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Infrared Spectra of Eighteen Halogen-Substituted Methanes

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In order to study how the vibrational frequencies of methane vary with halogen substitutions, the infrared spectra of the following halogen-substituted methanes have been studied with a prism spectrometer between 2 and 38 microns: Carbon tetrafluoride, chlorotrifluoromethane, dichlorodifluoromethane, trichlorofluoromethane, carbon tetrachloride, trichlorobromomethane, dichlorodibromomethane, fluoroform, difluorochloromethane, dichlorofluoromethane, chloroform, dichlorobromomethane, chlorodibromomethane, bromoform, iodoform, methylene fluoride, methylene chloride, and methylene iodide. Spectra are presented as obtained at room temperature in the vapor and liquid states, and in a few cases in solution. The bands are interpreted as fundamentals, overtones, combination, and difference bands. Tables and graphs display the regularities existing among the various fundamentals of these molecules and other halogen-substituted methanes. Force-constant calculations, using an approximate potential function with general constants transferred from one molecule to another are reported.

1. Introduction

The infrared absorption spectra of various halogen derivatives of methane have been studied by several investigators in various regions of the spectrum, and under varying degrees of dispersion [1].[1] The Raman spectra of these compounds have also been extensively studied [2]. The gradual improvement in infrared techniques, in particular the development of prism spectrographs using thallium bromide-iodide (KRS–5) as the dispersing medium, and the increasing practical importance of the fluorine-containing compounds (Freons) have made it seem worth while to carry out a comprehensive reinvestigation of these compounds over the wide spectral range of 2 to 38 μ, using prism spectrographs of various dispersing intervals, so that good dispersion is obtained throughout the entire region. Compounds were studied both in the vapor and liquid states, using in many cases comparatively thick cells in order to develop bands of low intensity.

A listing of the compounds studied, together with their boiling points and the phases in which they were observed, is given in table 1. Representatives of all types of halogen-substituted methanes except the methyl halides, which have been extensively studied under high resolution, were included.

Since the spectra were recorded with prism spectrographs, it was not possible to resolve the rotational fine-structure.

It should be possible to account for the observed absorption bands in terms of transitions among the various vibrational states of the molecules. The bands will be of three types: fundamentals, in which transition occurs from the ground vibrational level to a state in which one mode of vibration is singly excited; overtones and combinations, from the ground level to states in which there are two or three quanta of vibrational energy in one or more modes; and difference bands, in which transition is from one singly excited vibrational mode to other higher vibrational levels. In general the fundamentals will be the most intense bands, although in certain of the molecules, because of symmetry considerations, the intensity in the vapor phase should become zero. The combinations and overtones, lying at shorter wavelengths than the fundamentals, will be weaker, and the difference bands, which, in general, will be at longer wavelengths, will be very weak, except in the heavier molecules, where the fundamentals will be of such low energy that appreciable percentages of the molecules will be in excited states at room temperature. The following sections describe the experimental method, present the results, and discuss further the vibrational assignments.

2. Experimental Methods and Results

The infrared absorption spectra of 18 substituted methanes have been measured in the region 2 to 38 μ. They were measured in the liquid state, at room temperature whenever possible, and also several of the compounds, as listed in table 1, have been measured in both the liquid and vapor state. The eight Freons have been measured as gases, except trichlorofluoromethane, in the 23- to 38-μ region. In order to observe the bands of low intensity in liquids, a cell with a thickness of 1.6 mm was used. For the intense bands a film of liquid between windows constituted the cell. In such cases the cell thickness was of the order of 0.01 mm. For the measurement of the gases and vapors the cell thickness varied from 5 cm to 1 m. The pressure of the vapors was that of the saturated vapor at room temperature (approximately 25° C). For the Freons the pressure was atmospheric or less for the different cell lengths. The liquid-cell thickness, gas-cell length, and gas pressure are given on graphs of the results. The spectra were recorded on a Perkin-Elmer spectrometer.

In order to cover the region from 2 to 38 μ with good resolution, prisms of lithium fluoride, sodium chloride, potassium bromide, and thallium bromide-iodide were used. Sharp bands could be measured

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[1] Figures in brackets indicate the literature references at the end of this paper.

with an accuracy of 5 cm^{-1} or less for the entire region. The general method of measurement was the same as that used in previous studies [3].

The eight fluorinated methane derivatives were supplied by W. S. Murray, of Kinetic Chemicals, Wilmington, Del. They were all above 99 percent in purity, except carbon tetrafluoride, whose spectrum showed one band that could not be accounted for by combination or overtone bands. It appeared in the same position as an intense band in chlorotrifluoromethane at about 9 μ. The carbon tetrafluoride gas was tested for purity by F. L. Mohler on the mass spectrometer and found to be 98.2 percent pure. The Michigan Chemical Co. supplied the chlorodibromomethane, dichlorobromomethane, trichlorobromomethane, and dichlorodibromomethane, and some of the others were from Dow Chemical Co. The bromoform and chloroform were obtained from Eastman Kodak Co. and were purified by W. Harold Smith, of the Organic Chemistry Section. After the first purification, the chloroform showed a band in the 3.4-μ region in addition to the intense band at 3.3 μ. After the second purification, the band at 3.4 μ disappeared.

The results are presented as graphs of percentage absorption against wavelength and wave number in figures 1 to 12, inclusive. The conditions of measurement are stated on each graph. In general, the spectra are presented in groups of five molecules of similar structure, and the spectrum is divided into two portions, 2 to 15 μ, corresponding to measurements with sodium chloride and lithium fluoride prisms, and 15 to 38 μ, corresponding to measurements with potassium bromide and thallium bromide-iodide prisms.

Numerical values of the positions of maximum absorption that may be identified as band centers, and further data pertaining to their interpretation, are presented in tables 2 to 6, inclusive. These include the band centers in wave numbers; the approximate intensity, characterized as weak, strong, etc. (for a more quantitative estimate, the graphs should be consulted); the vibrational transition; and the symmetry of the transition. In addition to bands that appear in the infrared spectrum, there are given in parentheses the fundamental frequencies that do not appear, either because they fall outside the range of wavelengths studied, or because they have zero or very weak intensities. These frequencies are obtained either from the Raman effect or from combination and difference bands. The values given refer in general to the liquid state, except for compounds that are gaseous at room temperature. Cases where there is a pronounced difference between the two states will be mentioned in the discussion.

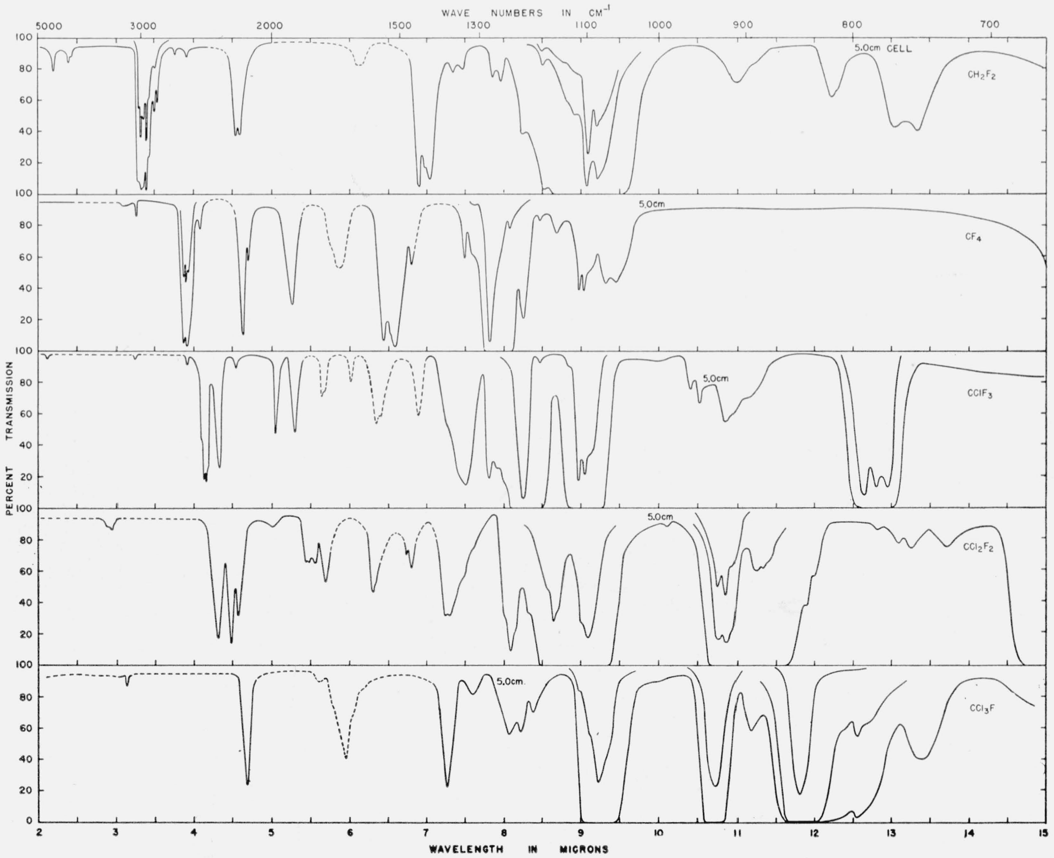

FIGURE 1. *Infrared spectra of gaseous* CH_2F_2, CF_4, $CClF_3$, CCl_2F_2, *and* CCl_3F *from 2 to 15* μ.

The pressure is atmospheric. The insert was measured at reduced pressures.

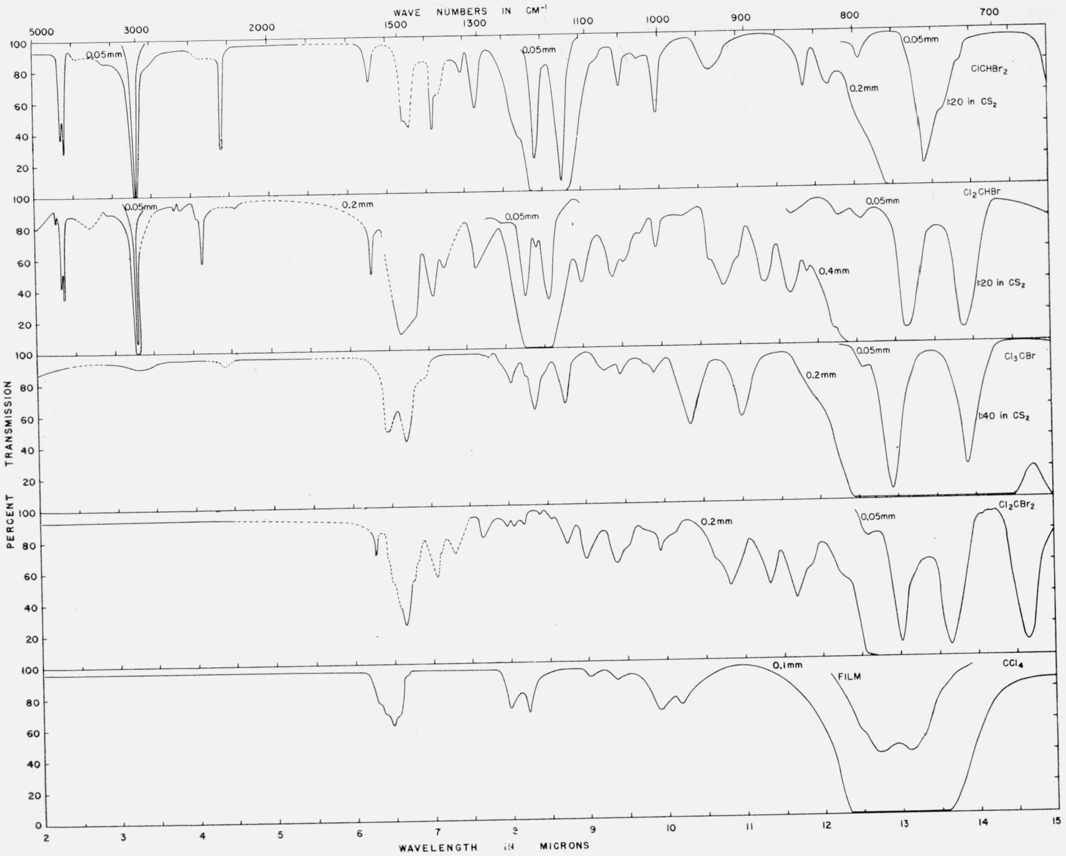

Figure 2. *Infrared spectra of* $CHBr_2Cl$, $CHBrCl_2$, $CBrCl_3$, CBr_2Cl_2, *and* CCl_4 *in the liquid state.*

Some strong bands near 14 μ were measured in solution.

