	1.12	2.55
	Total - Tor.	14.89	64.68	54.19	10.50
298	Tran. + Rot.	7.95	63.52	55.47	7.95
	Vib. - Tor.	9.54	6.08	2.07	4.01
	Total - Tor.	17.49	69.50	57.54	11.96
400	Tran. + Rot.	7.95	65.72	57.77	7.95
	Vib. - Tor.	12.18	9.28	3.49	5.77
	Total - Tor.	20.13	75.00	61.26	13.72
600	Tran. + Rot.	7.95	68.92	60.97	7.95
	Vib. - Tor.	15.68	14.02	5.52	8.54
	Total - Tor.	23.63	82.94	66.49	16.49
<u>$\text{CF}_2=\text{CFCl}$</u>					
270	Tran. + Rot.	7.95	65.72	57.72	7.95
	Vib.	10.31	7.15	2.60	4.54
	Tor.	(1.84)	(2.14)	(.96)	(1.18)
	Total	18.26	72.87	60.32	12.49
298	Tran. + Rot.	7.95	66.52	58.59	7.95
	Vib.	11.27	8.22	3.09	5.13
	Tor.	(1.87)	(2.34)	(1.09)	(1.25)
	Total	19.22	74.74	61.68	13.08
400	Tran. + Rot.	7.95	68.87	60.92	7.95
	Vib.	14.14	11.95	4.87	7.07
	Tor.	(1.92)	(2.88)	(1.47)	(1.41)
	Total	22.09	80.82	65.79	15.02
600	Tran. + Rot.	7.95	74.42	68.47	7.95
	Vib.	17.81	18.45	8.37	10.10
	Tor.	(1.96)	(3.67)	(2.08)	(1.59)
	Total	25.76	92.87	74.84	18.05

TABLE 72 (Cont.)
Calculated Thermodynamic Functions for
 $\text{CF}_2=\text{CH}_2$, $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CFCl}$, $\text{CF}_2=\text{CCl}_2$, CF_3-CH_3 , and Cyclic C_4F_8

T		C_p°	S°	$\frac{F_0-H_0^\circ}{T}$	$\frac{H_0-H_0^\circ}{T}$
Deg. K		Cal/Deg/Mole	Cal/Deg/Mole	Cal/Deg/Mole	Cal/Deg/Mole
<u>$\text{CF}_2=\text{CCl}_2$</u>					
298	Tran. + Rot.	7.95	67.32	59.37	7.95
	Vib.	12.15	9.55	3.75	5.79
	Tor.	(1.89)	(2.50)	(1.20)	(1.30)
	Total	20.10	76.87	63.12	13.74
400	Tran. + Rot.	7.95	69.67	61.72	7.95
	Vib.	14.93	13.50	5.74	7.76
	Tor.	(1.93)	(2.80)	(1.41)	(1.39)
	Total	22.88	83.17	67.46	15.71
600	Tran. + Rot.	7.95	73.02	65.07	7.95
	Vib.	18.38	20.27	9.47	10.80
	Tor.	(1.96)	(2.83)	(2.21)	(1.62)
	Total	26.33	93.29	74.54	18.75
<u>CF_3-CH_3</u>					
250	Tran. + Rot.	7.95	60.50	52.55	7.95
	Vib.	8.49	4.98	1.67	3.31
	Tor.	(1.82)	(2.00)	(.87)	(1.13)
	Total	16.44	65.48	54.22	11.26
298	Tran. + Rot.	7.95	62.02	54.07	7.95
	Vib.	10.55	6.65	2.34	4.31
	Rot.	(1.87)	(2.33)	(1.08)	(1.25)
	Total	18.50	68.67	56.41	12.26
400	Tran. + Rot.	7.95	64.32	56.37	7.95
	Vib.	14.75	10.34	3.91	6.43
	Rot.	(1.92)	(2.88)	(1.47)	(1.41)
	Total	22.52	74.66	60.28	14.38
600	Tran. + Rot.	7.95	67.52	59.57	7.95
	Vib.	20.48	17.44	7.25	10.20
	Rot.	(1.95)	(3.67)	(2.08)	(1.59)
	Total	28.43	84.96	66.82	18.15
<u>Cyclic C_4F_8</u>					
268	Tran. + Rot.	7.95	66.92	58.97	7.95
	Vib.	27.64	21.78	8.57	13.21
	Total	35.59	88.70	67.54	21.16
298	Tran. + Rot.	7.95	67.82	59.87	7.95
	Vib.	30.01	24.79	10.02	14.77
	Total	37.96	92.61	69.89	22.72
315	Tran. + Rot.	7.95	68.42	60.47	7.95
	Vib.	31.32	26.54	10.89	15.65
	Total	39.26	94.96	71.36	23.60
400	Tran. + Rot.	7.95	69.72	61.77	7.95
	Vib.	36.80	34.58	15.06	19.52
	Total	44.75	104.30	76.83	27.47
600	Tran. + Rot.	7.95	73.12	65.12	7.95
	Vib.	45.71	51.40	24.48	26.92
	Total	53.66	124.52	89.60	34.87

Russell, Golding, and Yost (38) have reported calorimetric data for $\text{CH}_3\text{-CF}_3$. Experimentally, the value 63.95 ± 0.10 cal/mole/deg was obtained for the entropy of the ideal gas at 224.40°K and 0.9330 atmosphere. Assuming free rotation of the methyl group, and using their own assignment of fundamental vibration frequencies (no torsional frequency) and the moments of inertia $I_A = 159.4$, $I_B = I_C = 166.7 \times 10^{-40}$ g cm^2 , they obtain a value of 1.47 ± 0.14 cal/mole/deg for the difference between the calorimetric and molecular values for the entropy, which corresponds, from the tables of Pitzer and Gwinn (86), to a value of 3450 cal/mole for the potential barrier hindering free rotation. Using the formula given by Glasstone (79, page 421),

$$\nu = \frac{\sigma_i}{2\pi} \sqrt{\frac{V^0}{2I}},$$

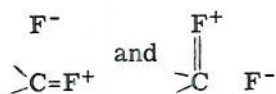
the reasonable value, 244 cm^{-1} , is obtained for the torsional frequency corresponding to this potential barrier. In the present calculations a different set of fundamentals has been used and the value $S^\circ_{224.4} (0.9330 \text{ Atm}) = 64.31$ cal/mole/deg obtained, as compared to the calorimetric value (38) 63.95 ± 0.10 cal/mole/deg. The difference between the present molecular value and that calculated by Russell, Golding, and Yost is due mainly to the lower value of 180 cm^{-1} adopted here for the uncertain torsional frequency, the difference in the assignments for the remaining fundamentals leading to a discrepancy of only 0.02 entropy units. In addition to the disagreement with the calorimetric value of the entropy, the torsional frequency of 180 cm^{-1} leads by the above equation to a low value of 1880 cal/mole for the barrier to rotation, whereas in the related molecules $\text{CH}_3\text{-CH}_3$ and $\text{CH}_3\text{-CCl}_3$ a barrier of about 3000 cal/mole has been obtained (38). Although the moments of inertia used in the calculations may not be correct, it appears that, if the calorimetric value of the entropy is correct to within ± 0.10 , as given, the torsional frequency of 180 cm^{-1} must be revised upwards in order to bring the value obtained from spectral data into agreement.

MOLECULAR FORCES

The most unusual feature of the spectral properties of fluorocarbons, at least in comparison with the spectra of hydrocarbons, is the high intensity of the infrared absorption and the weakness of the Raman scattering. As first found by Rank and Pace (16) for hexafluoroethane, the intensity of the Raman bands of most fluorocarbons is about one-tenth the intensity of the Raman bands of the corresponding hydrocarbons. In the infrared the intensity of absorption for fluorocarbons is always greater than for the corresponding hydrocarbons, sometimes by as much as a factor of ten. These intensity relationships are noted particularly in the case of bands known to correspond to vibrations involving mainly stretching of C-F bonds and, according to Torkington and Thompson (20), are not so pronounced in the case of molecules containing only one C-F bond. In the present studies, practically all the molecules contained carbon atoms with at least two attached fluorines.

These intensity relationships are undoubtedly due to the ionic character of the C-F bond which, in turn, is caused by the extreme electronegativity of the fluorine atom. According to Pauling (87) the C-F bond is 44 percent ionic, and an electric dipole therefore results from the corresponding charge distribution. In general, stretching vibrations of bonds of this type, which have associated with them a permanent dipole moment, give rise to strong infrared absorption and weak Raman scattering, whilst stretching of bonds which have no electric moment (such as in H_2 , O_2 , or N_2) produce strong Raman band but give no infrared spectrum.

It has also been proposed that, as a result of the ionic character of the C-F bond, attachment of two or more fluorines to a carbon atom fulfills the conditions for resonance between the structures



whereby a stronger bonding and greater molecular stability is obtained (87). These structures emphasize the ionic character and also introduce some double-bond character to the C-F link. The former would tend to decrease the Raman intensity while the latter would tend to increase the Raman intensity, but it is difficult to predict which effect should be the greater. It is clear from the intensity relationships only that the bond is highly ionic.

The fact that a bond is partially ionic does not imply that it is either strong or weak, although a contribution to the bond energy is to be expected in the case of resonance between ionic structures such as those just discussed. Nor does partial ionic character imply that the activation energy for chemical reactions involving the bond will be either enhanced or diminished in general. However, the concept of ionic character does play an important part in making a suitable choice of variables for describing interatomic forces, as will be discussed shortly.

The organic chemist is primarily concerned with the reactivity (or stability) of a compound and, in particular, with the reactivity at specific points (bonds) in the molecule. Since the heat of activation is not easily measured, there has been considerable interest in relating this to other measurable properties. For certain reactions such as pyrolysis, the activation energy is closely related to the bond energy, i.e., the energy required to rupture a bond. There have been many empirical relations proposed relating the bond energy to bond length and to other parameters, e.g., force constant, bond order, electronegativities, etc. In all these relationships the bond length is by far the predominant factor. This is usually measured by electron diffraction techniques, although for certain simple molecules bond distances have been more accurately determined from spectral data, particularly in the microwave region. It is now well-known (see Introduction) that in molecules which contain only one fluorine atom the C-F distance is only slightly shorter (1.38Å) than the normal covalent distance (1.41Å) given by Pauling, but that in compounds containing a CF₂ group the C-F distances are further decreased to about 1.36Å, apparently as a result of an increase in bond energy due to resonance. Brockway and Livingston (18) have obtained electron diffraction data for many fluorinated molecules and find consistently that for paraffinic, olefinic, and aromatic hydrocarbons the C-C bond distance contracts progressively as two or more fluorines are attached to the carbons forming the bond. And they correlate this with the decrease in chemical reactivity of the fluorinated compounds. However, Bauer (88), in a critical review of this work, contends that the accuracy of Brockway and Livingston's data does not justify all their conclusions. In particular, he questions the contraction of the aromatic ring upon fluorination. Also, it has recently been observed by improved electron diffraction techniques (see page 49) that the C=C distances in CH₂=CF₂ and CF₂=CF₂ are very nearly equal (~1.31Å), whereas Brockway and Livingston report values of 1.34 and 1.27Å respectively.

