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The Chemistry of SF₅Br and SF₅CF=CF₂ - Addition Reactions

Robin J. DeBuhr

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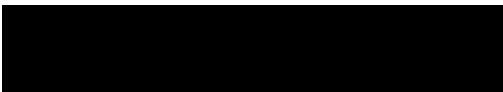
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AN ABSTRACT OF THE THESIS OF Robin J. DeBuhr for the Master of Science in Chemistry presented November 18, 1977.

Title: The Chemistry of SF_5Br and $SF_5CF=CF_2$ - Addition Reactions

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:


Gary L. Gard, Chairman


Alfred S. Levinson


Horace F. White

Addition reactions of pentafluorosulfur bromide (SF_5Br) with fluoroolefins were studied. Three new adducts were prepared, $SF_5CHFCHClBr$, $SF_5CH_2CH(CF_3)Br$, $SF_5CHFClBr$. SF_5Br and $CFCl=CHCl$ yielded a small amount of product but attempts to add SF_5Br to $CF_2=CFCOF$ were unsuccessful.

The mechanism for these addition reactions seems to involve a free radical addition pathway. Steric factors seem to be important in determining whether SF_5Br will add to fluoroolefins.

The new compounds, $SF_5CF(CF_3)COF$ and $SF_5CF(CF_3)CONH_2$ have been produced from $SF_5CF=CF_2$.

Analytical data, infrared, Raman, nmr and mass spectra are presented supporting the proposed structures for these new compounds.

THE CHEMISTRY OF SF₅Br AND SF₅CF=CF₂ - ADDITION REACTIONS

by

ROBIN J. DEBUHR

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE
in
CHEMISTRY

Portland State University
1977

TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH

The members of the Committee approve the thesis of
Robin J. DeBuhr presented November 18, 1977.

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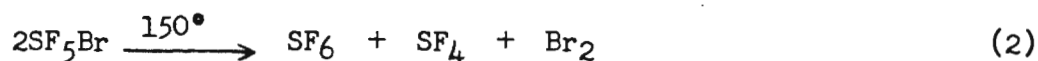
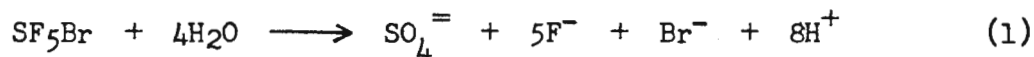
CHAPTER I

INTRODUCTION

SF₅Br Additions to Unsaturated Systems

Pentafluorosulfur bromide (SF₅Br) was first prepared in 1962 by C. Merrill by reacting SF₄ with Br₂ and BrF₅ at 100° under pressure (1). Another method was found in 1965 by B. Cohen and A. MacDiarmid which consisted of reacting Br₂ with S₂F₁₀ at 138° (2).

SF₅Br boils at 3.1° at one atmosphere, melts at -78.8° to -78.4°, and has a density of 2.098 g/cc at -20.1° (1). In the liquid state, SF₅Br has a faint yellow color. It hydrolyzes at room temperature (1) and decomposes at 150° according to the following equations:

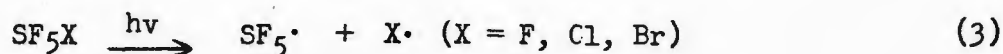


The infrared spectrum and the Raman spectrum of liquid SF₅Br have been reported (3). The results are tabulated in Table I. Since SF₅Br can be considered as a monosubstituted derivative of octahedral SF₆, it should belong to point group C_{4v}. The 11 fundamentals of SF₅Br of symmetry C_{4v} can be classified as 4A₁ + 2B₁ + B₂ + 4E. Of these, all 11 modes should be Raman active, whereas only the A₁ and E modes should be infrared active. Of the Raman lines, only the four A₁ modes should be polarized.

In addition to the infrared and Raman spectra the microwave spectrum of SF₅Br has been reported (4). The S-Br distance was found

to be $2.1902 \pm 0.0065 \text{ \AA}$ and S-F distance was $1.5970 \pm 0.0025 \text{ \AA}$.

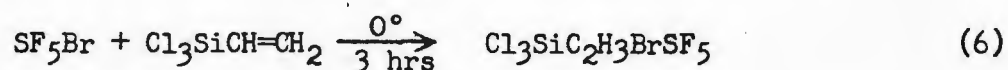
W. B. Fox and R. R. Smardzewski have studied the $\text{SF}_5\cdot$ radical (pentafluorosulfanyl radical) via the matrix isolation technique (5). The $\text{SF}_5\cdot$ radicals were produced either by vacuum ultraviolet photolysis of SF_6 and its derivatives or by the controlled fluorine attack on SF_4 :



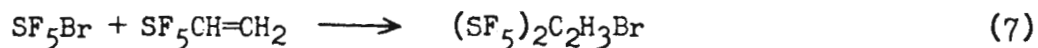
Pentafluorosulfur bromide has been found to be a valuable intermediate in incorporating SF_5 groups into molecules (6,7). It has also been shown that SF_5Br adds to a carbon-carbon triple bond in much the same way as it does to fluoroolefins (7). The results of these works are listed in Tables II through VII.

It has been found that SF_5Br adds more readily and directly than either SF_5Cl or S_2F_{10} to double and triple bonds. For more information on SF_5Cl and S_2F_{10} chemistry see Q. Wang's thesis (7).

Also, A. Berry and W. Fox have shown that SF_5Br addition to some vinylsilanes will occur (8). These reactions are as follows:



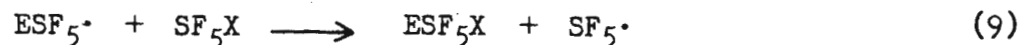
They also report in a later paper (9) the addition of SF_5Br to pentafluorosulfur ethene ($\text{SF}_5\text{CH}=\text{CH}_2$) to produce a bis(pentafluorosulfur)ethyl bromide.



Several additional reactions were tried with other highly halogenated pentafluorosulfur ethylene ($\text{SF}_5\text{CH}=\text{CHF}$, $\text{SF}_5\text{CH}=\text{CF}_2$, $\text{SF}_5\text{CF}=\text{CFH}$, $\text{SF}_5\text{CF}=\text{CF}_2$) (9) and SF_5Br but addition did not occur even under more rigid conditions.

The addition of SF_5Cl to fluoroolefins usually required ultraviolet excitation or thermal conditions involving a free radical initiator. With SF_5Br , the addition reaction usually proceeds either at room temperature or at elevated temperatures ($\sim 100^\circ$). It is interesting to note that the addition reaction of $\text{F}_5\text{S}-\text{SF}_5$, with olefins proceeds at best in very poor yield and in many cases not at all. This would suggest that the addition of two SF_5^\cdot radicals to a double bond is inefficient.

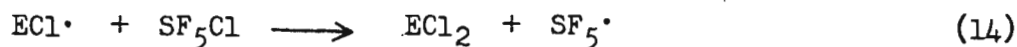
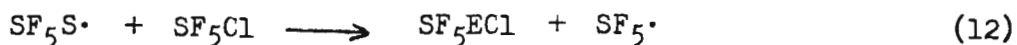
The mechanism for the thermal addition reaction of SF_5Br with fluoroolefins seems to follow a free radical addition pathway. For the most part, with SF_5Cl and SF_5Br additions, the SF_5^\cdot radical attacks the carbon bearing the hydrogens (6-11); however, exceptions to this will be discussed later in this thesis. The proposed steps for these additions are (10,11):



E = fluoroolefin; X = Br, Cl

With ultraviolet excitation, homolysis of the SF_5Cl molecule produces both SF_5^\cdot and Cl^\cdot radicals which then compete with each other

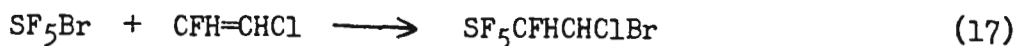
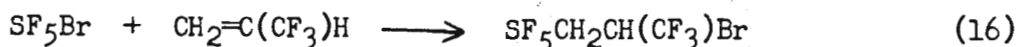
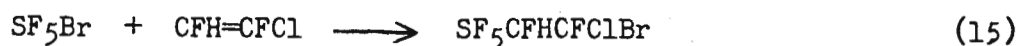
for the substrate as illustrated below (12,13).



E = olefin substrate

SF₅ compounds exhibit a wide range of useful and interesting properties. For example, SF₆ (14), CF₃SF₅ (14), SF₅CF=CF₂ (15), and SF₅-oxetanes (16) possess unusual dielectric strength while S₂F₁₀ (14), and SF₅CF=CF₂ (17) are biologically active. In addition, SF₆ (14), SF₅R_f (18), SF₅-oxetanes (16) and S₂F₁₀ (14) have high chemical stability towards concentrated acids and bases. It is expected that new SF₅ compounds will provide the basis for further study regarding the above properties and new SF₅-olefins should be useful in preparing surface active polymers.

The purpose of this work was to further study the thermal addition reaction of SF₅Br with fluoroolefins and in particular to determine the nature of the groups attached to double bonds that favored the addition of SF₅Br. Three new compounds were prepared:



Interestingly, SF_5Br formed only a small amount of product with $CFCl=CHCl$ and failed to add to $CF_2=CFCOF$.

The above three new compounds are clear, water-white, readily distillable liquids. They have been characterized via their infrared and Raman spectra, mass spectra, and nuclear magnetic spectra.

TABLE I

INFRARED AND RAMAN SPECTRA OF SF₅Br

<u>I.R. Gas</u>	<u>Raman (liq.)</u>	<u>Tentative Assignment and (1)</u> <u>Approx. Desc. of Vibration</u>	
894 vs	898 (0.2) dp	$\nu_8(E)$	ν asym (XF ₄)
849 vs (P,Q,R)	848 (0.02) dp	$\nu_1(A_1)$	ν (XF)
692 m (P,Q,R)	691 (7.6) dp	$\nu_2(A_1)$	ν sym (XF ₄)
	620 (0.3) dp	$\nu_5(B_1)$	ν sym out of phase (XF ₄)
591 m (P,Q,R)	586 (0.2) p	$\nu_3(A_1)$	δ sym out of plane (XF ₄)
575 m	575 (0.02) dp	$\nu_9(E)$	δ (FXF ₄)
	500 (0.2) (dp)	$\nu_7(B_2)$	δ sym in plane (XF ₄)
477 vw		$\nu_2 - \nu_{11}(E)$	
418 mv	419 (0.4) dp	$\nu_{10}(E)$	δ asym in plane (XF ₄)
271 mw	272 (10) p	$\nu_4(A_1)$	ν (X-Y)
	222 (0.6) dp	$\nu_{11}(E)$	δ (YXF ₄)

(1) X = S, Y = Br

TABLE II

SF₅Br AND FLUOROOLEFIN ADDUCTS

<u>Reactants</u>	<u>Reaction Cond.</u>	<u>BP (°C)</u>	<u>Adducts</u>
SF ₅ Br + CH ₂ =CHF	24 hrs RT	99.5-100.5	SF ₅ CH ₂ CHFBr
SF ₅ Br + CH ₂ =CF ₂	24 hrs RT	86-87	SF ₅ CH ₂ CF ₂ Br
SF ₅ Br + CHF=CF ₂	24 hrs RT	74-75	SF ₅ CHF ₂ CF ₂ Br
SF ₅ Br + CFC1=CF ₂	24 hrs RT	94-95	SF ₅ C ₂ F ₃ ClBr
SF ₅ Br + CH ₂ =CFC1	24 hrs RT	119°	SF ₅ CH ₂ CFC1Br
SF ₅ Br + CF ₂ =CHCl	14 days 100°	111-111.5	SF ₅ CF ₂ CHClBr

TABLE III

SF₅Br ADDITION TO TRIPLE BONDS

<u>Reactants</u>	<u>Reaction Cond.</u>	<u>BP (°C)</u>	<u>Products</u>
SF ₅ Br + CF ₃ C≡CH	4 days 100°	93±1°	SF ₅ CH=C(CF ₃)Br
SF ₅ Br + CH ₃ C≡CH	12 hrs RT	111-111.5	SF ₅ CH=C(CH ₃)Br

TABLE IV

INFRARED SPECTRAL DATA FOR SF₅Br - FLUOROOLEFIN ANDSF₅Br - TRIPLE BOND ADDUCTS(cm⁻¹)

SF ₅ CH ₂ CHBr	1416 (w), 1364 (w), 1307 (w), 1196 (w), 1086 (s), 1042 (s), 900 (vs), 874 (vs), 847 (vs), 751 (w), 681 (w)
SF ₅ CH ₂ CF ₂ Br	1416 (w), 1323 (w), 1274 (w), 1224 (m), 1189 (w), 1124 (s), 1047 (m), 955 (vs), 914 (m), 891 (vs), 873 (vs), 855 (vs), 797 (m), 741 (w), 694 (w)
SF ₅ CHFCF ₂ Br	1324 (w), 1295 (w), 1232 (s), 1161 (vs), 1060 (m), 983 (vs), 968 (s), 883 (vs), 808 (m), 775 (m), 758 (w), 706 (s)
SF ₅ C ₂ F ₃ ClBr	1214 (s), 1175 (w), 1117 (s), 1055 (w), 1020 (w), 936 (vs), 894 (vs), 854 (m), 816 (m), 760 (m), 724 (s), 685 (m)
SF ₅ CF ₂ CHClBr	1288 (m), 1225 (s), 1189 (m), 1163 (s), 1145 (s), 1032 (w), 960 (m), 885 (vs), 863 (vs), 815 (m), 792 (w), 778 (w), 731 (s), 702 (w), 660 (s), 600 (s), 588 (m, sh at 588 and 573)

TABLE IV (Cont.)

$\text{SF}_5\text{CH}_2\text{CFC1Br}$	1410 (w), 1149 (m-s), 1020 (s), 974 (w), 912 (vs), 870 (vs), 845 (vs), 790 (w), 720 (w), 664 (w), 618 (vw), 596 (s), 568 (m)
$\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$	3100 (vw), 1643 (m), 1435 (w-m), 1383 (m), 1296 (w), 1084 (m), 980 (s), 863 (s), 883 (s), 735 (m), 619 (m), 598 (s, sh at 575)
$\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ isomeric mixture	3100(m), 1630 (m,sh at 1637), 1336 (m), 1285 (w), 1262 (vs), 1226 (m), 1191 (vs,b), 1120 (w), 960 (v), 944 (vs), 882 (vs,b), 832 (w), 768 (m), 724 (m-w), 654 (m), 635 (m), 604 (m-s), 572 (w), 534 (w)

TABLE V
GAS CHROMATOGRAPHY DATA FOR SF₅Br-
FLUOROOLEFIN AND SF₅Br TRIPLE BOND ADDUCTS

<u>Adduct</u>	<u>Retention Time (minutes)</u>
SF ₅ CH ₂ CHBr*	35
SF ₅ CH ₂ CF ₂ Br*	15
SF ₅ CHFCF ₂ Br*	5.6
SF ₅ C ₂ F ₃ ClBr*	3.8
CCl ₄ *	7.5
CCl ₄ **	2.17
SF ₅ CH ₂ CFClBr**	4.33
SF ₅ F ₂ CHClBr**	3.17
CCl ₄ ***	7.3
SF ₅ CH=C(CH ₃)Br*	12
SF ₅ CH=C(CF ₃)Br***	1st G.C. isomer 3.7
	2nd G.C. isomer 6.5

* Column temp = 59±1°. He flow rate 2.5 ml/sec.

** Column temp = 118°. He flow rate 3 ml/sec.

*** Column temp = 59±1°. He flow rate 3 ml/sec.

TABLE VI

NMR SPECTRAL DATA FOR SF₅Br AND FLUOROOLEFIN ADDUCTS

Proposed Structure Skeletal Atom Number			Chemical Shifts, Band Centers*					
			S-F	SF ₄	CF	CF ₂	CH ₂	CH
(1)	SF ₅	CHFBr	-79.9	-66.4	139.2		4.27	6.95
(2)	SF ₅	CH ₂ CF ₂ Br	-77.3	-70.5		51.5	4.46	
(3)	SF ₅	CHF ₂ Br	-70.0	-53.7	163.5	63.1		5.58
(4)	SF ₅ C ₂ F ₃ ClBr ⁺		-65.4	-48.5	76.8	88.5		
			Coupling Constants**					
			J _{1,2} ^{H,F}	J _{2,3} ^{H,F}	J _{2,2} ^{H,H}	J _{2,3} ^{H,H}	J _{2,3} ^{H,H}	J _{3,3} ^{H,F}
(1)			8	24	***	***	***	50
(2)			7	14				
(3)			5		J _{2,3} ^{H,F} = 3	J _{2,3} ^{H,F} = 13		44

*Chemical shifts in parts per million upfield from CFCl₃ internal standard or downfield from Si(CH₃)₄ internal standard.

**Measured in cycles per second.

***Data unavailable as a detailed analysis of this compound is incomplete; J_{2,3}^{H,H} + J_{2,3}^{H,H} = 11 cps.

+Structure unknown.

TABLE VII

NMR SPECTRAL DATA FOR SF₅Br - FLUOROOLEFIN
AND SF₅Br - TRIPLE BOND ADDUCTS

Proposed Structure Skeletal Atom Number			Chemical Shifts Band Centers*			Coupling Constants**		
1	2	3	CH	CH ₂	CH ₃	H,F J _{1,1}	H,F J _{3,2}	H,F J _{3,2}
SF ₅	CH ₂	CFC1Br		4.5@				
SF ₅	CF ₂	CHClBr	5.9				12.6	6.0
SF ₅	CH	C(CF ₃)Br***	7.60			6.5		
SF ₅	CH	C(CF ₃)Br****	7.13			8.6		
SF ₅	CH	C(CH ₃)Br	6.76		2.57	7.8		

*Chemical shifts in parts per million downfield from Si(CH₃)₄ internal standard.

**Measured in cycles per second.

***First gas Chromatographic isomer

****Second gas Chromatographic isomer.

@Band center of multiplet of 13 major lines.

CHAPTER II

EXPERIMENTAL METHODS

Vacuum System

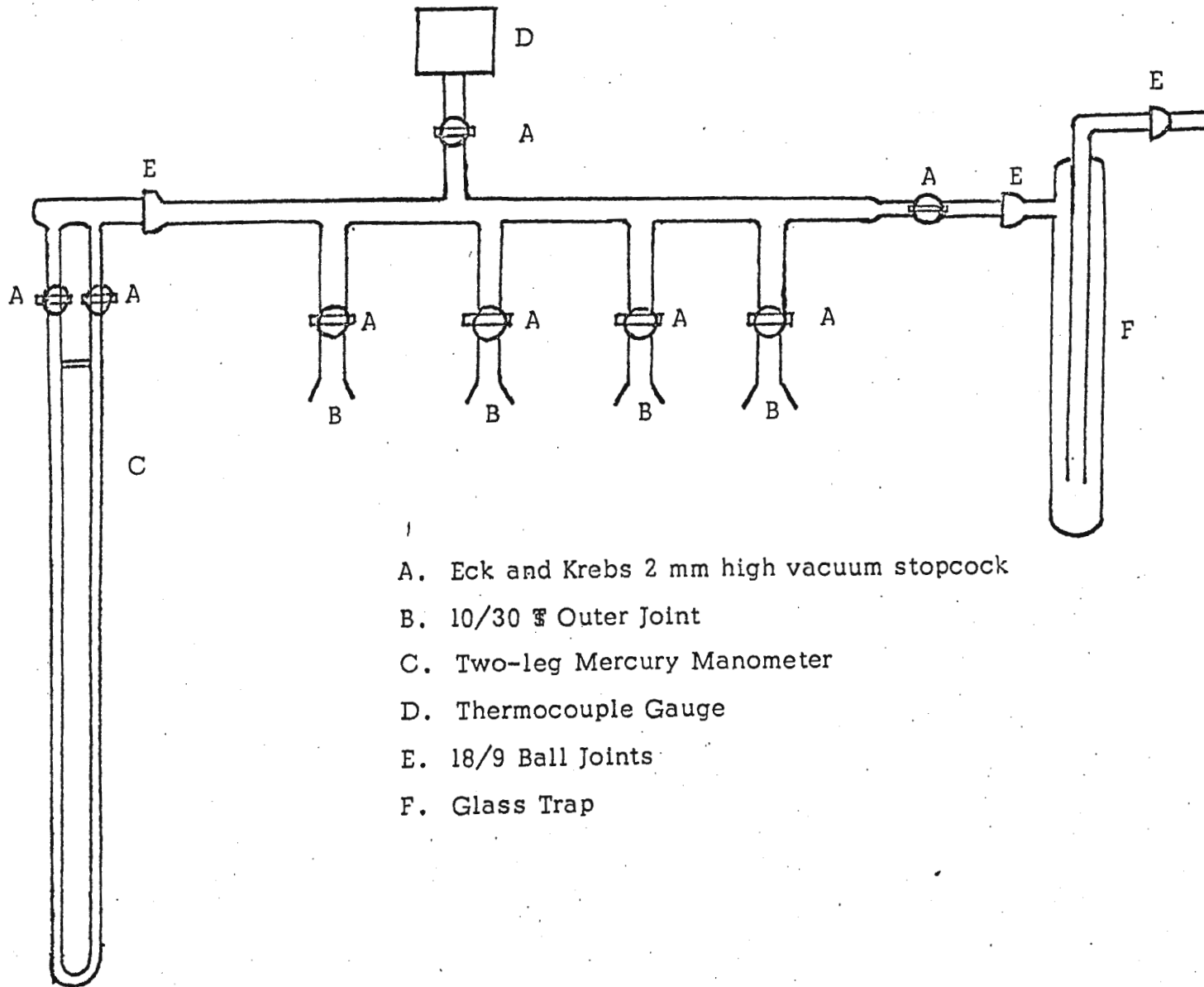
The vacuum system used in this work was an all glass system which consisted of a manifold connected to a Welch Duo-Seal rotary pump. The manifold consisted of 8 mm and 22 mm I.D. Pyrex glass tubing which was connected to the pump by a concentric liquid nitrogen cooled trap. The manifold was connected to a two leg mercury manometer and also had four taps for attaching vessels. The taps were Eck and Krebs 2 mm high vacuum stopcocks to which Pyrex 10/30 outer glass joints were attached. A Televac gauge was used to monitor the system and it usually attained a vacuum at 10^{-2} - 10^{-3} torr. All joints were lubricated with Apiezon-M grease. The system is illustrated in Figure I.

Reaction Vessels

Pyrex-glass Vessels

For room temperature reactions 1, 2, or 3 liter Pyrex-glass vessels were used. The vessels were equipped with a cold finger at the bottom for condensing reactants and had 2 mm high vacuum Teflon stopcocks for an outlet. The connecting portion consisted of 10/30 inner joints for attaching to the vacuum line.

Figure 1. Glass Vacuum Manifold



- A. Eck and Krebs 2 mm high vacuum stopcock
- B. 10/30 F Outer Joint
- C. Two-leg Mercury Manometer
- D. Thermocouple Gauge
- E. 18/9 Ball Joints
- F. Glass Trap

Metal High Pressure Vessels

Pentafluorosulfur bromide was prepared in a 75 ml monel vessel equipped with a Whitney stainless steel valve and tipped with a brass 10/30 inner joint. Higher temperature reactions using SF₅Br were carried out in various monel or stainless steel vessels with brass valves and 10/30 joints. The vessels were placed in an oven to heat to desired temperatures.

Physical Methods

Fractional Distillation

Products were purified by distilling in a Bantam-ware (Kontes) distillation apparatus. A heater and oil bath were used to provide heat and the column was connected to the atmosphere by a -78° trap.

Gas Chromatography

The purity of products was checked by gas chromatography by using an Aerograph Autoprep (Model A-700) gas chromatograph. Separations were carried out with a 10' x 3/8" column containing 20% Carbowax absorbed on "Chromosorb W."

Molecular Weights

Molecular weights were determined on the vacuum line using the vapor density method. The Pyrex-glass bulb was equipped with a Teflon stopcock and had a volume of 209.6 cm³.

Infrared Spectra

Infrared spectra were obtained using a Perkin-Elmer 467 Spectrometer. Gas samples were contained in a monel cell fitted with either AgCl windows or KRS-5 windows. The cell was equipped with a Whitney brass valve and 10/30 inner joint. The IR range was 4000-250 cm⁻¹.

Nuclear Magnetic Resonance

Nuclear magnetic resonance spectra were taken on a Varian Model EM-390 NMR.

Mass Spectra

Mass spectra were taken on a CEC 21-110 B double focus Mass Spectrometer with a 6 KV ion accelerator set at 70 volts. The internal standard used was Perfluorokerosine (PFK).

Chemical Analysis

Chemical analyses were performed by Beller Microanalytical Laboratory in Gottingen, West Germany.

Reagents

Pentafluorosulfur Bromide

SF_5Br was prepared by reaction of S_2F_{10} and Br_2 heated in a monel vessel to 130° for 16 hours as described by Fox et al. (19). No attempt was made to purify the SF_5Br other than transferring it out of the reaction vessel at -50° to -60° . Possible contaminants were SF_6 , SF_4 , S_2F_{10} and Br_2 .

Fluoroolefins

The following fluoroolefins; 1-chloro-2-fluoroethylene ($CHCl=CHF$), 3,3,3-trifluoropropene ($CF_3CH=CH_2$), 1-chloro-1,2-difluoroethylene ($CFCl=CHF$), 1,2-dichloro-1-fluoroethylene ($CFCl=CCl$), perfluoropropenal ($CF_2=CFCOF$), and trifluoroethylene ($CF_2=CFH$), were obtained from Peninsular Chem Research and used without purification. Their purity was checked by infrared analysis before use.

Carbonyl Fluoride

COF₂ was obtained from Peninsular Chem Research and used without purification. The purity was checked by infrared analysis before use.

Disulfur Decafluoride

S₂F₁₀ was a gift from Dr. Maude Tremblay, Centre Canadien de Recherches et Perfectionnement des Armes (CARDE), Quebec, Canada. The molecular weight was taken and found to be 254.89 g/mole (theor. = 254.1 g/mole). Its purity was also confirmed by infrared analysis.

Bromine

Analytical reagent bromine was purchased from Mallinckrodt and used without purification.

Cesium Fluoride

CsF was obtained from Mallinckrodt and was used after drying at 100° overnight.

Acetonitrile

CH₃CN was spectral grade obtained from Mallinckrodt and used after drying with MgSO₄.

Potassium Hydroxide

KOH was purchased from "Baker" and was used without further purification.