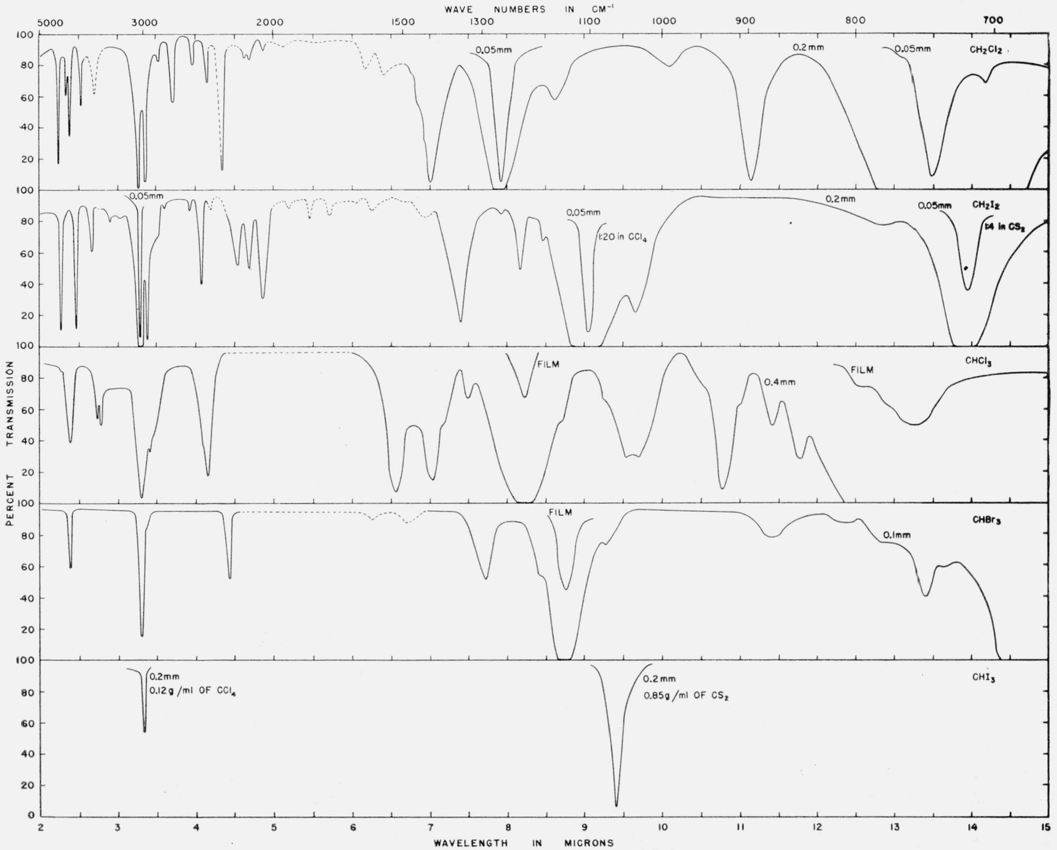

Figure 3. *Infrared spectra of* CH_2Cl_2, CH_2I_2, $CHCl_3$, $CHBr_3$, *in the liquid state and* CHI_3 *in solution from 2 to 15* μ.

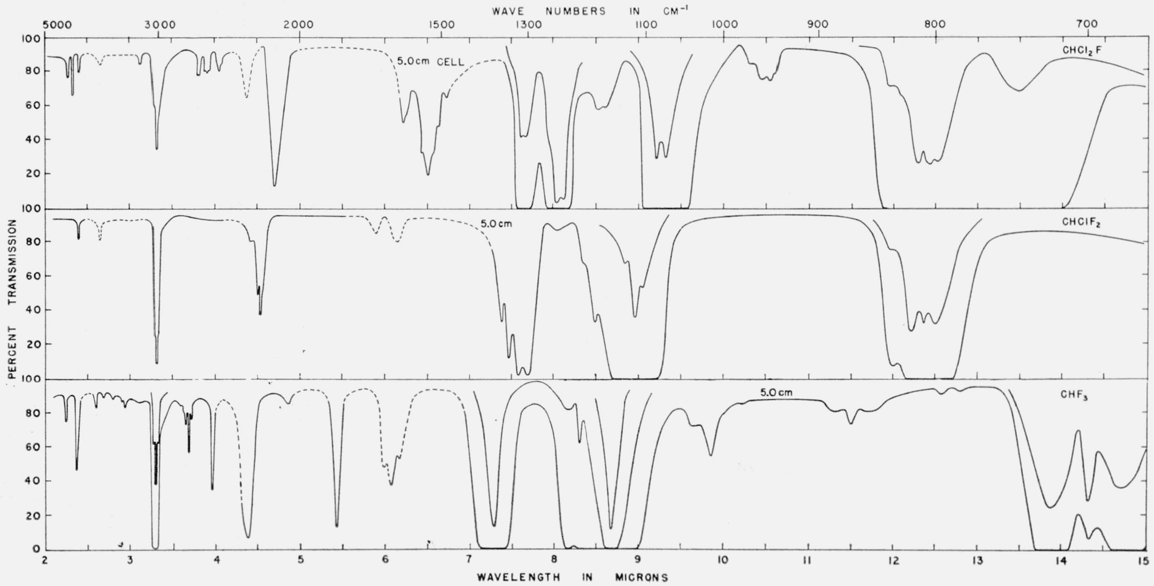

FIGURE 4. *Infrared spectra of gaseous* $CHCl_2F$, $CHClF_2$, *and* CHF_3 *from 2 to 15 μ.*

Pressure is atmospheric. Insert graphs are for pressures less than atmospheric.

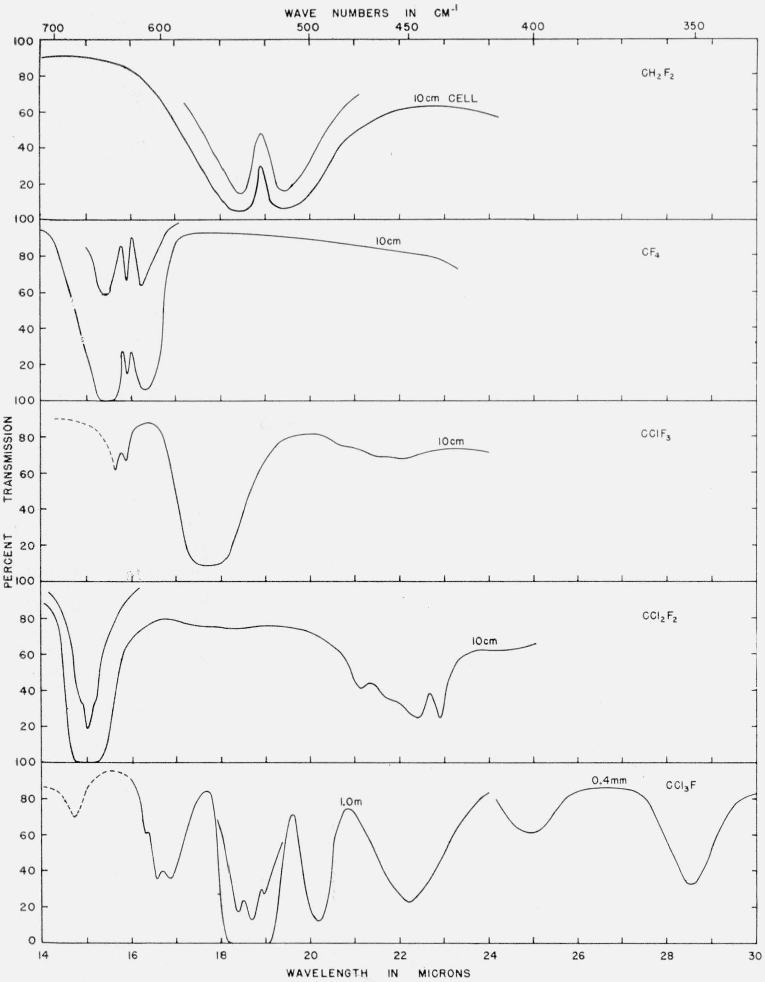

FIGURE 5. *Infrared spectra of gaseous* CH_2F_2, CF_4, $CClF_3$, CCl_2F_2, *and* CCl_3F *from 14 to 30 μ.*

Insert graphs are for pressures less than atmospheric. For CCl_3F the 0.4-mm cell refers to the liquid state.

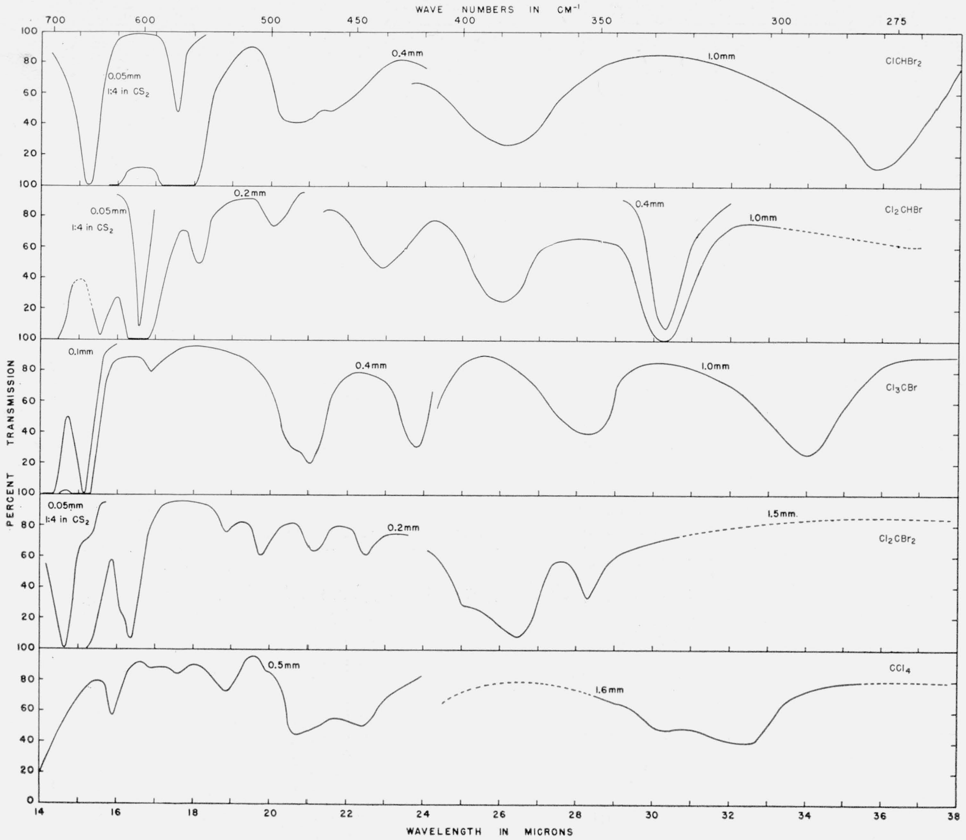

FIGURE 6. *Infrared spectra of* $CHBr_2Cl$, $CHBrCl_2$, $CBrCl_3$, CBr_2Cl_2, *and* CCl_4 *from 14 to 38 μ in the liquid state.*

The stronger bands near 16 μ were measured in solution.

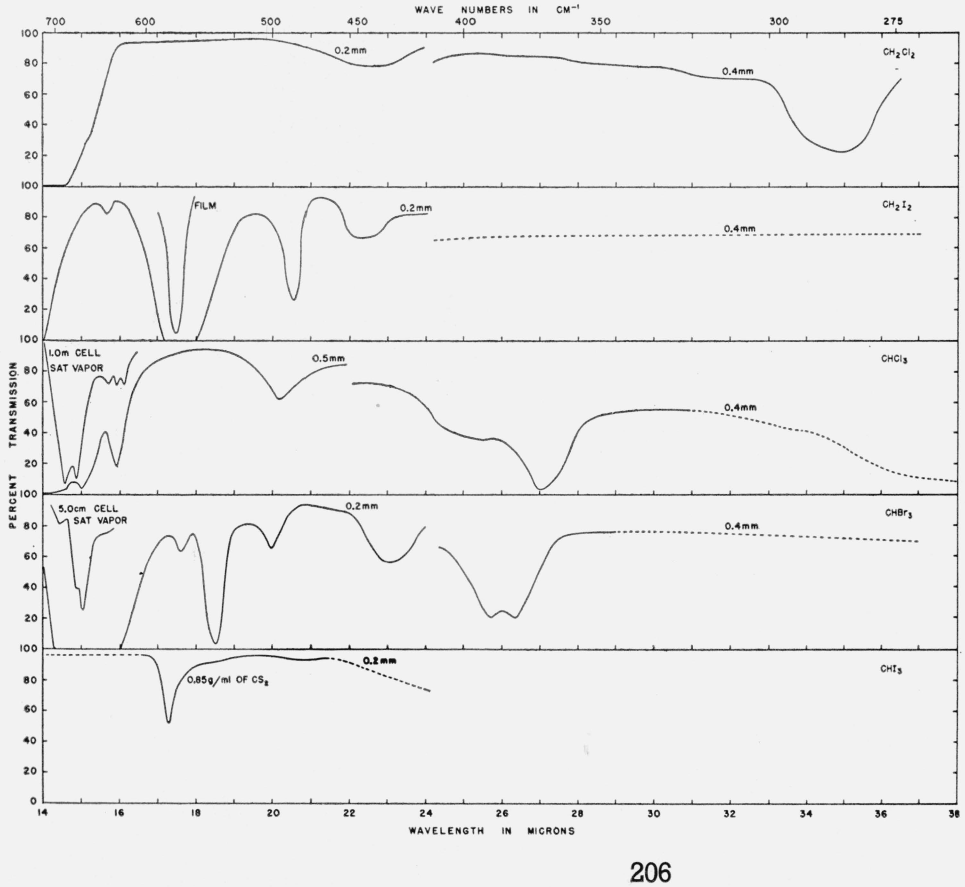

FIGURE 7. *Infrared spectra of* CH_2Cl_2, CH_2I_2, $CHCl_3$, $CHBr_3$, *in the liquid state, and* CHI_3 *in solution from 14 to 38 μ.*

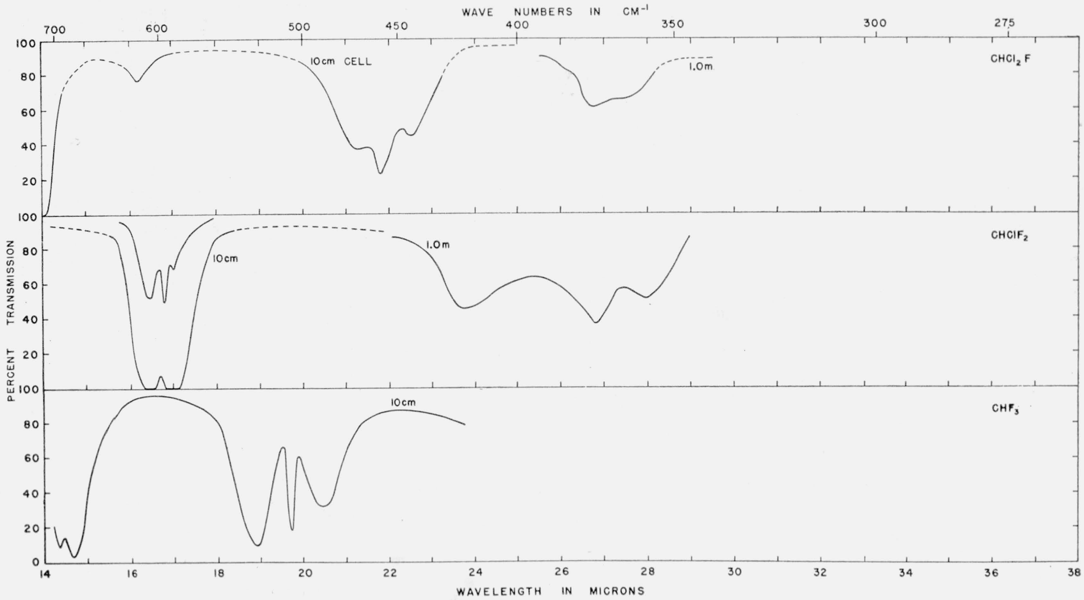

FIGURE 8. *Infrared spectra of gaseous* $CHCl_2F$, $CHClF_2$, *and* CHF_3 *from 14 to 38* μ.