The important point is that accurate values of various molecular constants, particularly the bond distances, are not now available. They must certainly be determined before any of the proposed relationships can be used to obtain information concerning bond energies and to draw conclusions about molecular reactivities. For most molecules, the bond distances will have to be determined by precise electron diffraction techniques, or perhaps

from microwave spectra, rather than from the infrared and Raman spectra. Of the other possible molecular constants to be used, the stretching force constants (force in dynes/cm for bond stretching) and/or other constants in the potential function for molecular vibrations are probably the most important and must be determined by spectral methods independently of bond distances. Further, these data must be obtained for groups of related molecules, rather than for a few different structures, in order to select the proper form of the potential function and the proper relationship between bond energy and molecular parameters. In the course of the present program, only a start has been made toward this end.

In the case of fluorinated olefins it has been observed that the C=C stretching frequency increases about 50 cm^{-1} per fluorine when two or more fluorines are substituted about the double bond. Since this effect is not observed in the case of other halogens, it cannot be due to the effect of the atomic masses on the vibration frequency and must evidently be due to differences either in bond lengths or interatomic forces of the fluorinated molecules. An increase in C=C stretching frequency would generally imply an increase in the force constant for the C=C bond, and this, in turn, would imply a decrease in the C=C distance since it is generally observed that the force constant increases as the bond distance decreases (on going from C-C to C=C to C \equiv C, for example). But if it be true that the C=C distance is the same in these molecules, then the increase in frequency due to fluorine must reflect unusual molecular forces introduced by the fluorine atoms. It is in this connection that the ionic character of the C-F bond becomes of interest. In the course of the work reported here on the interpretation of the spectra of olefins, it was found that a simple valency type potential, i.e., one in which only forces for the stretching and bending of bonds are assumed, was entirely unsatisfactory, except perhaps for predicting the frequency range pattern of the fundamentals. Further work has shown that this potential function must be modified so as to take into account the repulsive forces between nonbonded atoms, which are undoubtedly caused by the electric charge distributions in partially ionic bonds. The details of these results will be presented in a later report. They agree in principle with the recent results of Edgell and Byrd (28) who find that for $\text{CH}_2=\text{CF}_2$ a single force constant of 1.17×10^5 dynes/cm associated with changes of the F-F distance "adequately replaces several valency type interaction constants otherwise required" and at the same time allows the C-F bond stretching constant to assume a reasonable single bond value of 3.8×10^{-5} dynes/cm. Only when complete results of this type and accurate bond distances are obtained for several fluorinated olefins can bond energies be calculated for comparison with independent determinations of bond energies and selection of the correct relationships.

In the case of fluorinated paraffinic molecules, previous results (Table 16) and the present results for cyclic C_4F_8 (Appendix, Table 82) again show that interatomic forces in molecules containing CF_2 or CF_3 groups are not those expected for single covalent bonding. Valence forces are usually adequate in the case of covalent bonding, but in the case of fluorocarbons valence forces lead to values of the C-F stretching force constant which correspond to double or triple rather than to single bonds, the F-C-F angle constants are larger than normal, and a large number of interaction constants are required, those between C-F distances and F-C-F angles again being the largest. Thus, even though the force constants so far obtained for these molecules may be correct, they do not appear to be useful for making predictions concerning chemical stability or reactivity. For this purpose an attempt should be made to find a potential function which is adequate and which at the same time yields not more than one large force constant per bond, or per atom.

As regards fluorinated aromatic compounds, Brockway and Livingston's conclusion, that fluorine substituents effect a contraction of the ring, finds support in the observation that in some cases the ring frequencies involving C-C stretching are enhanced by the

substitution of fluorine for hydrogen. The increased frequency of these vibrations does not necessarily imply that the ring changes dimensions, however, for this could also be due either to an increase in bond forces or to a change in the nature (e.g., distribution) of the interatomic forces. As in the case of the previous discussion, accurate molecular dimensions and the results from detailed normal coordinate treatments are required to settle these points. But it seems apparent that the electronegativity of the fluorine atom is of fundamental importance and that many of the chemical as well as physical (spectral) properties of these fluorinated aromatics can be explained or predicted on the basis of ionic effects.

For example, if benzene is considered as an electronically unsaturated resonating ring structure to which hydrogens are attached by nonresonating bonds, then the replacement of one hydrogen by electronegative fluorine, as in fluorobenzene or fluorotoluene, would be expected to result in electrical interactions between the substituent and the ring, such that the quinoidal ring structure would be introduced as an additional resonant form. As already suggested, this accounts for the increase in frequency of certain ring vibrations, particularly in the case of the ν_8 vibration of the fluorotoluenes where the vibrational motions involve mainly a stretching of the C-C bonds between carbons 2,3 and 5,6. Also, certain of the ring frequencies increase more or less uniformly as successive fluorines are attached to the ring. It seems reasonable that these effects are due to stabilizing resonance interactions between the ring and the partially ionic C-F bonds. If this is the case, all bonds in these fluorinated aromatics are more ionic than in the corresponding hydrocarbons, and as a result the interatomic forces may be expected to differ from those associated with valency force field and to approach those of a central force field. In particular, the force constants and frequencies of vibrations involving stretching of partially ionic bonds will be enhanced, whereas the force constants and frequencies involving bending of those bonds will be diminished, at least for those vibrations in which other attractive or repulsive forces cannot be of importance.

According to the assignments in Table 64, fluorine substituents tend to diminish both the planar (ν_6) and nonplanar (ν_{16}) ring bending frequencies. And in the case of vibrations involving mainly C-H bonds, fluorine substituents tend to increase the stretching of ν_2 and ν_7 , whereas the nonplanar bending frequencies ν_{10} and ν_{17} tend to decrease. These observations indicate that fluorine substituents modify the ring forces so as to render the carbon bonds less directional, an effect which might also be expected in the case of fluorinated olefins where interaction of C-F and C=C bonds could result in ionic resonant structures. Recently this has been verified by the work of Sheppard and Sutherland (89) who show that in $\text{CH}_2=\text{CX}_2$ and $\text{CH}_2=\text{CHX}$ molecules the nonplanar C-H bending vibration of the CH_2 group is independent of the mass of X and depends only upon the force constant for C-H bending. This force constant decreases as the electronegativity of X increases in the series X = alkyl, bromine, chlorine, fluorine.

Thus, the spectral data indicate that in the case of aromatics and olefins the effect of fluorine substituents is to increase the strength and to decrease the directional properties of the bonds, thereby imparting to the molecule greater thermal stability and less geometric rigidity. This is in agreement with the belief that the C-F bond is highly ionic, particularly in the case of CF_2 or CF_3 groups and in aromatic and olefinic compounds where stabilization by resonance of ionic structures can occur.

SUMMARY AND CONCLUSIONS

The infrared and Raman spectra of $\text{CH}_2=\text{CF}_2$, $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CCl}_2$, and $\text{CF}_2=\text{CFCl}$ have been determined; and all fundamental vibration frequencies, except the twisting frequency of $\text{CF}_2=\text{CF}_2$, have been assigned. Nearly all of the observed spectral frequencies have been satisfactorily interpreted, and only a few of the assignments remain uncertain. Thermodynamic functions for these molecules (which have not been determined calorimetrically) have been computed from the spectral data. Although a previous assignment of fundamentals for one other olefin, $\text{CF}_2=\text{CF}-\text{CF}_3$, has been revised on the basis of new spectral data, the assignment is less certain than for the other olefins and one fundamental remains unassigned.

A complete assignment for methylfluoroform has been made and practically all of the observed frequencies interpreted. The methyl torsion frequency is somewhat uncertain, however, and the value selected leads to a low value (1880 cal.) for the potential barrier hindering free rotation and to a higher value for the entropy than that determined calorimetrically. New infrared data for methylchloroform confirm all but one of the fundamentals reported previously for this molecule.

All of the active fundamentals of cyclic C_4F_8 have been identified with reasonable certainty, and values for the six inactive fundamentals are also proposed on the basis of observed combination frequencies and the results of a normal coordinate treatment. However, comparison of the value for the specific heat computed from the assigned fundamentals with that determined calorimetrically indicates that one or more of the fundamentals, probably one of the inactive frequencies, is too low. When a valency-type force field is assumed, the normal coordinate treatment leads to a C-F stretching force constant of 6.06×10^5 dynes/cm, which is higher than would be expected for a normal covalent single bond. It was also necessary to include several relatively large constants for interaction between stretching of C-F bonds and bending of FCF angles.

The spectra of a group of nine fluorinated aromatic hydrocarbons—consisting of monofluoro-, 1,4-difluoro-, 1,2,4-trifluoro- and 1,2,4,5-tetrafluorobenzene, ortho- and para-fluorotoluene, benzonitrile, para-fluoro- and 2,5-difluorobenzonitrile—have been obtained for the liquid state, and tentative assignments of many of the fundamentals for these molecules are proposed. With the fundamentals of the parent molecule benzene as a starting point, the corresponding fundamentals were traced in the spectra of the fluorinated derivatives using as a guide the selection rules, the results of previous work on deuterated benzenes, and the appearance of the spectra. Although the assignments are incomplete and in some cases uncertain, practically all of the observed bands of appreciable intensity are accounted for either as fundamentals or as combinations involving the observed fundamentals.

The infrared and Raman spectra of several additional saturated fluorocarbons having straight-chain, branched-chain, or cyclic configuration have also been obtained, and the infrared spectra of fifteen other fluorinated samples have been recorded. These data show that spectral methods of analysis (i.e., compound identification, purity determination and analysis of mixtures) can be applied to fluorine-containing compounds quite as readily as to hydrocarbons or other classes of organic compounds. For these purposes, the spectral range from $500\text{--}800\text{ cm}^{-1}$ (12.5 to 20 microns) is the most useful; and either infrared or Raman techniques can generally be used, the choice depending upon the particular problem.

The spectral data for the compounds studied have also been correlated empirically using as a guide both the results of previous work and the new frequency assignments proposed here. In the case of fluorinated olefins, it has been shown that faulty relationships between molecular structure and spectral absorption can easily result from solely empirical correlation of a limited number of spectra, and it is concluded that this may occur even more readily in other types of fluorocarbons. However, it appears certain that an olefinic $=CF_2$ group has characteristic frequencies near 1750 and 1325 cm^{-1} , and possibly another near 550 cm^{-1} , which may be used to identify this structural group in an unknown sample. The spectral range of each characteristic frequency has been defined and some effects of the substituents adjacent to the $=CF_2$ group upon the exact position within this range are pointed out.