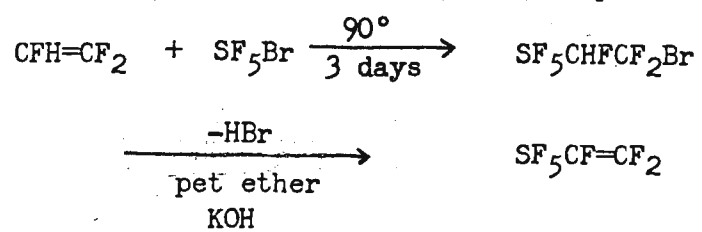
Petroleum Ether (90-120°)

Petroleum ether was also purchased from Mallinckrodt and used without further purification.

Pentafluorosulfur Trifluoroethylene

SF₅CF=CF₂ was prepared in the lab via a process developed by

G. L. Gard et al. (6). The reactions steps are:



Its purity was confirmed by infrared analysis.

Ammonia

NH₃ (anhydrous) was obtained from Matheson Gas Products Company.

Carbon Tetrachloride

CCl₄ was supplied in spectral grade from Mallinckrodt Supply Company.

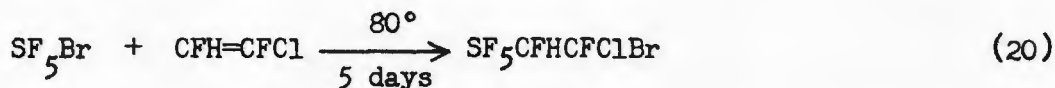
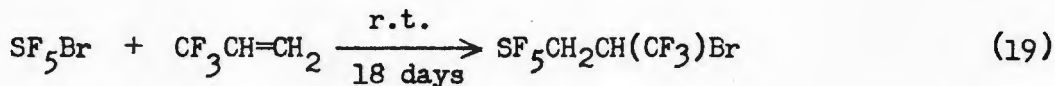
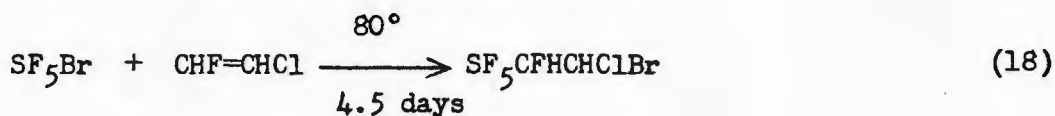
CHAPTER III

SYNTHESIS OF NEW ADDUCTS OF SF₅Br

WITH FLUOROOLEFINS

Introduction

Pentafluorosulfur bromide reacts with CHF=CHCl, CF₃CH=CH₂ and CFH=CFC1 according to the following equations:



With CFC1=CHCl (125°, 5 days) SF₅Br produced only a small amount of unidentifiable liquid, and with CF₂=C(COF)F (80°, 6 days) no reaction products were obtained.

In reacting SF₅Br with CF₂=CFH a white waxy polymer was produced along with SF₅CFHCF₂Br. This polymer was found to contain sulfur and bromine along with carbon, hydrogen and fluorine.

All of the new products were clear, colorless readily distillable liquids, and hydrolytically stable. For all products, one addition compound was formed. These have been identified by gas chromatography, mass spectra, nmr spectra, infrared and Raman spectra.

EXPERIMENTAL

Reaction of CHF=CHCl with SF₅Br

This reaction was first run in a one liter Pyrex vessel with 2.27×10^{-2} moles SF₅Br and 1.99×10^{-2} moles CHF=CHCl which were condensed into the vessel at -196° . It was observed that on warming to r.t. the yellow color of SF₅Br disappeared and a clear colorless liquid formed. The colorless liquid was allowed to stand for 12 days and was then distilled. There was not enough product formed to separate by distillation.

An improved method was found using a 200 ml Hoke monel vessel and an increase in temperature. Into this vessel 5.9×10^{-2} moles SF₅Br and 7.3×10^{-2} moles CHF=CHCl were condensed. The compounds were heated in an oven for 4.5 days at 80° . The products again were distilled and the portion boiling at 127.5° was collected. The yield was 49.5%. Since infrared spectrum (IR) showed olefin contamination, the product was washed with H₂O, dried with MgSO₄ and redistilled again, collecting the portion boiling at 127.5° .

Reaction of CF₃CH=CH₂ with SF₅Br

This reaction, using 5.4×10^{-2} moles SF₅Br and 5.83×10^{-2} moles CF₃CH=CH₂, was run in a 3 liter Pyrex reaction vessel at room temperature. The reactants were condensed into the vessel at -196° and allowed to warm slowly to room temperature. A colorless liquid formed. It was distilled at the end of 18 days and the colorless product was collected at 102.5° . No washing was needed. The yield was 39%.

Reaction of CHF=CFC1 and SF₅Br

The reaction was first run in a Pyrex 1-liter vessel. The quantities used were 2.6×10^{-2} moles SF₅Br and 1.94×10^{-2} moles CHF=CFC1. These were condensed into the vessel at -196° and allowed to warm to room temperature. After two days the colorless liquid was distilled and the product collected at 110.5°. The yield was 46%.

A better method for this reaction was found to consist of warming the reactants to 80° in a monel vessel. The reaction of 5.4×10^{-2} moles SF₅Br with 3.9×10^{-2} moles CHF=CFC1 for 5 days in the monel vessel at 80°, after distillation and collection of the 110.5° portion, gave a 70.2% yield. The IR again showed olefin contamination and the product was washed with H₂O and dried with MgSO₄.

Reaction of CFCl=CHCl and SF₅Br

This reaction was attempted in both the 1 liter Pyrex vessel at r.t. and the monel 200 ml vessel at 80°. Into the 1-liter vessel, 2.02×10^{-2} moles SF₅Br and 2×10^{-2} moles CFCl=CHCl were condensed. After 21 days at r.t. very little liquid was observed and when distilled no product could be isolated. Into the Hoke metal vessel, 4.18×10^{-2} moles SF₅Br and 3.42×10^{-2} moles CFCl=CHCl were condensed, and heated at 80° for 5 days. Again after distillation little product was observed. The cuts from the distillation were returned to the vessel and the temperature increased to 110° and then 125° for 5 days. A small amount of product was collected at 94° via distillation. There is some indication that a small amount of product is formed but it could not be purified nor could an accurate boiling point

or molecular weight be determined.

Reaction of $\text{CF}_2=\text{CFCOF}$ and SF_5Br

Into a one liter Pyrex vessel, 1.79×10^{-2} moles $\text{CF}_2=\text{CFCOF}$ and 3.18×10^{-2} moles SF_5Br were condensed at -196° . At room temperature there were no apparent signs of reaction. This reaction was then tried in a monel vessel at 80° for six days; 2.7×10^{-2} moles $\text{CF}_2=\text{CFCOF}$ and 3.6×10^{-2} moles SF_5Br were used this time. The material in the vessel was distilled and no product formation was observed. The major distillate was collected at $29-31^\circ$ which is the boiling point of the starting olefin.

Chemical Analysis

The compounds were analyzed by Beller Microanalytical Laboratory for C, H, S, Cl, Br, F. There was good agreement with calculated and experimental results as shown in Table VIII.

Physical Properties

The physical properties are summarized in Table IX. The molecular weights were found using a calibrated bulb and they agree well with the theoretical values.

Gas Chromatography

The gas chromatographs of $\text{SF}_5\text{CH}_2\text{CHBr}(\text{CF}_3)$ and $\text{SF}_5\text{CFHCFClBr}$ showed one peak (see Table X). We are at a loss to explain why $\text{SF}_5\text{CFHCHClBr}$ had a shoulder on it which we could not separate. With another column of the same type we observed only one major peak at 4.0 minutes retention time.

TABLE VIII

ELEMENTAL ANALYSES OF SF₅Br ADDUCTS

<u>Adducts</u>	<u>C</u>	<u>H</u>	<u>S</u>	<u>F</u>	<u>Cl</u>	<u>Br</u>
	(% by wt, Exp/Calc)					
SF ₅ CFHCHClBr	<u>9.04</u>	<u>.80</u>	<u>10.84</u>	<u>39.0</u>	<u>28.53</u>	<u>12.57</u>
	8.36	.69	11.1	39.7	27.92	12.2
SF ₅ CH ₂ CHBrCF ₃	<u>11.88</u>	<u>1.00</u>	<u>10.44</u>	<u>49.8</u>	<u>26.2</u>	----
	11.9	.99	10.6	50.2	26.4	
SF ₅ CFHCFC1Br	<u>8.00</u>	<u>.33</u>	<u>10.46</u>	<u>43.9</u>	<u>26.41</u>	<u>11.73</u>
	7.87	.328	10.5	43.6	26.2	11.5

TABLE IX

PHYSICAL PROPERTIES OF ADDUCTS

<u>Compounds</u>	<u>Mol. Wt. (g/mole)</u> <u>Exp/Calc</u>	<u>Boiling Points</u> <u>°C</u>
SF ₅ CFHCHClBr	290.1/287.4	127.5
SF ₅ CH ₂ CHBrCF ₃	299.1/303	102.5
SF ₅ CFHCFC1Br	300.6/305	111.2

TABLE X

GAS CHROMATOGRAPHY DATA FOR SF₅Br ADDUCTS

<u>Compound</u>	<u>Time (min.)</u>
CCl ₄	1.87
SF ₅ CFHCHClBr	5.90*
SF ₅ CH ₂ CHBrCF ₃	1.67
SF ₅ CFHCFC1Br	2.50

*Shoulder on peak. Using another 10 ft carbowax column there was observed 1 peak at 4 min; temp = 160°

Column temp. 130°

Detector temp. 160°

Inlet temp. 120°

Collector temp. 180°

Infrared Spectra

The infrared spectra for the new adducts are listed in Table XI and shown in Figures (2-5). The common feature in all spectra is the absorption bands due to the SF₅ group. These bands are centered near the 870 cm⁻¹ and can be directly related to the vibrational modes of the SF₅ group. Cross and coworkers found that the SF₅ group should have the most intense bands in the 850-920 cm⁻¹ range for the S-F stretching modes and in the 600 cm⁻¹ region for the deformation modes (20). Therefore, the bands at 872 cm⁻¹ and 900 cm⁻¹ for SF₅CFHCHClBr, 850 cm⁻¹, 870 cm⁻¹, and 927 cm⁻¹ for SF₅CH₂CH(CF₃)Br and 870 cm⁻¹ for SF₅CFHCFC1Br are assigned to the S-F stretching mode. The S-F deformation mode is located at 600 cm⁻¹ for all the adducts. For compounds with the C-F group the stretching absorption is usually located at 1000-1110 cm⁻¹. Therefore, in SF₅CFHCHClBr and in SF₅CFHCFC1Br the C-F stretch is assigned to 1100 cm⁻¹ and 1065 cm⁻¹ respectively, The C-F stretch in SF₅CH₂CH(CF₃)Br is assigned to the bands in 1115 cm⁻¹ to 1280 cm⁻¹ region.

In the reaction of CHCl=CFCl + SF₅Br the infrared spectrum shows the disappearance of the double bond and the presence of the S-F stretch in the 800-1000 cm⁻¹ range. Also, bands attributable to C-F stretch are present.

Mass Spectra

The major peaks in the mass spectra for the new SF₅Br adducts are listed in Table XII. The peaks for the possible SF₅Br + CHCl=CFCl adduct are listed although not all fragments are identified. There is, however, some evidence for the presence of an adduct. The other

TABLE XI

INFRARED SPECTRA OF NEW SF₅Br ADDUCTSSF₅CFHCHClBr (gas)

1368 (m)
 1345 (m)
 1270 (w)
 1150 (m, sh. 1175)
 1100 (m)
 1050 (w)
 932 (m)
 900 (s)
 872 (s)
 817 (m)
 717 (m-w)
 700 (m-w)
 630 (m)
 600 (m)
 567 (w)

SF₅CH₂CH(CF₃)Br (gas)

1480 (w)
 1410 (m, sh. at 1420 & 1427)
 1365 (w)
 1280 (s)
 1252 (s)
 1165 (vs, sh. at 1190)
 1115 (s)
 927 (vs)
 870 (vs, sh. at 895)
 850 (s)
 816 (s)
 600 (m-s)
 570 (m-s)
 540 (s)

SF₅CFHCFC1Br (gas)

1155 (m-s, sh. at 1195, 1255,
 1280, 1330)
 1120 (s)
 1065 (m, sh. at 1035)
 960 (m)
 870 (vs, sh. at 1005, 1025)
 815 (s)
 755 (w)
 645 (m, sh. at 665, 685, 705)
 600 (s)
 570 (m)
 540 (m)

CFC1=CHCl + SF₅Br (gas)

1270 (m)
 1209 (s)
 1130 (vs)
 1025 (s)
 973 (s)
 935 (s)
 800 (w)
 750 (m)
 670 (w)
 582 (w)

TABLE XII

MASS SPECTRA OF NEW ADDUCTS

SF₅CFHCHClBr

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
25	2.06	C ₂ H ₃ ⁺	82	22.68	C ₂ H ₂ ClF ⁺
26	8.25	C ₂ H ₂ ⁺	89	56.70	SF ₃ ⁺
28	81.44	N ₂ ⁺ , CO ⁺	91	3.09	CBr ⁺ , SF ₃ ⁺
31	5.15	CF ⁺	96	6.19	SF ₂ CHCH ⁺
32	28.87	CFH ⁺	98	3.09	BrF ⁺ , SF ₂ CHCH ⁺
44	17.53	CO ₂ ⁺ , CS ⁺	99	100	CHF ₂ CHCl ⁺
45	41.23	C ₂ H ₂ F ⁺	100	3.09	BrF ⁺
47	8.25	CCl ⁺	101	32.99	SF ₃ C ⁺ , CHF ₂ CHCl ⁺
48	3.09	CHCl ⁺			
49	9.28	CH ₂ Cl ₂ ⁺ , CCl ⁺	123	5.15	SCBr ⁺
51	8.25	SF ⁺ , CH ₂ Cl ⁺	124	3.09	SCHBr ⁺
60	2.06	C ₂ HCl ⁺	125	4.12	SCBr ⁺
61	2.06	C ₂ H ₂ Cl ⁺	126	3.09	SCHBr ⁺
64	4.12	SFCH ⁺	127	36.08	SF ₅ ⁺
67	4.12	SCl ⁺	129	10.31	SF ₂ C ₂ Cl ⁺ , SF ₅ ⁺
70	10.31	SF ₂ ⁺	138	9.28	SC ₂ HBr ⁺
77	4.12	?	140	11.34	SF ₅ CH ⁺ , SC ₂ HBr ⁺
78	8.25	CFCCl ⁺	142	3.09	SF ₅ CH ⁺
79	23.71	CHFCCl ⁺ , Br ⁺	158	26.80	SF ₅ CF ⁺
80	54.64	C ₂ H ₂ ClF ⁺	159	3.09	SF ₅ CFH ⁺
81	47.42	CHFCCl ⁺ Br ⁺	160	34.02	SF ₅ CH ₂ F ⁺ , SF ₅ CF ⁺

TABLE XII (con't)

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
162	34.02	SF ₅ CH ₂ F ⁺	89	55.56	SF ₃ ⁺
177	7.22	SF ₂ CH ₂ CBr ⁺	91	2.78	CBr ⁺ , SF ₃ ⁺
179	9.28	CF ₂ CHClBr ⁺	95	36.11	F ₃ CCHCH ₂ ⁺
286	2.06	SF ₅ CFCClBr ⁺	102	2.78	SF ₃ CH ⁺
288	3.09	parent	105	4.17	BrCHCH ⁺ , SF ₃ CH ₂ ⁺
<u>SF₅CH₂CH(CF₃)Br</u>			107	5.56	BrCHCH ⁺
25	5.56	C ₂ H ⁺	108	2.78	BrCHCH ₂ ⁺ , SF ₄ ⁺
26	27.78	C ₂ H ₂ ⁺	111	22.22	SBr ⁺
27	15.28	C ₂ H ₃ ⁺	113	20.83	SF ₃ C ₂ ⁺ , SBr ⁺
30	5.56	?	115	6.94	SF ₃ CHCH ⁺ , SF ₃ C ₂ ⁺
31	4.17	CF ⁺	127	100	SF ₅ ⁺
44	2.78	CO ₂ ⁺ , CS ⁺	129	11.11	CBrF ₂ ⁺ , SF ₅ ⁺
45	8.33	C ₂ H ₂ F ⁺	131	6.94	C ₂ F ₂ CF ₃ ⁺
49	4.17	?	175	63.89	CHCCF ₃ Br ⁺ , CH ₂ HCCF ₃ Br ⁺
50	22.22	CF ₂ ⁺	176	2.78	CHCHCF ₃ Br ⁺
65	2.78	SFCH ₂ ⁺	177	62.50	CH ₂ CHCF ₃ Br ⁺
69	34.7	CF ₃ ⁺	<u>SF₅CFHCFC1Br</u>		
70	13.89	SF ₂ ⁺	28	51.04	N ₂ ⁺ , CO ⁺
75	9.72	CHCCF ₂ ⁺	31	11.46	CF ⁺
76	2.78	CHCHCF ₂ ⁺	32	21.88	CFH ⁺
77	16.67	CH ₂ CHCF ₂ ⁺	35	2.08	Cl ⁺
81	2.78	CCF ₃ ⁺	44	6.25	CO ₂ ⁺ , CS ⁺
83	5.56	CH ₂ CF ₃ ⁺			

TABLE XII (con't)

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
47	5.21	CCl ⁺	117	62.50	SF ₂ CCl ⁺
48	2.08	CHCl ⁺	119	20.83	SF ₂ CCl ⁺
51	20.83	SF ⁺ , CH ₂ Cl ⁺	127	100	SF ₅ ⁺
63	7.29	SCF ⁺	128	3.12	SF ₅ H ⁺
66	3.21	CFCI ⁺	129	16.67	SCFCFCI ⁺
67	22.92	SCl ⁺			SF ₅ ⁺
69	7.29	CF ₃ ⁺ , SCl ⁺	142	4.17	SFCBr ⁺
70	33.33	SF ₂ ⁺	144	4.17	SFCBr ⁺
77	4.17	?	145	4.17	SFCHBr ⁺ , CFCI ₂ Br ⁺
79	5.21	CHCFCI ⁺ , Br ⁺	147	4.17	SFCHBr ⁺ , CFCI ₂ Br ⁺
81	17.71	CHCFCI ⁺ , Br ⁺	161	7.29	SF ₂ CBr ⁺
82	5.21	HBr ⁺ , SF ₂ C ⁺	163	7.29	SF ₂ CBr ⁺
85	2.60	SCFH ⁺	177	12.50	CHFCFCI ⁺
89	100	SF ₃ ⁺	179	14.58	CHFCFCI ₂ Br ⁺
91	7.29	CBr ⁺ , SF ₃ ⁺	181	3.12	CHFCFCI ₂ Br ⁺
97	2.08	CFCFCI ⁺			
98	41.67	CHFCFCI ⁺	<u>CHCl=CFCl + SF₅Br</u>		
		SFCCl ⁺	24	2.0	C ₂ ⁺
			25	7.3	C ₂ H ⁺
100	14.58	CHFCFCI ⁺	27	5.2	
		SFCCl ⁺ , BrF ⁺	28	10.4	N ₂ ⁺ , CO ⁺
105	2.08	SClF ₂ ⁺	31	12.5	CF ⁺
108	5.21	SF ₄ ⁺	32	3.1	CFH ⁺ , S ⁺
111	7.29	SBr ⁺ , CHFBr ⁺	35	11.4	Cl ⁺
113	7.29	SBr ⁺ , CHFBr ⁺	36	2.1	HCl ⁺

TABLE XII (con't)

<u>CHCl=CFC1 + SF₅Br (con't)</u>					
37	4.2	Cl ⁺	129	18.7	SF ₂ C ₂ Cl ⁺ , SF ₅ ⁺
43	4.2	C ₂ F ⁺	131	3.1	SF ₂ C ₂ Cl ⁺
44	45.8	CO ₂ ⁺ , CS ⁺	133	34.3	SF ₂ C ₂ Cl ⁺
47	36.4	CCl ⁺	134	2.1	SF ₂ C ₂ HCl ⁺
48	12.5	CHCl ⁺	135	21.8	SC ₂ Br ⁺
49	10.4	CCl ⁺	137	3.1	SC ₂ Br ⁺
50	4.2	CHCl ⁺	155	7.3	SC ₂ HFBr ⁺
51	4.2	SF ⁺	177	4.7	CF ₂ CHClBr ⁺
54	3.1	SFH ⁺ , ClF ⁺	179	6.2	CF ₂ CHClBr ⁺
59	6.25	C ₂ Cl ⁺	193	2.1	CHClCFC1Br ⁺
60	14.6	C ₂ HCl ⁺	195	4.2	CHClCFC1Br ⁺
61	2.1	C ₂ Cl ⁺	212	5.2	CF ₂ CHCl ₂ Br ⁺
62	9.4	C ₂ HCl ⁺	214	8.3	CF ₂ CHCl ₂ Br ⁺
99	19.8	SFCHCl ⁺	216	3.1	CF ₂ CHCl ₂ Br ⁺
100	4.2	BrF ⁺			
101	6.25	SF ₃ C ⁺ , SFCHCl ⁺			
108	6.25	SF ₄ ⁺			
113	4.2	SF ₂ CCF ⁺ , CClCFC1 ⁺			
114	100	SF ₂ CHCF ⁺ , CHClCFC1 ⁺			
115	8.3	?			
116	100	SF ₂ CCl ⁺ , CHClCFC1 ⁺			
117	4.2	SF ₂ CCl ⁺			
118	27.1	SF ₂ CHCl ⁺ , CHClCFC1 ⁺			
127	100	SF ₅ ⁺			

three compounds all exhibit strong peaks at $m/e = 89$, $m/e = 51$ and $m/e = 127$, which are SF_3^+ , SF^+ and SF_5^+ respectively. In $SF_5CH_2CH(CF_3)Br$ there was a strong CF_3^+ at $m/e = 69$. Only one compound, $SF_5CHFCHClBr$, had a good parent peak.

Nuclear Magnetic Resonance Spectra

Proton nmr spectra were recorded for the compounds $SF_5CHFCHClBr$, $SF_5CH_2C(CF_3)HBr$, and $SF_5CHFCFC1Br$ (see Fig. 6-8). The data available from the spectra are given in Table XIII. Due to the fluorine splitting of the protons and the asymmetric centers on the molecules the spectra are rather complex and not all of the coupling constants could be determined; however enough information is present to determine the structures as presented in the table.

For compound $SF_5CFHCHClBr$ there are two protons being split into doublets by the fluorine on the carbon. The SF_4 portion of the SF_5 group then splits one of these protons into a pentet with $J_{H_2F_1} = 5.4$ cycles. This gives two five line patterns which are split into doublets by the proton-proton interaction $J_{H_2H_3} = 1.2$ cycles. The remaining proton H_3 which formed a doublet with the fluorine F_3 , was again split into a doublet by H_2 with the same coupling constant $J_{H_2H_3} = 1.2$ cycles. If the addition of SF_5Br had been reversed the proton on the $CHFBr$ portion would have had a fairly simple splitting pattern and this proton would have had the larger J value and would not have been split into the pentet.

TABLE XIII

NMR SPECTRAL DATA FOR SF₅Br - FLUOROOLEFINS ADDUCTS

Suggested Structure				Chemical Shifts	Coupling Constants	
1	2	3	4	(ppm)	(cycles)	
SF ₅	CHF	CHClBr		$\delta_2 = 5.83$ $\delta_3 = 6.25$	$J_{H_2F_2} = 43.2$	$J_{H_3F_2} = 19.8$
					$J_{H_2F_1} = 5.4$	$J_{H_2H_3} = 1.2$
SF ₅	CH ₂	CHBr	CF ₃	$\delta_3 = 4.5$ $\delta_2 \cong 4.13$	$J_{H_3F_4} = 9$	$J_{H_2H_3\text{cis}} = 2.88$
SF ₅	CHF	CFClBr		$\delta = 5.6$	$J_{H_2F_2} = 41.4$	$J_{H_2F_1} \cong 6$

The spectrum for compound $\text{SF}_5\text{CH}_2\text{CH}(\text{CF}_3)\text{Br}$ is very complex and not all of the coupling constants could be obtained. The set of peaks farther downfield belong to proton H_3 and the group of peaks at 4.13 ppm belong to proton H_2 . Because of the asymmetric centers on this molecule there is both cis and trans coupling between proton H_3 and proton H_2 . Proton H_3 is split into a doublet by the cis proton, a doublet by the trans proton, and a quartet by the fluorine F_4 ; from the possible overlapping it was determined $J_{\text{H}_3\text{H}_2 \text{ cis}} < J_{\text{H}_3\text{F}_4} < J_{\text{H}_3\text{H}_2 \text{ trans}}$, $J_{\text{H}_3\text{H}_2 \text{ cis}} = 2.88$ cycles, $J_{\text{H}_3\text{F}_4} = 9$ cycles and $J_{\text{H}_3\text{H}_2 \text{ trans}}$ was indeterminable due to overlapping. If the SF_5Br addition had occurred in the opposite way the protons CH_2 would have a very simple splitting pattern. Very little can be said about these protons from this spectrum other than to get an approximate chemical shift of $\delta_2 \approx 4.13$ ppm. This problem is due to the proton being in different environments and to the overlap and possible collapsing of peaks due to close J values.

Compound $\text{SF}_5\text{CFHCFC1Br}$ gives another rather complex spectrum again due to the asymmetry of the compound. The single proton has a chemical shift of 5.6 ppm. The largest coupling constant is the doublet with value $J_{\text{H}_2\text{F}_2} = 41.4$ cycles, this compares very well with the value for the same type of coupling in the compound $\text{SF}_5\text{CFHCHClBr}$, where $J_{\text{H}_2\text{F}_2} = 43.2$ cycles. Again in this molecule one has a cis-trans splitting between H_2 , F_3 and this causes overlap and collapsing of peaks. Also, the F_1H_2 coupling which is a pentet is involved. If in this compound addition had occurred the opposite way there would be no complex pattern as the proton would not be split by the SF_4 group and simple doublets would be observed.

Polymerization of Trifluoroethylene in the Presence of SF₅Br

1. Experimental and Discussion

In the reaction of SF₅Br and CF₂=CFH to form the liquid SF₅CFHCF₂Br from which SF₅CF=CF₂ is produced, a white waxy solid was formed inside the vessel. This occurred when 0.1 moles CF₂=CFH and 9.3×10^{-2} moles SF₅Br were heated together in a Hoke 200 ml stainless steel vessel at 90° for four days; to this mixture 6.4×10^{-2} moles of CF₂=CFH were added and after two days at room temperature an additional 5.2×10^{-2} moles of SF₅Br were added. This final mixture was heated at 90° for three days. Seven grams of the crude liquid adduct was transferred out of the vessel leaving behind 9 grams of a white solid polymer.