Pressure is atmospheric. Insert graph is for a pressure less than atmospheric.

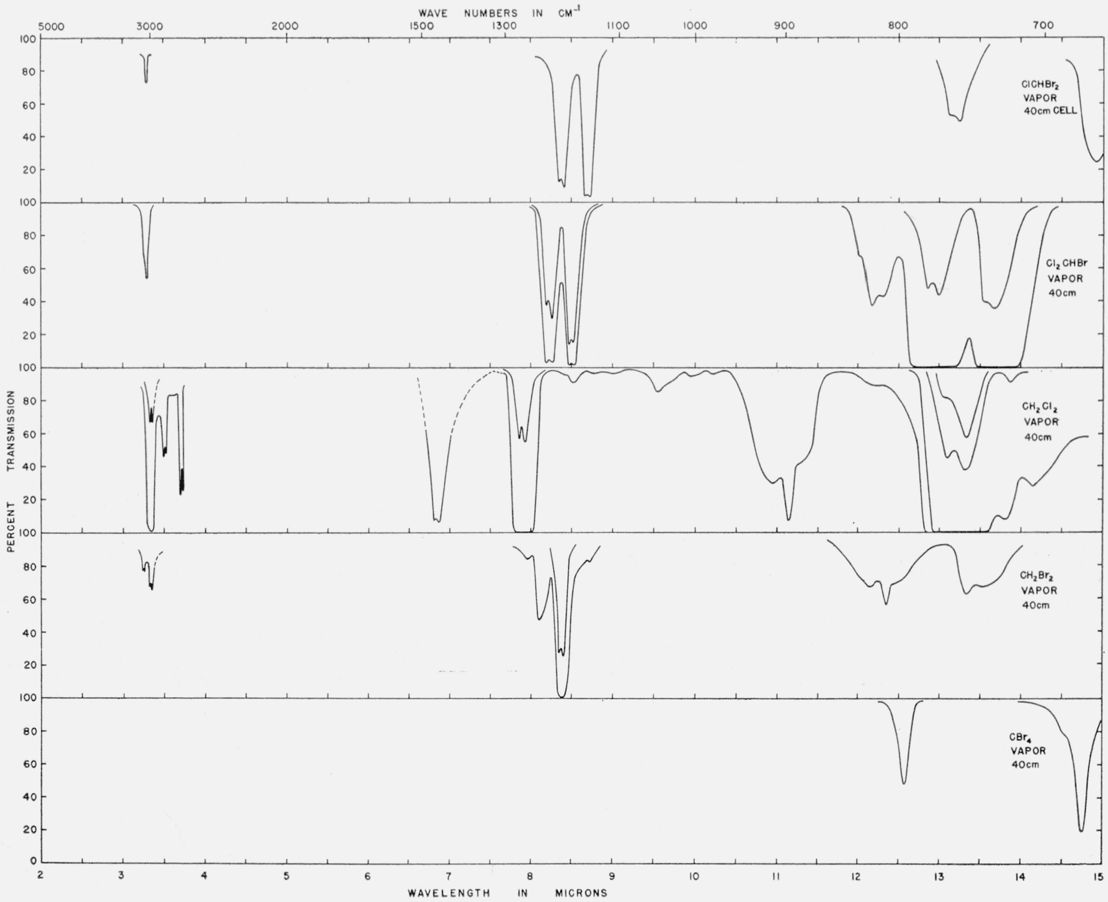

FIGURE 9. *Infrared spectra of vapors at saturation pressures at room temperature of* $CHBr_2Cl$, $CHBrCl_2$, CH_2Cl_2, CH_2Br_2, *and* CBr_4, *from 2 to 15* μ.

The insert curves are for reduced vapor pressures.

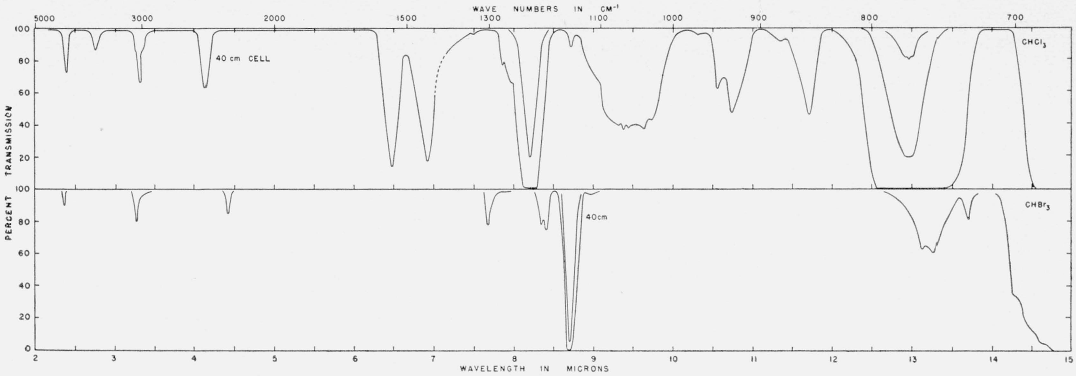

Figure 10. *Infrared spectra of vapors saturated at room temperature of* $CHCl_3$, *and* $CHBr_3$ *from 2 to 15 μ.*

The inserts are for reduced pressure.

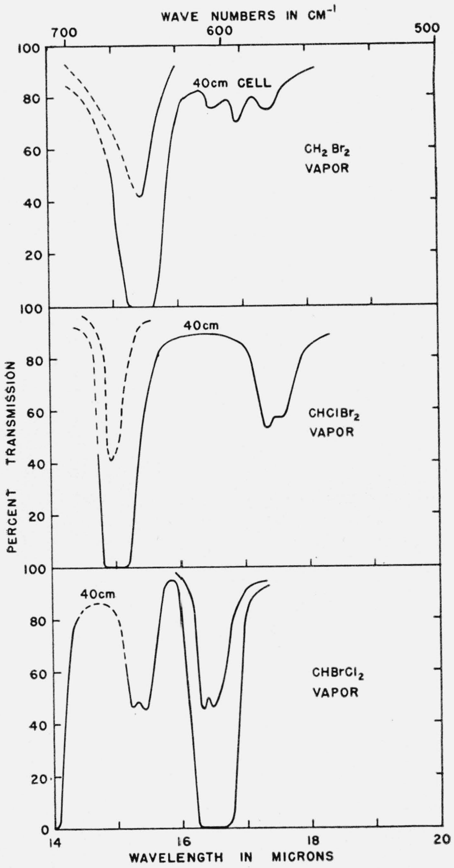

Figure 11. *Infrared spectra of saturated vapors of* CH_2Br_2, $CHBr_2Cl$, *and* $CHBrCl_2$ *from 14 to 20 μ.*

Insert curves are for reduced pressure.

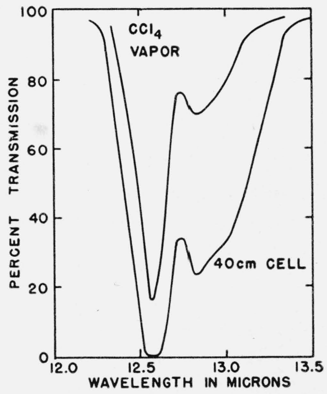

Figure 12. *Infrared absorption spectra of saturated vapor of* CCl_4 *at room temperature.*

Insert curve is for reduced pressure.

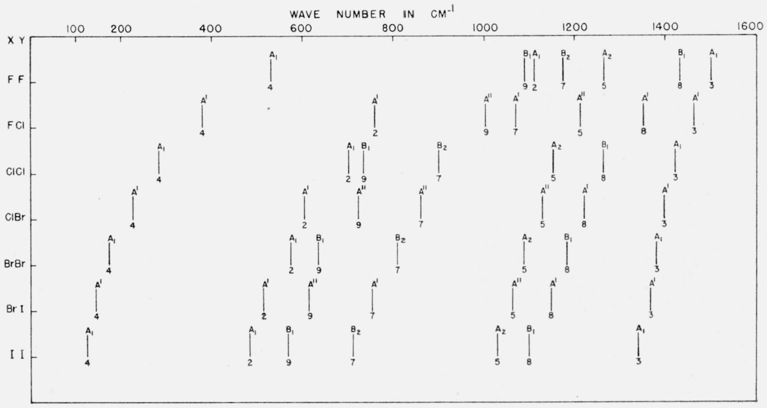

Figure 13. *Comparison of the positions of the fundamental bands of molecules of type* CH_2XY.

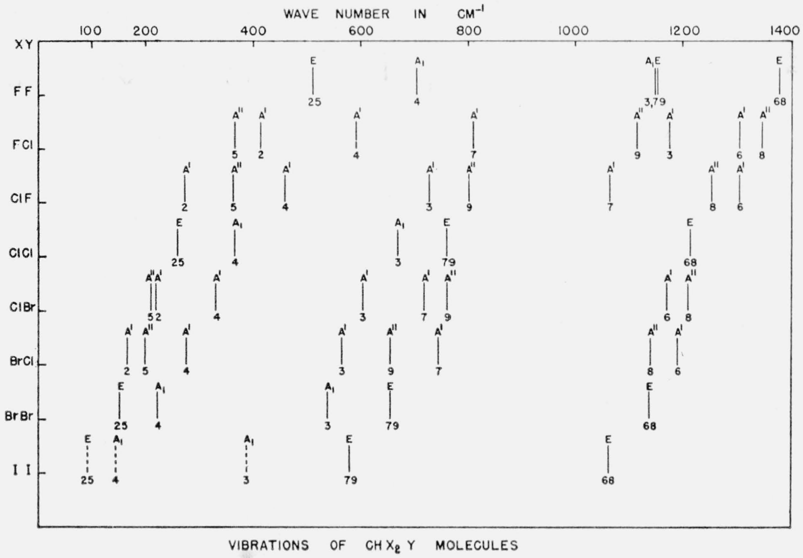

FIGURE 14. *Comparison of the positions of the fundamental bands of molecules of type* CHX_2Y.

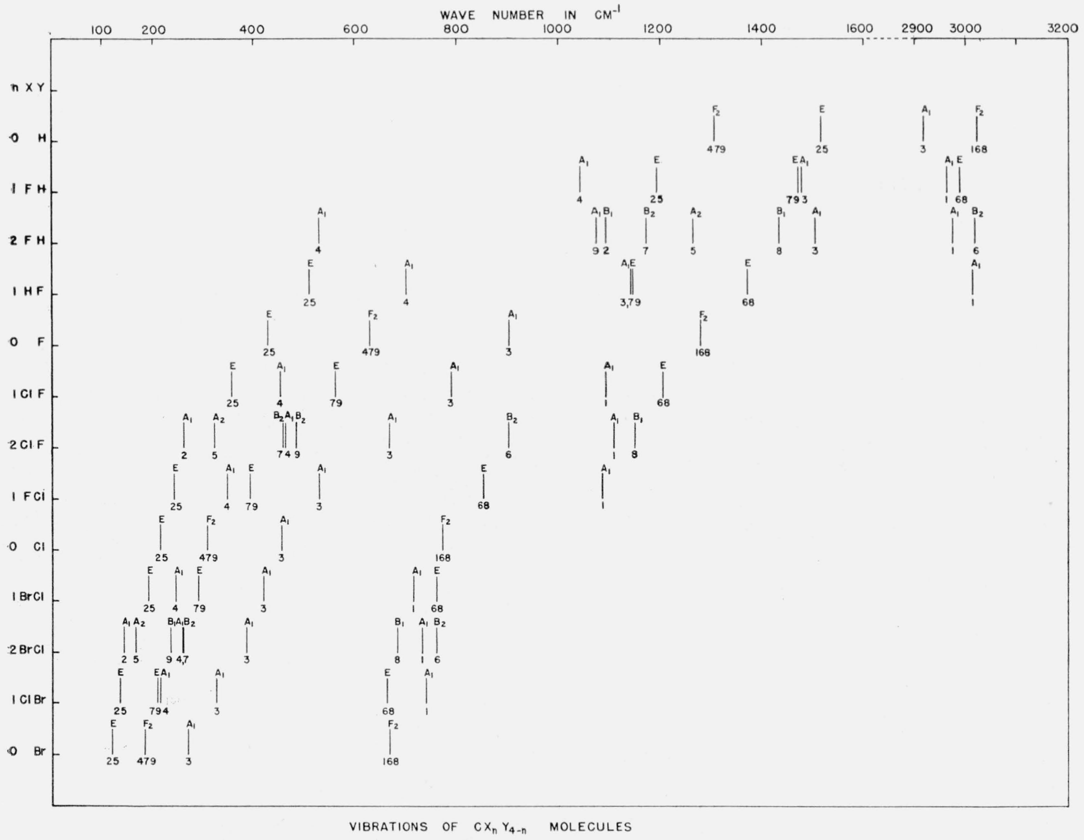

FIGURE 15. *Comparison of the positions of the fundamental bands of molecules of the type* CX_nY_{4-n}.