In the case of saturated fluorocarbons, no useful relationships between molecular structure and infrared absorption have been found. In these compounds the CF_3 and CF_2 groups do not have useful characteristic frequencies as do the CH_3 and CH_2 groups in hydrocarbons. In the case of aromatic hydrocarbon derivatives, however, both fluorine and CF_3 group substituents on the ring appear to exhibit three characteristic absorption frequencies. These substituents may therefore be identified either singly or together, or in the presence of other alkyl substituents. In addition, it has been found that fluorine or fluorinated substituents on a benzene ring produce only a slight modification of the characteristic ring frequencies known for hydrocarbons and other substituted aromatics. This indicates that for substituted benzenes, not only the identity of the ring substituents but also their number and position can usually be determined by infrared methods. Spectral methods may therefore be particularly useful for structural determination in connection with the chemistry of fluorinated aromatic compounds.

Finally, the relationship between the spectral data and the interatomic forces in fluorinated hydrocarbons has been considered briefly. In view of the extreme electro-negativity of the fluorine atom, the intensity relationships between the infrared and Raman spectra, the nature of the force-field which must be employed to account for the observed fundamental vibration frequencies, and the known molecular structure of certain of the fluorinated compounds studied, it is concluded that the C-F bond is highly ionic, particularly in the presence of other C-F bonds or other unsaturated bonds in which case the atom(s) tend to promote molecular stability by the formation of resonant ionic structures. There is also some spectral evidence to indicate that the configuration of the molecule under these conditions is essentially as predicted by the theory of directed valence but that the directional properties of the bonds are relaxed in accordance with the increased ionic character, thereby rendering the molecule less rigid and probably more independent of steric effects.

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APPENDIX

Normal Coordinate Treatment of Perfluorocyclobutane

SYMMETRY OF THE PERFLUOROCYCLOBUTANE MOLECULE

The spectral evidence for the configuration of perfluorocyclobutane has been discussed by Edgell (46). He concluded from rather meager data that the symmetry is D_{4h} , the carbon ring forming a plane square and each CF_2 group lying in a plane perpendicular to that of the carbon atoms. Since the spectra obtained in the present research are much more complete, the question needs to be considered again.

The symmetry D_{4h} includes a center of symmetry, and the selection rules forbid the appearance of frequencies corresponding to the same vibration in both the Raman and infrared spectra. If one of the carbon atoms were out of the plane of the other three, no symmetry center would be present, and a number of coincidences of infrared and Raman frequencies would be expected. Also, the number of allowed infrared fundamentals would be more than twice as great as for the symmetry D_{4h} . In the observed spectra several coincidences do occur, namely at 438, 569, 659, 767, and 1220, and at 1337 cm^{-1} , but four of these bands are very weak in the Raman spectrum and are observed only in the liquid state in which the selection rules may possibly break down. The other two may well be accidental coincidences, in view of the large number of frequencies observed. The number of strong infrared bands observed is six, in precise agreement with the predictions based on the symmetry D_{4h} . The small number of strong infrared bands observed may also be considered an argument against the use of the V_h model (distortion of the ring in the plane), since with this symmetry eight infrared fundamentals should appear.

Wilson (90) has given convincing evidence that ordinary cyclobutane has the symmetry D_{4h} . This may be considered as further evidence for the assumption, adopted here, that perfluorocyclobutane has the symmetry D_{4h} .

INTERNAL AND SYMMETRY COORDINATES

The set of symmetry operations that transform a molecule into itself always forms a mathematical group. Any set of matrices that is isomorphic or homomorphic with the symmetry group is said to represent the group. Although any number of sets of matrices may be found that will represent a given group, only certain of these will have the property that they cannot be reduced by similarity transformations.

The characters, i.e., sums of diagonal elements, of all the irreducible representations of the symmetry group D_{4h} are given in Table 73. The symbols listed in the column headings for the symmetry operations are: I , the identity operation; $2C_4$, right and left rotation of 90° ; C_2 , rotation of 180° about the 4-fold axis; $2C_2'$, rotations of 180° about the two axes parallel to C-C bonds; $2C_2''$, rotations of 180° about the two diagonal axes; σ_h , reflection in the plane of the carbon atoms; $2\sigma_v$, reflections in the two vertical planes parallel to the C-C bonds; $2\sigma_d$, reflections in the diagonal planes; $2S_4$, right and left rotations of 90° followed by reflections in the plane of the carbon atoms; and i , inversion in the symmetry center. The row headings on the left are the standard symbols used to designate the different representations. The number of normal vibrations of the cyclobutane molecule that transform under symmetry operations according to each of the irreducible representations

A_{1g}
 A_{1u}
 A_{2g}
 A_{2u}
 B_{1g}
 B_{1u}
 B_{2g}
 B_{2u}
 E_g
 E_u

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TABLE 73
Characters for the Symmetry Group D_{4h}

	I	$2C_4$	C_4^2	$2C_2$	$2C_2'$	σ_h	2σ	$2\sigma_d$	$2S_4$	i	No. of Normal Vibrations for C_4F_8
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	3
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	1
A_{2g}	+1	+1	+1	-1	-1	+1	-1	-1	+1	+1	1
A_{2u}	+1	+1	+1	-1	-1	-1	+1	+1	-1	-1	2
B_{1g}	+1	-1	+1	+1	-1	+1	+1	-1	-1	+1	2
B_{1u}	+1	-1	+1	+1	-1	-1	-1	+1	+1	-1	3
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	3
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	1
E_g	+2	0	-2	0	0	-2	0	0	0	+2	3
E_u	+2	0	-2	0	0	+2	0	0	0	-2	4

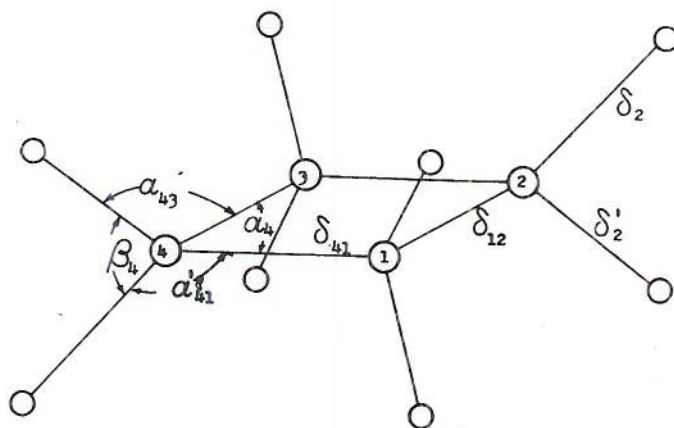
can readily be found by well-known group-theoretical methods; this number is given for each representation in the last column of Table 73. The numbers given for the doubly degenerate species E_g and E_u refer to pairs of equivalent vibrations.

The internal coordinates to be used for the C_4F_8 molecule are: the changes from the equilibrium values in the four C-C-C angles, designated by α_i ; in the four F-C-F angles, designated by β_i ; in the sixteen C-C-F angles, designated by α_{ij} (or α'_{ij}); in the eight C-F distances, designated by δ_i (or δ'_i); in the four C-C distances, designated by δ_{ij} ; and an out-of-plane distortion of the carbon ring, designated by γ . The subscripts $i, j = 1, 2, 3, 4$ refer to different carbon atoms, and the primes refer to fluorine atoms lying "below" the "horizontal" plane of the carbon atoms. Figure 42 illustrates the numbering of the coordinates, of which there are a total of 37. Since the molecule has only 30 vibrational degrees of freedom, seven dependency relations exist among them.

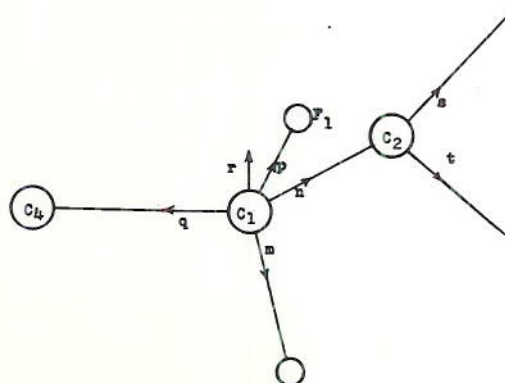
If the vibrational motions are assumed to be small, the potential energy of the distorted molecule can be expressed as a quadratic form in the coordinates. The kinetic energy is a quadratic form in the time derivatives of the coordinates. From these two expressions the secular equation for the normal frequencies could be written. It would be a determinantal equation of 37th degree in the frequencies. This could be reduced to the 30th degree by means of the dependency relations. The solution of such an equation would be a prohibitive task.

However, the complexity of the problem can be greatly reduced by the use of symmetry coordinates. These are defined as linear combinations of the internal coordinates having the property of transforming under symmetry operations according to irreducible representations of the symmetry group. It can be shown that, when a complete set of such coordinates is used, the secular equation will factor into equations of lower degree. There will be one equation for each of the symmetry species given in Table 73; the degree of each will be equal to the number of normal vibrations of that species.

Symmetry coordinates can be obtained in a straightforward manner by means of a method devised recently by Nielsen and Berryman (91). A set of 37 symmetry coordinates for cyclobutane is listed in Table 74. The seven dependency relations among the symmetry coordinates are listed at the bottom of the table. The general nature of the symmetry coordinates is illustrated in Figure 43.



a. Numbering of internal coordinates.



b. Orientations of unit vectors.

Figure 42 - Internal coordinates and unit vectors for perfluorocyclobutane

WILSON'S F-G MATRIX METHOD FOR SECULAR EQUATIONS

Wilson (92) has devised a method for setting up the secular equation for polyatomic molecules which is very convenient when internal coordinates, such as changes in bond distances and bond angles, are used. If F is a symmetric matrix such that twice the potential energy of the molecule is given by

$$2V = R'FR, \quad (1)$$

where R is a column matrix whose elements are the coordinates used to express the displacements of the atoms from their equilibrium positions and R' is the transpose of this matrix, and if G is a symmetric matrix such that twice the kinetic energy of the vibrational motion is given by

$$2T = R'G^{-1}R, \quad (2)$$

where \dot{R} is a column matrix whose elements are the time derivatives of the elements of R and \dot{R}' is the transpose of \dot{R} , then the secular equation may be written

$$|GF - E \lambda| = 0. \quad (3)$$

Here E is a unit matrix, GF is the matrix product of G and F , and

$$\lambda = 4 \pi^2 \nu^2, \quad (4)$$

where ν is a vibration frequency. Wilson has shown further that the determinantal equation (3) may be expanded as an algebraic equation in λ of the form:

$$\sum_{s=0}^N (-\lambda)^{N-s} \sum_{k < l < \dots} \sum_{i < j < \dots} \begin{vmatrix} G_{ki} & G_{kj} & \dots \\ G_{li} & G_{lj} & \dots \\ \dots & \dots & \dots \end{vmatrix} \begin{vmatrix} F_{ki} & F_{kj} & \dots \\ F_{li} & F_{lj} & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0 \quad (5)$$

where N is the number of rows (or columns) in the matrix G (or F), and where the sum is extended over all different sets of s letters k, l , etc., with $k < l < m$, etc., and over all different sets of s letters $i < j < \dots$, these to be chosen from the N possible values.