The white waxy material is insoluble in water but dissolves in acetone and has a broad melting range, from 130° to 160°. In this range the product becomes more and more liquid-like, without exhibiting a sharp characteristic melting point. An infrared spectrum was taken and showed the presence of characteristic bands in the C-F region and S-F region. Figure 9 contains the infrared spectra for this material.

An elemental sample analysis of the white waxy solid gave the following: C(27.34%), H(1.19%), S(1.44%), F(68.2%), Br(2.01%).

It is obvious that the SF₅Br was incorporated into the polymer and was probably responsible for the polymerization of CF₂=CFH.

The polymerization of CF₂=CF₂ by SF₅Br is poorly understood particularly with regard to the experimental conditions that favor its formation. Further studies of the preparation and properties of this polymer are in order.

Discussion

Table XIV contains a summary of all olefin systems in which attempts have been made to add SF_5Br with thermal excitation.

Part A of Table XIV clearly demonstrates that any olefin containing a CH_2 group will add SF_5Br under normally mild thermal conditions. The SF_5 group in all cases adds to the CH_2 portion of the double bond; large bulky groups [SF_5 , $Si(CH_3)_3$] attached to the other carbon of the double bond do not appear to alter or prevent this addition.

Part B of Table XIV indicates that SF_5 addition to olefins at a CHF group is prevented when the groups attached to the other carbon of the double bond contains a SF_5 group. In part C, SF_5 addition at the CF_2 group is prevented when bulky groups are attached to the other carbon of the double bond. Part D clearly demonstrates the steric effects opposing SF_5 addition. In replacing fluorine with chlorine ($CHF = CFC1$ and $CHCl = CFC1$) enough steric repulsion is present to prevent SF_5 addition.

To a first order approximation it seems possible to conclude that steric factors are important in determining the fate of SF_5Br addition to fluoroolefins. This effect is also present in $CF_3(SF_5)CFCF(SF_5)CF_3$ which is unstable at elevated temperatures (greater than 50°) and decomposes to $CF_3CF=CF_2$ and S_2F_{10} .

TABLE XIV

OLEFINIC SYSTEMS - ADDITION OF SF₅Br

<u>Olefin</u>	<u>Product</u>	<u>Conditions</u>
A. CH ₂ = CH ₂	SF ₅ CH ₂ CH ₂ Br	Not Available
CH ₂ = CHF	SF ₅ CH ₂ CHFBr	R.T., 24 hrs.
CH ₂ = CF ₂	SF ₅ CH ₂ CF ₂ Br	R.T., 24 hrs.
CH ₂ = CFCl	SF ₅ CH ₂ CFClBr	R.T., 24 hrs.
CH ₂ = C(CF ₃)H	SF ₅ CH ₂ CH(CF ₃)Br	R.T., 18 days
CH ₂ = CH(SF ₅)	SF ₅ CH ₂ CH(SF ₅)Br	70°, 8 hrs.
CH ₂ = CH/Si(CH ₃) ₃ /	SF ₅ CH ₂ CH/Si(CH ₃) ₃ /Br*	25°, 1 hr
CH ₂ = CH(SiCl ₃)	SF ₅ CH ₂ CH(SiCl ₃)Br	0°, 3 hrs.
B. CHF = CF ₂	SF ₅ CHF CF ₂ Br	R.T., 24 hrs.
CHF = CHCl	SF ₅ CHFCHClBr	80°, 4.5 days
CHF = CFCl	SF ₅ CHF CFClBr	80°, 5 days
CHF = CF(SF ₅)	None	**
CHF = CH(SF ₅)	None	**
C. CF ₂ = CFCl	SF ₅ CF ₂ CFClBr*	R.T., 24 hrs.
CF ₂ = CHCl	SF ₅ CF ₂ CHClBr	100°, 14 days
CF ₂ = CF(COF)	None	80°, 6 days
CF ₂ = CH(SF ₅)	None	**
CF ₂ = CF(SF ₅)	None	**
D. CHCl = CFCl	Small Amount	125°, 5 days
CHBr = CHSF ₅	None	**

* Structure not proven conclusively.

** Range of conditions (T = 120-180°; times 18 hrs-7 days; SF₅Br: olefin ratios of 2:1 + 1:2)

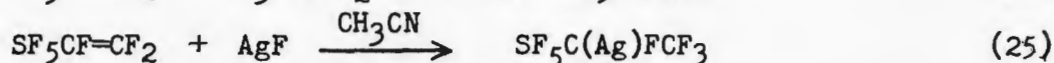
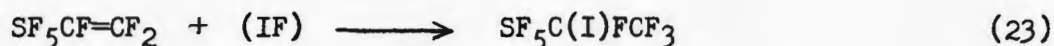
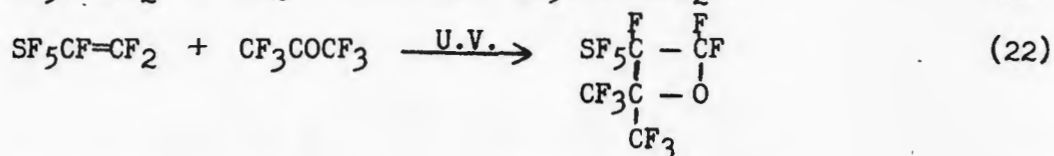
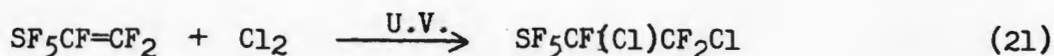
CHAPTER IV

DERIVATIVES OF TRIFLUOROVINYLSULFUR PENTAFLUORIDE (SF₅CF=CF₂)

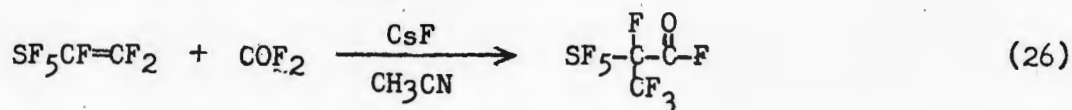
I. Introduction

Roberts et al. (11) reported the preparation of SF₅CF=CF₂ via the dehydrohalogenation of SF₅CFHCF₂Cl. The olefin is a clear colorless liquid with a boiling point of 19° and a normal Trouton constant of 20.5

SF₅CF=CF₂ is an important reagent for preparing useful SF₅ carbon compounds. Some of the reactions that have been reported are (11,16,21-23):

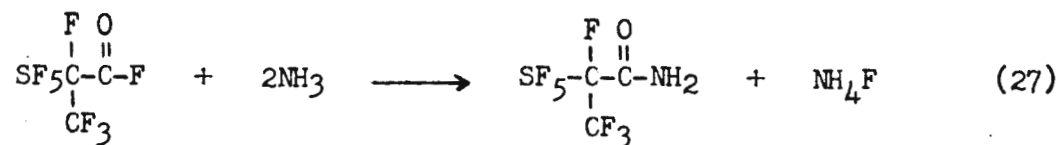


Based on the chemistry of SF₅CF=CF₂ and the work reported by Fawcett and coworkers (24) where they found that carbonyl fluoride (COF₂) in the presence of CsF and CH₃CN will add to double bonds of fluoroolefins the following reaction was elucidated:



Due to the difficulty of separating SF₅CF(CF₃)COF from the reaction

mixture, the following reaction of $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ with NH_3 was also elucidated:



II. Reaction of $\text{SF}_5\text{CF}=\text{CF}_2$ and COF_2

1. Experimental and Discussion

$\text{SF}_5\text{CF}=\text{CF}_2$ (3.75×10^{-2} moles) and COF_2 (5.4×10^{-2} moles) were condensed into a 75 ml stainless steel vessel containing 30 ml CH_3CN and 10 grams of CsF . The CH_3CN was dried over P_4O_{10} and distilled directly into the reaction vessel. CsF was dried under vacuum at 100° for 5 hrs. The reactant materials were heated at 50° for 2 hrs., 75° for 2 hrs., and 100° for 5 hrs. The products were a colorless volatile liquid mixture that could not be separated by distillation because the product $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ boils close to room temperature and appeared to azeotrope with the excess COF_2 . Purification was achieved by a trap to trap transfer at -120° , -78° , and -50° . The -50° trap contained essentially pure $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ as determined by the absence of infrared absorption bands attributable to COF_2 .

The analysis of this pure fraction via its molecular weight, its elemental analysis, its characteristic infrared and mass spectra (Tables XV and XVI) is supportive of its structure. See Figure 10 for actual infrared spectrum.

The molecular weight of the product was found to be 269 g per mole (theor. 274 g/mole). The elemental analysis was as follows: Found: C(14.53%), S(9.35%), F(70.9%). Theoretical: C(13.1%), S(11.7%), F(69.3%). Due to the possible contamination by a small amount of COF_2 , the above values are within acceptable limits.

The infrared spectrum of $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ is listed in Table XV. By analogy with numerous spectra of acid fluorides, the absorption at 1880 cm^{-1} is assigned to the C=O. In $\text{SF}_5\text{OCF}_2\text{COF}$ this absorption band was found at 1898 cm^{-1} . The absorption bands at 845 and 890 cm^{-1} are due to the S-F stretching vibrations while the band at 600 cm^{-1} is due to the S-F deformation mode. The C-F stretching modes are found in the 1200 to 1300 cm^{-1} region.

The major mass spectrum peaks for $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ are listed in Table XVI. Strong peaks of 100% intensity were found for the CF_3^+ , COF_3^+ , SF_3^+ , SF_5^+ , and C_2F_5^+ ion groups. The fragmentation pattern is supportive for the proposed structure.

III. Reaction of $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ with NH_3

In an attempt to separate $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ from the other reaction products, its reaction with ammonia was studied. It is anticipated that the $\text{SF}_5\text{CF}(\text{CF}_3)\text{CONH}_2$ formed in this reaction could be used to reform the acid fluoride in subsequent reactions.

1. Experimental and Discussion

Impure $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ (1.13×10^{-2} moles) and NH_3 (2.9×10^{-2} moles) were condensed into a 75 ml stainless steel vessel. After standing overnight at room temperature the volatile materials were pumped away into a trap cooled to -196° . In a dry box the solid

mixture of $\text{SF}_5\text{CF}(\text{CF}_3)\text{CONH}_2$ and NH_4F were transferred to a sample bottle (weight of products transferred was 1.2 grams).

It was found that the amide is soluble in CCl_4 , and the NH_4F was easily removed from the product mixture by dissolving the amide in CCl_4 and filtering away the insoluble NH_4F . Removal of the CCl_4 solvent left a white solid product (0.5 grams). The white solid product has a melting point of 32-34°.

The analysis of the white solid via its elemental analysis and its characteristic infrared spectrum is supportive of the proposed structure, $\text{SF}_5\text{CF}(\text{CF}_3)\text{CONH}_2$. The elemental analysis was as follows: Found: C(14.65, 14.85), H(0.65, 0.84), S(10.51, 9.34), N(5.4), F(63.6). Theoretical: C(13.3), H(0.74), S(11.8), N(5.17), F(63.1).

The infrared spectrum of $\text{SF}_5\text{CF}(\text{CF}_3)\text{CONH}_2$ is listed in Table XVII. The disappearance of the $[\text{C}(\text{O})\text{F}]$ absorption at 1880 cm^{-1} and the appearance of a new absorption at 1740 cm^{-1} $[\text{C}(\text{O})\text{NH}_2]$ and new absorptions 3200 cm^{-1} and 3420 cm^{-1} $[\text{N-H stretch in C}(\text{O})\text{NH}_2]$ as well as retention of the SF_5 and C-F absorptions indicate that the amide was formed. The absorption peak at 1010 cm^{-1} is assigned to the C-N stretch. The actual spectrum is shown in Figure 11.

V. Conclusions

The work reported in this section clearly establishes the existence of two new compounds - $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ and $\text{SF}_5\text{CF}(\text{CF}_3)\text{CONH}_2$. However, more work is needed to increase the yield of the acid fluoride as well as the amide, and more work is needed to expand the chemistry of these two new compounds.

TABLE XV

INFRARED SPECTRUM OF SF₅CF(CF₃)COF (GAS)

<u>cm⁻¹</u>	<u>Intensity</u>
1880	s
1240	vs with sh. at 1910 & 1180 cm ⁻¹
1145	s
975	m with sh. at 1000 & 1020 cm ⁻¹
890	s
845	s
750	w
695	w-m
640	vw
600	m
570	w

TABLE XVI

MASS SPECTRUM OF SF₅CF(CF₃)COF

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
28	9.38	CO ⁺
31	27.08	CF ⁺
32	2.08	S ⁺
38	2.08	F ⁺
39	3.12	?
40	8.33	C ₂ O ⁺
41	16.67	?
47	19.79	CFO ⁺
50	8.33	CF ₂ ⁺
51	7.29	SF ⁺
62	1.56	C ₂ F ₂ ⁺
63	5.21	SFC ⁺
69	100	CF ₃ ⁺
70	20.83	SF ₂ ⁺
81	5.21	C ₂ F ₃ ⁺
85	100	COF ₃ ⁺
86	5.21	SF ₂ O ⁺
87	3.12	C ₃ FS ⁺
89	100	S ³² F ₃ ⁺
90	2.08	S ³³ F ₃ ⁺
91	8.33	SFCCO ⁺ , S ³⁴ F ₃ ⁺
93	5.21	C ₃ F ₃ ⁺

TABLE XVI (Cont.)

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
100	17.71	$C_2F_4^+$
101	7.29	SF_3C^+
104	3.12	?
108	3.12	SF_4^+
113	3.12	$SF_3C_2^+$
119	100	$C_2F_5^+$
120	2.08	SF_4C^+
127	100	$S^{32}F_5^+$
128	3.12	$CFCOCF_3^+$, $S^{33}F_5^+$
129	9.38	$S^{34}F_5^+$
131	14.58	$C_3F_5^+$
147	3.12	?

TABLE XVII

INFRARED SPECTRUM OF $\text{SF}_5\text{CF}(\text{CF}_3)\text{CONH}_2$ (solid)

<u>cm⁻¹</u>	<u>Strength</u>
3420	m
3320	m
3240	m
3200	m
1740	s
1600	m
1360	w-m
1275	m-s
1230	s
1195	s
1140	m
1010	m
880	vs
840	vs
775	vs
750	vs
680	w
600	m
575	w
540	vw

CHAPTER V

RAMAN SPECTRA FOR SF₅Br ADDUCTS

Raman spectra for the three new SF₅Br adducts discussed in this thesis (SF₅CHFCFClBr, SF₅CH₂CH(CF₃)Br, SF₅CHFCHClBr) and for three other adducts [SF₅CH=C(CF₃)Br, SF₅CH=C(CH₃)Br, and SF₅CF₂CHClBr] prepared in our laboratories have been recorded by Dr. Thomas Loehr of the Oregon Graduate Center. The Raman spectra were obtained by Dr. Loehr on a Jarrell-Ash 25-300 spectrometer using a radiation of 5145 Å Argon laser for excitation; 90° viewing was used. The Raman radiation was detected by a S-20 phototube which was thermo-electrically cooled. The photon counting mode was used. Samples (liquids) were contained in a sealed 0.25" I.D. Pyrex-glass tube.

Figures 12-17 contain the Raman spectra as recorded for the above compounds. The abbreviations SR and SL found in each Figure refer to the scan rate (cm⁻¹ per sec.) and slit width (cm⁻¹), respectively, for each run. In Tables XVIII-XXII, the Raman bands along with their respective relative intensities are listed. The compound, SF₅CF₂CHClBr decomposed slowly during this study and as a result only a few Raman bands were obtained.

For SF₅Br adducts containing C-H bonds, the Raman spectra contained bands in the 3000 cm⁻¹ range. For SF₅CHFCHClBr, the 3012 and 2978 cm⁻¹ bands are assigned to the C-H stretching vibration of the -CHCl group and the -CHSF₅ group, respectively. This is based on the observation that in SF₅CHFCFClBr the only C-H stretching frequency was found at 2978 cm⁻¹. Furthermore, it seems reasonable to assign the C-H

stretching frequency of the $-\text{CH}(\text{CF}_3)\text{Br}$ group in $\text{SF}_5\text{CH}_2\text{CH}(\text{CF}_3)\text{Br}$ to the band located at 3016 cm^{-1} by analogy to the similar group, $-\text{CHClBr}$ in $\text{SF}_5\text{CHFCHClBr}$ where the C-H stretching frequency is located at 3012 cm^{-1} . In $\text{SF}_5\text{CH}_2\text{CH}(\text{CF}_3)\text{Br}$ the band at 2976 cm^{-1} is attributable to C-H stretch of the CH_2 group.

For the isomeric mixture, $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$, the observed bands at 3091 and 3047 cm^{-1} are attributable to the C-H stretching frequencies for the entgegen and zusammen isomers. In $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$, the band at 3097 cm^{-1} is most likely due to the C-H stretch of the $\text{SF}_5\text{CH}=\text{C}$ group; this by analogy to the C-H band in $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$. The band at 2937 cm^{-1} in $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ is assigned to the C-H stretch frequency of the CH_3 group.

For the SF_5 adducts the stretching frequencies in $1600\text{--}1700\text{ cm}^{-1}$ range are assigned to the C=C stretching frequencies. For $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$, this band is found at 1643 cm^{-1} while for the isomeric mixture of $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ the bands are located at 1687 and 1636 cm^{-1} .

Carbon-fluorine stretching vibrations have been established to be in the $1400\text{--}1000\text{ cm}^{-1}$ range (25) and are strong in the infrared but weak in the Raman. Due to C-F vibrational coupling with C-C stretching frequencies (26), some difficulties are encountered in assigning various C-F stretching modes. Most of the bands we see in this region, however, are probably due to C-F stretching frequencies. The frequency range $850\text{--}1000\text{ cm}^{-1}$ is designated as the C-C stretching region although assignment of this mode has not been well established (25). However, assignments for the C-C stretch have been reported for fluorocarbons (27) and fall within this frequency range. Since some of the molecules

presented in this thesis contain a Raman band in this region and some do not, it is difficult to make any definite assignment.

One of the strongest Raman bands in the spectra of CF_3 containing compounds (28) is a CF_3 deformation mode at about 750 cm^{-1} . In $\text{SF}_5\text{CH}_2\text{CH}(\text{CF}_3)\text{Br}$ and $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$, the Raman bands at 727 and 769 or 719 cm^{-1} , respectively, could be due to the CF_3 deformation mode. The C-S stretching frequency assignments in $(\text{CF}_3)_2\text{S}_2$ are sym. 446 cm^{-1} and asym. 450 cm^{-1} (28). The Raman bands in this region are present in some of our SF_5 adducts but are shifted to lower frequency in others. A definite assignment must wait further work.

It has been noted that in the infrared spectrum of SF_5Br , strong bands located at 849 and 894 cm^{-1} were present [849 cm^{-1} assigned to (S-F); 894 cm^{-1} assigned to asym (SF_4)]. With the SF_5 adducts, intense infrared absorption bands appear in $850\text{--}920 \text{ cm}^{-1}$ region due to S-F stretching modes. In the Raman spectra of our SF_5 adducts, bands attributable to these S-F stretching modes are either absent or extremely weak. This is exactly the same behavior as noted for SF_5Br . In SF_5Br , the Raman band assigned to the sym (SF_4) mode, located at 691 cm^{-1} , is strong. For all SF_5 adducts, a strong Raman band is located in the region $669\text{--}694 \text{ cm}^{-1}$ and probably represents the sym (SF_4) mode in these molecules.

All of these adducts contain a C-Br band and the C-Br stretching frequency in the Raman is usually strong. For CH_3Br , the Raman band is located at 609 cm^{-1} . For all the SF_5 adducts, a Raman band is located in the $595\text{--}612 \text{ cm}^{-1}$ region and could be assigned to the C-Br stretching frequencies. However, it is also possible that the stronger Raman bands

located in $620-667\text{ cm}^{-1}$ region represent the C-Br stretch. Further studies are needed to solve this assignment.

TABLE XVIII

RAMAN SPECTRUM FOR SF₅CHFCHClBr

<u>cm⁻¹</u>	<u>Rel. Int.</u>	<u>cm⁻¹</u>	<u>Rel. Int.</u>
3012	94.6	658	5.4
2978	88.5	631	55.0
1343	12.8	600	28.7
1291	22.7	485	3.9
1261	14.9	430	33.7
1175	12.6	403	28.7
1142	9.5	330	54.2
977	25.9	273	44.8
774	74.0	255	100
735	11.3	191	47.3
714	97.8	166	95.7
697	8.4	68	11.2
669	64.9		

TABLE XIX

RAMAN SPECTRA FOR $\text{SF}_5\text{CH}_2\text{CH}(\text{CF}_3)\text{Br}$

<u>cm⁻¹</u>	<u>Rel. Int.</u>	<u>cm⁻¹</u>	<u>Rel. Int.</u>
3016	75.8	687	32.9
2976	100	667	76.6
1423	16.4	599	22.7
1369	3.3	531	19.0
1302	4.5	386	18.5
1285	14.5	317	64.9
1252	1.8	263	47.9
1194	18.5	209	89.8
1171	3.5	188	28.9
1115	11.7	149	3.5
1066	1	121	38.1
727	38.2		

TABLE XX
RAMAN SPECTRUM FOR SF₅CFHCFC1Br

<u>cm⁻¹</u>	<u>Rel. Int.</u>	<u>cm⁻¹</u>	<u>Rel. Int.</u>
2978	56.1	648	90.6
1333	9.4	612	45.0
1274	13.2	541	68.1
1282	15.0	435	39.9
1225	17.8	306	67.8
1153	8.1	259	73.7
1117	10.7	247	81.2
1065	1.1	227	86.8
971	1.6	188	92.9
807	66.0	167	100
782	29.5	123	38.6
686	81.2	73	.5
667	31.1		

TABLE XXI

RAMAN SPECTRA FOR $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ AND $\text{SF}_5\text{CF}_2\text{CHClBr}$

<u>$\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$</u>		<u>$\text{SF}_5\text{CF}_2\text{CHClBr}$</u>	
<u>cm^{-1}</u>	<u>Rel. Int.</u>	<u>cm^{-1}</u>	<u>Rel. Int.</u>
3097	51.5	812	44
2937	100	789	42.4
1643	24.8	736	62.7
1435	20.5	677	88.1
1384	22.1	662	100
1297	18.3	612	76.3
1088	12.9	392	57.6
738	94.3	366	49.1
684	48.3	271	71.2
620	57.7	243	81.1
595	69.8	167	6.7
499	30.5		
481	26.0		
422	42.4		
335	50.5		
288	26.7		
192	86.9		
137	67.1		
89	6.3		

TABLE XXII

RAMAN SPECTRUM FOR SF₅CH=C(CF₃)Br*

<u>cm⁻¹</u>	<u>Rel. Int.</u>	<u>cm⁻¹</u>	<u>Rel. Int.</u>
3091	63.9	649	44.7
3047	73.1	609	28.2
1687	16.8	535	6.3
1636	23.1	508	38.5
1339	13.8	488	49.5
1289	13.3	401	2.5
1266	15.1	356	45.0
1227	19.6	337	9.4
1199	21.3	316	6.1
1174	22.9	249	82.5
1153	24.9	224	18.1
1070	2.9	196	13.2
891	19.4	176	72.1
769	36.4	159	55.5
719	75.2	100	79.1
694	100		

*This compound was a mixture of two isomers.