TABLE 1. *Some physical properties of the compounds measured*

Compound	Formula	Boiling point [a]	Observed as—		
			Gas	Liquid	Solution
		° C			
Carbon tetrafluoride (Freon 14)	CF_4	−128	×		
Chlorotrifluoromethane (Freon 13)	CF_3Cl	−80	×		
Dichlorodifluoromethane (Freon 12).	CF_2Cl_2	−28	×		
Trichlorofluoromethane (Freon 11)	CCl_3F	24. 1	×		
Carbon tetrachloride	CCl_4	76. 77	×	×	
Trichlorobromomethane	CCl_3Br	104. 07		×	×
Dichlorodibromomethane	CCl_2Br_2	135±		×	×
Fluoroform (Freon 23)	CHF_3	−82. 2	×		
Difluorochloromethane (Freon 22)	CHF_2Cl	−40. 8	×		
Dichlorofluoromethane (Freon 21)	$CHFCl_2$	8. 9	×		
Chloroform	$CHCl_3$	61. 26 58 to 61. 5	×	×	
Dichlorobromomethane	$CHCl_2Br$	91 to 92	×	×	×
Chlorodibromomethane	$CHClBr_2$	120	×	×	×
Bromoform	$CHBr_3$	149. 5	×	×	
Iodoform	CHI_3	Sublimes			×
Methylene fluoride (Freon 32)	CH_2F_2	−51. 6	×		
Methylene chloride	CH_2Cl_2	40. 1	×	×	×
Methylene iodide	CH_2I_2	Decomposes 180	×	×	×

[a] These values are principally from the Handbook of Physics and Chemistry.

3. Discussion

3.1. The Fundamental Frequencies

Each of the related methane derivatives reported in this paper has nine fundamental frequencies of vibration. The general theory of the vibrations of such molecules has been discussed in many places and need not be repeated here. It will suffice to recall that when there are atoms of different kinds joined to the carbon atom, the symmetry of the molecule is less than when all four linked atoms are alike, and that the particular degree of symmetry governs the degeneracy of the vibrations, the general form of the molecular motions, and the resulting activity in both the infrared and the Raman spectrum. The pertinent information derivable from such symmetry considerations is summarized in table 7. The symmetry class of overtones, combinations, and difference bands of the various fundamentals follow well-known rules and are given in tables 2 to 6.

The numerical values of the fundamentals show regular variations when going from one molecule to another in which a single substituent has been altered. This is a qualitative consequence of the facts that in all these substituted methanes the forces between the central atom and a particular peripheral atom are to a first approximation independent of the other peripheral atoms, and that these forces vary regularly with the mass of the peripheral atom. A more quantitative discussion will be given later. The relative positions and groupings of the numerical values are also affected by the symmetry. The conventional system of numerical identification of the fundamentals is based on the symmetry. This system fails to display the regularities existing among molecules of different symmetry. Accordingly, in this paper, one purpose of which was to show the consistency of all the frequencies of a large number of related compounds of different symmetry, use is made of an unconventional numbering system. The system closely resembles the conventional one for molecules of the type CH_2X_2, where there are no degeneracies. For molecules of higher symmetry than C_{2v}, where degeneracy occurs, the degenerate frequencies have been assigned two or three numbers, so that all nine frequencies may be identified. The relation between the numbers adopted here and those that would follow from application of the conventional rules is shown in table 8. This table also collects in one place the numerical values of the fundamentals of all the molecules, the spectra of which are reported in this paper, as well as of related molecules that have recently been studied in this laboratory [4].

TABLE 2. *The observed bands and their assignments of* CF_4, CF_3Cl, CF_2Cl_2, *and* $CFCl_3$

ν	Intensity	Band	Symmetry
Molecule CF_4 (Freon 14) molecular symmetry T_d			
cm^{-1}			
[437](R)	----	ω_{25}	E
630	s	ω_{479}	F_2
[904] (R)	----	ω_3	A_1
1067	w	$\omega_{25}+\omega_{479}$	$F_2(+F_1)$
1277	s	$2\omega_{479}$ ω_{168}	$F_2(+A_1+E)$ F_2
1468	w	$2\omega_{25}+\omega_{479}$	$2F_2(+F_1)$
1517	m	$\omega_{479}+\omega_3$	F_2
1555	m	--------	----------------
1698	w	$\omega_{25}+\omega_{168}$	$F_2(+F_1)$
1901	m	$3\omega_{479}$ $\omega_{479}+\omega_{168}$	$2F_2(+A_1+F_1)$ $F_2(+A_1+E+F_1)$
2123	w	$2\omega_{479}+\omega_3$	$F_2(+A_1+E)$
2160	m	$\omega_3+\omega_{168}$	F_2
2447	vw	$\omega_{479}+2\omega_3$	F_2
2565	m	$2\omega_{168}$	$F_2(+A_1+E)$
3081	vw	$2\omega_3+\omega_{168}$	F_2
Molecule CF_3Cl (Freon 13) molecular symmetry C_{3v}			
[356] (R)	----	ω_{25}	E
[470] (R)	----	--------	----------------
450?	vw	ω_4	A_1
563	m	ω_{79}	E
635	w	$\omega_{68}-\omega_{79}$? $\omega_1-\omega_4$	A_1
781	s	ω_3	A_1
921	w	$\omega_{25}+\omega_{79}$	$E+A_1(+A_2)$
950	w	$2\omega_4$	A_1
1105	s	ω_1	A_1
1132?	w	$2\omega_{79}$	$2E+A_1$
1181?	w	--------	----------------
1212	s	ω_{68}	E
[1279]	m	$\omega_4+\omega_3$	A_1
1335	m	$\omega_{79}+\omega_3$	E
1451?	m	$\omega_{25}+\omega_1$	E
1575	w	$2\omega_3$ $\omega_4+\omega_1$ $\omega_{25}+\omega_{68}$	$3A_1+E(+A_2)$
1667	vw	$\omega_4+\omega_{68}$	E
1887	w	$\omega_3+\omega_1$	A_1
1984	w	$\omega_3+\omega_{68}$	E
2208	vw	$2\omega_1$	A_1
2315	m	$\omega_1+\omega_{68}$	E
2417	m	$2\omega_{68}$	$E+A_1$
2554	vw	$\omega_{79}+\omega_3+\omega_{68}$	$E+A_1(+A_2)$
3104	vw	$\omega_3+\omega_1+\omega_{68}$	E

Table 2. *The observed bands and their assignments of* CF_4, CF_3Cl, CF_2Cl_2, *and* $CFCl_3$—Continued

ν	Intensity	Band	Symmetry
Molecule CF_2Cl_2 (Freon 12) molecular symmetry C_{2v}			
cm^{-1}			
[261] (R)	----	ω_2	A_1
[318] (R)	----	ω_5	A_2
437	w	ω_7	B_1
[455] (R)	----	ω_4	A_1
446	w	ω_4	----------------
473	w	ω_9	B_2
667	s	ω_3	A_1
728	w	$\omega_2+\omega_9$	B_2
755	w	$\omega_5+\omega_7$	B_2
781	vw	$\omega_5+\omega_9$	B_1
837	w	$\omega_8-\omega_5$ $\omega_1-\omega_2$	A_1 A_1
882	s	$\omega_4+\omega_7$	B_1
922	vs	ω_6	B_1
987?	vw	$\omega_3+\omega_5$	A_2
1101	s	$\omega_3+\omega_4$ ω_1	A_1 A_1
1159	s	ω_8	B_2
1236	m	$\omega_5+\omega_6$	B_2
1335	w	$2\omega_3$	A_1
1372	w	$\omega_7+\omega_6$ $\omega_4+\omega_6$ $\omega_9+\omega_6$	A_1 B_1 A_2?
1473	vw	$\omega_5+\omega_8$	B_1
1587	w	$\omega_9+\omega_1$ $\omega_4+\omega_8$ $\omega_7+\omega_8$	B_2 B_2 A_2
1754	w	$\omega_3+\omega_1$ $2\omega_4+2\omega_7$	A_1 A_1
1795	w	$\omega_4+\omega_6+\omega_7$	A_1
1832	w	$2\omega_6$	A_1
1996	vw	$\omega_4+\omega_7+\omega_1$ $\omega_6+\omega_1$	B_1
2188	w	$2\omega_1$	A_1
2242	m	$\omega_1+\omega_8$	B_2
2325	m	$2\omega_8$	A_1
3413	vw	$\omega_1+2\omega_8$	A_1
Molecule $CFCl_3$ (Freon 11) molecular symmetry C_{3v}			
[248] (R)	----	ω_{25}	E
350	w	ω_4	A_1
401	vw	ω_{79}	E
451	w	$\omega_{68}-\omega_{79}$?	A_1
495	w	$\omega_{68}-\omega_4$? $2\omega_{25}$	$E+A_1$
535	m	ω_3	A_1
603	w	$\omega_{25}+\omega_4$ $\omega_{68}-\omega_{25}$	E
680	w	$2\omega_4$	A_1
748	w	$\omega_4+\omega_{79}$	E
797	m	$\omega_{25}+\omega_3$	E
847	vs	ω_{68}	E
895	w	$\omega_4+\omega_3$	A_1
932	s	$\omega_{79}+\omega_3$	E
1085	s	ω_1 $2\omega_3$	A_1
1115?	m	$\omega_{25}+\omega_{68}$	$E+A_1+A_2$
1193	w	$\omega_4+\omega_{68}$ $\omega_{79}+\omega_{68}$	E $E+A_1(+A_2)$
1215	w		
1239	w		
1317	w	$\omega_{25}+\omega_1$	E
1376	m	$\omega_3+\omega_{68}$	E
1678?	w	$2\omega_{68}$ $2\omega_4+\omega_1$	$E+A_1$ A_1
1775?	vw	$\omega_{79}+\omega_3+\omega_{68}$	$E+A_1+A_2$
2132	m	$2\omega_1$	A_1
3195	vw	$3\omega_1$	A_1

Table 3. *The observed bands and their assignments of* CCl_4, CCl_3Br, *and* CCl_2Br_2

ν	Intensity	Band	Symmetry
Molecule CCl_4 molecular symmetry T_d			
cm^{-1}			
[218] (R)	----	ω_{25}	(E)
309	w	$\omega_3+\omega_{479}-\omega_3$ ω_{479}	F_2
319			
329			
446	w	$\omega_{168}-\omega_{479}$	F_2
482	w	$\omega_3+\omega_{479}-\omega_{479}$	F_2
[458] (R)	----	ω_3	(A_1)
501	vw	$\omega_{479}+\omega_{25}$	$F_2(+F_1)$
531	w	$\omega_{168}-\omega_{25}$	F_2
569	vw	$\omega_3+\omega_{479}-\omega_{25}$	F_2
635	w	$2\omega_{479}$	$F_2(+E+A_1)$
762	s	ω_{168}	F_2
785	s	$\omega_3+\omega_{479}$	F_2
982	w	$\omega_{168}+\omega_{25}$	$F_2(+F_1)$
1006	w	$\omega_3+\omega_{479}+\omega_{25}$	$F_2(+F_1)$
1068	vw	$\omega_{168}+\omega_{479}$	$F_2(+F_1+E+A_1)$
1107	vw	$\omega_3+2\omega_{479}$	$F_2(+E+A_1)$
1218	w	$\omega_{168}+\omega_3$	F_2
1253	w	$2\omega_3+\omega_{479}$	F_2
1529	w	$2\omega_{168}$	$F_2(+E+A_1)$
1546	w	$\omega_{168}+\omega_3+\omega_{479}$	$F_2(+F_1+E+A_1)$
1575	w	$2\omega_3+2\omega_{479}$	$F_2(+E+A_1)$
Molecule CCl_3Br molecular symmetry C_{3v}			
[187] (R)	----	ω_{25}	E
[243] (R)	----	ω_4	A_1
294	w	ω_{79}	E
353	w	$\omega_{68}-\omega_3$ $2\omega_{25}$	E $E+A_1$
420	w	ω_3	A_1
475	m	$2\omega_4$ $\omega_1-\omega_4$	A_1 A_1
490	w	$\omega_{79}+\omega_{25}$	$E+A_1(+A_2)$
592	vw	$2\omega_{79}$ $\omega_3+\omega_{25}$ $\omega_{68}-\omega_{25}$	$E+A_1$ E A_1
664	s	$\omega_3+\omega_4$	A_1
719	vs	ω_1	A_1
773	vs	ω_{68}	E
796	m	$2\omega_{79}+\omega_{25}$	$2E+A_1(+A_2)$
908	w	$\omega_1+\omega_{25}$	E
966	w	$\omega_1+\omega_4$ $\omega_{68}+\omega_{25}$	A_1 $E+A_1(+A_2)$
1010	vw	$\omega_{68}+\omega_4$	E
1046	vw	$\omega_1+2\omega_{25}$	$E+A_1$
1080	vw	$2\omega_3+\omega_4$	A_1
1143	w	$\omega_1+\omega_3$	A_1
1193	w	$\omega_{68}+\omega_3$	E
1242	vw	$\omega_1+\omega_{68}-\omega_4$	E
1440	w	$2\omega_1$	A_1
1493	w	$\omega_1+\omega_{68}$	E
1545	w	$2\omega_{68}$	$E+A_1$
2270	vw	$2\omega_{68}+\omega_1$	$E+A_1$

TABLE 3. *The observed bands and their assignments of* CCl_4, CCl_2Br, *and* CCl_2Br_3—Continued