TABLE 74
Internal Symmetry Coordinates for Perfluorocyclobutane
and Dependency Relations

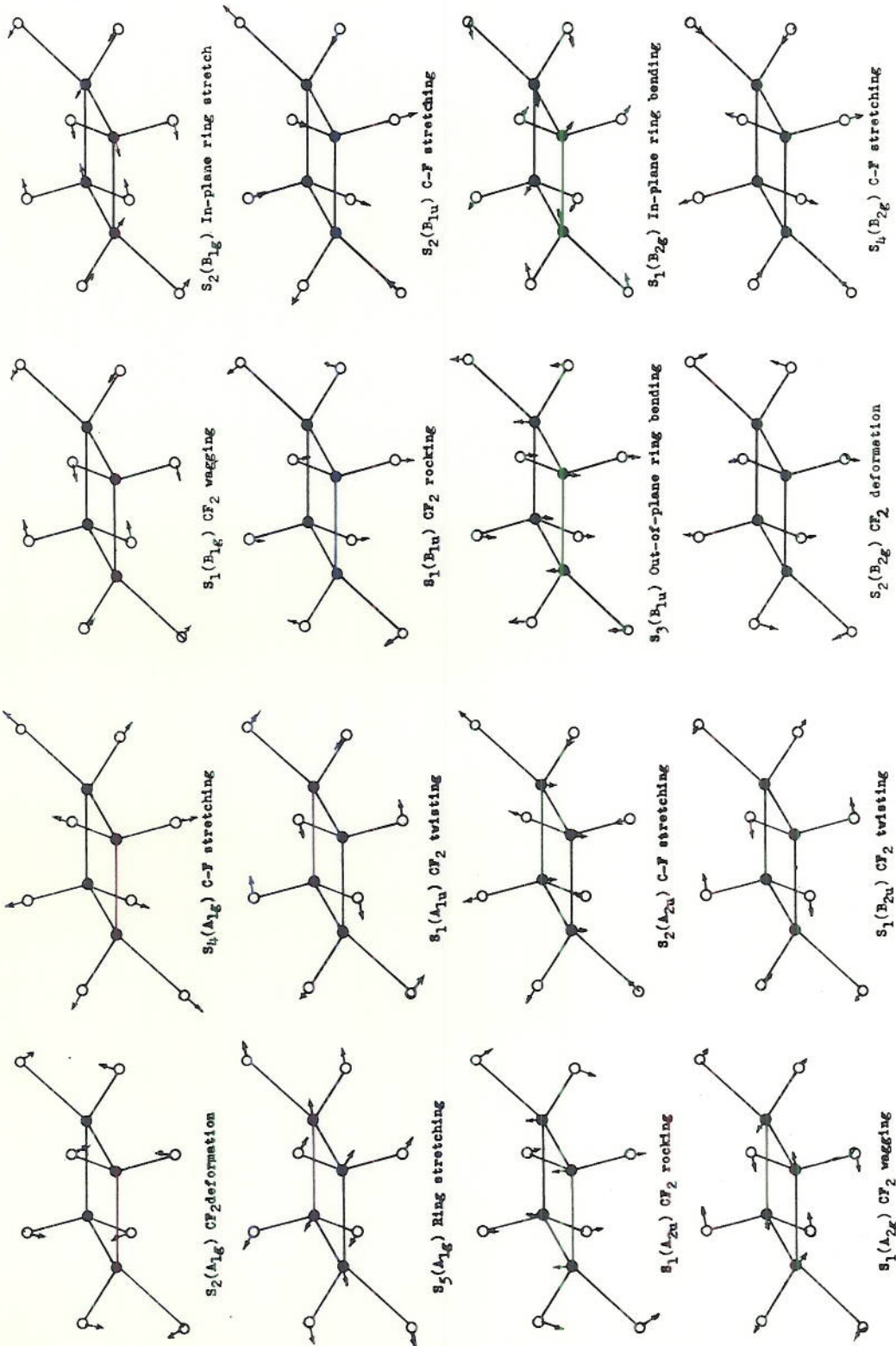
Definition of Coordinates	
$s_1(A_{1g}) = 2^{-1} (a_1 + a_2 + a_3 + a_4)$	
$s_2(A_{1g}) = 2^{-1} (\beta_1 + \beta_2 + \beta_3 + \beta_4)$	
$s_3(A_{1g}) = 2^{-2} (a_{12} + a_{21} + a_{23} + a_{32} + a_{34} + a_{43} + a_{41} + a_{14}$ $+ a_{12} + a_{21} + a_{23} + a_{32} + a_{34} + a_{43} + a_{41} + a_{14})$	
$s_4(A_{1g}) = (2\sqrt{2})^{-1} (\delta_1' + \delta_2' + \delta_3' + \delta_4' + \delta_1 + \delta_2 + \delta_3 + \delta_4)$	
$s_5(A_{1g}) = 2^{-1} (\delta_{12} + \delta_{23} + \delta_{34} + \delta_{41})$	
$s_1(A_{1u}) = 2^{-2} (a_{12} - a_{21} + a_{23} - a_{32} + a_{34} - a_{43} + a_{41} - a_{14}$ $- a_{12} + a_{21} - a_{23} + a_{32} - a_{34} + a_{43} - a_{41} + a_{14})$	
$s_1(A_{2g}) = 2^{-2} (a_{12} - a_{21} + a_{23} - a_{32} + a_{34} - a_{43} + a_{41} - a_{14}$ $+ a_{12} - a_{21} + a_{23} - a_{32} + a_{34} - a_{43} + a_{41} - a_{14})$	
$s_1(A_{2u}) = 2^{-2} (a_{12} + a_{21} + a_{23} + a_{32} + a_{34} + a_{43} + a_{41} + a_{14}$ $- a_{12} - a_{21} - a_{23} - a_{32} - a_{34} - a_{43} - a_{41} - a_{14})$	
$s_2(A_{2u}) = (2\sqrt{2})^{-1} (\delta_1 + \delta_2 + \delta_3 + \delta_4 - \delta_1' - \delta_2' - \delta_3' - \delta_4')$	
$s_1(B_{1g}) = 2^{-2} (a_{12} + a_{21} - a_{23} - a_{32} + a_{34} + a_{43} - a_{41} - a_{14}$ $+ a_{12} + a_{21} - a_{23} - a_{32} + a_{34} + a_{43} - a_{41} - a_{14})$	

TABLE 74 (Cont.)
Internal Symmetry Coordinates for Perfluorocyclobutane
and Dependency Relations

Definition of Coordinates
$s_2(B_{1g}) = 2^{-1}(\delta_{12} - \delta_{23} + \delta_{34} - \delta_{41})$
$s_1(B_{1u}) = 2^{-2}(a_{12} - a_{21} - a_{23} + a_{32} + a_{34} - a_{43} - a_{41} + a_{14} - a_{12} + a_{21} + a_{23} - a_{32} - a_{34} + a_{43} + a_{41} - a_{14})$
$s_2(B_{1u}) = (2\sqrt{2})^{-1}(-\delta_1 + \delta_2 - \delta_3 + \delta_4 + \delta'_1 - \delta'_2 + \delta'_3 - \delta'_4)$
$s_3(B_{1u}) = \gamma$
$s_1(B_{2g}) = 2^{-1}(a_1 - a_2 + a_3 - a_4)$
$s_2(B_{2g}) = 2^{-1}(\beta_1 - \beta_2 + \beta_3 - \beta_4)$
$s_3(B_{2g}) = 2^{-2}(a_{12} - a_{21} - a_{23} + a_{32} + a_{34} - a_{43} - a_{41} + a_{14} + a_{12} - a_{21} - a_{23} + a_{32} + a_{34} - a_{43} - a_{41} + a_{14})$
$s_4(B_{2g}) = (2\sqrt{2})^{-1}(\delta_1 - \delta_2 + \delta_3 - \delta_4 + \delta'_1 - \delta'_2 + \delta'_3 - \delta'_4)$
$s_1(B_{2u}) = 2^{-2}(a_{12} + a_{21} - a_{23} - a_{32} + a_{34} + a_{43} - a_{41} - a_{14} - a_{12} - a_{21} + a_{23} + a_{32} - a_{34} - a_{43} + a_{41} + a_{14})$
$s_{1a}(B_g) = (2\sqrt{2})^{-1}(a_{12} + a_{21} - a_{34} - a_{43} - a_{12} - a_{21} + a_{34} + a_{43})$
$s_{1b}(B_g) = (2\sqrt{2})^{-1}(a_{23} + a_{32} - a_{41} - a_{14} - a_{23} - a_{32} + a_{41} + a_{14})$
$s_{2a}(B_g) = (2\sqrt{2})^{-1}(a_{23} - a_{32} - a_{41} + a_{14} - a_{23} + a_{32} + a_{41} - a_{14})$
$s_{2b}(B_g) = (2\sqrt{2})^{-1}(-a_{12} + a_{21} + a_{34} - a_{43} + a_{12} - a_{21} - a_{34} + a_{43})$
$s_{3a}(B_g) = (2\sqrt{2})^{-1}(\delta_1 + \delta_2 - \delta_3 - \delta_4 - \delta'_1 - \delta'_2 + \delta'_3 + \delta'_4)$
$s_{3b}(B_g) = (2\sqrt{2})^{-1}(-\delta_1 + \delta_2 + \delta_3 - \delta_4 + \delta'_1 - \delta'_2 - \delta'_3 + \delta'_4)$
$s_{1a}(B_u) = 2^{-1}(a_1 - a_2 - a_3 + a_4)$
$s_{1b}(B_u) = 2^{-1}(a_1 + a_2 - a_3 - a_4)$
$s_{2a}(B_u) = 2^{-1}(\beta_1 - \beta_2 - \beta_3 + \beta_4)$
$s_{2b}(B_u) = 2^{-1}(\beta_1 + \beta_2 - \beta_3 - \beta_4)$
$s_{3a}(B_u) = (2\sqrt{2})^{-1}(a_{12} - a_{21} - a_{34} + a_{43} + a_{12} - a_{21} - a_{34} + a_{43})$
$s_{3b}(B_u) = (2\sqrt{2})^{-1}(a_{23} - a_{32} - a_{41} + a_{14} + a_{23} - a_{32} - a_{41} + a_{14})$
$s_{4a}(B_u) = (2\sqrt{2})^{-1}(-a_{23} - a_{32} + a_{41} + a_{14} - a_{23} - a_{32} + a_{41} + a_{14})$
$s_{4b}(B_u) = (2\sqrt{2})^{-1}(a_{12} + a_{21} - a_{34} - a_{43} + a_{12} + a_{21} - a_{34} - a_{43})$