Figure 2. Infrared Spectrum for SF₅CH₂CFCHClBr

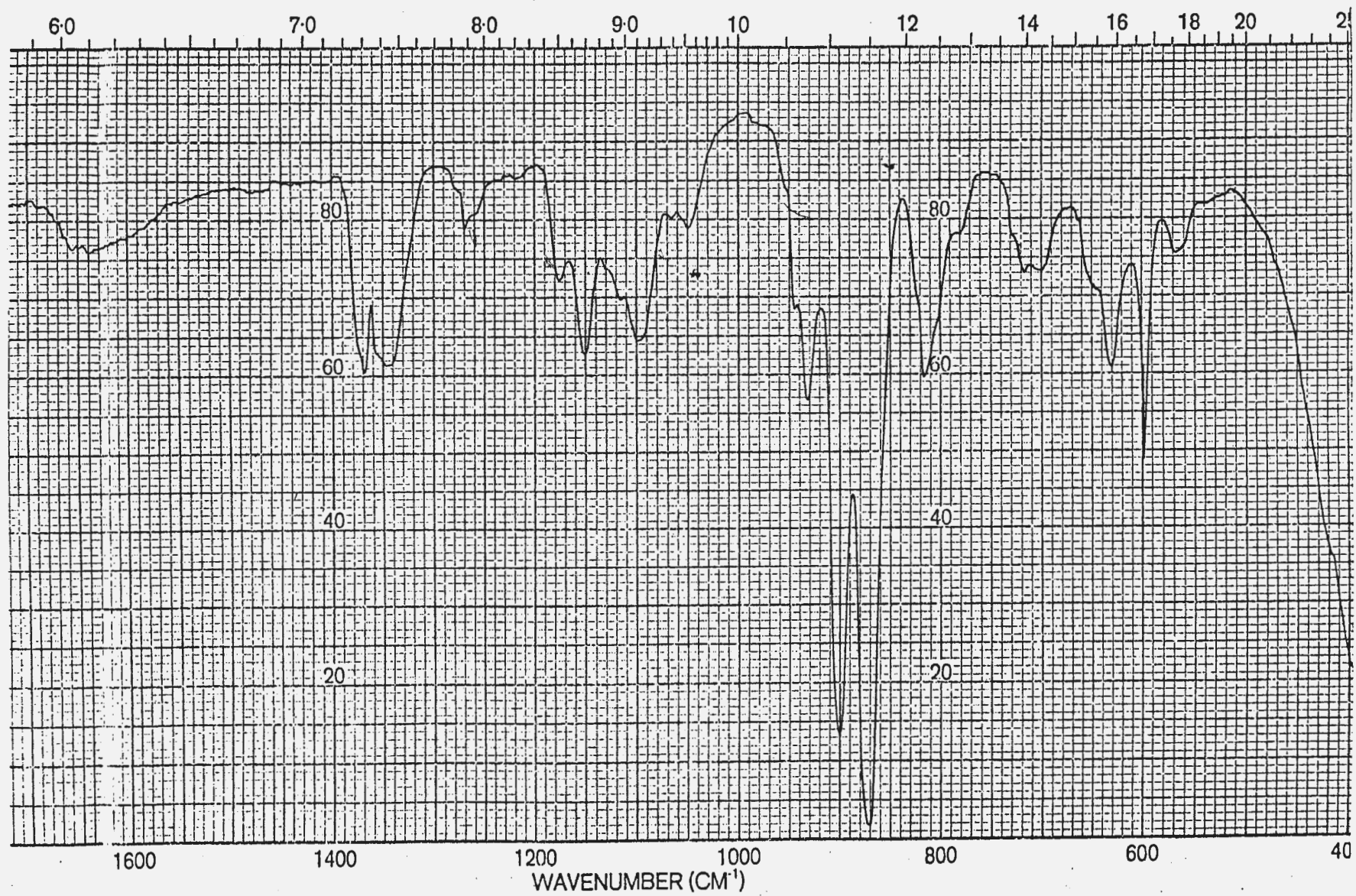


Figure 3. Infrared Spectrum for $\text{SF}_5\text{CH}_2\text{CH}(\text{CF}_3)\text{Br}$

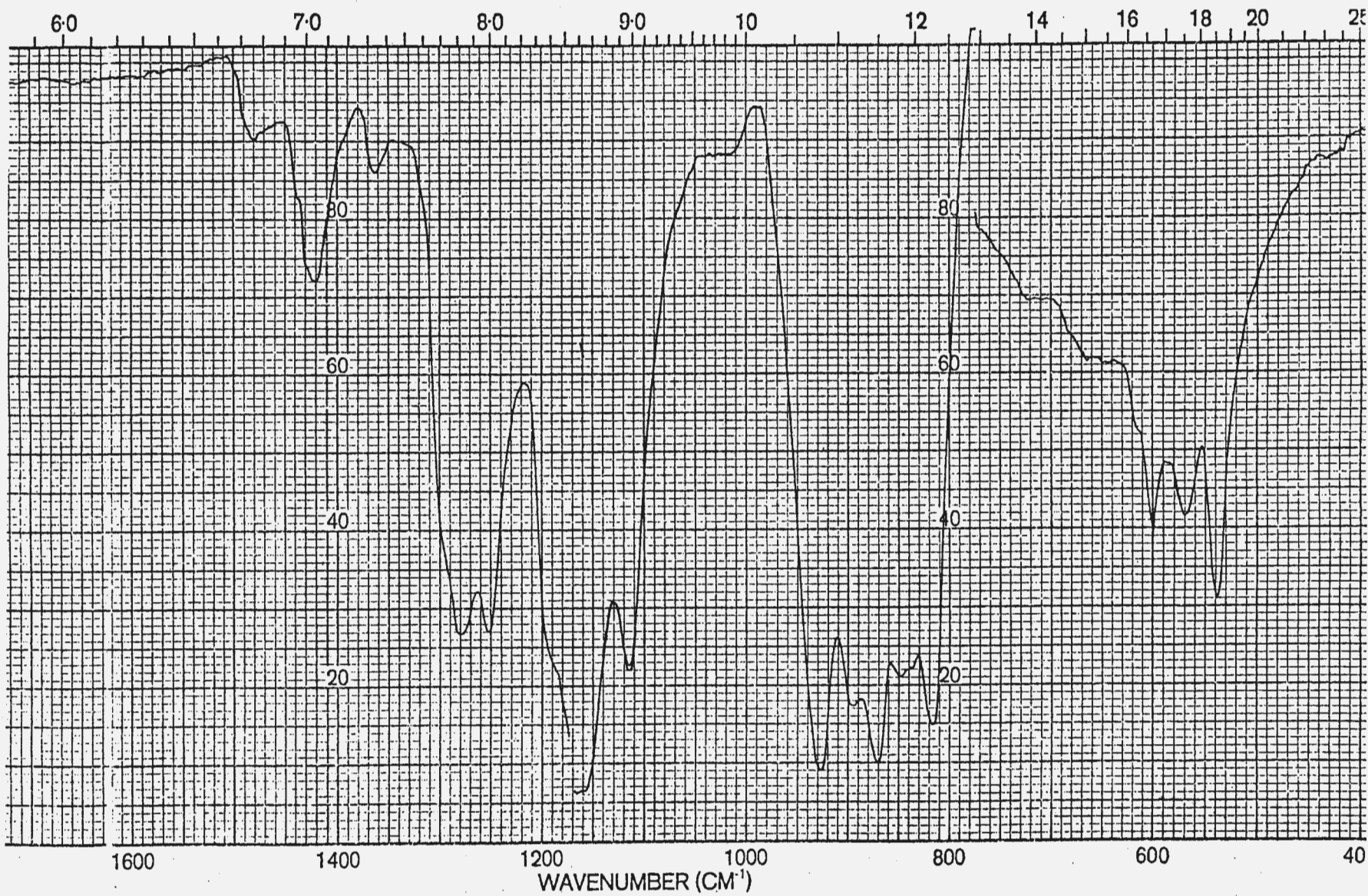


Figure 4. Infrared Spectrum for SF₅CHFCFCIBr

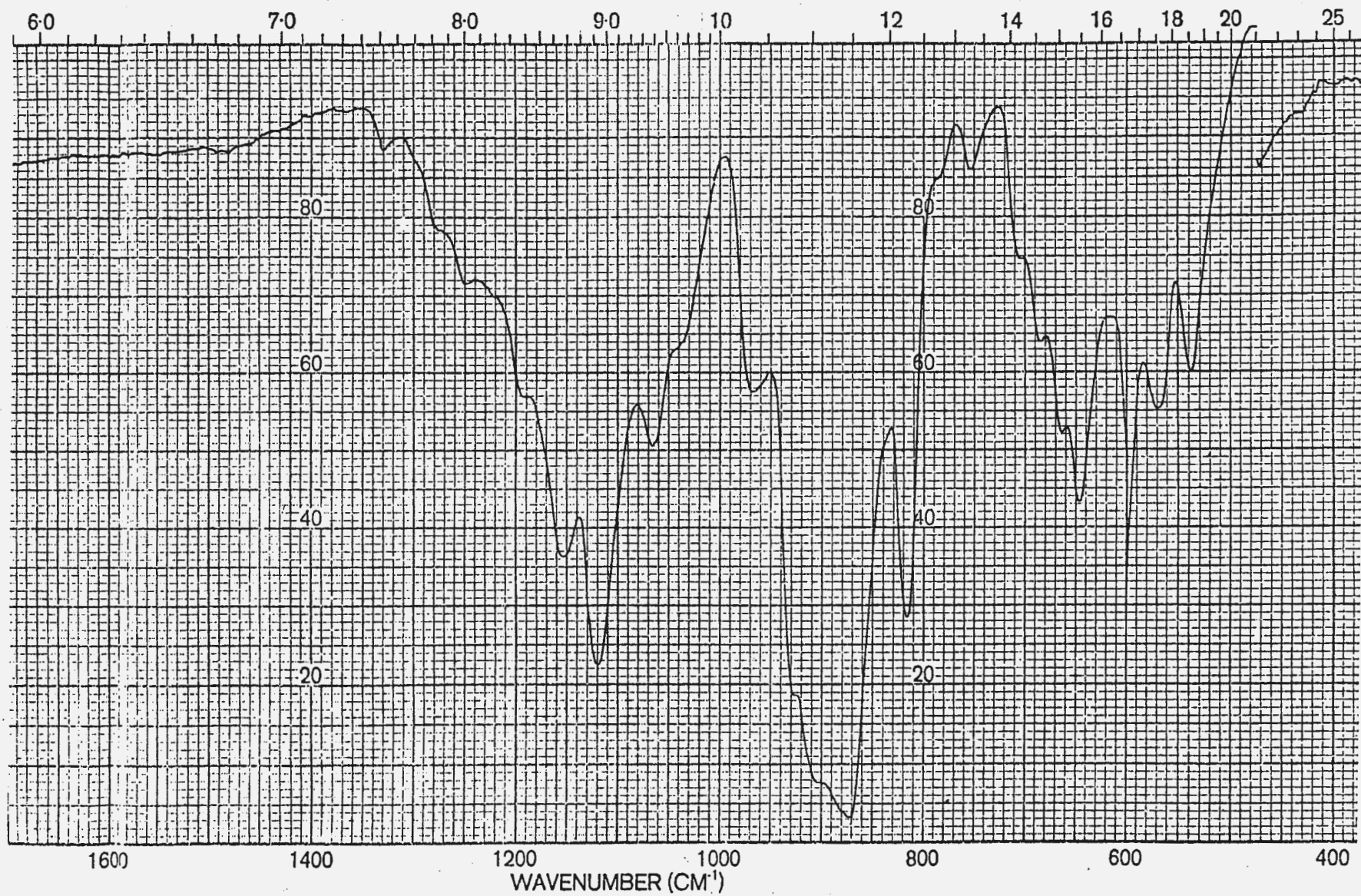


Figure 5. Infrared Spectrum for SF₆Br + CFCl=CHCl

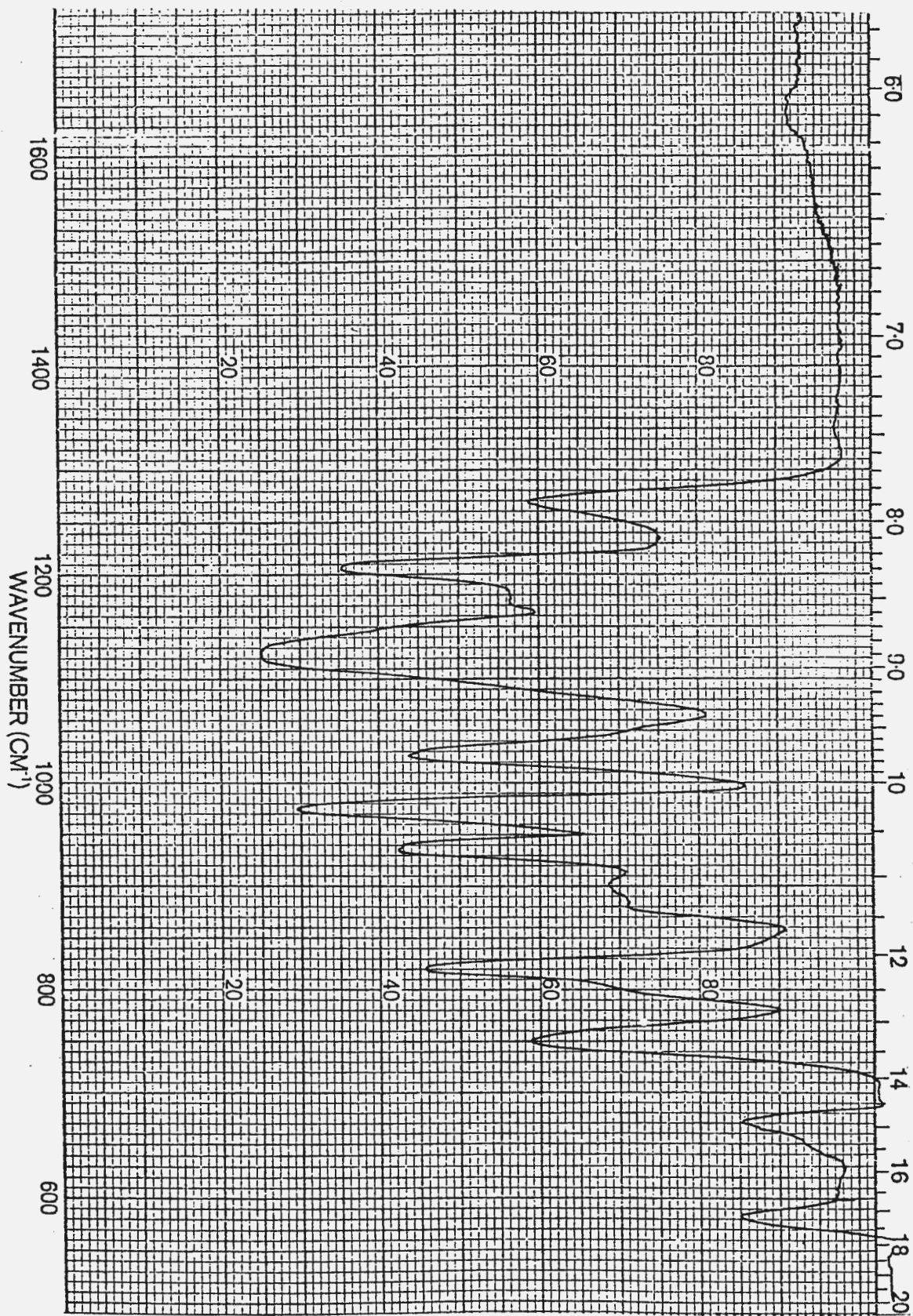
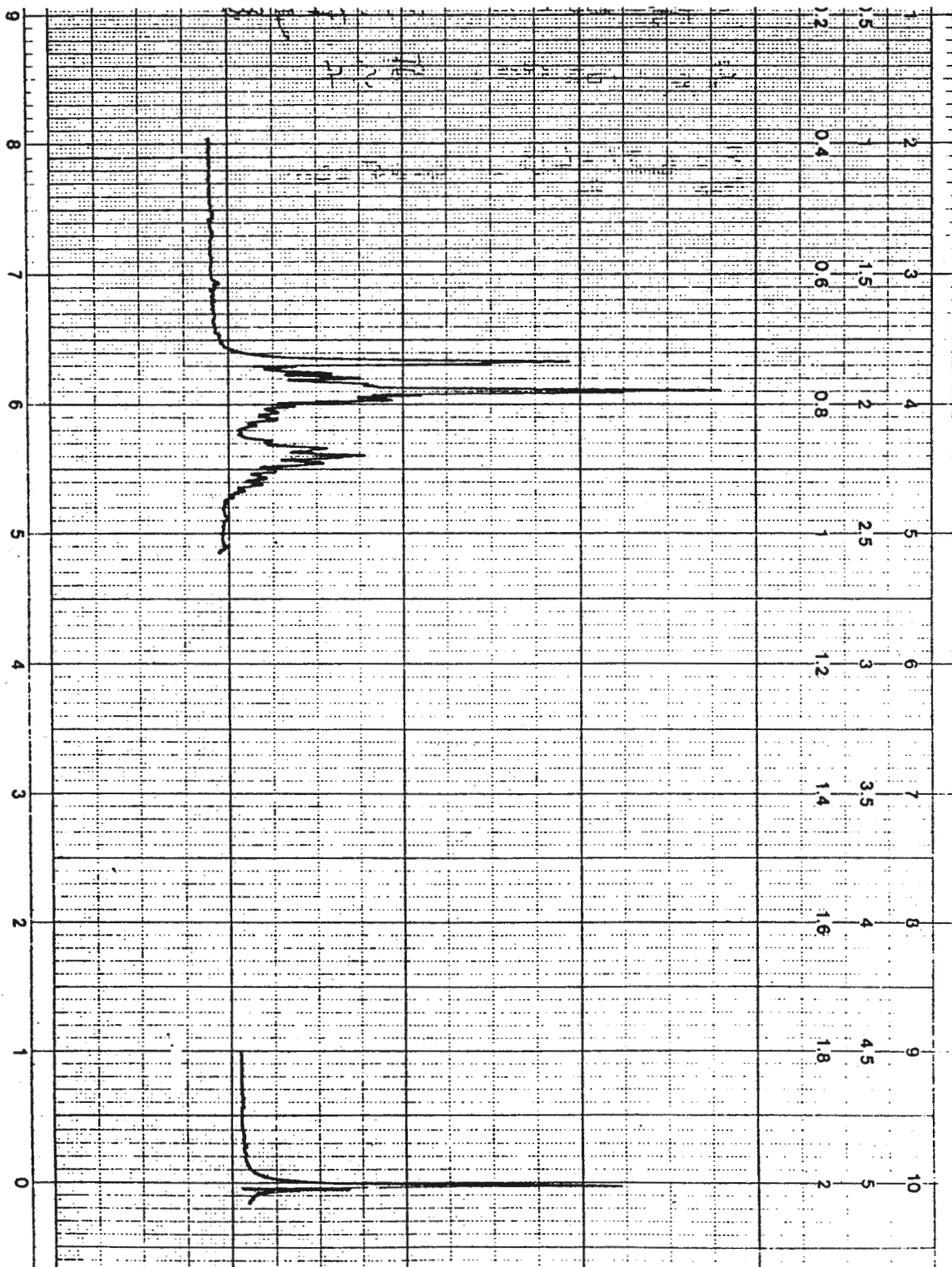


Figure 6. NMR Proton Spectrum for SF₅CHFCFClBr



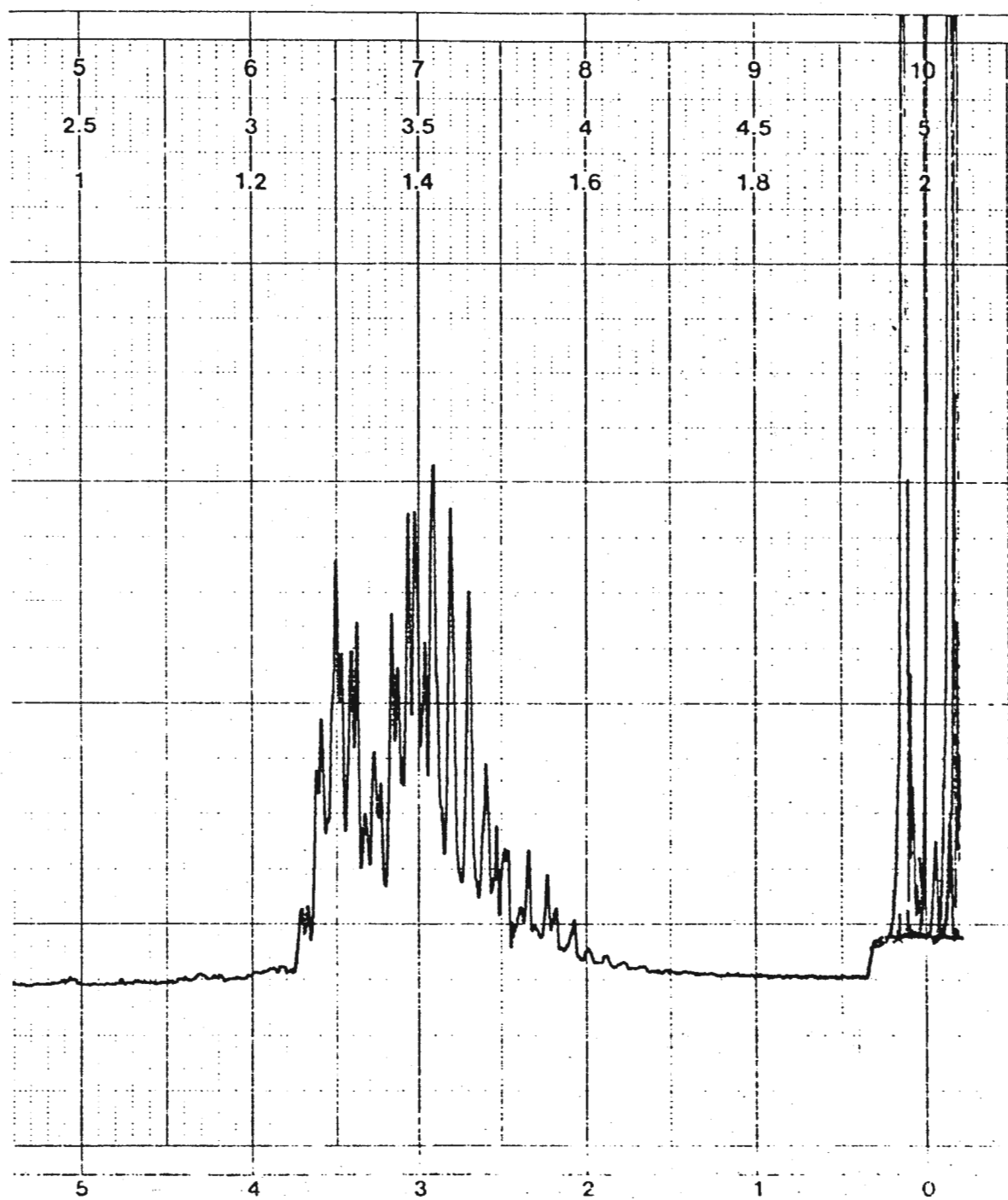


Figure 7. NMR Proton Spectrum for SF₅CH₂CH(CF₃)Br

Figure 8. NMR Proton Spectrum for SF₅CHFCFClBr

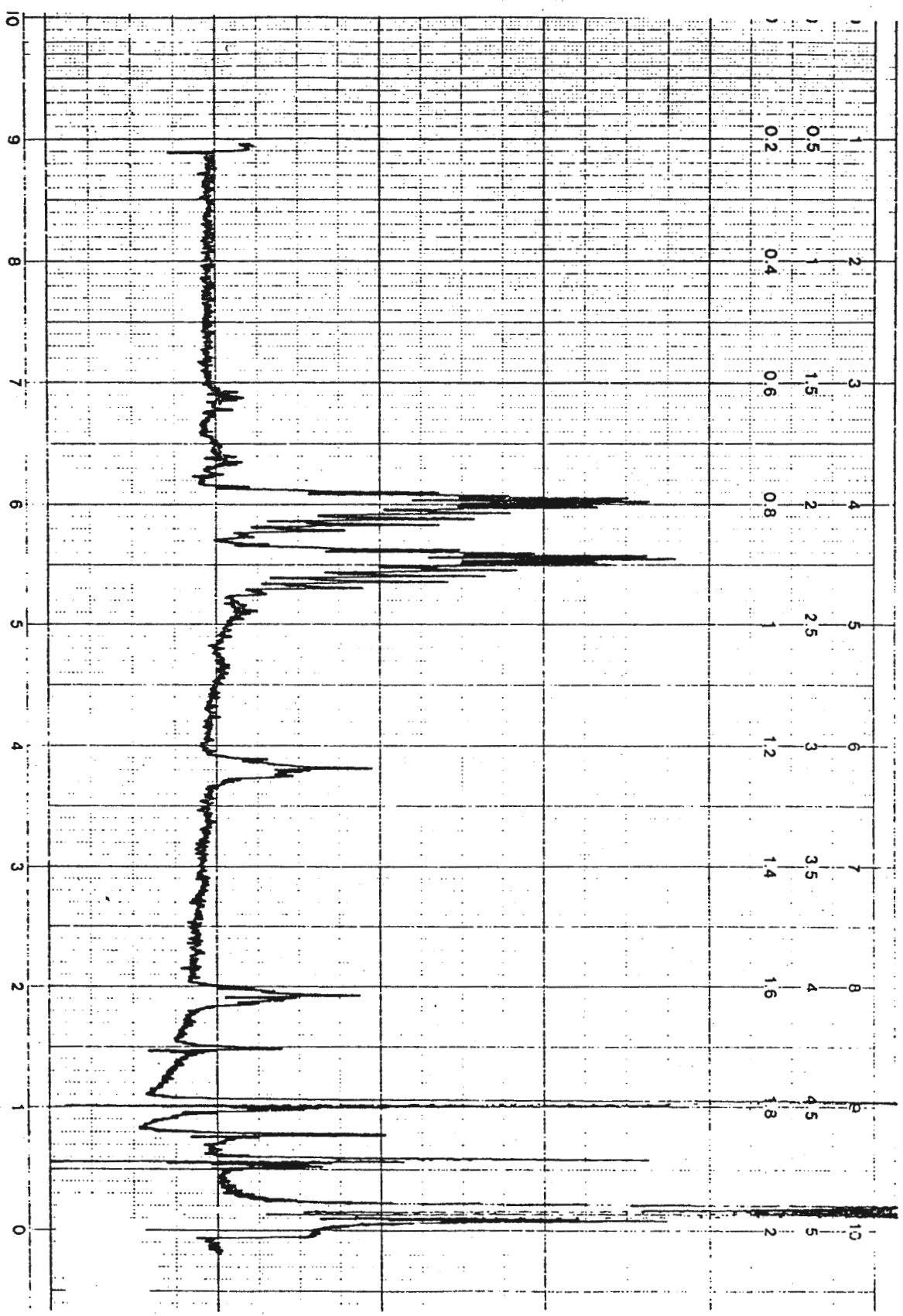


Figure 9. Infrared Spectrum for SF₅Br - CF₂=CFH Polymer

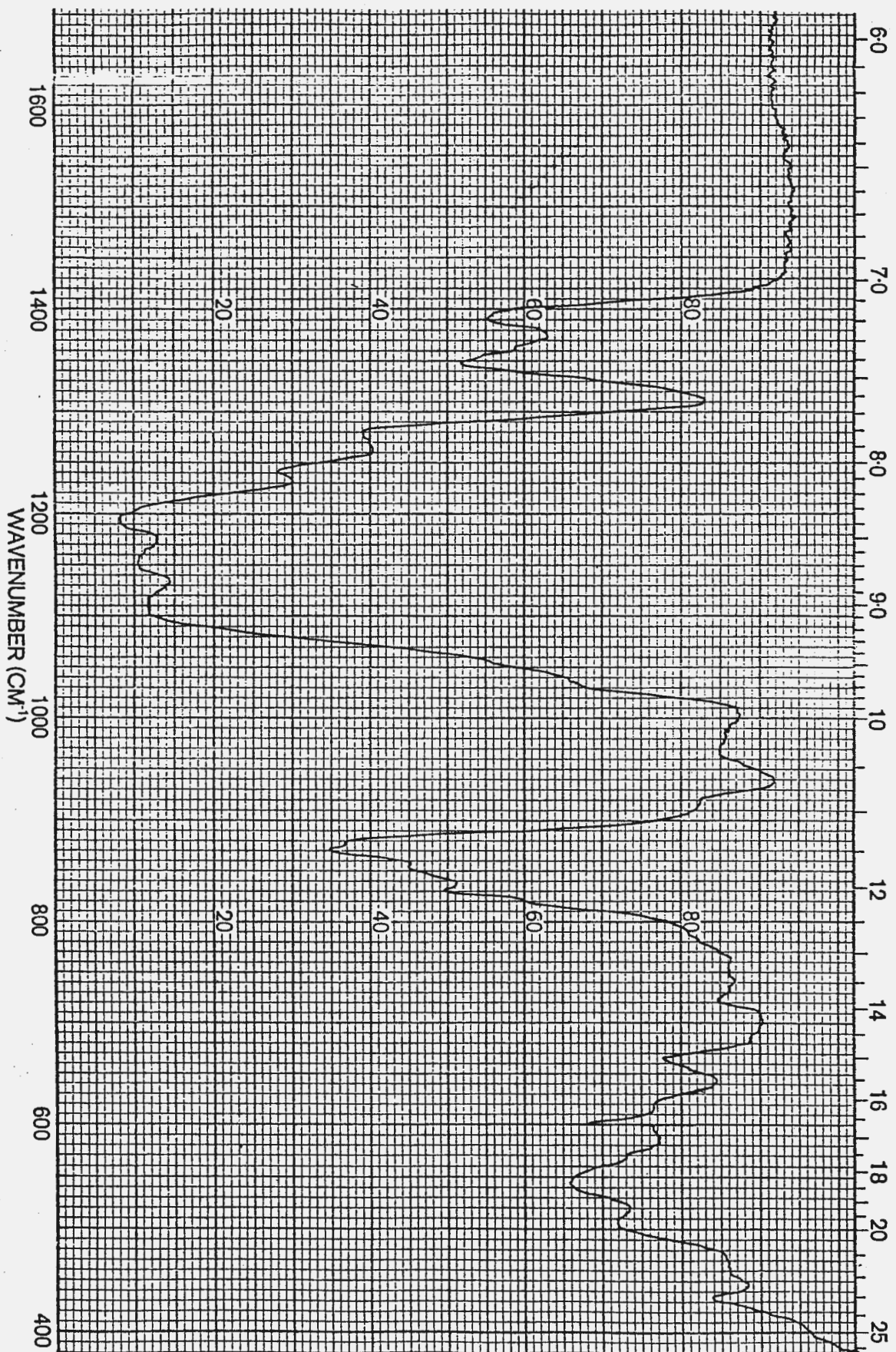


Figure 10. Infrared Spectrum for $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$