ν	Intensity	Band	Symmetry
Molecule CCl_2Br_2 molecular symmetry C_{2v}			
cm^{-1}			
[141](R)	----	ω_2	A_1
[164](R)	----	ω_5	(A_2)
[230](R)	----	ω_9	B_1
[252](R)	----	ω_7	B_2
[252](R)	----	ω_4	A_1
353	w	$\omega_9+\omega_2$	B_1
377	w	ω_3	A_1
398	w	$\omega_7+\omega_2$	B_2
		$\omega_9+\omega_5$	B_2
443	w	$2\omega_9$	A_1
		$\omega_8-\omega_{74}$	$B_1(+A_2)$
472	w	$\omega_9+\omega_{74}$	$B_1(+A_2)$
505	w	$2\omega_{74}$	$2A_1+B_2$
529	w	$\omega_3+\omega_2$	A_1
		$\omega_3+\omega_5$	A_2
610	m	$\omega_3+\omega_{974}$	$A_1+B_1+B_2$
		$\omega_6-\omega_2$	B_2
683	vs	ω_8	B_1
733	vs	ω_1	A_1
768	vs	ω_6	B_2
793	m	$\omega_6+\omega_5-\omega_2$	B_1
818	w	$\omega_8+\omega_2$	B_1
844	vw	$\omega_8+\omega_5$	B_2
858	w	$\omega_1+\omega_2$	A_1
882	w	$\omega_6+\omega_2$	B_2
		$\omega_1+\omega_5$	(A_2)
923	w	$\omega_8+\omega_9$	A_1
		$\omega_6+\omega_5$	B_1
939	vw	$\omega_8+\omega_{47}$	$B_1(+A_2)$
991	vw	$\omega_1+\omega_{47}$	A_1+B_2
1005	w	$\omega_6+\omega_{947}$	$(A_2)+A_1+B_2$
1067	w	$\omega_8+\omega_3$	B_1
1112	w	$\omega_1+\omega_3$	A_1
1144	w	$\omega_6+\omega_3$	B_2
1171	vw	$\omega_6+\omega_9+\omega_5$	A_1
1190	vw	$\omega_1+2\omega_9$	A_1
1221	vw	$\omega_8+\omega_3+\omega_5$	B_2
1241	vw	$\omega_1+\omega_3+\omega_2$	A_1
1256	vw	$\omega_6+\omega_3+\omega_2$	B_2
1307	w	$\omega_8+\omega_3+\omega_9$	A_1
1362	w	$2\omega_8$	A_1
1416	w	$\omega_1+\omega_8$	B_1
1470	vw	$2\omega_1$	A_1
1503	m	$\omega_1+\omega_6$	B_2
1540	vw	$2\omega_6$	A_1
1592	w	$2\omega_8+\omega_9$	B_1

TABLE 4. *The observed bands and their assignments of* CHF_3, CHF_2Cl, $CHFCl_2$, *and* $CHCl_3$

ν	Intensity	Band	Symmetry
Molecule CHF_3 (Freon 23) molecular symmetry C_{3v}			
cm^{-1}			
507	m	ω_{25}	E
700	m	ω_4	A_1
870	w	$\omega_{68}-\omega_{25}$	A_1
1014	w	$2\omega_{25}$	$E+A_1$
1035	vw		
1150?	vs	ω_3	A_1
1152	vs	ω_{79}	E
1206	s	$\omega_{25}+\omega_4$	E
1372	m	ω_{68}	E
1647	m	$\omega_{25}+\omega_{79}$	$2E+A_1(+A_2)$
1842	m	$(\omega_{25}+\omega_{68}?)$	$E+A_1(+A_2)$
		$\omega_4+\omega_3$	A_1
		$\omega_4+\omega_{79}$	E
2045	vw	$\omega_4+\omega_{68}$	E
2278	m	$\omega_3+\omega_{79}$	2E
		$2\omega_{79}$	A_1
2523	m	$\omega_3+\omega_{68}$	2E
		$\omega_{79}+\omega_{68}$	$A_1(+A_2)$
2716	w	$2\omega_{68}$	$E+A_1$
3031	s	ω_1	A_1
3407	vw	$2\omega_{68}+\omega_4$	$E+A_1$
3445	vw	$3\omega_{79}$	
4212	w	$\omega_3+\omega_1$	A_1
		$\omega_{79}+\omega_1$	E
4448	vw	$\omega_{68}+\omega_1$	E
Molecule CHF_2Cl (Freon 22) molecular symmetry C_s			
365	w	ω_5	A″
422	w	ω_2	A′
595	s	ω_4	A′
809	vs	ω_7	A′
833	m	$2\omega_2$	A′
1116	vs	ω_9	A″
1178	m	ω_3	A′
		$\omega_5+\omega_7$	A′
1198	w	$2\omega_4$	A′
1244	vw	$\omega_2+\omega_7$	A′
1311	s	ω_6	A′
1347	m	ω_8	A″
1625?	w	$2\omega_7$	A′
1695?	vw	$\omega_5+\omega_6$	A″
		$\omega_5+\omega_8$	A′
		$\omega_4+\omega_9$	A′
2222	m	$2\omega_9$	A′
3023	m	ω_1	A′
3769?	vw	$\omega_7+\omega_1?$	A′
4167	vw	$\omega_9+\omega_1$	A″
Molecule $CHFCl_2$ (Freon 22) molecular symmetry C_s			
[276](R)	----	ω_2	A′
368	w	ω_5	A″
458	w	ω_4	A′
742	s	$\omega_2+\omega_5?$	A″
		$(\omega_2+\omega_4)$	A′
		$\omega_3?$	
804	vs	ω_9	A″
835	s	$\omega_5+\omega_4$	A″
955?	w	$\omega_6-\omega_5$	A″
		$\omega_8-\omega_2$	A″
1079	s	$\omega_2+\omega_9$	A″
		ω_7	A′
1166	w	$\omega_5+\omega_9$	A′
1242	s	ω_8	A″
1260	w	$\omega_4+\omega_9$	A″
1304	s	ω_6	A′
1494	w	$\omega_5+\omega_7$	A″
1536	m	$\omega_4+\omega_7$	A′
1608	w	$2\omega_9$	A′
		$\omega_5+\omega_8$	A′
2123	m	$2\omega_7$	A′
		$\omega_9+\omega_6$	A″
2280?	w	$\omega_8+\omega_7$	A″
2463	w	$2\omega_8$	A′

TABLE 4. *The observed bands and their assigments of* CHF_3, CHF_2Cl, $CHFCl_2$, *and* $CHCl_3$—Continued

ν	Intensity	Band	Symmetry
Molecule $CHFCl_2$ (Freon 21) molecular symmetry C_s			
cm^{-1}			
2557	vw	$\omega_6+\omega_8$	A''
2616	vw	$2\omega_6$	A'
3023	m	ω_1	A'
3184	vw	$3\omega_7$	A'
3780?	vw	$\omega_1+\omega_3$	A'
4144	vw	$\omega_7+\omega_1$	A'
4303	w	$\omega_6+\omega_1$	A'
4398	vw	$4\omega_7$?	A'
Molecule $CHCl_3$ molecular symmetry C_{3v}			
[261](R)	----	ω_{25}	E
370	m	ω_4	A_1
392	w	$\omega_3-\omega_{25}$	$E+A_1$
488	w	$2\omega_{25}$ $\omega_{79}-\omega_{25}$	$E+A_1$ A_1
629	m	$\omega_4+\omega_{25}$	E
667	s	ω_3	A_1
755	vs	ω_{79} $2\omega_4$	E A_1
849	m	$\omega_{68}-\omega_4$	E
929	m	$\omega_3+\omega_{25}$	E
951	w	$\omega_{68}-\omega_{25}$	A_1
1031	m	$\omega_3+\omega_4$	A_1
1049	m	$\omega_{79}+\omega_{25}$	$E+2A_1$
1145	w	$\omega_{79}+\omega_4$	E
1214	s	ω_{68}	E
1333	w	$2\omega_3$	A_1
1393	m	$\omega_{79}+\omega_4+\omega_{25}$	$E+2A_1$
1420	m	$\omega_3+\omega_{79}$	E
1524	m	$2\omega_{79}$	$E+A_1$
2410	m	$2\omega_{68}$	$E+A_1$
3040	m	ω_1	A_1
3597	w	$3\omega_{68}$	$E+A_1+A_2$
3663	w	$\omega_1+\omega_3$	A_1
4202	m	$\omega_1+\omega_{68}$	E

TABLE 5. *The observed bands and their assignments of* $CHCl_2Br$, $CHClBr_2$, $CHBr_3$, *and* CHI_3

ν	Intensity	Band	Symmetry
Molecule $CHCl_2Br$ molecular symmetry C_s			
cm^{-1}			
[215] (R)	----	ω_5	A''
220 (R)	----	ω_2	A'
330	m	ω_4	A'
383	w	$\omega_3-\omega_{25}$	$A'+A''$
437	w	$2\omega_{25}$	$2A'+A''$
495	w	$\omega_7-\omega_{25}$	$A'+A''$
552	w	$\omega_4+\omega_{25}$ $\omega_9-\omega_{25}$	$A'+A''$ $A'+A''$
604	s	ω_3	A'
643	m	$2\omega_4$	A'
719	vs	ω_7	A'
760	vs	ω_9	A''
795	m	$\omega_3+\omega_5$	A''
814	w	$\omega_3+\omega_2$	A'
843	vw	----------	----------
858	w	$\omega_6-\omega_4$	A''
884	w	$\omega_8-\omega_4$	A'
916	w	$\omega_7+\omega_{25}$	$A'+A''$
924	w	$\omega_3+\omega_4$	A'
942	w	$\omega_9+\omega_{25}$ $\omega_6-\omega_{25}$	$A'+A''$ $A'+A''$
1004	vw	$\omega_8-\omega_{25}$	$A'+A''$
1052	w	----------	----------
1066	w	$\omega_7+\omega_4$	A'
1114	w	$\omega_9+\omega_4$	A''
1168	s	ω_6	A'
1189	m	$2\omega_3$	A'
1211	s	ω_8	A''
1312	w	$\omega_3+\omega_7$	A'
1385	vw	$\omega_3+\omega_9$ $\omega_6+\omega_{25}$	A'' $A'+A''$
1414	vw	$2\omega_7$ $\omega_8+\omega_{25}$	A' $A'+A''$
1506	w	$2\omega_9$	A'
1592	w	$\omega_{68}+\omega_4$	$A'+A''$
2421	w	$2\omega_{68}$	$2A'+A''$
3040	s	ω_1	A'
3077	vw	$2\omega_6+\omega_7$	A'
3802	vw	$\omega_1+\omega_9$	A''
4237	m	$\omega_1+\omega_6$	A'
4291	w	$\omega_1+\omega_8$	A''
4504	vw	$\omega_1+2\omega_9$	A'
Molecule $CHClBr_2$ molecular symmetry C_s			
[168] (R)	----	ω_2	A'
[201] (R)	----	ω_5	A''
278	w	ω_4	A'
383	w	$\omega_3-\omega_{25}$ $2\omega_{25}$	$A'+A''$ $2A'+A''$
460	w	$\omega_4+\omega_2$ $\omega_9-\omega_5$	A' A'
492	w	$\omega_4+\omega_5$ $\omega_9-\omega_2$	A'' A''
570	s	ω_3	A'
657	vs	ω_9	A''
733	m	$\omega_3+\omega_2$	A'
746	s	ω_7	A'
796	m	$\omega_3+\omega_5$	A''
821	w	$\omega_2+\omega_9$	A''
844	w	$\omega_3+\omega_4$ $\omega_9+\omega_5$	A' A'
937	w	$\omega_7+\omega_{25}$ $\omega_9+\omega_4$	$A'+A''$ A''
1004	w	$\omega_7+\omega_4$	A'
1029	vw	$\omega_6-\omega_2$	A'
1053	w	$\omega_2+\omega_5+\omega_9$	$A'+A''$
1144	vs	ω_8 $2\omega_3$	A'' A'
1189	s	ω_6	A'
1218	w	$\omega_3+\omega_9$	A''
1309	w	$2\omega_9$	A'
1340	vw	$\omega_8+\omega_5$ $\omega_6+\omega_2$	A'' A''
1410	w	$\omega_7+\omega_9$	A''
1473	w	$\omega_6+\omega_4$	A'
1488	w	$2\omega_7$	A'
1592?	w	$\omega_5+\omega_7+\omega_9$	A''
2278	m	$2\omega_{68}$	$2A'+A''$
3034	s	ω_1	A'
4203	m	$\omega_1+\omega_8$	A''
4257	w	$\omega_1+\omega_6$	A'

TABLE 5. *The observed bands and their assignments of* $CHCl_2Br$, $CHClBr_2$, $CHBr_3$, *and* CHI_3—Continued

ν	Intensity	Band	Symmetry
Molecule $CHBr_3$ molecular symmetry C_{3v}			
cm^{-1}			
[154](R)	----	ω_{25}	E
[222](R)	----	ω_4	A_1
[300?](R)	----	$2\omega_{25}$	$E+A_1$
380	m	$\omega_4+\omega_{25}$	E
389	m	$\omega_3-\omega_{25}$	E
435	w	$2\omega_4$	A_1
501	w	$\omega_{79}-\omega_{25}$	A_1
541	m	ω_3	A_1
668	vs	ω_{79}	E
694?	m	$\omega_3+\omega_{25}$	E
762	w	$\omega_3+\omega_4$	A_1
873	w	$\omega_{79}+\omega_4$	E
1078	w	$2\omega_3$	A_1
1142	vs	ω_{68}	E
1188	m	$\omega_3+\omega_{79}$	E
1295	m	$2\omega_{79}$ $\omega_{68}+\omega_{25}$	$E+A_1$ $E+2A_1$
1493?	vw	$2\omega_{79}+\omega_{25}$	$2E+A_1$
1597?	vw	$\omega_3+\omega_{68}$	E
2257	w	$2\omega_{68}$	$E+A_1$
3040	m	ω_1	A_1
4202	w	$\omega_1+\omega_{68}$	E
Molecule $CHBr_3$ molecular symmetry C_{3v}			
[92]?(R)	----	ω_{25}	E
[145]?(R)	----	ω_4	A_1
[385](R)	----	ω_3	A_1
581	m	ω_{79}	E
1064	m	ω_{68}	E
[3040](R)	----	ω_1	A_1

TABLE 6. *The observed bands and their assignments of* CH_2F_2, CH_2Cl_2, *and* CH_2I_2