TABLE 74 (Cont.)
Internal Symmetry Coordinates for Perfluorocyclobutane
and Dependency Relations

Definition of Coordinates
$s_{5a}(E_u) = (2\sqrt{2})^{-1} (+\delta_1 - \delta_2 - \delta_3 + \delta'_4 + \delta'_1 - \delta'_2 - \delta'_3 + \delta'_4)$ $s_{5b}(E_u) = (2\sqrt{2})^{-1} (+\delta_1 + \delta_2 - \delta_3 - \delta_4 + \delta'_1 + \delta'_2 - \delta'_3 - \delta'_4)$ $s_{6a}(E_u) = 2^{-\frac{1}{2}} (\delta_{23} - \delta_{41})$ $s_{6b}(E_u) = 2^{-\frac{1}{2}} (-\delta_{12} + \delta_{34})$
Dependency Relations
$s_1(A_{1g}) = 0$ $s_1(A_{1g}) + \sqrt{2} s_2(A_{1g}) + \sqrt{5} s_3(A_{1g}) = 0$ $s_1(E_{2g}) + \sqrt{2} s_2(E_{2g}) + \sqrt{5} s_3(E_{2g}) = 0$ $DS_{1a}(E_u) - \sqrt{2} s_{6a}(E_u) = 0$ $DS_{1b}(E_u) - \sqrt{2} s_{6b}(E_u) = 0$ $2s_{1a}(E_u) + 2\sqrt{2} s_{2a}(E_u) + \sqrt{10} [s_{3a}(E_u) + s_{4a}(E_u)] = 0$ $2s_{1b}(E_u) + 2\sqrt{2} s_{2b}(E_u) + \sqrt{10} [s_{3b}(E_u) + s_{4b}(E_u)] = 0$

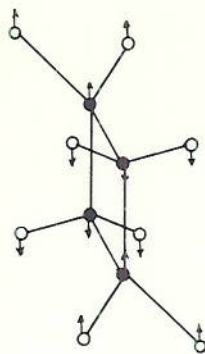


$S_1(A_{2g})$ CF₂ wagging

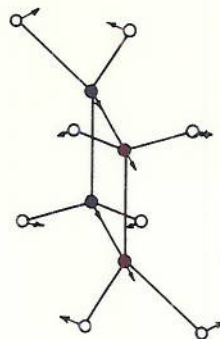
$S_1(E_{2u})$ CF₂ twisting

$S_2(A_{2g})$ CF₂ wagging

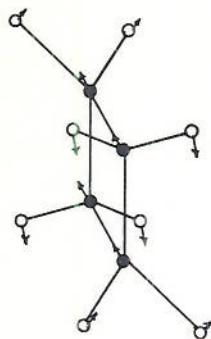
$S_2(E_{2g})$ CF₂ twisting



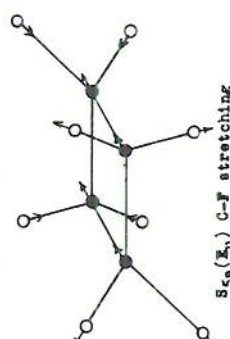
$S_{1A}(E_u)$ In-plane ring stretch



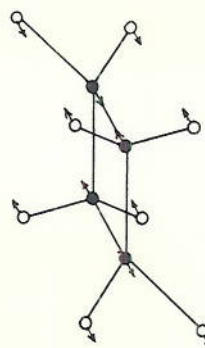
$S_{2A}(E_u)$ CF₂ deformation



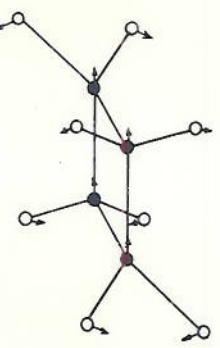
$S_{3A}(E_u)$ CF₂ wagging



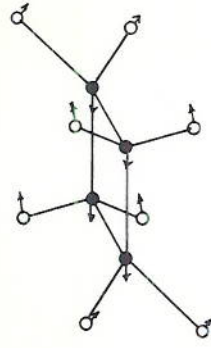
$S_{5A}(E_u)$ C-F stretching



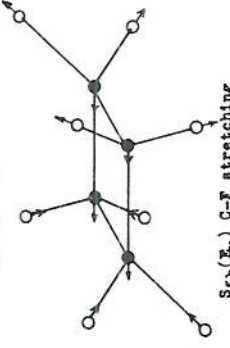
$S_{1B}(E_u)$ In-plane ring stretch



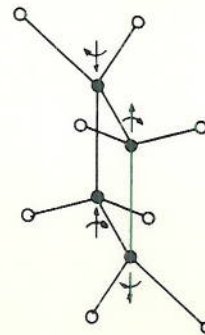
$S_{2B}(E_u)$ CF₂ deformation



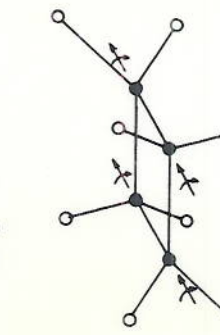
$S_{3B}(E_u)$ CF₂ wagging



$S_{5B}(E_u)$ C-F stretching



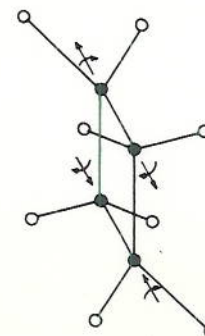
$S_{1A}(E_g)$ CF₂ twisting



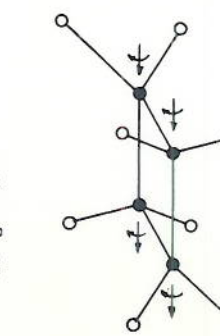
$S_{2A}(E_g)$ CF₂ twisting



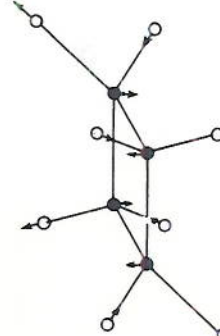
$S_{3A}(E_g)$ C-F stretching



$S_{1B}(E_g)$ CF₂ twisting



$S_{2B}(E_g)$ CF₂ twisting



$S_{3B}(E_g)$ C-F stretching

Figure 43 - Symmetry coordinates for perfluorocyclobutane

The F Matrix

The potential function that has been considered for perfluorocyclobutane is given by the following quadratic expression in the internal coordinates

$$\begin{aligned}
 2V = & r \sum_1^4 \alpha_1^2 + u \sum_1^4 \beta_1^2 + s(\alpha_{12}^2 + \alpha_{14}^2 + \alpha_{21}^2 + \alpha_{23}^2 + \alpha_{32}^2 + \alpha_{34}^2 + \alpha_{43}^2 + \alpha_{41}^2 + \alpha_{12}'^2 + \alpha_{14}'^2 \\
 & + \alpha_{21}'^2 + \alpha_{23}'^2 + \alpha_{32}'^2 + \alpha_{34}'^2 + \alpha_{43}'^2 + \alpha_{41}'^2) + x \sum_1^4 (\delta_1^2 + \delta_1'^2) + y(\delta_{12}^2 + \delta_{23}^2 + \delta_{34}^2 + \delta_{41}^2) \\
 & + v\gamma^2 + 2b[\delta_{12}(\alpha_1 + \alpha_2) + \delta_{23}(\alpha_2 + \alpha_3) + \delta_{34}(\alpha_3 + \alpha_4) + \delta_{41}(\alpha_4 + \alpha_1)] + 2c[\beta_1(\delta_1 \\
 & + \delta_1') + \beta_2(\delta_2 + \delta_2') + \beta_3(\delta_3 + \delta_3') + \beta_4(\delta_4 + \delta_4')] + 2f[\delta_{12}(\alpha_{12} + \alpha_{21} + \alpha_{12}' + \alpha_{21}') \\
 & + \delta_{23}(\alpha_{23} + \alpha_{32} + \alpha_{23}' + \alpha_{32}') + \delta_{34}(\alpha_{34} + \alpha_{43} + \alpha_{34}' + \alpha_{43}') + \delta_{41}(\alpha_{41} + \alpha_{14} + \alpha_{41}' + \alpha_{14}')] \\
 & + 2g[\delta_1(\alpha_{12} + \alpha_{14}) + \delta_2(\alpha_{21} + \alpha_{23}) + \delta_3(\alpha_{32} + \alpha_{34}) + \delta_4(\alpha_{43} + \alpha_{41}) + \delta_1'(\alpha_{12}' + \alpha_{14}') \\
 & + \delta_2'(\alpha_{21}' + \alpha_{23}') + \delta_3'(\alpha_{32}' + \alpha_{34}') + \delta_4'(\alpha_{43}' + \alpha_{41}')] + 2h(\alpha_{12}\alpha_{21} + \alpha_{23}\alpha_{32} + \alpha_{34}\alpha_{43} \\
 & + \alpha_{41}\alpha_{14} + \alpha_{21}\alpha_{12}' + \alpha_{23}\alpha_{32}' + \alpha_{34}\alpha_{43}' + \alpha_{41}\alpha_{14}') + 2k[(\delta_1 + \delta_1')(\delta_{12} + \delta_{41}) \\
 & + (\delta_2 + \delta_2')(\delta_{12} + \delta_{23}) + (\delta_3 + \delta_3')(\delta_{23} + \delta_{34}) + (\delta_4 + \delta_4')(\delta_{34} + \delta_{41})] + 2a \sum_1^4 \delta_i \delta_i' \quad (6)
 \end{aligned}$$

where (d being the equilibrium C-F distance and D being the equilibrium C-C distance): $f_{90} = r/D^2$, $f_{\beta} = u/d^2$, and $f_{\alpha} = s/d^2$ are the restoring force constants for changes in the C-C-C, F-C-F, and F-C-C angles respectively; $f_d = x$, $f_D = y$, and $f_{\gamma} = v$ are the restoring force constants for changes in the C-F distance, the C-C distance, and the distance of one carbon from the plane of the other three, respectively; and where $f_{90D} = b/D$, $f_{\beta d} = c/d$, $f_{\alpha D} = f/D$, $f_{\alpha d} = g/d$, $f_{\alpha\alpha} = h/d^2$, $f_{dD} = k$, and $f_{dd} = a$ are interaction constants for the cross product term of a C-C-C angle change with an adjacent C-C distance change, an F-C-F angle change with an adjacent C-F distance change, an F-C-C angle change with an adjacent C-C distance change, an F-C-C angle change with the adjacent C-F distance change, two F-C-C angle changes on the same side of the carbon plane with the C-C bond in common, a C-F bond change with the change of a C-C bond to the same carbon, and a C-F bond change with the change of the other C-F bond to the same carbon, respectively. The letters without subscripts are used to save writing; the f's having subscripts may all be expressed in dynes/cm, as is commonly done for force constants.