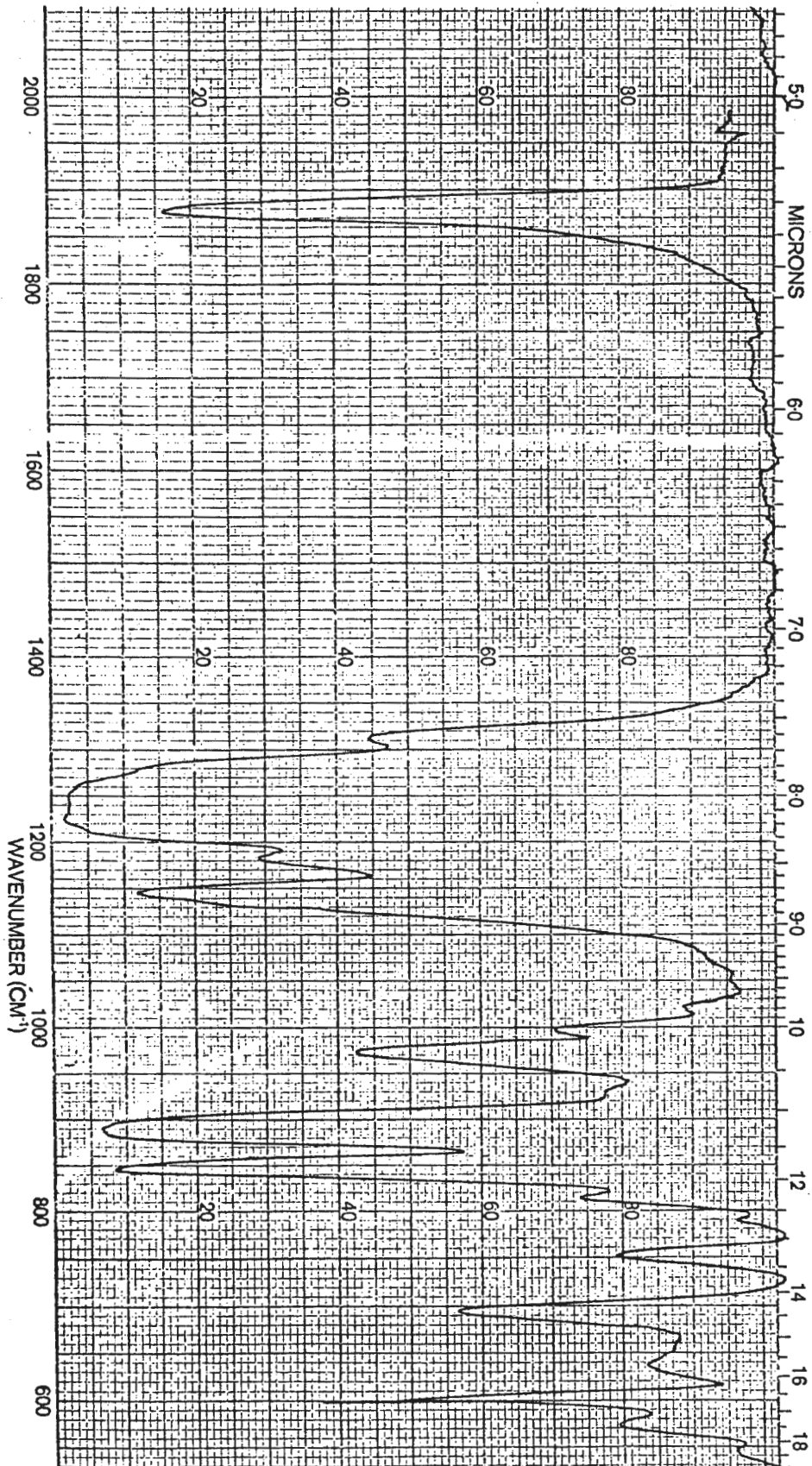
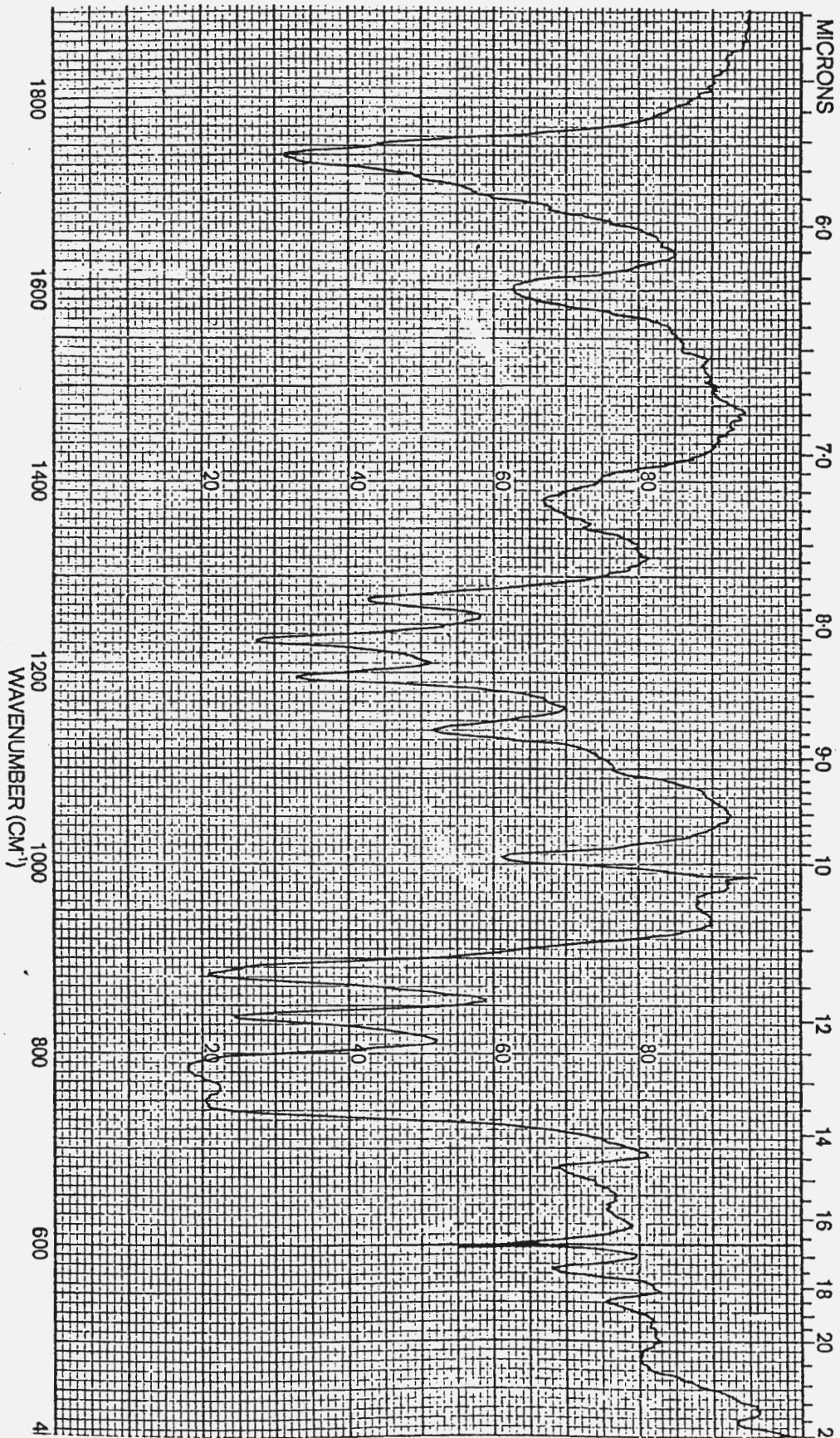


Figure 11. Infrared Spectrum for SF₅CF(CF₃)(CONH₂)



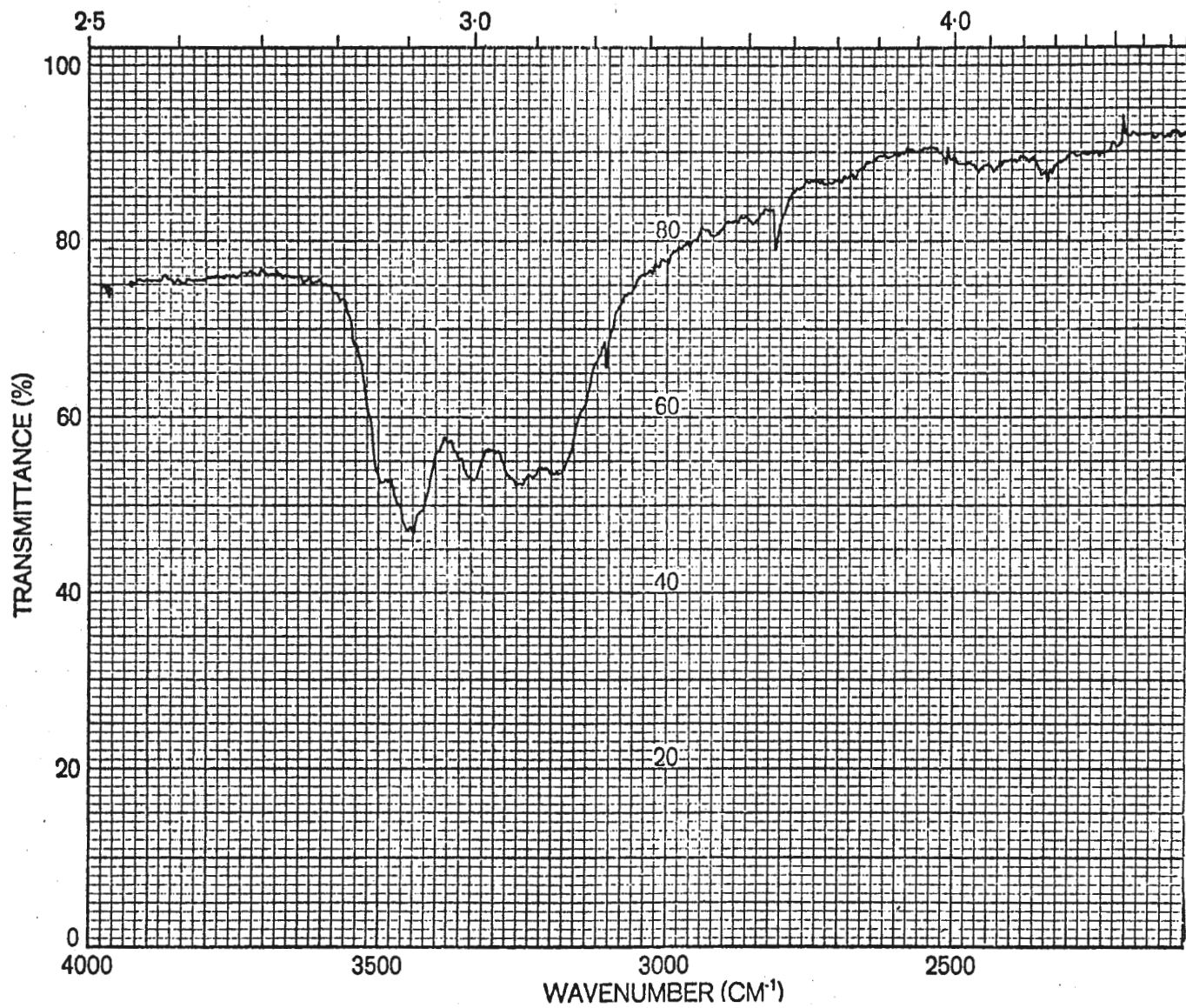
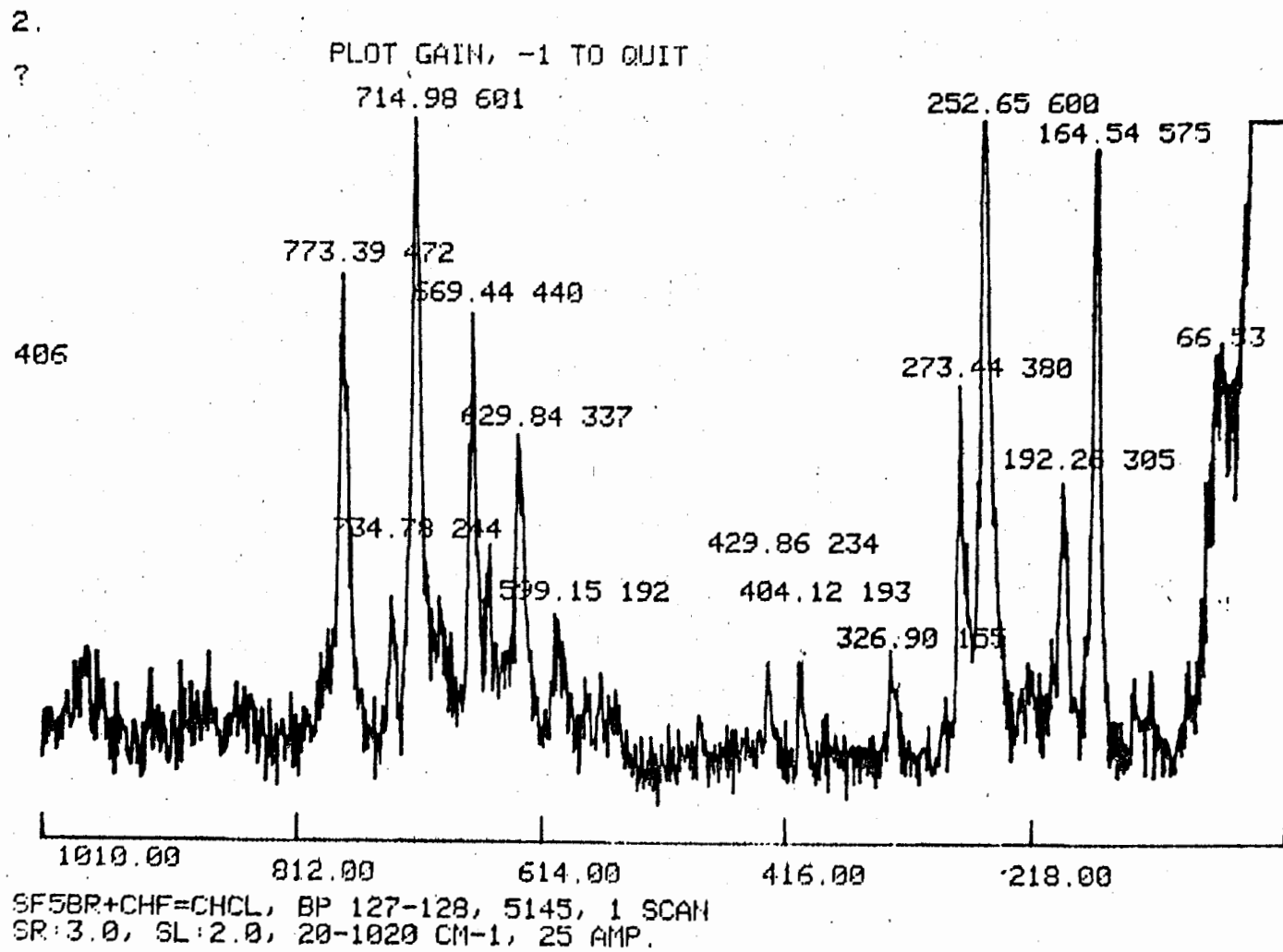


Figure 11. (Cont.)

Figure 12. Raman Spectrum for SF₅CHFCHClBr



PLOT GAIN, -1 TO QUIT

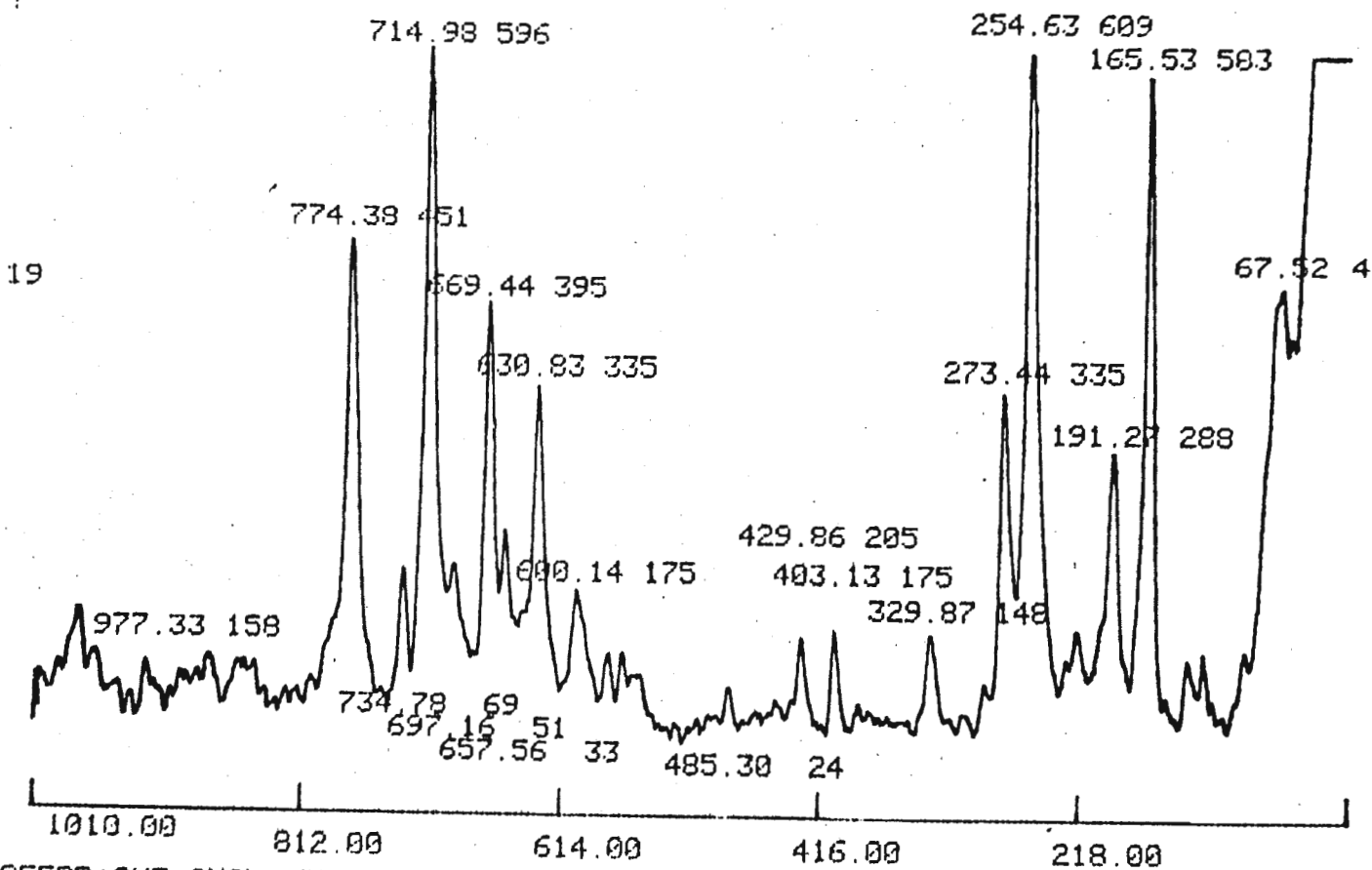


Figure 12. (Cont.)

SF5BR+CHF=CHCL, BP 127-128, 5145, 1 SCAN
SR:3.0, SL:2.0, 20-1020 CM-1, 25 AMP.

72.

PLOT GAIN, -1 TO QUIT

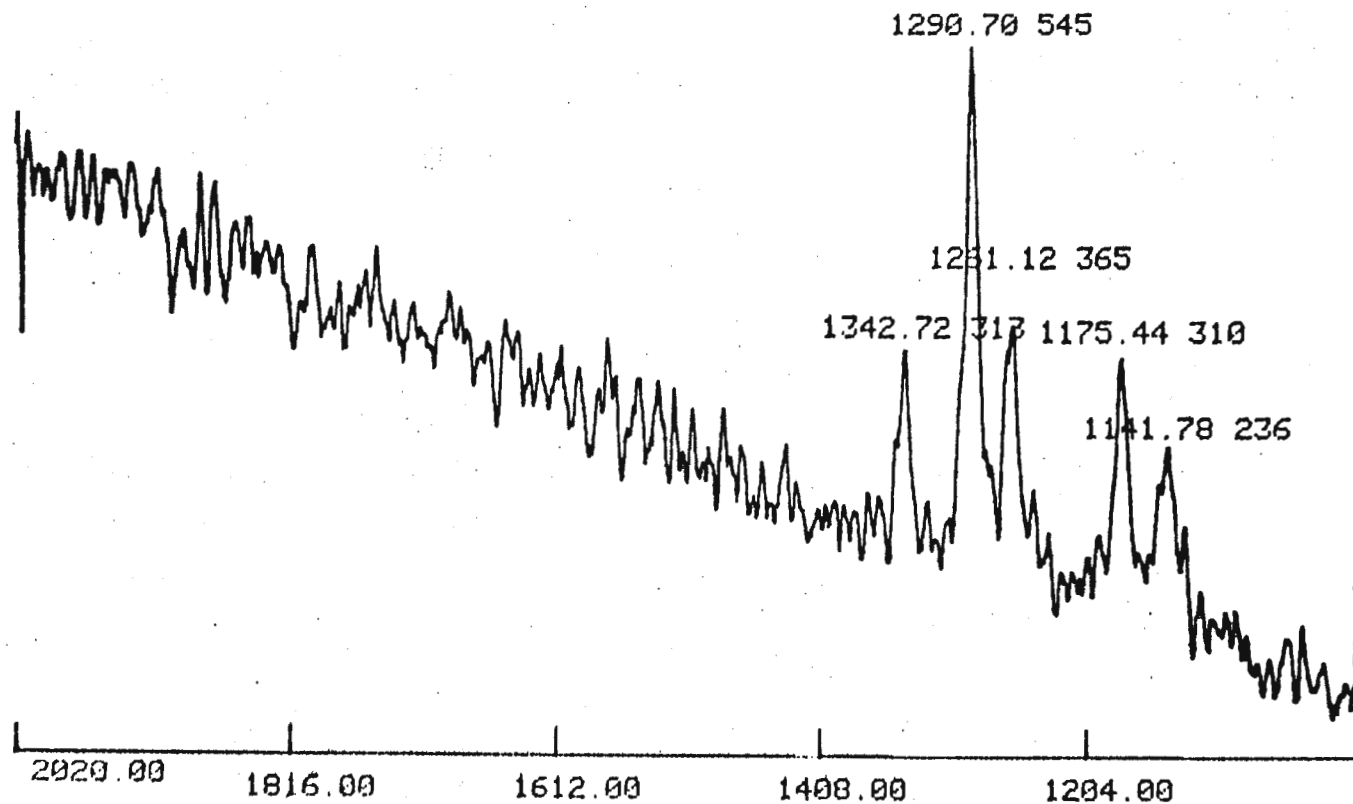


Figure 12. (Cont.)

SF5BR+CHF=CHCL, BP 127-128, 5145, 4 SCANS
SR:3.0, SL:2.0, 1000-2000 CM-1, 25 AMP.

?2.