ν	Intensity	Band	Symmetry
Molecule CH_2F_2 (Freon 32) molecular symmetry C_{2v}			
cm^{-1}			
529	s	ω_4	A_1
757	w	$\omega_5-\omega_4$	A_2
816	w	----------	--------
910	w	$\omega_8-\omega_4$	B_1
1090	vs	ω_9	B_1
1116	s	ω_2	A_1
1176	m	ω_7	B_2
1262	w	ω_5	A_2
1349	w	----------	--------
1435	s	ω_8	B_1
(1508)	----	ω_3	A_1
1623	vw	$\omega_4+\omega_{29}$	A_1+B_1
2183	m	$2\omega_{29}$	$2A_1+B_1$
2551	vw	$2\omega_5$ $\omega_8+\omega_{29}$	A_1 A_1+B_1
2838	m	$2\omega_8$	A_1
2945	m	$\omega_3+\omega_8$	B_1
2949	s	ω_1	A_1
3012	s	ω_6	B_2
4161	w	$\omega_1+\omega_7$ $\omega_6+\omega_{29}$	$2B_2+A_2$
4550	w	$\omega_6+\omega_3$	B_2

TABLE 6. *The observed bands and their assignments of* CH_2F_2, CH_2Cl_2, *and* CH_2I_2—Continued

ν	Intensity	Band	Symmetry
Molecule CH_2Cl_2 molecular symmetry C_{2v}			
cm^{-}			
286	w	ω_4	A_1
444	w	$\omega_9-\omega_4$	B_1
706	m	ω_2	A_1
742	vs	ω_9	B_1
898	m	ω_7	B_2
991	w	$\omega_2+\omega_4$	A_1
1159	vw	ω_5	A_2
1262	s	ω_8	B_1
1424	m	ω_3	A_1
1562	vw	$\omega_4+\omega_8$	B_1
1621	vw	$\omega_7+\omega_{29}$	A_1+B_2
1945	vw	$\omega_2+\omega_8$	B_1
2053	vw	$\omega_5+\omega_7$	B_1
2132	vw	$\omega_3+\omega_2$	A_1
2155	vw	$\omega_3+\omega_9$	B_1
2304	m	$\omega_7+\omega_3$	B_2
2410	w	$\omega_8+\omega_5$	B_2
2525	w	$2\omega_8$	A_1
2688	m	$\omega_1-\omega_4$ $\omega_3+\omega_8$	A_1 B_1
2833	vw	$2\omega_3$	A_1
2985	s	ω_1	A_1
3048	s	ω_6	B_2
3690	w	$\omega_1+\omega_2$	A_1
3952	w	$\omega_6+\omega_7$	A_1
4219	m	$\omega_6+\omega_5$	B_1
4273	w	$\omega_6+\omega_8$	B_1
4464	m	$\omega_6+\omega_3$	B_2
Molecule CH_2I_2 molecular symmetry C_{2v}			
[128](R)	----	ω_4	A_1
444	w	$\omega_9-\omega_4$	B_1
486	m	ω_2	A_1
572	s	ω_9	B_1
639	w	$\omega_2+\omega_4$	A_1
717	m	ω_7	B_2
1035	w	ω_5	A_2
1107	vs	ω_8	B_1
1182	vw	$\omega_2+\omega_7$	B_2
1225	w	$\omega_4+\omega_8$	B_1
1351	m	ω_3	A_1
1435	vw	$2\omega_7$	A_1
1597	w	$\omega_2+\omega_8$	B_1
1748	w	$\omega_5+\omega_7$	B_1
1842	w	$\omega_3+\omega_2$	A_1
1923	vw	$\omega_3+\omega_9$	B_1
2062	m	$2\omega_5$ $\omega_3+\omega_7$	A_1 B_2
2132	m	$\omega_5+\omega_8$	B_2
2204	m	$2\omega_8$	A_1
2390	vw	$\omega_3+\omega_5$	A_2
2456	m	$\omega_3+\omega_8$	B_1
2551	vw	$\omega_6-\omega_2$	B_2
2850	w	$\omega_1-\omega_4$	A_1
2967	s	ω_1	A_1
3049	vs	ω_6	B_2
3450	vw	$\omega_1+\omega_2$	A_1
3759	m	$\omega_6+\omega_7$	A_1
4065	m	$\omega_1+\omega_8$ $\omega_6+\omega_5$	B_1 B_1
4397	m	$\omega_3+\omega_6$	B_2

TABLE 7. *Symmetry effects in the vibrations of molecules of the type* C—$X_1X_2X_3X_4$ *having tetrahedral symmetry when* $X_1=X_2=X_3=X_4$

Structure	Typical molecule	Molecular symmetry group	Vibrational subgroups	Number and degeneracy of vibrations in each subgroup		Infrared activity	Raman activity	
							Polarized	Depolarized
$X_1=X_2=X_3=X_4$	CF_4	T_d	A_1	1	1	0	×	
			E	1	2	0	×	
			F_2	2	3	×		×
$X_1=X_2=X_3\neq X_4$	CF_3Cl	C_{3v}	A_1	3	1	×	×	
			E	3	2	×		×
$X_1=X_2\neq X_3=X_4$	CF_2Cl_2	C_{2v}	A_1	4	1	×	×	
			A_2	1	1	0		×
			B_1	2	1	×		×
			B_2	2	1	×		×
$X_1=X_2\neq X_3\neq X_4$	$CHFCl_2$	C_s	A'	6	1	×	×	
			A''	3	1	×		×
$X_1\neq X_2\neq X_3\neq X_4$	CHFClBr	--------	--------	9	1	×		×

Degradation of the symmetrical vibrations in structures of lower symmetry

$$\begin{array}{ccccccc}
T_d & \longrightarrow & C_{3v} & \longrightarrow & C_{2v} & \longrightarrow & C_s \\
6F_2 & \longrightarrow & \left\{\begin{matrix}4E\\2A_1\end{matrix}\right\} & \longrightarrow & \left\{\begin{matrix}2B_1\\2B_2\\2A_1\end{matrix}\right\} & \longrightarrow & \left\{\begin{matrix}2A''\\4A'\end{matrix}\right. \\
2E & \longrightarrow & 2E & \longrightarrow & \left\{\begin{matrix}A_1\\A_2\end{matrix}\right\} & \longrightarrow & \left\{\begin{matrix}A'\\A''\end{matrix}\right. \\
A_1 & \longrightarrow & A_1 & \longrightarrow & A_1 & \longrightarrow & A'
\end{array}$$

TABLE 8. *Fundamental frequencies of methane derivatives, numbered and characterized in different ways*

Conventional No.		Methane derivative												
		CF_4	CF_3Cl	CF_2Cl_2	$CFCl_3$	CCl_4	CCl_3Br	CCl_2Br_2	$CClBr_3$	CBr_4	CHF_3	CHF_2Cl	$CHFCl_2$	$CHCl_3$
1	ν,cm^{-1}	904	1105	1101	1085	458	719	733	747	267	3031	3023	3023	3040
	Adopted No	3	1	1	1	3	1	1	1	3	1	1	1	1
	Character	$\nu_{F,s}$	$\nu_{F,s}$	$\nu_{F,s}$	ν_F	$\nu_{Cl,s}$	$\nu_{Cl,s}$	$\nu_{Cl.s}$	ν_{Cl}	$\nu_{Br,s}$	ν_H	ν_H	ν_H	ν_H
2	ν,cm^{-1}	437	781	667	535	218	420	377	329	123	1150	1311	1304	667
	Adopted No	25	3	3	3	25	3	3	3	25	3	6	6	3
	Character	δ_F	ν_{Cl}	$\nu_{Cl,s}$	$\nu_{Cl,s}$	δ_{Cl}	ν_{Br}	$\nu_{Br,s}$	$\nu_{Br,s}$	δ_{Br}	$\nu_{F,s}$	δ_H	δ_H	$\nu_{Cl,s}$
3	ν,cm^{-1}	1277	470	455	350	773	243	252	215	669	700	1178	1079	370
	Adopted No	168	4	4	4	168	4	4	4	168	4	3	7	4
	Character	$\nu_{F,a}$	$\delta_{F,s}$	$\delta_{F,s}$	$\delta_{Cl,s}$	$\nu_{Cl,a}$	$\delta_{Cl,s}$	$\delta_{Cl,s}$	$\delta_{Br,s}$	$\nu_{Br,a}$	$\delta_{F,s}$	$\nu_{F,s}$	ν_F	$\delta_{Cl,s}$
4	ν,cm^{-1}	630	1212	261	847	319	773	141	675	183	1372	809	742	1214
	Adopted No	479	68	2	68	479	68	2	68	479	68	7	3	68
	Character	$\delta_{F,a}$	$\nu_{F,a}$	$\delta_{Cl,s}$	$\nu_{Cl,a}$	$\delta_{Cl,a}$	$\nu_{Cl,a}$	$\delta_{Br,s}$	$\nu_{Br,a}$	$\delta_{Br,a}$	$\nu_{F,a}$	ν_{Cl}	$\nu_{Cl,s}$	δ_H
5	ν,cm^{-1}		563	318	401		294	164	214		1152	595	458	755
	Adopted No		79	5	79		79	5	79		79	4	4	79
	Character		$\delta_{F,a}$	δ	δ_F		$\delta_{Cl,a}$	δ	δ_{Cl}		δ_H	$\delta_{F,s}$	δ_F	$\nu_{Cl,a}$
6	ν,cm^{-1}		356	906	248		187	768	141		507	422	276	261
	Adopted No		25	6	25		25	6	25		25	2	2	25
	Character		δ_{Cl}	$\nu_{Cl,a}$	$\delta_{Cl,a}$		δ_{Br}	$\nu_{Cl,a}$	$\delta_{Br,a}$		$\delta_{F,a}$	δ_{Cl}	$\delta_{Cl,s}$	$\delta_{Cl,a}$
7	ν,cm^{-1}			437				252				1347	1242	
	Adopted No			7				7				8	8	
	Character			δ_{FCl}				$\delta_{Cl,a}$				δ_H	δ_H	
8	ν,cm^{-1}			1159				683				1116	804	
	Adopted No			8				8				9	9	
	Character			$\nu_{F,a}$				$\nu_{Br,a}$				$\nu_{F,a}$	$\nu_{Cl,a}$	
9	ν,cm^{-1}			473				230				365	368	
	Adopted No			9				9				5	5	
	Character			δ_{FCl}				$\delta_{Br,a}$				δ_{FCl}	δ_{FCl}	

TABLE 8. *Fundamental frequencies of menthane derivatives, numbered and characterized in different ways*—Continued

Conventional No.		Methane derivative											
		$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	CHI_3	CH_2F_2	CH_2ClF	CH_2Cl_2	CH_2ClBr	CH_2Br_2	CH_2I_2	CH_3F	CH_4
1	ν, cm^{-1}	3040	3034	3040	(3040)	2949	2993	2985	2987	2988	2967	2964	2915
	Adopted No.	1	1	1	1	1	1	1	1	1	1	1	3
	Character	ν_{H}	ν_{H}	ν_{H}	ν_{H}	$\nu_{\mathrm{H,s}}$	$\nu_{\mathrm{H,s}}$	$\nu_{\mathrm{H,s}}$	$\nu_{\mathrm{H,s}}$	$\nu_{\mathrm{H,s}}$	$\nu_{\mathrm{H,s}}$	$\nu_{\mathrm{H,s}}$	$\nu_{\mathrm{H,s}}$
2	ν, cm^{-1}	1168	1189	541	385	1508	1470	1424	1402	1385	1351	1475	1533
	Adopted No.	6	6	3	3	3	3	3	3	3	3	3	25
	Character	δ_{H}	δ_{H}	$\nu_{\mathrm{Br,s}}$	$\nu_{\mathrm{I,s}}$	$\delta_{\mathrm{H,s}}$	$\delta_{\mathrm{H,s}}$	$\delta_{\mathrm{H,s}}$	$\delta_{\mathrm{H,s}}$	$\delta_{\mathrm{H,s}}$	$\delta_{\mathrm{H,s}}$	$\delta_{\mathrm{H,s}}$	δ_{H}
3	ν, cm^{-1}	719	746	222	145	1116	1351	706	1225	579	486	1048	3020
	Adopted No.	7	7	4	4	2	8	2	8	2	2	4	168
	Character	$\nu_{\mathrm{Cl,s}}$	ν_{Cl}	$\delta_{\mathrm{Br,s}}$	$\delta_{\mathrm{I,s}}$	$\nu_{\mathrm{F,s}}$	δ_{HF}	$\nu_{\mathrm{Cl,s}}$	δ_{HCl}	$\nu_{\mathrm{Br,s}}$	$\nu_{\mathrm{I,s}}$	ν_{F}	$\nu_{\mathrm{H,a}}$
4	ν, cm^{-1}	604	570	1142	1064	529	1068	286	728	174	128	2982	1304
	Adopted No.	3	3	68	68	4	7	4	9	4	4	68	479
	Character	ν_{Br}	$\nu_{\mathrm{Br,s}}$	δ_{H}	δ_{H}	$\delta_{\mathrm{F,s}}$	ν_{F}	$\delta_{\mathrm{Cl,s}}$	ν_{Cl}	δ_{Br}	δ_{I}	$\nu_{\mathrm{H,a}}$	$\delta_{\mathrm{H,a}}$
5	ν, cm^{-1}	330	278	668	581	1262	760	1159	606	1096	1035	1471	--------
	Adopted No.	4	4	79	79	5	2	5	2	5	5	79	--------
	Character	$\delta_{\mathrm{Cl,s}}$	δ_{Cl}	$\nu_{\mathrm{Br,a}}$	$\nu_{\mathrm{I,a}}$	δ	ν_{Cl}	δ	ν_{Br}	δ	δ	$\delta_{\mathrm{H,a}}$	--------
6	ν, cm^{-1}	220	168	154	92	3012	385	3048	226	3065	3049	1196	--------
	Adopted No.	2	2	25	25	6	4	6	4	6	6	25	--------
	Character	δ_{Br}	$\delta_{\mathrm{Br,s}}$	$\delta_{\mathrm{Br,a}}$	$\delta_{\mathrm{I,a}}$	$\nu_{\mathrm{H,a}}$	δ_{Cl}	$\nu_{\mathrm{H,a}}$	δ_{Br}	$\nu_{\mathrm{H,a}}$	$\nu_{\mathrm{H,a}}$	δ_{HF}	--------
7	ν, cm^{-1}	1211	1144	--------	--------	1176	3048	898	3060	813	717	--------	--------
	Adopted No.	8	8	--------	--------	7	6	7	6	7	7	--------	--------
	Character	δ_{H}	δ_{H}	--------	--------	δ_{HF}	$\nu_{\mathrm{H,a}}$	δ_{HCl}	$\nu_{\mathrm{H,a}}$	δ_{HBr}	δ_{HI}	--------	--------
8	ν, cm^{-1}	760	657	--------	--------	1435	1236	1262	1130	1190	1107	--------	--------
	Adopted No.	9	9	--------	--------	8	5	8	5	8	8	--------	--------
	Character	$\nu_{\mathrm{Cl,a}}$	$\nu_{\mathrm{Br,a}}$	--------	--------	δ_{HF}	δ_{HF}	δ_{HCl}	δ_{HCl}	δ_{HBr}	δ_{HI}	--------	--------
9	ν, cm^{-1}	215	201	--------	--------	1090	1004	742	852	639	572	--------	--------
	Adopted No.	5	5	--------	--------	9	9	9	7	9	9	--------	--------
	Character	δ_{ClBr}	δ_{ClBr}	--------	--------	$\nu_{\mathrm{F,a}}$	δ_{HCl}	$\nu_{\mathrm{Cl,a}}$	δ_{HBr}	$\nu_{\mathrm{Br,a}}$	$\nu_{\mathrm{I.a}}$	--------	--------

The regularities mentioned in the preceding paragraph are displayed in figures 13 to 15, inclusive. In these graphs the frequencies of related molecules are plotted, the molecules being arranged vertically in order of increasing molecular weight. The regular decrease in frequency with increasing weight of the substituent, and the way in which the degenerate frequencies in the more symmetrical molecules break up in the less symmetrical ones and then regroup, is to be noted.