This potential function contains the so-called valence force constants for each internal coordinate, i.e., for the bond lengths and the interbond angles. Interaction constants are included for products of changes of two C-F bonds to the same carbon atom and for products of changes of C-C and C-F bonds to the same carbon atom. Interaction constants are also included for products of the change in each interbond angle with that in each of the bonds forming its sides. Because of the extreme electronegativity of fluorine, repulsions between fluorine atoms may be expected to influence the potential function. Hence, it seems reasonable to consider additional interaction terms for any pairs of coordinates whose relative values will markedly influence the distances between neighboring fluorine atoms. For this reason there has been included an interaction constant for the products of changes in F-C-C angles lying on the same side of the carbon plane and having a C-C bond in common.

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α_1
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 β_2
 β_3
 β_4
 α_{12}
 α_{14}
 α_{21}
 α_{23}
 α_{32}
 α_{34}
 α_{43}
 α_{41}
 α_{12}'
 α_{14}'
 α_{21}'
 α_{23}'
 α_{32}'
 α_{34}'
 α_{43}'
 α_{41}'
 δ_1
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It is necessary to express the potential energy in terms of the symmetry coordinates. When the linear transformation from internal coordinates to symmetry coordinates (given explicitly on page 167) is written in matrix notation,

$$S = UR, \quad (8)$$

where S is a column matrix whose elements are the symmetry coordinates in the same order as listed in Table 74, the 37 by 37 matrix U is an orthogonal matrix. Therefore, its inverse is equal to its transpose, so that

$$R = U'S \text{ and } R' = S'U. \quad (9)$$

Substitution of equations (9) into equation (7) gives

$$2V = S'FS, \quad (10)$$

where

$$F = U \mathcal{F} U'. \quad (11)$$

On carrying out the matrix multiplication indicated in equation (11), the F matrix given in Table 76 is obtained.

It can be seen from this matrix that the potential energy expressed in terms of symmetry coordinates contains no products of coordinates belonging to different representations. The complete G matrix expressed in terms of symmetry coordinates will have a diagonal block form that is the same as that of the F matrix. For such matrices, it may be recalled, the product matrix GF will also have a diagonal block form, each block being the matrix product of the corresponding G and F blocks. Thus it becomes evident that the determinantal secular equation,

$$|GF - E\lambda| = 0, \quad (3)$$

can be split up into a number of equations of lower degree, each such equation being associated with a given symmetry species. In what follows each symmetry species will be treated separately.

The orders of the F matrices for A_{1g} , B_{2g} , and E_u may be reduced by means of the dependency relations given in Table 74. Specifically, one may write out the quadratic form,

$$S'FS = \sum_{ij} S_i F_{ij} S_j,$$

for a given species, eliminate certain coordinates by expressing them in terms of the others, and write down the smaller matrix corresponding to the new quadratic form. In A_{1g} , S_1 is identically zero, so that it may simply be ignored; S_3 may be expressed in terms of S_2 by the second dependency relation. In B_{2g} , S_3 may be expressed in terms of S_1 and S_2 . In E_u , values S_{6a} , S_{6b} , S_{4a} , and S_{4b} may be eliminated similarly. With these eliminations the F matrices listed separately for each symmetry type are given in Table 77. Since the matrices are symmetric, only terms on and above the diagonal are given. One further change has been made in the doubly degenerate representations E_g and E_u . All nonzero elements in these matrices occur in 2×2 blocks, each of which is a constant times the 2×2 unit matrix. Each of these blocks has been listed as a single element in Table 77. This amounts to using only one instead of both of each pair of degenerate coordinates.

A_{1g}
 A_{2u}
 A_{2g}
 A_{2u}
 B_{1g}
 B_{1u}
 B_{2g}
 B_{2u}
 E_g
 E_u

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TABLE 76
F Matrix for Perfluorocyclobutane

		A_{1g}				A_{1u}		A_{2g}		A_{2u}		B_{1g}		B_{1u}		B_{2g}		B_{2u}		E_g				E_u								
		S_1	S_2	S_3	S_4	S_5	S_1	S_1	S_1	S_2	S_1	S_2	S_1	S_2	S_3	S_4	S_1	S_2	S_3	S_4	S_{1a}	S_{1b}	S_{2a}	S_{2b}	S_{3a}	S_{3b}	S_{4a}	S_{4b}	S_{5a}	S_{5b}	S_{6a}	S_{6b}
A_{1g}	S_1	r	0	0	0	2b																										
	S_2	0	u	0	$\sqrt{2}c$	0																										
	S_3	0	0	s+h	$\sqrt{2}f$	2f																										
	S_4	0	$\sqrt{2}c$	$\sqrt{2}f$	$x+4\sqrt{2}k$																											
	S_5	2b	0	2f	$2\sqrt{2}k$	y																										
A_{1u}	S_1					s-h																										
	S_2					s-h																										
A_{2g}	S_1																															
	S_2																															
A_{2u}	S_1																															
	S_2																															
B_{1g}	S_1																															
	S_2																															
B_{1u}	S_1																															
	S_2																															
	S_3																															
B_{2g}	S_1																															
	S_2																															
	S_3																															
	S_4																															
B_{2u}	S_1																															
	S_2																															
E_g	S_{1a}																															
	S_{1b}																															
	S_{2a}																															
	S_{2b}																															
	S_{3a}																															
	S_{3b}																															
E_u	S_{4a}																															
	S_{4b}																															
	S_{5a}																															
	S_{5b}																															
	S_{6a}																															
	S_{6b}																															
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	S_{8a}																															
	S_{8b}																															
	S_{9a}																															
	S_{9b}																															
	S_{10a}																															
	S_{10b}																															

The G Matrices

Wilson (92) has shown that the elements of the G matrix for each symmetry type for nondegenerate vibrations may be obtained from

$$G_{jl} = \sum_p \mu_p g_p \bar{S}_j(t) \cdot \bar{S}_l(t) \quad (12)$$

and for doubly degenerate vibrations from

$$G_{jl} = 1/2 \sum_p \mu_p g_p (\bar{S}_{ja}(t) \cdot \bar{S}_{la}(t) + \bar{S}_{jb}(t) \cdot \bar{S}_{lb}(t)) \quad (13)$$

where j and l refer to the symmetry coordinates used in determining the vectors S ; p refers to a set of symmetrically equivalent atoms, a typical one of which is t ; μ_p is the reciprocal of the mass of the typical atom t ; g_p is the number of equivalent atoms in the p 'th set; and the summations extend over all sets of equivalent atoms in the molecule.

The vectors S are given by

$$\bar{S}_j(t) = \sum_k U_{jk} \bar{s}_{kt}, \quad (14)$$

where U_{jk} are elements of the matrix defining the symmetry coordinates, and where the \bar{s}_{kt} are certain vectors which may be expressed in terms of unit vectors arbitrarily directed along the chemical bonds. If \bar{r}_ϵ is a unit vector from atom t toward atom t' and R_k is the change in the length of this bond from its equilibrium value, then

$$\bar{s}_{kt} = -\bar{r}_\epsilon, \quad \bar{s}_{kt'} = +\bar{r}_\epsilon. \quad (15)$$

If R is the change in the bond angle formed by the atom $t'-t''$, with t at the apex, then the vectors are

$$\begin{aligned} \bar{s}_{kt'} &= \epsilon (\cos \phi \bar{r}_\epsilon - \bar{r}_\tau) / \sin \phi, \\ \bar{s}_{kt''} &= \tau (\cos \phi \bar{r}_\tau - \bar{r}_\epsilon) / \sin \phi, \\ \bar{s}_{kt} &= [(\tau - \epsilon \cos \phi) \bar{r}_\epsilon + (\epsilon - \gamma \cos \phi) \bar{r}_\tau] / \sin \phi, \end{aligned} \quad (16)$$

where the unit vectors \bar{r}_ϵ and \bar{r}_τ point out from the apex atom toward t' and t'' , respectively; ϕ is the equilibrium value of the angle; and ϵ and τ are the reciprocals of the bond lengths tt' and tt'' , again respectively.

The unit vectors used in the present case are designated by \bar{s} , \bar{t} , \bar{m} , \bar{n} , \bar{p} , \bar{q} , and \bar{r} ; their orientations are shown in Figure 42b. From these vectors, \bar{s}_{kt} for $t = F_1$ and $t = C_1$ may be obtained by means of equations (15) and (16). The nonzero \bar{s}_{kt} vectors are listed in Table 78, where α and β are the equilibrium values of the F-C-C and F-C-F angles, respectively; τ and ϵ are the reciprocals of the equilibrium values of the C-C and C-F distances; and where $M = (\csc \beta - \cot \beta)$, $\Omega = \tau \csc \alpha - \epsilon \cot \alpha$, and $\Lambda = \epsilon \csc \alpha - \tau \cot \alpha$. Three multiplication tables of scalar products of vectors are given in Table 79; the first is for the unit vectors, the second for the vectors \bar{s}_{kF_1} ; and the third for the vectors \bar{s}_{kC_1} .

In perfluorocyclobutane there are only two symmetrically equivalent sets of atoms, the 4 carbon and the 8 fluorine atoms. Equations (12) and (13) may for this case be rewritten specifically as

$$G_{jl} = 8\mu \bar{s}_j^{F1} \cdot \bar{s}_l^{F1} + 4\eta \bar{s}_j^{C1} \cdot \bar{s}_l^{C1} \quad (17)$$

$$G_{lj} = 4\mu (\bar{s}_{ja}^{F1} \cdot \bar{s}_{la}^{F1} + \bar{s}_{jb}^{F1} \cdot \bar{s}_{lb}^{F1}) + 2\eta (\bar{s}_{ja}^{C1} \cdot \bar{s}_{la}^{C1} + \bar{s}_{jb}^{C1} \cdot \bar{s}_{lb}^{C1}), \quad (18)$$

where μ and η are reciprocals of the masses of fluorine and carbon atoms, respectively.