PLOT GAIN, -1 TO QUIT

3011.78 576

2978.12 539

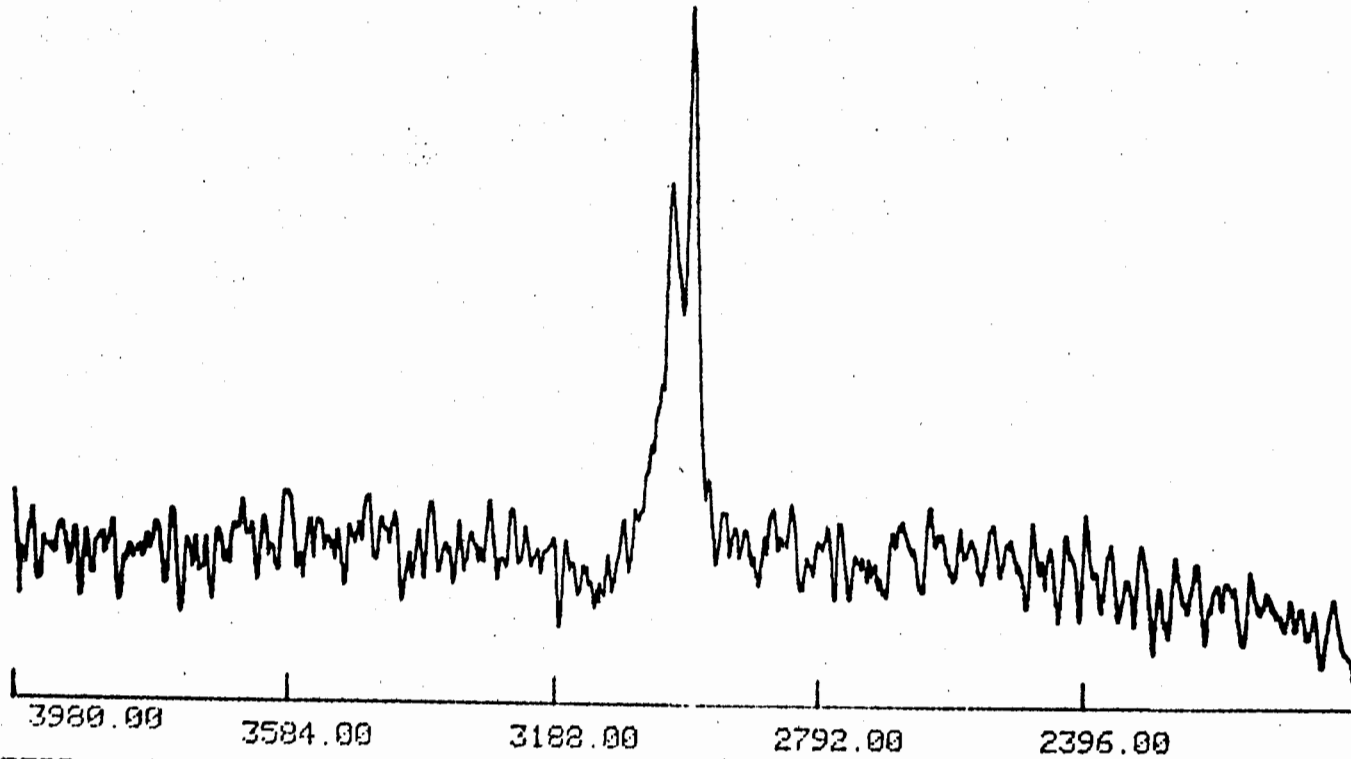
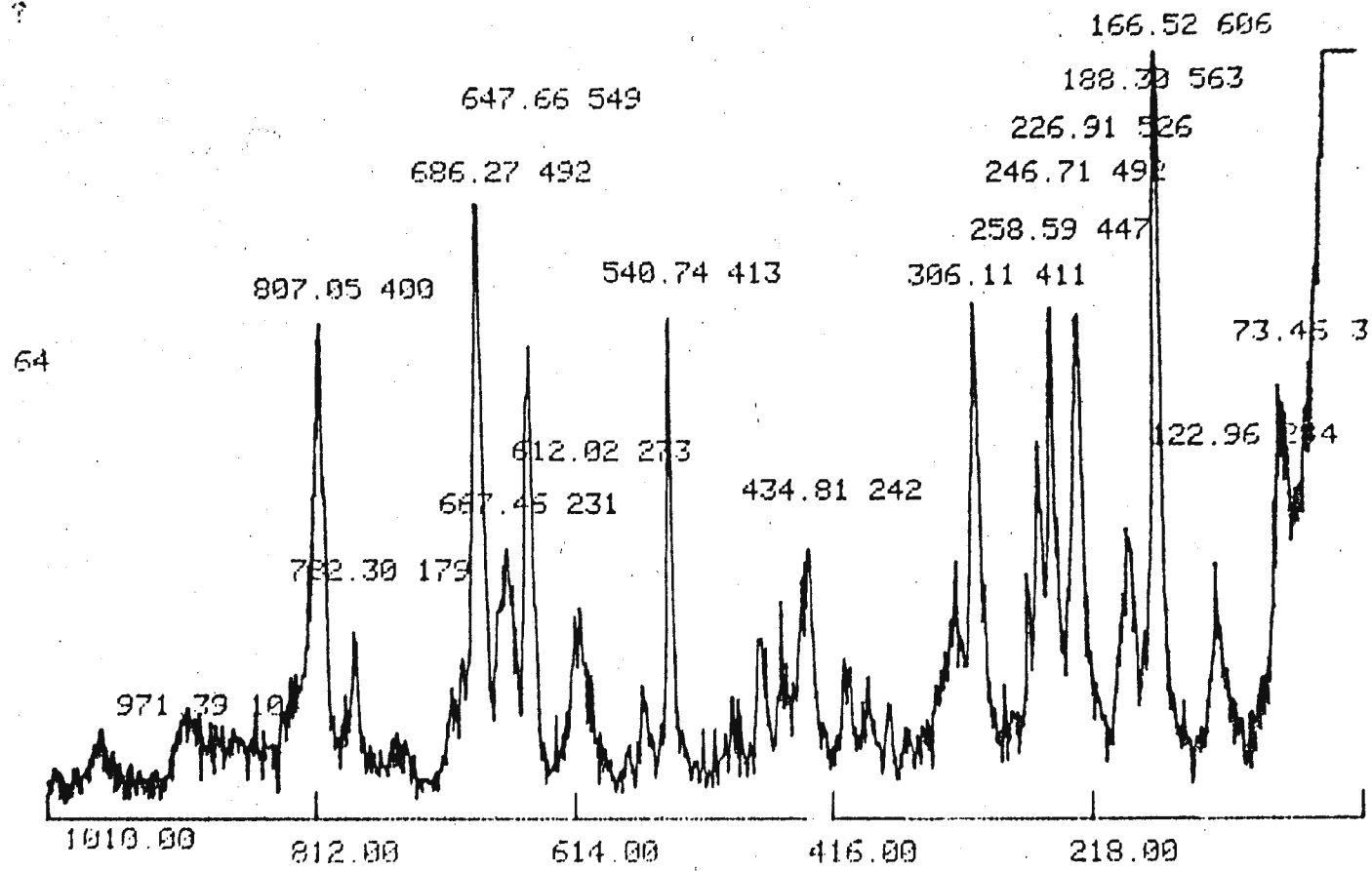


Figure 12. (Cont.)

SF5BR+CHF=CHCL, BP 127-128, 5145, 1 SCAN
SR:3.0, SL:2.0, 2000-4000 CM-1, 25 AMP.

1.5

PLOT GAIN: -1 TO QUIT



SF5BR+CFCL=CFH, BP 110.5, 5145, 1 SCAN
SR:3.0, SL:2.0, 20-1020 CM-1, 25 AMP.

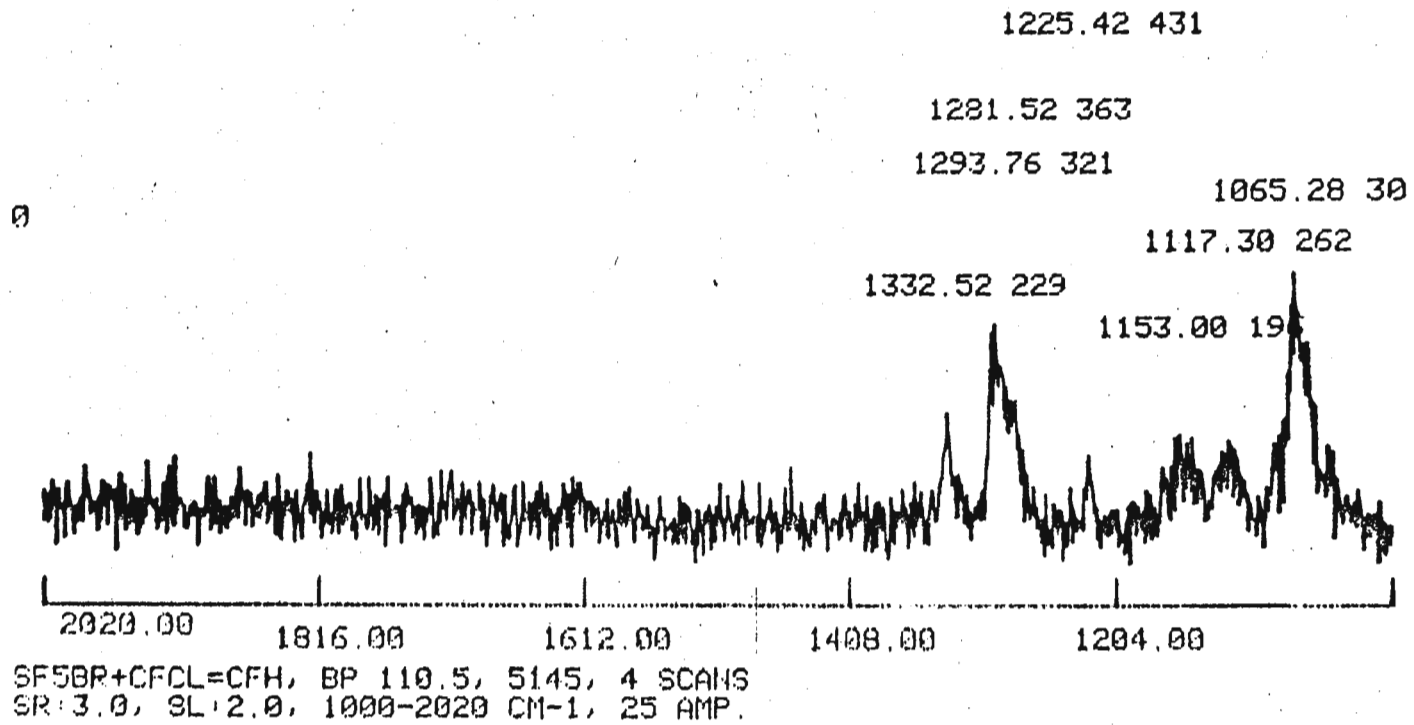
Figure 13. Raman Spectrum for SF₅CHFCFClBr

1.5

PLOT GAIN, -1 TO QUIT

?

Figure 13. (Cont.)

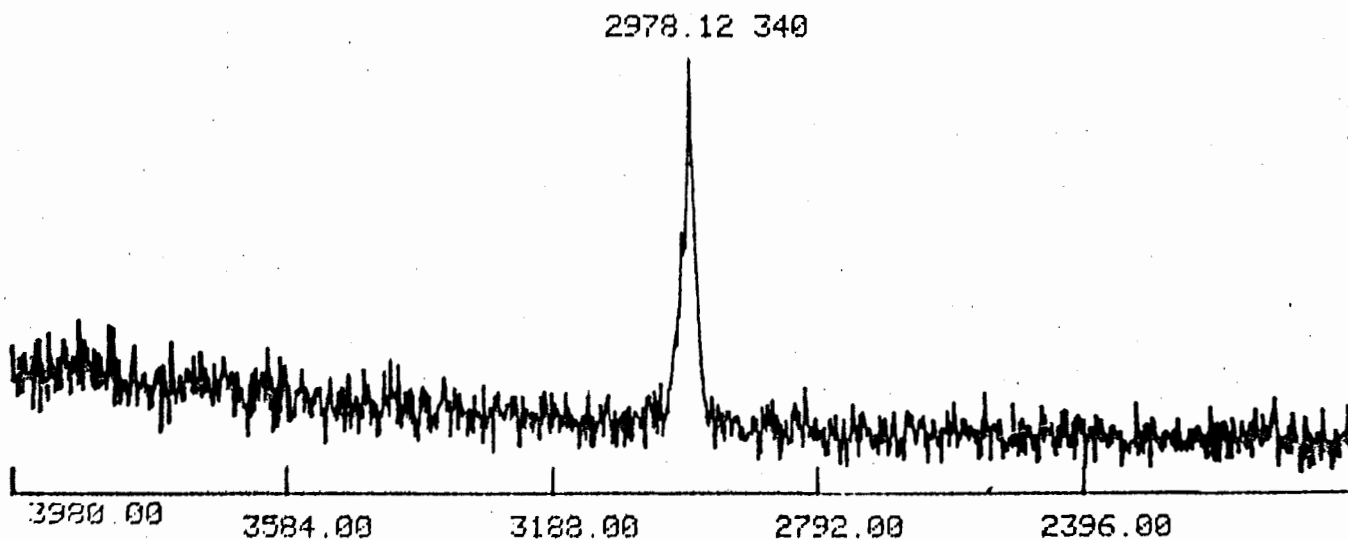


1.5

PLOT GAIN, -1 TO QUIT

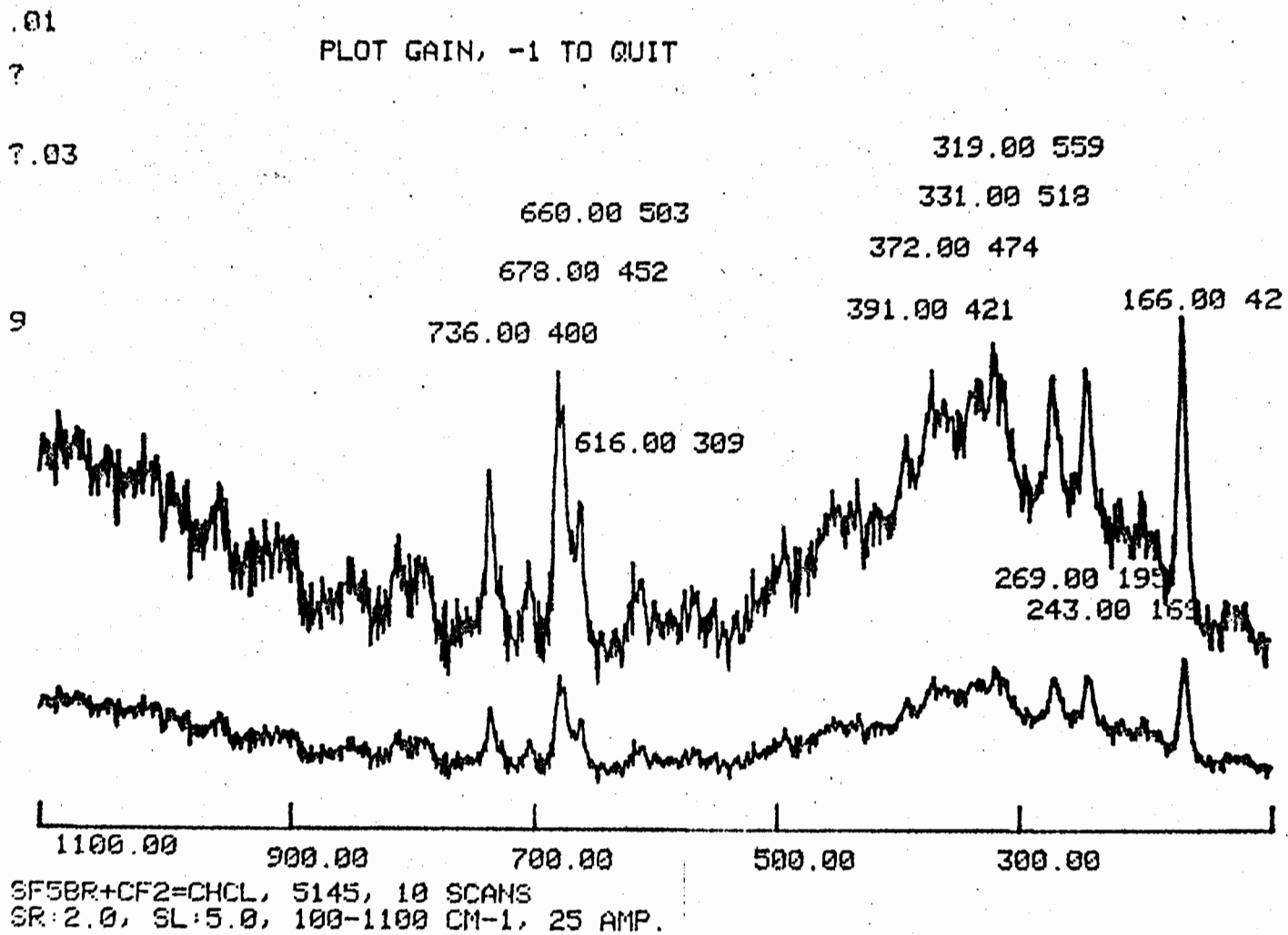
?

Figure 13. (Cont.)



SF5BR+CFCL=CHF, BP 110.5, 5145, 1 SCAN
SR:3.0, SL:2.0, 2000-4000 CM-1, 25 AMP.

Figure 14. Raman Spectrum for SF₅CF₂CHClBr



7.05

PLOT GAIN, -1 TO QUIT

662.00 592

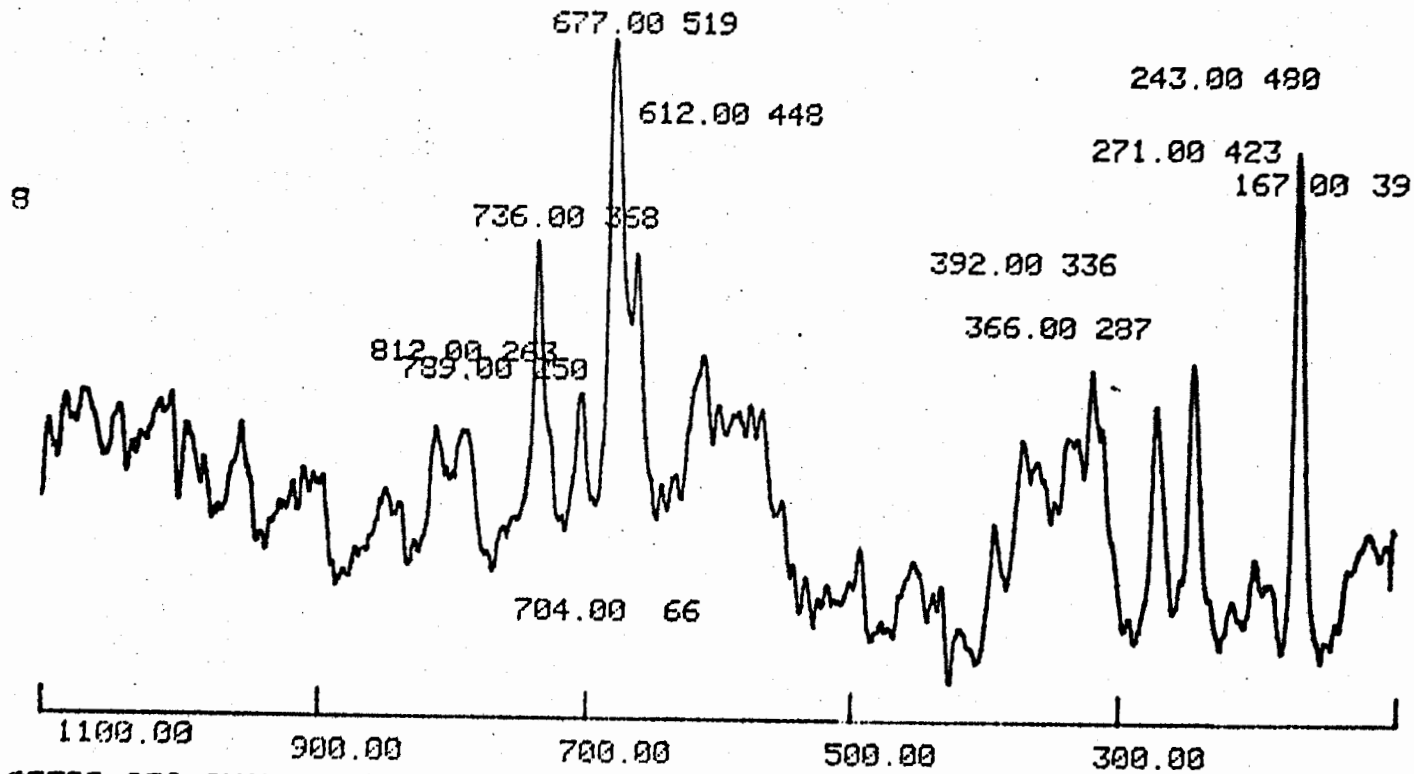


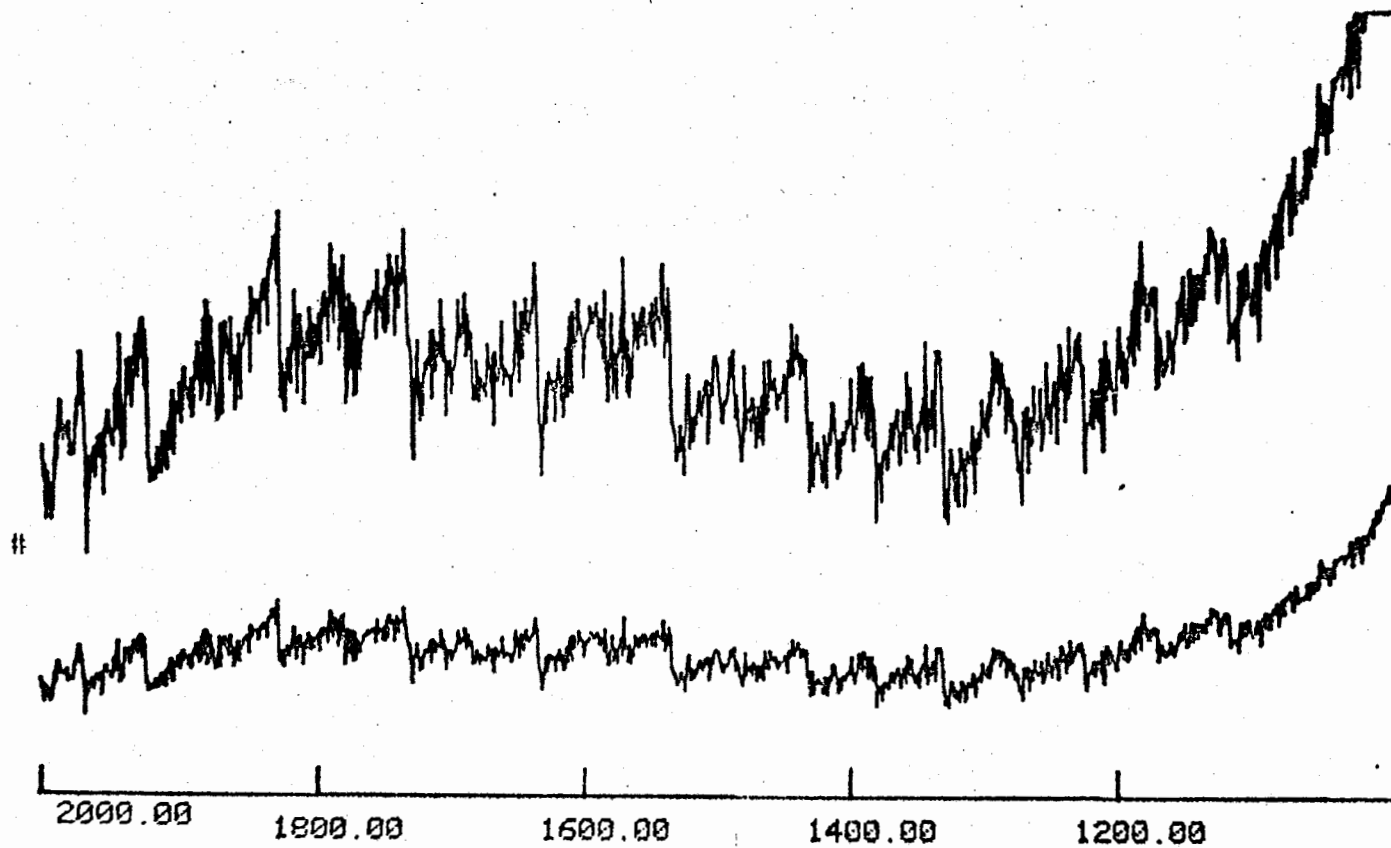
Figure 14. (Cont.)

SF5BR+CF2=CHCL, 5145, 10 SCANS
SR:2.0, SL:5.0, 100-1100 CM-1, 25 AMP.

.01

7.03

PLOT GAIN, -1 TO QUIT



SF5BR+CF2=CHCL, BP 111.5-112, 5145, 10 SCANS
SR:2.0, SL:5.0, 1000-2000 CM-1, 230+ AMP.

Figure 14. (Cont.)

1.
?