Another often-used method of identifying the fundamentals, which also possesses a degree of physical significance, is to characterize them by the type of intramolecular motion involved. In this method, ν_x signifies the stretching of a bond connecting the carbon atom with the x substituent, and δ_x signifies the bending of such a bond. All the molecules considered will have four ν's and five δ's. When there are several identical bonds, the suffix *s* or *a* may be added, according to whether the motion of the identical atoms is symmetrically toward the central atom or otherwise. In molecules as light as those considered here, this method often has limited meaning, since the motions in each fundamental mode cannot be localized as closely as the method would imply; in the δ modes in particular all the atoms participate in the motion. Nevertheless, a characterization of the fundamentals by this method is also included in table 8 and will be referred to in later discussion. For some such cases no suffix can be given; in others, a double suffix identifies the two atoms most prominently involved.

The relative intensity of the various fundamentals is not displayed in figures 13 to 15. The intensity depends on a number of factors, principally the symmetry of the motion and the distribution of electrical charge within the molecule. From the spectral graphs and tables it will be noted that there is a general parallelism in the intensities of corresponding bands in the various molecules of like symmetry. It should be noted that, although for molecules of symmetry C_{2v}, the A_2 frequency ω_5 should be inactive, it does appear in all the molecules considered, if it falls in the observable frequency range. It is always quite weak, however, and its appearance may readily be explained as due to a breakdown of the strict selection rules because of intermolecular forces, particularly in the liquid state, or to Coriolis interactions with nearby active frequencies, or to a combination of these causes.

3.2. Force Constant Calculations

For a quantitative verification of the assignment of fundamentals, recourse must be had to a calculation in terms of the atomic masses, atomic dimensions, and a suitable set of force constants of the potential energy. In the most general potential function there are many more disposable constants than there are observed frequencies, so that various approximations must be introduced. Certain of the constants, especially those involving interactions between motions of different types, may be set equal to zero; other constants may be assumed to have the same numerical value in different molecules. Many such treatments have been reported for most of the molecules considered here. One of the more successful of the recent simpler calculations was that of Decius [5], who was able to calculate 82 frequencies in 14 normal and deuterated chloro-bromo-methanes from 28 constants, with a mean accuracy of 1.1 percent.

In order to substantiate some of our assignments, and to determine whether a similar treatment may be applied to compounds containing fluorine, the calculations of Decius have been extended to the molecules CF_4, CF_3H, CF_2H_2, CFH_3, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_3Br, CCl_2Br_2, and $CClBr_3$, for which all nine frequencies were computed; and to the less symmetrical molecules CHF_2Cl, $CHFCl_2$, $CHCl_2Br$, $CHClBr_2$, CH_2FCl, and CH_2ClBr, for which only the three frequencies of symmetry A'' were computed. (To evaluate the remaining six frequencies of the latter molecules would involve the expansion and solution of a sixth-order determinant.) In these calculations the constants and molecular dimensions of Decius were adopted when applicable (one apparent numerical error or misprint, for f^1_β in C—Cl, was corrected). New values for the corresponding constants involving fluorine were adopted, which gave a fair over-all fit of the data considered. It is probable that additional computations would yield somewhat better values of these constants, but this does not seem useful, in view of the approximations involved. The constants used are listed in Decius' notation in table 9. Calculations on "mixed" molecules, that is, those containing more than one halogen, require additional constants. For these are used the geometric mean of the corresponding constants involving a single halogen. For example, since the constant f^2_{C-X}, corresponding to the interaction of motion along two $C-X^1$ bonds, $C-X^i_j \cdot C-X^i_k$, is 0.96 (in units of 10^5 dyne/cm) for $X^1=F$ and 0.332 for $X^1=Cl$, the constant for interaction of motion along C—F and C—Cl would be $[(0.96)\cdot(0.332)]^{1/2}=0.565$. The constants involving

TABLE 9.—*Force constants for halomethanes (after Decius)*

The following constants are assumed to be zero: f^1_{Rr}, $f^1_{R\eta}$, f^2_r, $f^1_{r\alpha}$, $f^2_{r\alpha}$, $f^1_{r\beta}$, $f^1_{r\eta}$, $f^2_{r\eta}$, $f^1_{\alpha\beta}$, $f^2_{\alpha\beta}$, $f^2_{\beta\eta}$, f^2_η, and f^3_η.

The numerical units are 10^5 dyne cm^{-1} for two stretching coordinates, 10^{-3} dyne for bending and stretching, and 10^{-11} dyne cm for two bending coordinates.

$r_0C-F=1.35$ A, $r_0C-Cl=1.75$ A, r_0 $C-Br=1.88$ A, $r_0C-H=1.093$ A, all $\alpha_0=\beta_0=\eta_0=109°28'$

Constant	Terms involved	$X^i=F$	$X^i=Cl$	$X^i=Br$
f^1_R	$C-X^i_j\cdot C-X^i_j$	6.26	3.383	2.840
f^2_R	$C-X^i_j\cdot C-X^i_k$	0.96	0.332	0.186
f^1_r	$C-H_i\cdot C-H_i$	5.04	5.04	5.04
$f^1_{R\alpha}$	$C-X^i_j\cdot H-C-X^i_j$	0.40	0.340	0.305
$f^2_{R\alpha}$	$C-X^i_j\cdot H-C-X^i_k$	−.21	−.164	−.152
$f^1_{R\beta}$	$C-X^i_j\cdot X^i_j-C-X^i_k$	.34	.338	.342
$f^2_{R\beta}$	$C-X^i_j\cdot X^i_k-C-X^i_l$	−.34	−.249	−.190
f^1_α	$H_j-C-X^i_j\cdot H_j-C-X^i_j$	.875	.687	.589
f^2_α	$H_j-C-X^i_j\cdot H_j-C-X^i_k$	.050	.009	−.005
f^3_α	$H_j-C-X^i_j\cdot H_k-C-X^i_j$	−.048	−.034	−.026
f^4_α	$H_j-C-X^i_j\cdot H_k-C-X^i_k$	−.145	−.065	−.060
f^1_β	$X^i_j-C-X^i_k\cdot X^i_j-C-X^i_k$	1.75	1.236	1.061
f^2_β	$X^i_j-C-X^i_k\cdot X^i_j-C-X^i_l$	0.17	0.092	0.134
f^3	$X^i_j-C-X^i_k\cdot X^i_l-C-X^i_m$	−.10	−.037	.039
f^1_η	$H_j-C-H_k\cdot H_j-C-H_k$	.530	.530	.530

TABLE 10. *Comparison of calculated and observed frequencies*

$$\left(\Delta=\frac{100(\nu_{obs}-\nu_{calc})}{\nu_{obs}}\right)$$

ω	$\nu_{calc.}$	Δ
	CF_4	
3	904	0.0
25	437	.0
168	1234	3.4
479	613	2.7
	CF_2H_2	
1	3005	1.9
3	1466	2.8
4	1154	−3.0
2	537	−1.5
5	1262	0.0
6	3082	−2.3
7	1108	5.8
8	1475	−2.8
9	1150	−5.5
	CF_3Cl	
1	1096	0.8
3	744	4.7
4	460	2.2
68	1191	1.8
79	562	0.2
25	358	−.5
	$CFCl_3$	
1	1125	−3.7
3	524	2.1
4	363	−3.7
68	813	4.0
79	420	−4.8
25	243	2.0
	CCl_2Br_2	
1	734	−0.1
3	364	3.5
4	251	0.4
2	147	−4.3
5	168	−2.5
6	772	−0.5
7	260	−3.2
8	676	1.0
9	229	0.4
	CHF_2Cl	
8	1366	−1.4
9	1132	−1.4
5	391	−7.1
	$CHFCl_2$	
8	1221	−1.8
9	791	1.6
5	392	−6.6
	$CHCl_2Br$	
8	1221	−4.4
9	749	1.5
5	219	−1.9

ω	$\nu_{calc.}$	Δ
	CF_3H	
1	3047	−0.5
3	1139	1.0
4	665	5.0
68	1369	0.2
79	1140	−1.2
25	532	−4.8
	CFH_3	
1	2960	0.1
3	1452	1.6
4	1125	7.3
68	3072	−3.0
79	1479	0.5
25	1181	1.3
	CF_2Cl_2	
1	1126	−2.3
3	648	2.8
4	463	−1.8
2	262	−0.4
5	331	−4.1
6	867	4.3
7	433	0.9
8	1168	−.8
9	460	2.8
	CCl_3Br	
1	699	−2.9
3	450	−7.1
4	235	−3.3
68	768	0.7
79	294	.0
25	174	6.9
	CBr_3Cl	
1	751	−0.5
3	324	1.6
4	215	0.0
68	678	−.5
79	215	−.4
25	137	2.8
	$CHBr_2Cl$	
8	1135	0.8
9	651	.9
5	205	−2.0
	CH_2FCl	
6	3080	−1.1
5	1214	1.8
9	1005	−0.1
	CH_2ClBr	
6	3077	−0.6
5	1142	−1.1
7	846	−0.7

bending of X^1-C-X^1 bonds and their interactions are obtained similarly, without introducing further new constants.

The resulting computed frequencies are compared with the observed fundamentals in table 10. It is seen that, in general, the agreement is good. The greatest deviation is 7.3 percent, and the average deviation of 85 frequencies in 16 molecules is 2.22 percent. This degree of fit was obtained by introducing 13 new constants, in addition to the 28 taken from Decius. Better agreement is not to be expected in view of the approximations introduced. Inasmuch as the very accurate results of microwave spectroscopy show that the interatomic distances are not constant, particularly for the C—F bond, and that the angles are not tetrahedral, it is clear that the force constants must vary to some extent. The interaction constants are relatively large: the particularly high value of f_R^2 for C—F (0.96×10^5 dyne cm^{-1}) is to be noted. This is a further reflection of the importance of specific forces arising from the highly polar C—F linkage, and indicates that for a truly accurate calculation, one should take into account all the ignored interactions, perhaps basing them on some more general force field [6]. The present comparison serves merely to confirm the choice of fundamentals and to demonstrate the approximate similarity of the carbon-halogen bonds in a large number of halomethanes.

It should be noted that the C—F constants, particularly the major ones involving the stretching, are in good agreement with a very recently published calculation based on much the same data and methods [7]. It should also be mentioned that preliminary calculations indicate that the C—F constants used also give adequate agreement with observation in such molecules as C_2F_6, CF_3-CH_3, CF_3-CCl_3, etc.

There are not enough data on the iodine compounds to derive constants for this bond, but approximate values extrapolated from the series F→Cl→Br→I may be seen to give adequate agreement with the few observations.

3.3. Overtone, Combination, and Difference Bands

In addition to the fundamentals, the bands that appear in the spectrum must be attributed to overtones, combinations, and differences of the fundamentals. They have been so assigned in tables 2 to 6. The assignments appear eminently reasonable, in that the selection rules are obeyed, in the molecules of higher symmetry, with the exception of an occasional weak combination of symmetry A_2 in C_{2v}; that binary combinations are in general much stronger than those involving three frequencies; and that difference bands arise only from relatively low vibrational frequencies.

Under the dispersion of prism instruments, it is not always possible to make an unambiguous assignment of these higher-order bands. As will be noted in tables 2 to 6, there are many instances in which two or more combinations can be offered as probable, and many other such have not been listed separately. The magnitude of the anharmonic corrections, by which the frequencies of the overtones and combinations differ from the sum of the fundamentals, ranges from +10 to −50 cm^{-1}, and, with nine fundamentals, such overlapping is common. Unless much higher resolution is available, it is unprofitable to attempt to distinguish between the possibilities, except to note that the assignments that are set forth show a consistent behavior in a large number of molecules. Indeed, because of the possibility of Fermi resonance among levels of like symmetry, it is often meaningless to distinguish between close-lying levels. Some of the more striking and definite examples of this effect occur in CCl_4 and CCl_2F_2 and will be discussed in more detail later. In a very heavy molecule of low symmetry, such as CCl_2Br_2, the number of possible difference bands of appreciable intensity arising from the five fundamentals below 300 cm^{-1} is particularly large. It will be noted in figure 6 that in these molecules there is a rather strong background of structureless absorption throughout the region 280 to 500 cm^{-1}, which undoubtedly arises from such overlappings.