The vectors $S_j(t)$ occurring in equations (17) or (18) may be obtained in terms of the \bar{s}_{kt} for each species by means of equation (14). The scalar products may be evaluated by means of Table 79. The G matrices thus obtained for each symmetry type are given in Table 80, in terms of the symbols defined above. Since they are symmetrical, only the elements on and above the main diagonal are given. The redundant symmetry coordinates,

TABLE 78
The skt Vectors for Perfluorocyclobutane

$\vec{s}_{\delta_1 F_1} = \vec{p}$	$\vec{s}_{\beta_1 C_1} = \epsilon (\csc \beta - \cot \beta) (\vec{p} + \vec{m})$
$\vec{s}_{\alpha_{12} F_1} = \epsilon \cot \alpha \vec{p} - \epsilon \csc \alpha \vec{n}$	$\vec{s}_{\alpha_{12} C_1} = \mathcal{Q} \vec{p} + \Lambda \vec{n}$
$\vec{s}_{\alpha_{14} F_1} = \epsilon \cot \alpha \vec{p} - \epsilon \csc \alpha \vec{q}$	$\vec{s}_{\alpha'_{12} C_1} = \mathcal{Q} \vec{m} + \Lambda \vec{n}$
$\vec{s}_{\beta_1 F_1} = \epsilon \cot \beta \vec{p} - \epsilon \csc \beta \vec{m}$	$\vec{s}_{\alpha_{14} C_1} = \mathcal{Q} \vec{p} + \Lambda \vec{q}$
$\vec{s}_{\delta_1 C_1} = -\vec{p}$	$\vec{s}_{\alpha'_{14} C_1} = \mathcal{Q} \vec{m} + \Lambda \vec{q}$
$\vec{s}_{\delta'_1 C_1} = -\vec{m}$	$\vec{s}_{\alpha_{21} C_1} = -\tau \cot \alpha \vec{n} - \tau \csc \alpha \vec{s}$
$\vec{s}_{\delta_{12} C_1} = -\vec{n}$	$\vec{s}_{\alpha'_{21} C_1} = -\tau \cot \alpha \vec{n} - \tau \csc \alpha \vec{t}$
$\vec{s}_{\delta_{41} C_1} = -\vec{q}$	$\vec{s}_{\alpha_{41} C_1} = \tau \csc \alpha \vec{t} - \tau \cot \alpha \vec{q}$
$\vec{s}_{\alpha_1 C_1} = \tau (\vec{n} + \vec{q})$	$\vec{s}_{\alpha'_{41} C_1} = \tau \csc \alpha \vec{s} - \tau \cot \alpha \vec{q}$
$\vec{s}_{\alpha_2 C_1} = -\tau \vec{q}$	$\vec{s}_{\gamma C_1} = \vec{r}$
$\vec{s}_{\alpha_4 C_1} = -\tau \vec{n}$	

which were eliminated in computing the F matrices, have been ignored in computing the G matrices.

In order to compute numerical values for the G matrix elements it is necessary to have values for interatomic distances and angles. No electron diffraction data are available for the perfluorocyclobutane molecule, so it is necessary to assume plausible values. The C-F distance was taken as 1.36Å, since this value has been observed for several difluoromethanes. The C-C distance was taken as 1.53Å, the distance commonly observed in saturated hydrocarbons. The F-C-F angle was assumed to be 112°. With these dimensions the numerical values for the G matrices were computed; the numbers obtained for the matrix elements are given in Table 80 after the algebraic expressions. Numbers of order of magnitude 10^{38} have the dimension $\text{g}^{-1} \text{cm}^{-2}$, those of order 10^{30} the dimension $\text{g}^{-1} \text{cm}^{-1}$, and those of order 10^{22} the dimension g^{-1} .

CALCULATION OF FREQUENCIES AND ASSIGNMENT OF OBSERVED FREQUENCIES

From the F matrices in Table 77 and the G matrices in Table 80, the expanded secular equation for any symmetry species may be written down by means of equation (5). The degree of the equation in λ is equal to the dimension of the F (or G) matrix. The labor of evaluating the determinants occurring in the expansion increases rapidly as the degree of the equation increases. Thus a third degree equation required the evaluation of nine 2×2 and one 3×3 determinant minors for F or G, whereas a fourth degree equation requires thirty-six 2×2 , sixteen 3×3 minors, and one 4×4 determinant minor for the F and the same number for the G matrix.

TABLE 79
Scalar Products of Vectors

UNIT VECTORS					S _{HF} VECTORS				
\vec{M}	\vec{N}	\vec{P}	\vec{Q}	\vec{R}	\vec{S}_{HF}	\vec{S}_{H2F}	\vec{S}_{H4F}	\vec{S}_{H6F}	\vec{S}_{H8F}
\vec{M}	1	$\cos \alpha$	$\cos \beta$	$\cos \alpha \cos \beta$	1				
\vec{N}	$\cos \alpha$	1	$\cos \alpha$	0	0	ϵ^2			
\vec{P}	$\cos \beta$	$\cos \alpha$	1	$\cos \alpha \sin \beta$	0	$-\epsilon^2 \cot^2 \alpha$	ϵ^2		
\vec{Q}	$\cos \alpha$	0	$\cos \alpha$	1	0	$\epsilon^2 \cot \alpha$	$\epsilon^2 \cot \alpha$	ϵ^2	
\vec{R}	$-\sin \beta$	0	$\sin \beta$	0	0	$\epsilon^2 \cot \alpha$	$\epsilon^2 \cot \alpha$	ϵ^2	ϵ^2

S _{HC} VECTORS					S _{HF} VECTORS				
\vec{S}_{HC}	\vec{S}_{HF}	\vec{S}_{H2F}	\vec{S}_{H4F}	\vec{S}_{H6F}	\vec{S}_{HF}	\vec{S}_{H2F}	\vec{S}_{H4F}	\vec{S}_{H6F}	\vec{S}_{H8F}
\vec{S}_{HC}	1								
\vec{S}_{HC}	$\cos \beta$								
\vec{S}_{HC}	$\cos \alpha$	1							
\vec{S}_{HC}	$\cos \alpha$	0	1						
\vec{S}_{HC}	$-2\pi \cos \alpha$	$-T$	$-T$						
\vec{S}_{HC}	$-\epsilon M(1 + \cos \beta)$	$-2\epsilon M \cos \alpha$	$4\pi \epsilon M \cos \alpha$	$2\epsilon M^2(1 + \cos \beta)$					
\vec{S}_{HC}	$-(1 + \Lambda \cos \alpha)$	$-(\Lambda \cos \alpha)$	$-\Lambda \cos \alpha$	$\pi^2 \Lambda \cos \alpha$					
\vec{S}_{HC}	$-(\Lambda \cos \beta + \Lambda \cos \alpha)$	$-(\Lambda \cos \alpha)$	$-(\Lambda \cos \alpha)$	$\pi^2 \Lambda \cos \alpha$					
\vec{S}_{HC}	$-(1 + \Lambda \cos \alpha)$	$-(\Lambda \cos \alpha)$	$-(\Lambda \cos \alpha)$	$\pi^2 \Lambda \cos \alpha$					
\vec{S}_{HC}	$-(\Lambda \cos \beta + \Lambda \cos \alpha)$	$-(\Lambda \cos \alpha)$	$-(\Lambda \cos \alpha)$	$\pi^2 \Lambda \cos \alpha$					
\vec{S}_{HC}	$-\sin \beta$	0	0	0					

TABLE 80
G Matrices for Perfluorocyclobutane

A_{1g}	$G_{11} = 2\mu\epsilon^2 + 2\eta\epsilon^2(1 - \cos\beta) = 10.89 \times 10^{38}$, $G_{12} = -\sqrt{2}\eta\epsilon \csc\beta(1 - \cos^2\beta) = -4.84 \times 10^{30}$, $G_{13} = -4\eta\epsilon M \cos\alpha = 8.66 \times 10^{30}$, $G_{22} = \mu + \eta(1 + \cos\beta) = 6.31 \times 10^{22}$, $G_{23} = 2\sqrt{2}\eta \cos\alpha = -5.81 \times 10^{22}$, $G_{33} = 2\eta = 10.05 \times 10^{22}$
A_{1u}	$G_{11} = \mu\epsilon^2 \csc^2\alpha = 2.03 \times 10^{38}$
A_{2g}	$G_{11} = \mu\epsilon^2 \csc^2\alpha + 2\eta \csc^2\alpha [\epsilon^2 + \tau^2(1 + \cos\beta) - 4\epsilon\tau \cos\alpha] = 20.7 \times 10^{38}$
A_{2u}	$G_{11} = \mu\epsilon^2(1 - \cot^2\alpha) + 4\eta(1 - 2\cos^2\alpha)\epsilon^2 \cot^2\alpha = 2.78 \times 10^{38}$, $G_{12} = 2\sqrt{2}\eta\epsilon \cot\alpha(1 - 2\cos^2\alpha) = -3.09 \times 10^{30}$, $G_{22} = \mu + 2\eta(1 - 2\cos^2\alpha) = 10.08 \times 10^{22}$
B_{1g}	$G_{11} = \mu\epsilon^2 \csc^2\alpha + 2\eta\epsilon^2 \csc^2\alpha = 8.47 \times 10^{38}$, $G_{12} = -2\eta\epsilon \csc\alpha = -8.04 \times 10^{30}$, $G_{22} = 2\eta = 10.05 \times 10^{22}$
B_{1u}	$G_{11} = \mu\epsilon^2(1 - \cot^2\alpha) + 4\eta(1 - 2\cos^2\alpha)(\Omega + \tau \csc\alpha)^2 = 43.2 \times 10^{38}$, $G_{12} = 2\sqrt{2}\eta(1 - 2\cos^2\alpha)(\Omega + \tau \csc\alpha) = 17.0 \times 10^{30}$, $G_{13} = 4\eta \sin\beta/2(\Omega + \tau \csc\alpha) = 29.0 \times 10^{30}$, $G_{22} = \mu + 2\eta(1 - 2\cos^2\alpha) = 10.08 \times 10^{22}$, $G_{23} = 2\sqrt{2}\eta \sin\beta/2 = 11.78 \times 10^{22}$, $G_{33} = 4\eta = 20.1 \times 10^{22}$
B_{2g}	$G_{11} = 8\eta\tau^2 = 17.16 \times 10^{38}$, $G_{12} = 8\eta\tau\epsilon M \cos\alpha = -11.31 \times 10^{38}$, $G_{13} = -4\sqrt{2}\eta\tau \cos\alpha = 7.34 \times 10^{30}$, $G_{22} = 2\mu\epsilon^2 + 8\eta\epsilon^2 M^2 \cos^2\alpha = 10.89 \times 10^{38}$, $G_{23} = -4\sqrt{2}\eta\epsilon M \cos^2\alpha = -4.84 \times 10^{30}$, $G_{33} = \mu + 4\eta \cos^2\alpha = 6.31 \times 10^{22}$
B_{2u}	$G_{11} = \mu\epsilon^2 \csc^2\alpha = 2.03 \times 10^{38}$
E_g	$G_{11} = \mu\epsilon^2 + 2\eta\epsilon^2 \cot^2\alpha(1 - 2\cos^2\alpha) = 2.41 \times 10^{38}$, $G_{12} = 2\eta(\epsilon^2 \cot^2\alpha - 2\tau\epsilon \csc\alpha \cot\alpha)(1 - 2\cos^2\alpha) - \mu\epsilon^2 \cot^2\alpha = 3.49 \times 10^{38}$, $G_{13} = 2\eta\epsilon \cot\alpha(1 - 2\cos^2\alpha) = -2.18 \times 10^{30}$, $G_{22} = \mu\epsilon^2 + 2\eta(\Omega + \tau \csc\alpha)^2(1 - 2\cos^2\alpha) = 22.6 \times 10^{38}$, $G_{23} = 2\eta(\Omega + \tau \csc\alpha)(2\cos^2\alpha - 1) = -12.01 \times 10^{30}$, $G_{33} = \mu + 2\eta(1 - 2\cos^2\alpha) = 10.08 \times 10^{22}$
E_u	$G_{11} = 4\eta\tau^2 = 8.58 \times 10^{38}$, $G_{12} = 4\eta\tau M \cos\alpha = -5.66 \times 10^{38}$, $G_{13} = 2\sqrt{2}\eta\tau(\Omega \cos\alpha + \tau \cot\alpha) = -6.39 \times 10^{38}$, $G_{14} = -2\sqrt{2}\eta\tau \cos\alpha = 3.67 \times 10^{30}$, $G_{22} = 2\mu\epsilon^2 + 8\eta\epsilon^2 M^2 \cos^2\alpha = 10.89 \times 10^{38}$, $G_{23} = \sqrt{2}\mu\epsilon^2 M \cot\alpha + 2\sqrt{2}\eta\epsilon M(2\Omega \cos^2\alpha + \epsilon \cot\alpha) = -1.47 \times 10^{38}$, $G_{24} = -4\sqrt{2}\eta\epsilon M \cos^2\alpha = -4.84 \times 10^{30}$, $G_{33} = \mu\epsilon^2 + 2\eta(4\tau^2 \cot^2\alpha + 2\epsilon^2 \cos^2\alpha \cot^2\alpha + \epsilon^2 - \epsilon^2 \cot^2\alpha - 4\tau\epsilon \cot^2\alpha \cos\alpha) = 11.04 \times 10^{38}$, $G_{34} = -2\eta(2\Omega \cos^2\alpha + \epsilon \cot\alpha) = -0.05 \times 10^{30}$, $G_{44} = \mu + 4\eta \cos^2\alpha = 6.31 \times 10^{22}$