PLOT GAIN, -1 TO QUIT

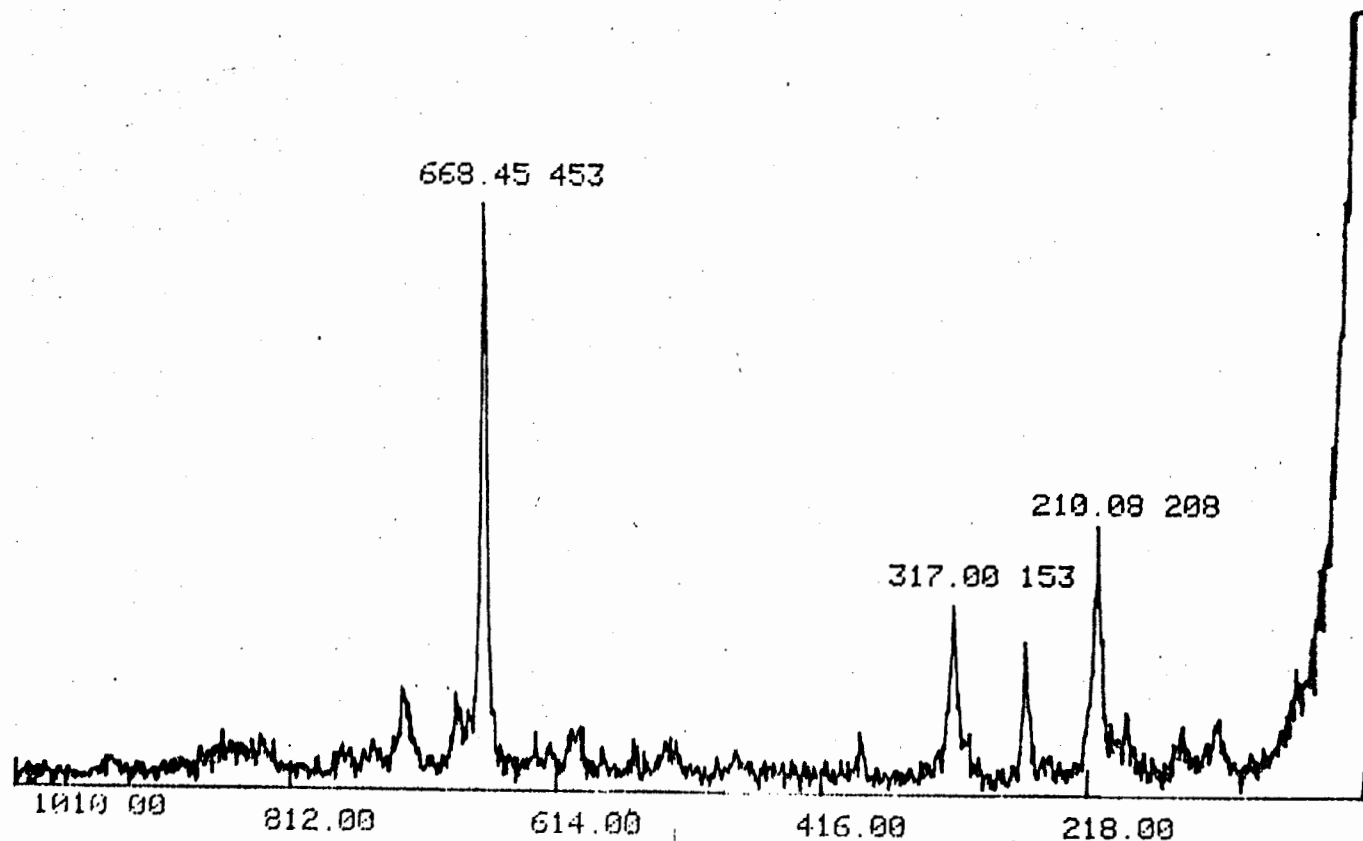
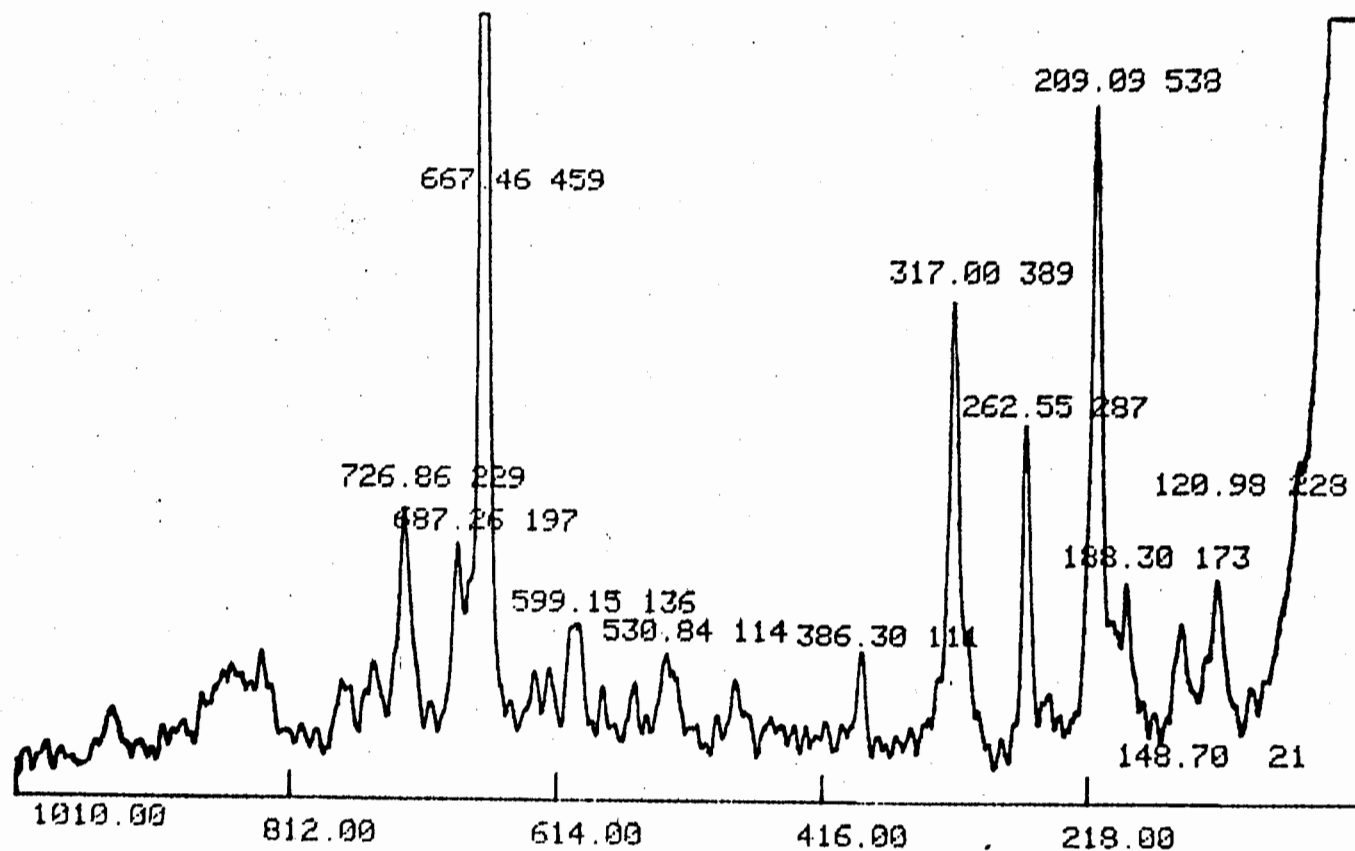


Figure 15. Raman Spectrum for SF₅CH₂CH(CF₃)Br

SF5BR+CF3CH=CH2, BP 102.5, 5145, 1 SCAN
SR:3.0, SL:2.0, 20-1020 CM-1, 25 AMP

3.
?

PLOT GAIN, -1 TO QUIT



SF5BR+CF3CH=CH2, BP 102.5, 5145, 1 SCAN
SR:3.0, SL:2.0, 20-1020 CM-1, 25 AMP.

Figure 15 (Cont.)

73.

PLOT GAIN, -1 TO QUIT

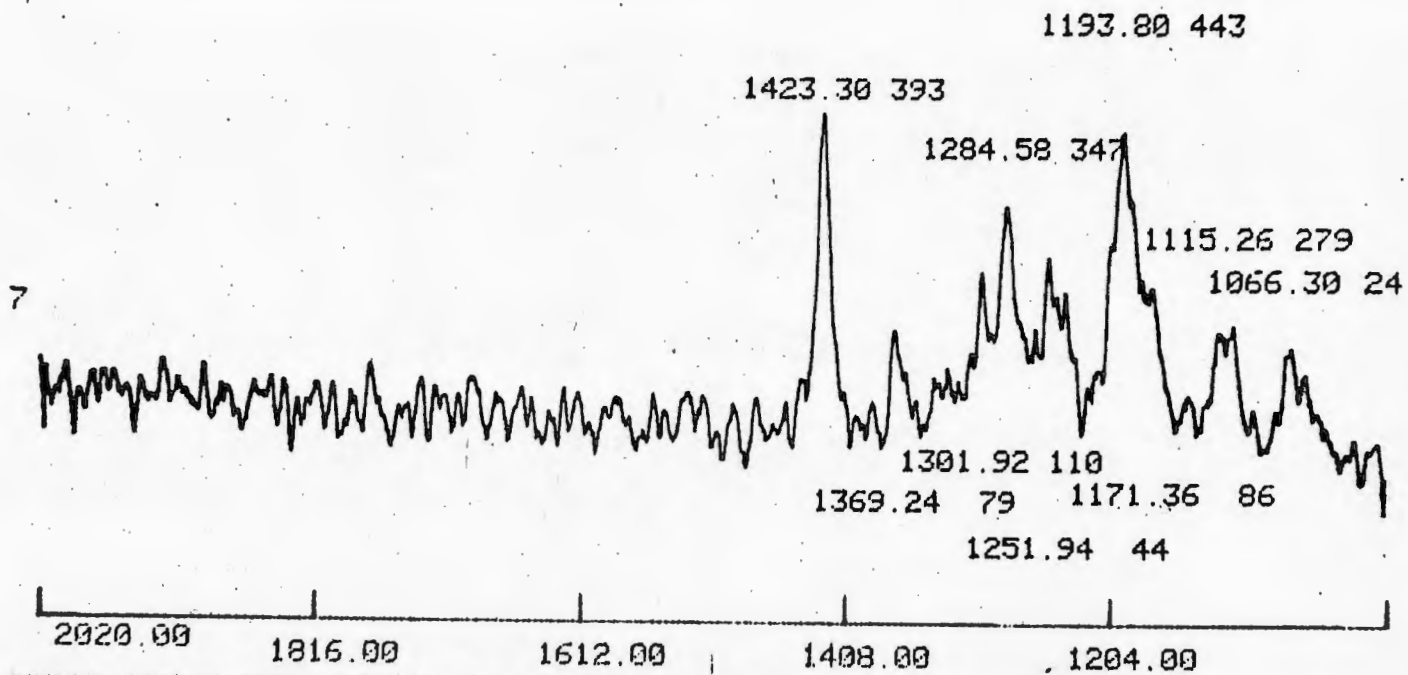


Figure 15. (Cont.)

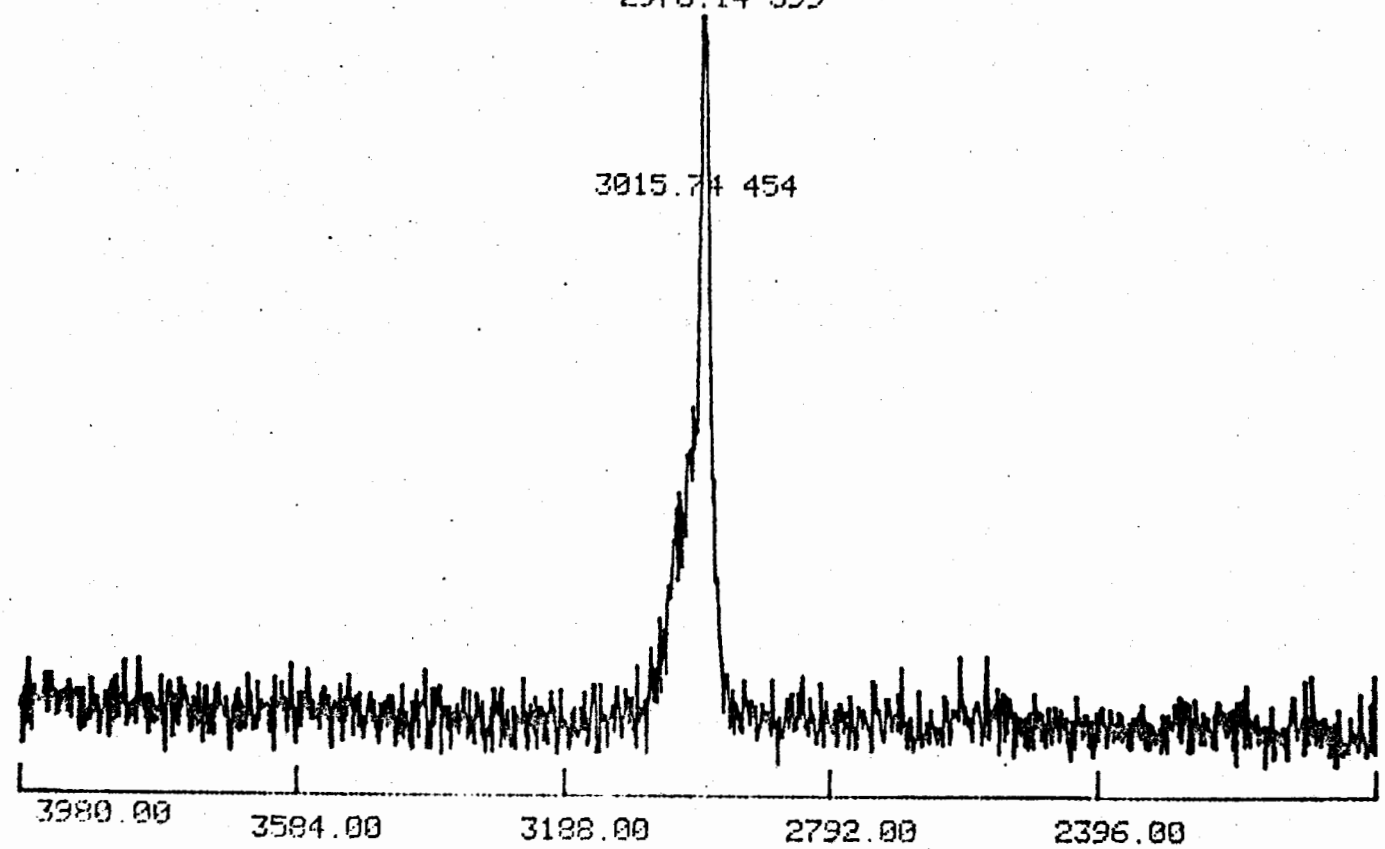
SF5BR+CF3CH=CH2, BP 102.5, 5145, 4 SCANS
SR: 3.0, SL: 2.0, 1000-2000 CM-1; 25 AMP.

2.
?

PLOT GAIN, -1 TO QUIT

2976.14 599

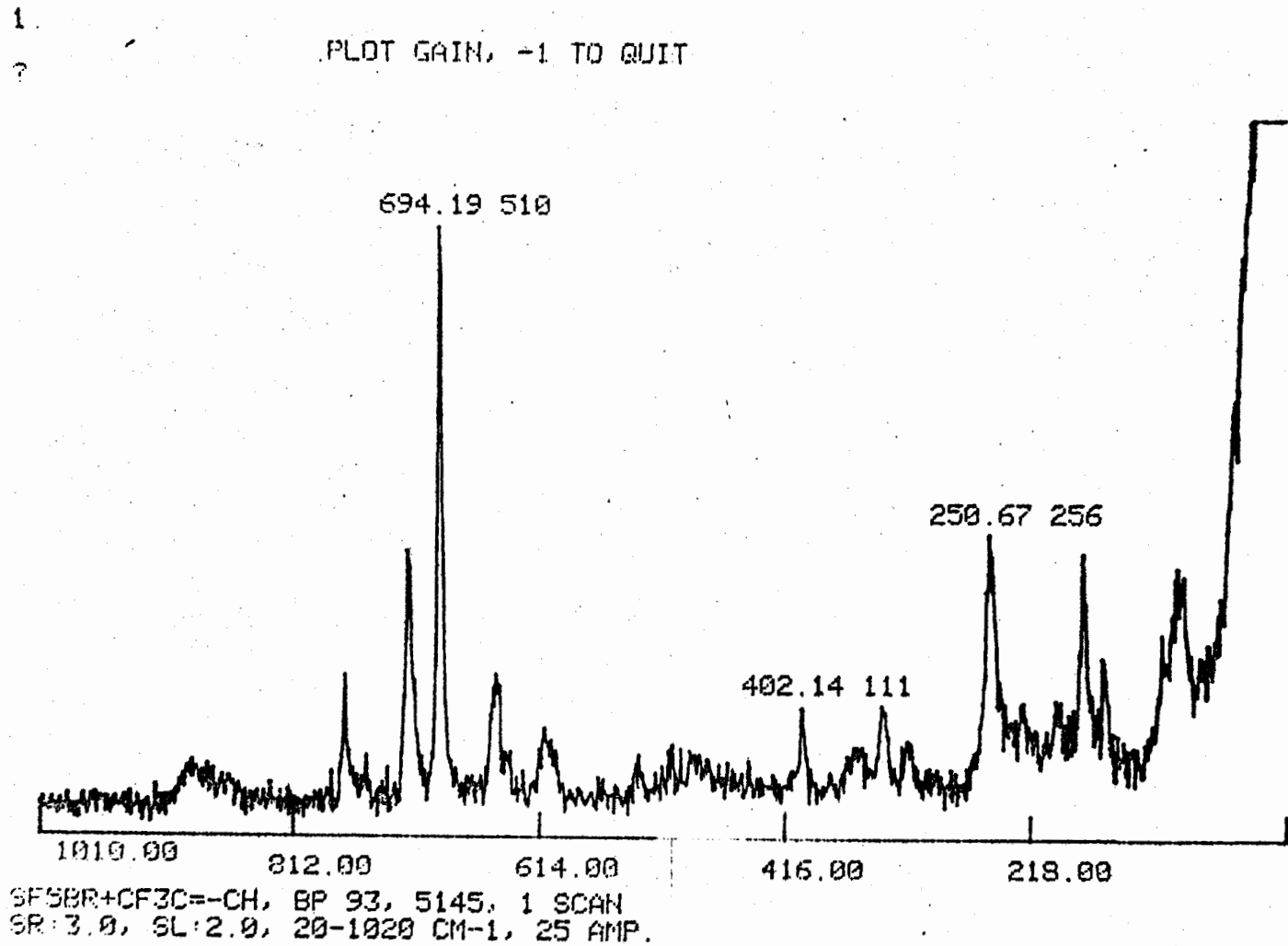
3015.74 454



SF5BR+CF3CH=CH2, BP 102.5, 1 SCAN, 5145
SR:3.0, SL:2.0, 2000-4000 CM-1

Figure 15. (Cont.)

Figure 16. Raman Spectrum for SF₅CH=C(CF₃)Br



2.

?

PLOT GAIN, -1 TO QUIT

694.19 602

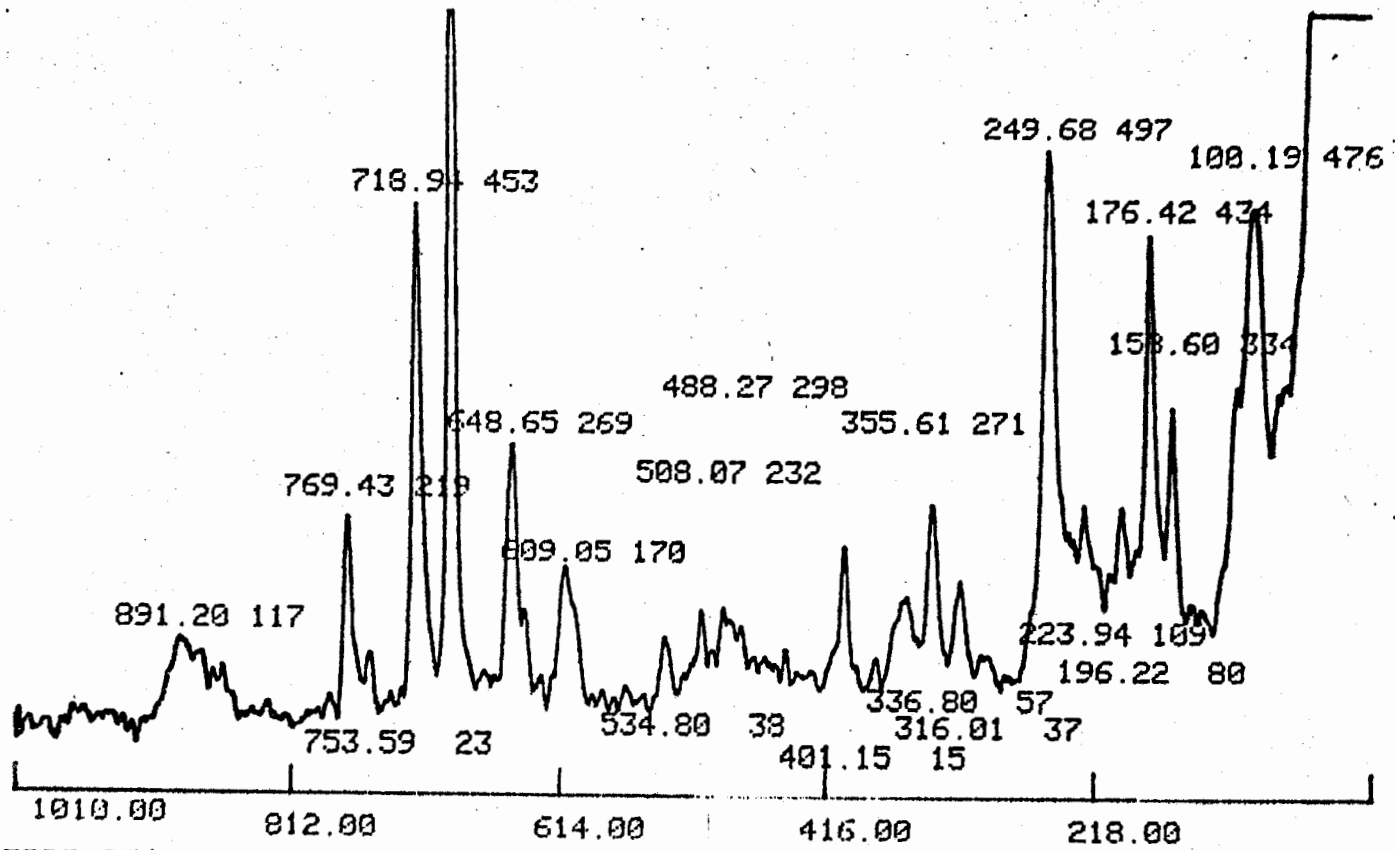


Figure 16. (Cont.)

SF5BR+CF3C=CH, BP 93, 5145, 1 SCAN
SR:3.0, SL:2.0, 20-1020 CM-1, 25 AMP.

72.

PLOT GAIN, -1. TO QUIT

1070.38 63

1153.00 590

1174.42 553

1198.90 512

1227.46 471

1266.22 366

1289.68 322

1338.64 252

1636.48 555

1687.48 405

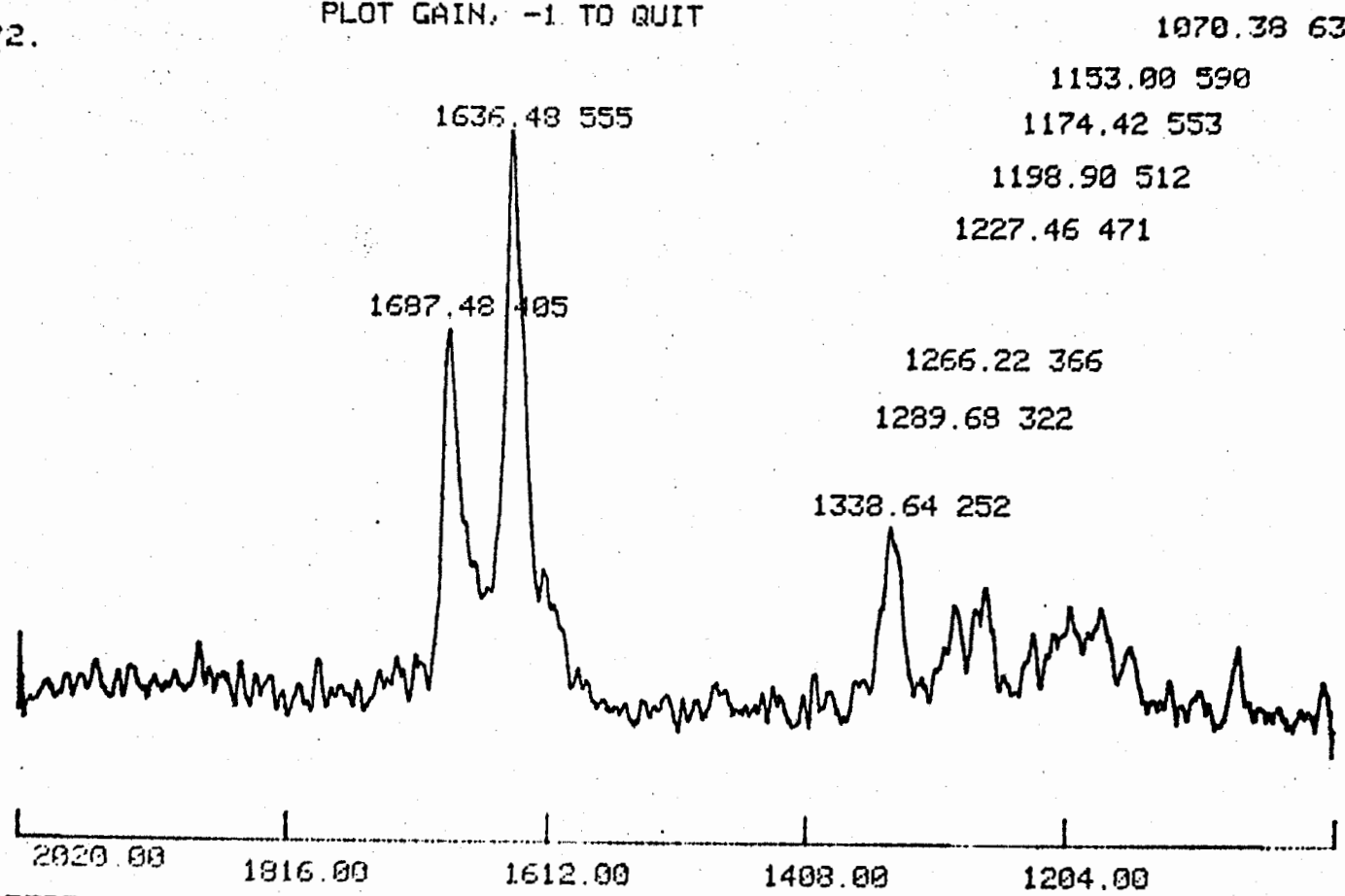


Figure 16. (Cont.)

SF5BR+CF3C=-CH, BP 93, 5145, 4 SCANS
SR:3.0, SL:2.0, 1000-2020 CM-1, 25 AMP.

72.