It should be mentioned that a number of the overtone and combination bands of the methylene-halide compounds CH_2F_2, CH_2FCl, CH_2Cl_2, CH_2ClBr, and CH_2Br_2 have been studied under very high resolving power in the region 1.6 to 2.5 μ. The results will be reported separately. They show the expected large number of bands, with the rotational structure partially resolved, and further confirm the vibrational assignments reported in this paper.

3.4. Liquid-Vapor Shifts

As mentioned above, a number of the compounds of low boiling point have been studied both as liquids and as vapors, at room temperature. As is commonly observed, the vapor spectra show more indications of partially resolved rotational structure (P, Q, and R branches), but otherwise do not differ appreciably from those of the liquids, except for slight shifts of the central absorption frequencies. Some of these shifts are listed in table 11. It will be noted that the frequencies for the vapor are consistently higher than for the liquid, and that the magnitude of the shift is in general greater, especially on a percentage basis, for the stretching frequencies involving the halogens (ν_X's) than for the bending frequencies or for the hydrogen-stretching frequencies. This is undoubtedly due to the fact that the shifts result from partial association in the liquid, which is predominantly due to forces between the dipoles localized in the carbon-halogen bonds.

The fluorine compounds CH_2F_2 and CHF_3 were studied in this research only in the gaseous state. Their Raman spectra have, however, been studied in the liquid. Since the C—F bond is considerably more polar than C—Cl, one might expect the ν_F frequencies to show quite large liquid-vapor shifts, and these have been observed. These two molecules have also been listed in table 11, the Δ now referring to the shift between our adopted infrared frequencies and the most recent Raman data [8].

TABLE 11. *Frequency differences ($\nu_{vapor}-\nu_{liquid}$) for some halomethanes*

Vibration	$\Delta\nu$ cm^{-1}	Vibration	$\Delta\nu$
$CHCl_3$		$CHCl_2Br$	
$\omega_3\nu_{\mathrm{Cl,s}}$	+13	$\omega_7\nu_{\mathrm{Cl,s}}$	+12
$\omega_{79}\nu_{\mathrm{Cl,a}}$	+17	$\omega_9\nu_{\mathrm{Cl,a}}$	+13
$\omega_{68}\delta_{\mathrm{H}}$	+5	$\omega_6\delta_{\mathrm{H}}$	+8
$\omega_1\nu_{\mathrm{H}}$	+15	$\omega_8\delta_{\mathrm{H}}$	+6
$CHClBr_2$		$CHBr_3$	
$\omega_9\nu_{\mathrm{Br,a}}$	+14	$\omega_{68}\delta_{\mathrm{H}}$	+7
$\omega_7\nu_{\mathrm{Cl}}$	+12	$\omega_1\nu_{\mathrm{H}}$	+18
$\omega_8\delta_{\mathrm{H}}$	+7		
$\omega_6\delta_{\mathrm{H}}$	+5		
CH_2Cl_2		CH_2F_2	
$\omega_4\nu_{\mathrm{Cl,s}}$	+9	$\omega_2\delta_{\mathrm{F,s}}$	−3
$\omega_9\nu_{\mathrm{Cl,a}}$	+15	$\omega_9\nu_{\mathrm{F,a}}$	+35
$\omega_7\delta_{\mathrm{HCl}}$	0	$\omega_4\nu_{\mathrm{F,s}}$	+38
$\omega_5\delta_{\mathrm{HCl}}$	+4	$\omega_7\delta_{\mathrm{HF}}$	+6
$\omega_3\delta_{\mathrm{H,s}}$	+38	$\omega_8\delta_{\mathrm{HF}}$	0
$\omega_1\nu_{\mathrm{H,s}}$	+14	$\omega_1\nu_{\mathrm{H,s}}$	−14
		$\omega_6\nu_{\mathrm{H,a}}$	−18
CHF_3			
$\omega_{25}\delta_{\mathrm{F,a}}$	+1		
$\omega_4\delta_{\mathrm{F,s}}$	+3		
$\omega_3\nu_{\mathrm{F,s}}$	+33		
$\omega_{79}\delta_{\mathrm{F,a}}$	−7		
$\omega_{68}\nu_{\mathrm{H}}$	−6		
$\omega_1\nu_{\mathrm{H}}$	−26		

3.5. Discussion on Particular Molecules

It does not seem necessary to discuss all the assignments for each molecule, since in most cases the assignments are in substantial agreement with the work of other investigators who have studied these molecules, either by the infrared or Raman spectra. In a few instances, however, where certain points have been discussed in the literature, it seems desirable to justify our choices further. It should be pointed out that in many cases final decisions can hardly be reached until the rotational fine structure of the bands in question is studied under very high resolution.

3.6. CF_4

The bands may all be assigned as F_2 combinations or overtones of the two infrared active frequencies 629 cm^{-1} and 1,277 cm^{-1}, and the Raman-active 437 cm^{-1} (E) and 904 cm^{-1} (A_1). The fact that these pairs are each nearly in the ratio 1:2 would make it possible for Fermi resonance to appear in many of the combinations; however, as the observations give a band of high intensity at each position, it appears that the interactions are not strong, and that the resonance is only partial. There is a very weak peak at ~1,238 cm^{-1}, which may correspond to the weaker component of the $2\nu_{479}$, ν_{168} F_2 pair; the corresponding combinations with ν_1 also appear at 2,123 and 2,160 with a relative intensity of about 1:5. The unresolved rotational envelopes of the 629 and 1,277 cm^{-1} fundamentals are quite different, the former showing well separated *P*, *Q*, and *R* branches, with a $P-R$ distance of ~33 cm^{-1}, whereas in the latter this distance is much less and unresolved. This is due to the interaction with the rotation of angular momentum of vibration, and is in qualitative agreement with calculation: the ζ-factor for the valence vibration ν_{168} should be about +0.68 and for ν_{479} about −0.18, so that the rotational spacings for the two bands should be in the ratio (0.32/1.18)~0.3. The combination bands of these fundamentals with ν_3 show the same behavior; for example, 1,532 is found with a $P-R$ spacing of ~38 cm^{-1}, whereas 2,160 is narrow and unresolved.

3.7. CF_3Cl

The two lowest-frequency fundamentals, ω_{25}(E) and $\omega_4(A_1)$ are very weak in the infrared, but appear strongly in the Raman spectrum of the liquid. Although a weak band appears at 450 cm^{-1}, in the infrared spectrum, it seems preferable to adopt 470 cm^{-1} of the Raman spectra for the vapor-phase frequency of ω_4, as this accounts for the weak absorption at 635 cm^{-1} as a difference band and gives satisfactory agreement in a number of combinations.

3.8. CF_2Cl_2

The force-constant calculations definitely require that there be five (deformation) frequencies below 500 cm^{-1} and only four above 600 cm^{-1}. Hence the assignment of both the strong bands at 882 and 922 cm^{-1} as fundamentals cannot be correct; it is very reasonable to consider this a case of Fermi resonance, with the original ω_6 fundamental (B_1) at 906 cm^{-1} split by interaction with the combination $\omega_4(A_1)455+\omega_7(B_1)437$. The region from 420 to 480 cm^{-1} must be studied under higher resolution before the values for the three overlapping frequencies ω_6, ω_4, and ω_9 can be considered certain. The value of 455 cm^{-1} for ω_4 is from the Raman effect.

3.9. $CFCl_3$

As in the other chloro-fluoromethanes, the deformation fundamentals are very weak, but Raman-effect measurements enable a choice to be made between the fundamentals and the equally intense difference bands at wavelengths greater than 20μ. The combination band at 932 cm^{-1} is more intense than the fundamentals on which it is based. This may result from a partial Fermi resonance with the very intense ω_{68}. The ν_{F} frequency shows a +17 cm^{-1} shift from the liquid value found in the Raman effect [9].

3.10. CCl_4

This much-studied molecule shows one of the earliest-recognized examples of Fermi resonance in the strong pair at 762 to 785 cm^{-1}. The unsplit position of the ω_{168} is taken as the exact center, 773 cm^{-1}, since the two bands are nearly of equal intensity, in the liquid. In the vapor the resonance with 319+458 is less exact, the intensity ratio now being about 4:1, the higher frequency component being the stronger. This is in accord with the general observation that the vapor-liquid shift is greatest for the asymmetric valence vibrations. It is of considerable interest that the doubling also appears in two difference bands, arising from ω_{25} and ω_{479}.

3.11. CCl_3Br and CCl_2Br_2

In these heavy molecules many fundamentals lie beyond the limit of our observation, but are known from the Raman effect. There is considerable absorption without definite structure beyond 20 μ, corresponding to many possible overlapping difference and combination bands of the deformation frequencies.

3.12. CHF_3

This molecule has been studied under very high resolution in the photographic infrared [10]. We have also examined a number of the combination bands under high resolution. The only question in the frequency assignment concerns the value of ω_3, the $\nu_{F,s}$ fundamental. Its intensity and polarization in the Raman spectrum definitely prove that in the liquid it falls at 1,116 cm^{-1}. In the infrared spectrum of the gas there is no indication of any weak absorption to longer wavelengths of the 1,152 cm^{-1} peak. It is therefore believed that the $\nu_{F,s}$ and $\nu_{F,a}$ fundamentals overlap at this point, the difference from the Raman effect being due to the vapor-liquid shift, whereas the weak band at 1,209 cm^{-1} is a combination tone. A high-resolution study of this region would be of interest. Our force-constant calculations, in agreement with those of Rank, Shull, and Pace, confirm the assignments of 700 cm^{-1} to A_1 and 507 cm^{-1} to E symmetry, although the rotational envelopes of the two bands are nearly identical.

3.13. CHF_2Cl

The assignment of the $\omega_3(\nu_{F,s})$ fundamental differs from that of Glockler, Edgell, and Leader [11] obtained from the Raman effect. There are two medium-intensity bands to choose between, at 833 and 1,178 cm^{-1}. The higher value fits much better with the related molecules. The low frequency, which is fairly strong in the Raman effect, and which may well be accounted for as 2×422 cm^{-1}, undoubtedly gains in intensity by partial Fermi resonance with ω_7, at 809 cm^{-1}.

3.14. $CHFCl_2$, $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$

In all these molecules, there is little question as to the assignment of fundamentals, when the infrared and Raman results are both considered. All show absorption in the long-wavelength region. The 262 cm^{-1} fundamental of $CHCl_3$ is relatively strong, but occurs just at the long-wavelength limit of the TlBr-I prism.

3.15. CHI_3

The results for this molecule are quite incomplete. Because of its physical properties (solid at room temperature and above, subliming with decomposition) it could be studied only in solution. Its chemical instability prevented the use of high concentration, and rapid surveys of the spectrum were required. The Raman frequencies, and rough force-constant calculations, show that two of the fundamentals lie at very long wavelengths. The few bands observed find a natural interpretation by analogy with the corresponding molecules.

3.16. CH_2F_2

This molecule has been investigated recently under high resolution [12]. As mentioned above, high-resolution studies in the 1.6 to 2.5 μ, region have also been made in the radiometry laboratory of the Bureau. The assignment of fundamentals differs from that of the above authors, but is in agreement with the one very recently offered by Rank, Shull, and Pace, [8] and with the force-constant calculations. The Raman-effect data leave no doubt that in the liquid ω_3 is at 1,508 cm^{-1}. This $\nu_{H,s}$ frequency might well be very weak in the infrared and escape detection, since it falls in a region where the H_2O absorption masks weak bands. The band structures found by Stewart and Nielsen are equally well accounted for by the assignment, since the B_1 combination at 2,945 cm^{-1} can be ascribed to $\omega_3+\omega_8$. As mentioned above in connection with table 11, a relatively large liquid-vapor shift may be invoked to reconcile the Raman and infrared measurements in the region of 1,100 cm^{-1}. The depolarized Raman line at 1,054 cm^{-1} can be attributed to ω_9, rather than to $2\omega_4$ which should be polarized. The ω_5 frequency, whose A_2 symmetry should make it inactive, appears weakly at 1,262 cm^{-1}, presumably due to Coriolis interaction with ω_7 (B_2) at 1,176 cm^{-1}, or to breakdown of the strict selection rules induced by the strong polar intermolecular forces. There are two weak bands, at 816 and 1,349 cm^{-1} which cannot be assigned. They may be due to impurities.

3.17. CH_2Cl_2 and CH_2I_2

These molecules show no unexpected effects. There is a close parallelism among the spectra of all the methylene halides. These will be discussed at greater length in connection with high-resolution studies in the overtone region.

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4. References

[1] G. Herzberg, Infrared and Raman spectra of polyatomic molecules (D. van Nostrand Co., Inc., New York, N. Y., 1945).

[2] K. W. F. Kohlrausch, Ramanspektren (Becker & Erler, Leipzig, 1943).

[3] E. K. Plyler, R. Stair, and C. J. Humphreys, J. Research NBS **38**, 211 (1947) RP1769.

[4] E. K. Plyler, H. W. Smith, and N. Acquista, J. Research NBS **44**, 503 (1950) RP2097.

[5] J. C. Decius, J. Chem. Phys. **16**, 214 (1948),

[6] T. Simanouti, J. Chem. Phys. **17**, 245 (1949).

[7] E. L. Pace, J. Chem. Phys. **18**, 881 (1950).

[8] D. H. Rank, E. R. Shull, and E. L. Pace, J. Chem. Phys. **18**, 885 (1950).

[9] J. P. Zietlow, F. F. Cleveland, and A. G. Meister, J. Chem. Phys. **18**, 1076 (1950).

[10] H. J. Bernstein and G. Herzberg, J. Chem. Phys. **16**, 30 (1948).

[11] G. Glockler, W. F. Edgell, and G. R. Leader, J. Chem. Phys. **9**, 224 (1941).

[12] H. B. Stewart and H. H. Nielsen, Phys. Rev. **75**, 640 (1949).

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