The total number of fundamental frequencies is greater than the number of force constants in the potential function. However, for each single species the number of force constants required is greater than the number of frequencies. Thus, in no case can force constants be evaluated from the frequencies of a single species. Further difficulties are, except in the case of A_{1g} , caused by the lack of knowledge of the species to which the observed fundamentals belong.

It seems certain that eight fundamentals are observed in the Raman spectrum in addition to the three belonging to A_{1g} . Of these, three must belong to E_g , three to B_{2g} , and two to B_{1g} . There are five observed infrared bands that seem to be fundamentals, as well as one infrared-active band, outside the observed range at 285 cm^{-1} , which was located by its overtone in the Raman spectrum and verified by combination bands. Two of these are to be assigned to A_{2u} and four to E_u . Finally, there are six inactive fundamentals,

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one each belonging to A_{1u} , A_{2g} , and B_{2u} , and three to B_{1u} . These may be observed in combination bands, but their determination is feasible only after the frequencies are calculated, so that one knows where to look.

It was hoped that an approximate calculation of frequencies could be made first with a simple valence potential function, that is, using only diagonal elements in the \mathcal{F} matrix (Table 75). These values could then be used to assign the observed frequencies to the proper species, after which a refinement in calculations would be undertaken. From the A_{1g} fundamentals, the only set identified with certainty, one should be able to evaluate y , $x + a$, and $u + 2/5 (s + h)$. However, it was found impossible to fit the observed frequencies 359, 699, and 1431 cm^{-1} with the use of a simple valence potential. The set of force constants that would most nearly fit gave frequencies of 331, 610, and 1469 cm^{-1} . This indicated that interaction constants were certainly not to be neglected in final calculations. Preliminary rough calculations proved to be valuable, however, in assigning the observed bands to the different species. Thus, rough calculations in which interaction constants were set equal to zero indicated that either 1220 or 1285 cm^{-1} and one of the low frequencies, 273, 258, or 192 cm^{-1} must be assigned to B_{1g} ; that the lower A_{2u} fundamental must lie well below 435 cm^{-1} ; and that 1285, 439, and one of the low frequencies, 273, 258, or 192 cm^{-1} should be assigned to E_g .

When interaction constants are considered, the secular equation for each species contains more force constants than can be evaluated from the observed frequencies. The two species, E_g and A_{2u} , when considered simultaneously, can be used to evaluate force constants. Only the four independent constants, s , $x - a$, g , and h , enter these equations, while five equations may be written for the five frequencies belonging to these species. Now, the infrared band at 1239 cm^{-1} can be assigned to A_{2u} on the basis of infrared combinations. Using the four equations obtained from this frequency and the frequencies 1285, 439, and 273 cm^{-1} , as suggested above for E_g , four force constants were evaluated: $x - a = 5.63 \times 10^5 \text{ dyne/cm}$, $s = 1.17 \times 10^{-11} \text{ dyne/cm}$, $h = 0.32 \times 10^{-11} \text{ dyne/cm}$, and $g = 0.39 \times 10^{-3} \text{ dyne}$. This assignment for E_g was verified by later calculations, whereas other assignments tried led to absurd results. The second frequency belonging to A_{2u} was calculated at 278 cm^{-1} . By means of the B_{1g} secular equation, two further force constants were evaluated: $y = 4.07 \times 10^5 \text{ dyne/cm}$ and $f = -0.05 \times 10^{-3} \text{ dynes}$. The Raman bands at 1220 and 258 cm^{-1} were used for the B_{1g} fundamentals. The other plausible choice, 1220 and 192 cm^{-1} , yielded unreasonable force constants.

Next the A_{1g} secular equation and frequencies were used. Although only three frequencies belong to this species, four force constants were considered by treating one of them as a parameter. If the interaction constant, k , is assigned the value $0.2 \times 10^5 \text{ dyne/cm}$, a solution for the other three is $x + a = 6.49 \times 10^5 \text{ dyne/cm}$, $u = 1.44 \times 10^{-11} \text{ dyne/cm}$, and $c = 0.55 \times 10^{-3} \text{ dyne}$. If k is set equal to zero, there is obtained $x + a = 5.52 \times 10^5$, $u = 1.92 \times 10^{-11}$, and $c = 0.95 \times 10^{-3}$. If k is set equal to -0.2×10^5 , no real solution exists for the others.

One Raman-active species, B_{2g} , remains to be treated. Five of the force constants evaluated above enter the secular equation for this species, as does the still unknown angle constant r . If the assignments for the other species are correct, there remain only 192, 347, 660, and 1008 cm^{-1} of the intense Raman bands, three of which must belong to B_{2g} . If 192 cm^{-1} is used to evaluate r , the other two can be calculated. This was done for each of the two sets of values above for k , $x + a$, u , and c . The first of the two sets was found to give the best results: 192, 554, and 1066 cm^{-1} . Although this fits the observed 192, 660, and 1008 cm^{-1} only roughly, the assignment is clearly indicated. It does not seem that the agreement here could be improved materially by choosing another value for k . The other intense Raman band at 347 cm^{-1} is very probably the overtone of an

inactive fundamental, the intensity being enhanced by the band's proximity to the very intense A_{1g} fundamental at 359 cm^{-1} .

For E_u , the infrared-active species having a fourth degree secular equation, all force constants are known except b , an interaction constant for C-C stretching and C-C-C angle change. If this constant is given the value, $b = -0.17 \times 10^{-3}$ dyne, approximately the average of the values indicated by the two frequencies 1340 and 285 cm^{-1} which were assigned to E_u , on the basis of infrared combinations, there is obtained 1399 , 935 , 544 , and 275 cm^{-1} . This definitely indicates the assignment 1340 , 963 , 569 , and 285 cm^{-1} and furnishes a strong indication that the earlier work is essentially correct.

The inactive frequencies remain to be calculated. Using the force constants given above the values obtained for the A_{1u} , A_{2g} , and B_{2u} fundamentals are 221 , 705 , and 292 cm^{-1} respectively. In the secular equation for the other inactive species, B_{1u} , to which three frequencies belong, there occurs the constant v , for out-of-plane distortion of the carbon ring, about whose magnitude nothing is known. Inspection of the secular equation showed that a frequency between about 140 and 200 cm^{-1} would lead to absurdly high values of v . In the range below 140 cm^{-1} some evidence could be found in combination bands for a B_{1u} fundamental at 86 cm^{-1} . Using this, the value of 0.58×10 dynes/cm was found for v . The three calculated frequencies belonging to B_{1u} were then calculated at 1453 , 568 , and 86 cm^{-1} .

TABLE 81
Calculated and Observed Frequencies for Perfluorocyclobutane

Species	Calculated Frequencies cm^{-1}	Observed Frequencies cm^{-1}	Species	Calculated Frequencies cm^{-1}	Observed Frequencies cm^{-1}
A_{1g}	1431* 699* 359*	1431 699 359	B_{2g}	1066 554 192*	1008 660 192
A_{1u}	221	(173)	B_{2u}	292	(250)
A_{2g}	705	(745)	E_g	1285* 439* 273*	1285 439 273
A_{2u}	1239* 278	1239 (338)	E_u	1399 935 544 277	1340 963 569 285
B_{1g}	1220* 258*	1220 258			
B_{1u}	1453 568 86*	(1385) (613) (86)			

* These frequencies were used to evaluate force constants.

TABLE 82
Force Constants for Perfluorocyclobutane

Description	Symbols	Value dyne/cm
<u>Valence Force Constants</u>		
C-F bond	x	6.06×10^5
C-C bond	y	4.07
C-C-C angle	r/D^2	0.07
F-C-C angle	s/dD	0.56
F-C-F angle	u/d^2	0.78
C distance out of plane	v	0.58
<u>Interaction Constants</u>		
C-C-C angle with C-C dist.	b/D	-0.11
F-C-F angle with C-F dist.	c/d	0.40
F-C-C angle with C-C dist.	f/D	-0.03
F-C-C angle with C-F dist.	g/d	0.29
F-C-C angle with F-C-C angle	h/d^2	0.17
C-C dist. with C-F dist.	k	0.20
C-F dist. with C-F dist.	a	0.43

The complete list of calculated and observed fundamentals is given in Table 81, where experimental values for the inactive frequencies are listed in parentheses. These were evaluated by searching near the computed values for frequencies that could be used in binary combinations to explain infrared or Raman bands not interpreted by binary sums of the active fundamentals. Several of the inactive frequencies listed in the observed column must be regarded as doubtful, since only a few combinations could be found in which they occurred.

The agreement between calculated and observed frequencies is perhaps as good in most instances as could be expected in view of the uncertainty in the molecular dimensions. The calculations are precise enough to establish with some confidence the assignment of the observed fundamentals.

The force constants evaluated are listed in Table 82. These must not be considered as highly accurate in view of the uncertainty in molecular dimensions and of the inaccurate fit between computed and observed frequencies belonging to B_{2g} . It seems likely that the inaccuracy in B_{2g} may be due to the failure to include interaction terms between C-C stretches in the potential function. Inclusion of such terms, however, would probably require the evaluation of six force constants from six simultaneous equations, an almost prohibitive task.

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