PLOT GAIN, -1 TO QUIT

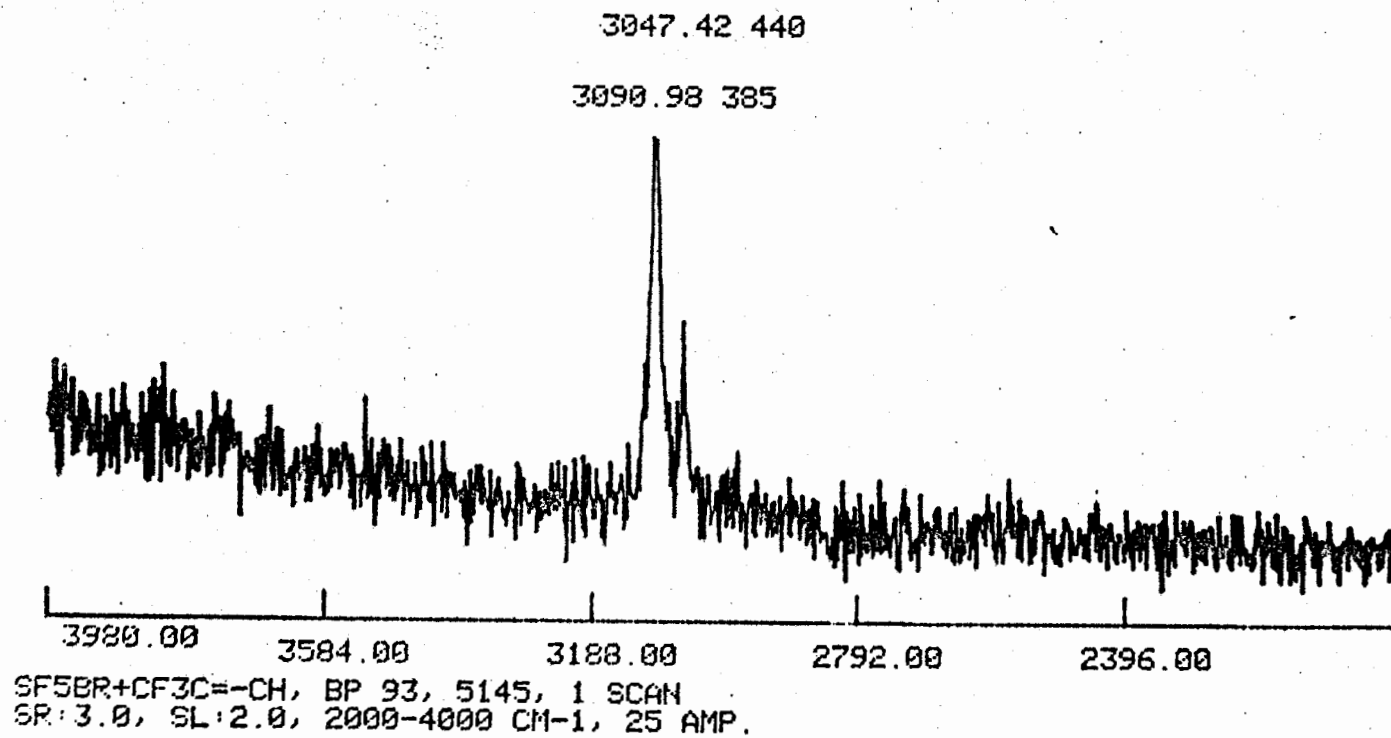
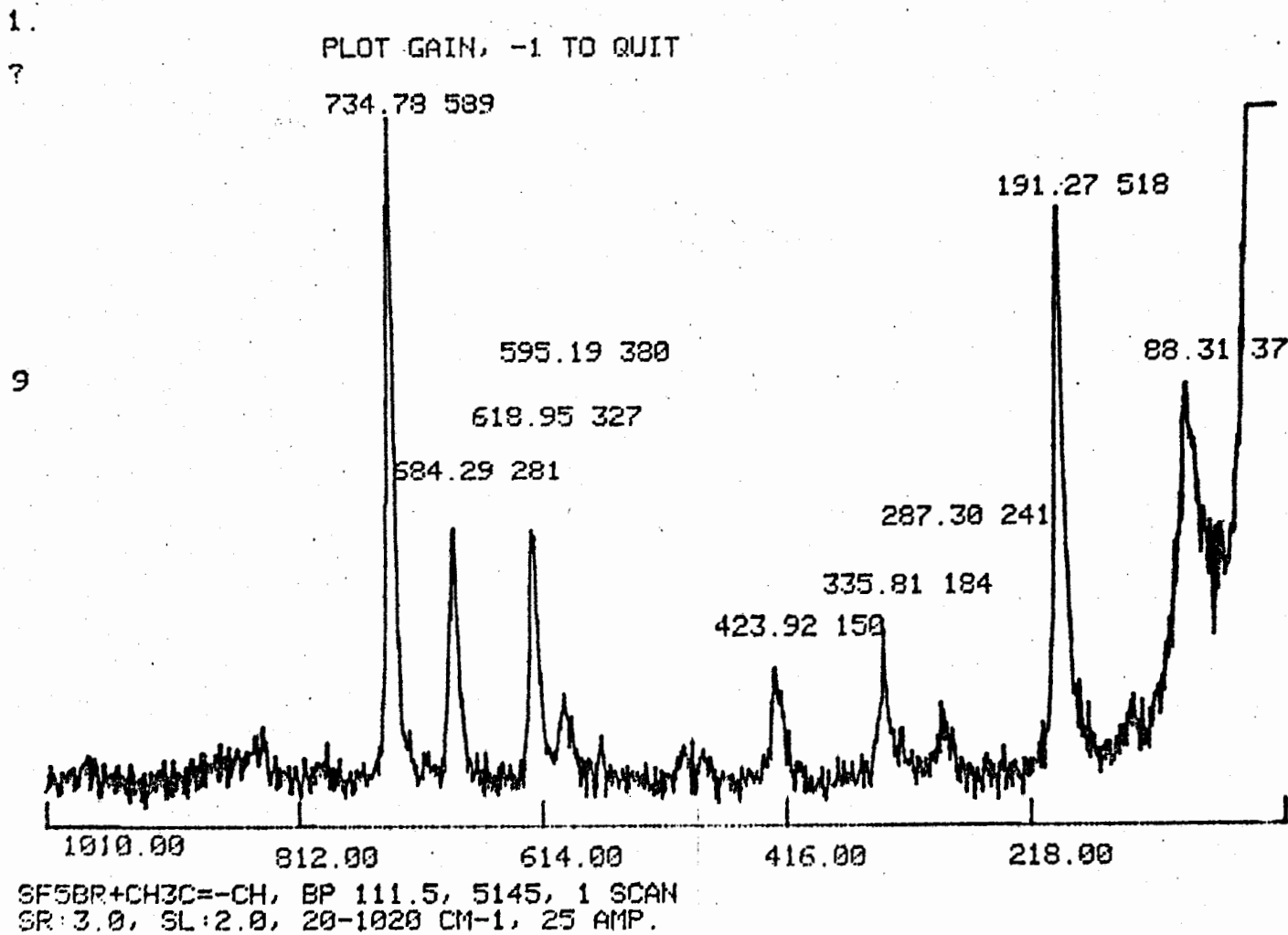


Figure 16. (Cont.)

Figure 17. Raman Spectrum for SF₅CH=C(CH₃)Br



1.
?

PLOT GAIN, -1 TO QUIT

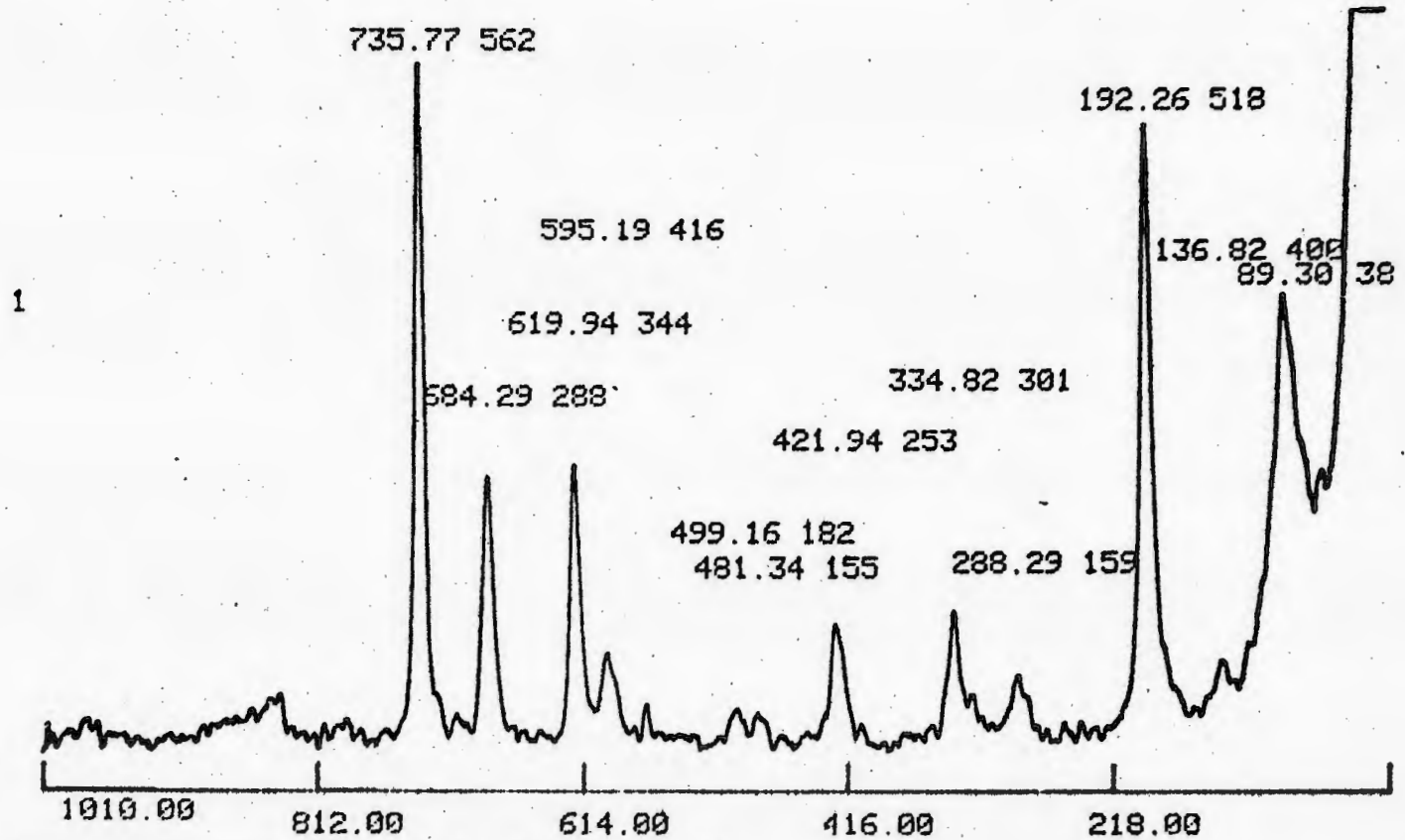


Figure 17. (Cont.)

SF5BR+CH3C=-CH, BP 111.5, 5145, 1 SCAN
SR:3.0, SL:2.0, 20-1020 CM-1, 25 AMP.

PLOT GAIN, -1 TO QUIT

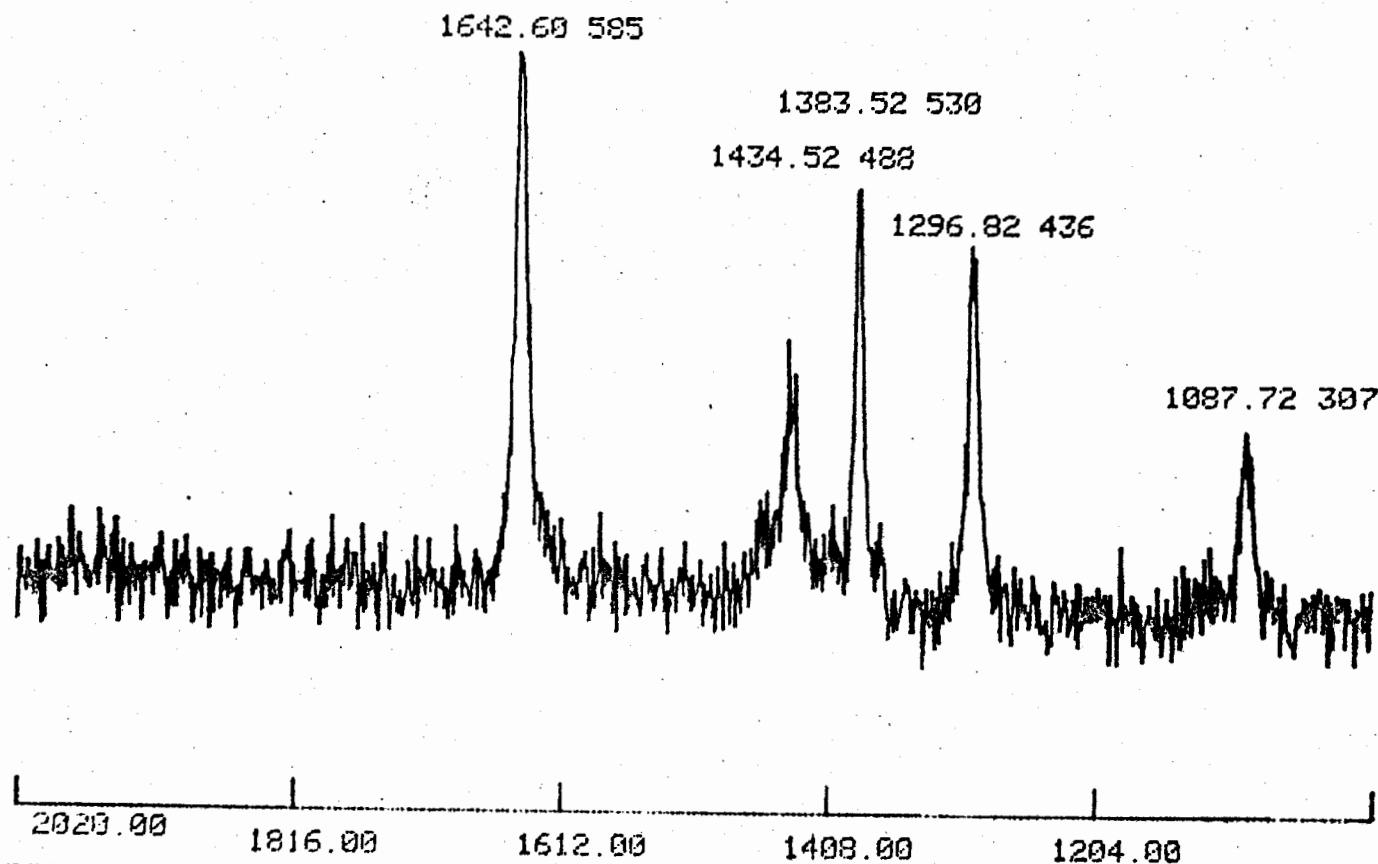


Figure 17. (Cont.)

SF5BR+CH3C=-CH, BP 111.5, 5145, 4 SCANS
SR:3.0, SL:2.0, 1000-2020 CM-1, 25 AMP.

1.
?

PLOT GAIN, -1 TO QUIT

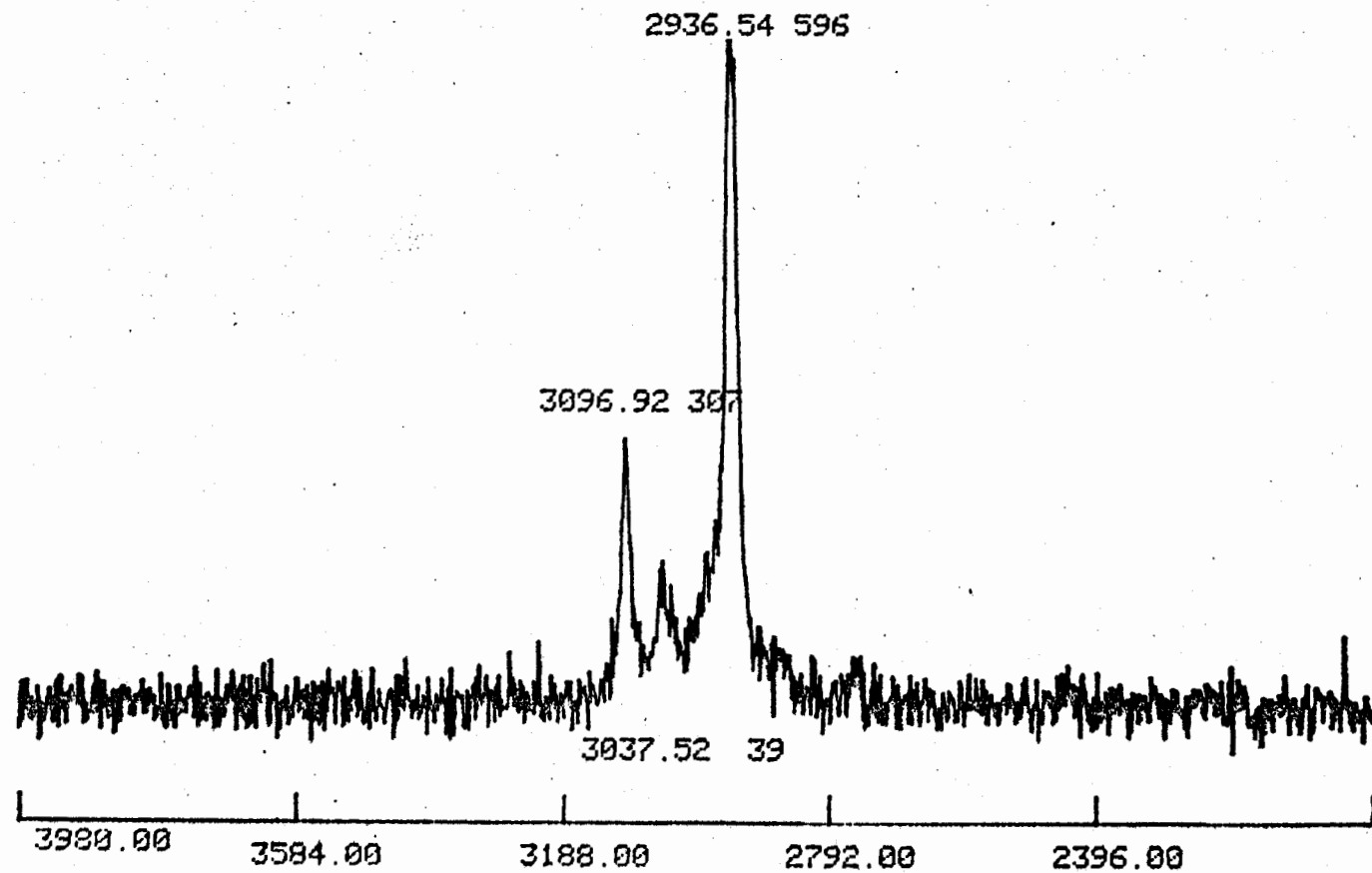


Figure 17. (Cont.)

SF5BR+CH3C=-CH, BP 111.5, 5145, 1 SCAN
SR:3.0, SL:2.0, 2000-4000 CM-1, 25 AMP.

CHAPTER VI

CONCLUSIONS

It is known that carbon compounds containing a SF_5 group have interesting and useful properties. The compounds SF_6 , SF_5CF_3 , $SF_5CF=CF_2$ and SF_5 -oxetanes have high dielectric strength and one of them, SF_6 , is used today in high voltage transformers. In general, these compounds have good to outstanding dielectric properties, which they retain to high frequencies and are useful as dielectric coolants in electronic equipment. Other compounds such as S_2F_{10} , $SF_5CF=CF_2$ and $SF_5N=CF_2$ are biologically active. Disulfur decafluoride (S_2F_{10}) is toxic to rats while $SF_5CF=CF_2$ and $SF_5N=CF_2$ are effective fumigants. Sulfur hexafluoride (SF_6) SF_5R_f , $SF_5C_6H_5X$ ($X = NH_2, NO_2$), and SF_5 -oxetanes have unusual chemical and thermal stability. The stability of these SF_5 compounds makes them useful as stable liquid materials, e.g. fluids for high temperature power transmissions, hydraulic systems, or liquid-coupled mechanical drives. Some of the SF_5 compounds, particularly the arylsulfur pentafluorides, are useful as solvents for highly fluorinated polymers (solutions of Teflon and Kel-F are useful in making cellulosic compositions waterproof). It is thought that compounds containing a SF_5 group should have interesting surface active and anesthetic properties, however, these predictions have not been verified. Therefore, because of the properties, uses, and potential uses of these compounds, a need exists to prepare new SF_5 compounds which will provide the basis for further studies.

One proven effective way of preparing new SF_5 compounds is by the addition of SF_5Br to fluoroolefins. The work presented in this thesis was carried out in order to prepare new SF_5 compounds and to study the factors that favored this reaction. Hopefully, a relationship can be found between the types of groups present in fluoroolefins and the direction of addition of the SF_5 group. The new compounds produced in this thesis were $SF_5CFHCFClBr$, $SF_5CH_2CH(CF_3)Br$, and $SF_5CFHCHClBr$. The SF_5Br and $CFCl=CHCl$ reaction produced a very small amount of product while with $CF_2=CFCOF$ no products were obtained.

Table XIV at the end of Chapter III contains all the olefin systems in which attempts have been made to add SF_5Br under thermal conditions. Group A of Table XIV shows that the SF_5 group adds to the CH_2 portion of the olefin and that the other carbon of the double bond, having large bulky groups, does not prevent this addition. Group B of Table XIV contains addition to the CFH group and shows that no addition will occur when the other carbon contains a SF_5 group. Group C of Table XIV, contains addition to the CF_2 groups and shows that SF_5 addition does not occur when bulky groups are attached to the second carbon. Finally, group D of Table XIV shows that SF_5 addition to olefins containing only $CHCl + CFCl$ groups and $CHBr + CHSF_5$ groups does not occur to any appreciable extent.

The conclusion drawn from the data in Table XIV is that steric repulsion is an important factor that determines SF_5Br addition. More compounds of the type illustrated in part D need to be studied in order to confirm this observation. This opens up an area of further research in the study of SF_5 compounds.

During the reaction of SF_5Br and trifluoroethylene, an interesting side reaction occurred. A polymer of trifluoroethylene containing sulfur and bromine was prepared. The properties of this polymer have not as yet been fully investigated. A method of preparing polymers in which SF_5 groups are present is needed. It is possible that further studies of this system will suggest just such a method. It is anticipated that polymers containing SF_5 groups will have unusual properties (good solid state dielectric properties).

A characterization of the new adducts was accomplished by the analysis of infrared spectra, mass spectra, nuclear magnetic resonance spectra and an initial attempt was made to interpret the Raman spectra of SF_5Br adducts. The Raman spectra of two SF_5Br triple bond adducts, $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$, $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$, and four SF_5Br -fluoroolefin adducts, $\text{SF}_5\text{CHFCHClBr}$, $\text{SF}_5\text{CH}_2\text{CH}(\text{CF}_3)\text{Br}$, $\text{SF}_5\text{CHFClBr}$ and $\text{SF}_5\text{CF}_2\text{CFHBr}$ were taken. For the compound, $\text{SF}_5\text{CF}_2\text{CFHBr}$, decomposition occurred and a complete Raman spectrum was not obtained. An initial attempt was made to identify definite groups. The C-H peaks and C=C peaks were readily identified. However, the C-F, C-Cl, C-Br and SF_5 peaks were not so easily identified (See Chapter V).

Much more work needs to be done on the Raman spectra of these compounds. This could be accomplished by synthesizing model compounds (such as $\text{SF}_5\text{CHFCH}_2\text{Br}$ and $\text{SF}_5\text{CH}_2\text{CH}_2\text{Br}$) in order to study specific peaks. Also, Raman spectra could be taken of SF_5Br adducts already known and internal comparisons could be made.

Another method of preparing SF_5 compounds involves the addition of functional groups to $\text{SF}_5\text{CF}=\text{CF}_2$. Carbonyl fluoride (COF_2) was added

to $\text{SF}_5\text{CF}=\text{CF}_2$ to form $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$. This new compound was not easily separated from COF_2 and so it was allowed to react with NH_3 to form the more easily separable amide $[\text{SF}_5\text{CF}(\text{CF}_3)\text{CONH}_2]$. The two new compounds were identified by infrared and elemental analysis.

Much more work needs to be done in this area. The $-\text{COF}$ derivative has a boiling point near room temperature and an improved method for synthesis needs to be developed. The quantity of the product was small and work needs to be done to improve yields as well as separation. Other organic reactions could be attempted with the COF derivative, such as formation of the acid. In addition, COF_2 reactions with other SF_5 -olefins might also be tried.

It is believed that either $\text{SF}_5\text{CF}(\text{CF}_3)\text{COF}$ or $\text{SF}_5\text{CF}(\text{CF}_3)\text{CONH}_2$ can be used to prepare novel SF_5 compounds that will be effective dielectrics and surface-active agents. It is conceivable that polymer systems containing the $\text{SF}_5\text{CF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{C}$ - group can also be made. These compounds have opened the door to a new exciting area of chemistry.

BIBLIOGRAPHY

1. C. Merrill, Ph.D. Thesis, University of Washington, Seattle, Wash. (1962).
2. B. Cohen and A. G. MacDiarmid, Inorg. Chem., 4, 1782 (1965).
3. K. O. Christe, E. C. Curtis and C. J. Schack, Spectrochim. Acta., 33A, 69 (1977).
4. E. W. Neuwar and A. W. Jache, J. Chem. Phys., 39, 596 (1963).
5. R. R. Smardzewski and W. B. Fox, J. Fluorine Chem., 7, 456 (1976).
6. J. Stewart, L. Kegly, H. F. White and G. L. Gard, J. Org. Chem., 34, 760 (1969).
7. Qui-Chee Wendy Wang, M.S. Thesis, Portland State University, Portland, OR. (1976).
8. A. D. Berry and W. B. Fox, J. Fluorine Chem., 6, 175 (1975).
9. A. D. Berry and W. B. Fox, J. Fluorine Chem., 7, 449 (1976).
10. H. L. Roberts, et al., J. Chem. Soc., 2066 (1961).
11. H. L. Roberts, et al., J. Chem. Soc., 2070 (1961).
12. J. C. Walton, et al., Trans. Faraday Soc., 65, 2103 (1969).
13. J. C. Walton, et al., Trans. Faraday Soc., 66, 2039 (1970).
14. G. H. Cady, "Fluorine Containing Compounds of Sulfur," Advances in Inorganic Chemistry and Radiochemistry, Vol. 2 (1960).
15. G. L. Gard, C. Woolf and R. Shaw, British Patent, No. 1,167,228 (1969).
16. C. Woolf and G. L. Gard, United States Patent, No. 3,448,121 (1969).
17. E. E. Gilbert and G. L. Gard, United States Patent No. 3,475,453 (1969).
18. R. D. Dresdner, T. J. Kao and J. A. Young, J. Am. Chem. Soc., 80, 3007 (1958).
19. T. A. Kovacina, A. D. Berry and W. B. Fox, J. Fluorine Chem., 7, 430 (1976).

20. L. H. Cross, G. Cushing and H. L. Roberts, Spectrochim. Acta., 17, 364 (1961).
21. G. L. Gard and C. Woolf, J. Fluorine Chem., 1, 487 (1971/72).
22. A. W. Marcellis and R. E. Eibeck, J. Fluorine Chem., 5, 71 (1975).
23. R. E. Nofhle and W. B. Fox, J. Fluorine Chem., 9, 219 (1977).
24. F. S. Fawcett, C. W. Tullock and D. D. Coffman, J. Am. Chem. Soc., 84, 4275 (1962).
25. J. K. Brown and K. J. Morgan, "Advan. Fluorine Chem.," 4, 253 (1963).
26. E. C. Tuazon, W. G. Fateley and F. F. Bentley, Appl. Spectrosc., 25, 374 (1971).
27. E. L. Pace, A. C. Plaush and H. V. Samuelson, Spectrochim. Acta., 22, 993 (1966).
28. H. A. Carter, C. S.-C Wang and J. M. Shreeve, Spectrochim. Acta., 29A, 1479 (1973).