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Infrared Absorption Spectra of Hexafluoroethane and of Chloropentafluoroethane

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In the present paper the infrared absorption spectra of hexafluoroethane and chloropentafluoroethane have been studied. The spectra examined ranged from 2 to 40 microns, and for this purpose lithium fluoride, sodium chloride, potassium bromide, and thallium bromide-iodide (KRS5) prisms were used. The substances studied were in the gaseous state.

This work was undertaken to compare the spectra of two molecules of the same type of structure but with much different properties of symmetry. The spectrum of hexafluoroethane has been previously measured in the infrared to 22 microns, and only small differences are noted in the present work from the previous study. Tables are included, which classify the observed spectra of hexafluoroethane and chloropentafluoroethane as fundamental, combination, and overtone bands

I. Introduction

This paper presents the results obtained in the study of the infrared absorption spectra of two fluorocarbons, hexafluoroethane and chloropentafluoroethane, from 2 μ to 40 μ.

In spite of the interest in fluorocarbons, in view of their characteristics, no data were available on the infrared absorption spectrum of chloropentafluoroethane. The infrared absorptance of hexafluoroethane has been studied by J. R. Nielsen, C. M. Richards, and H. L. McMurry [1],[2] and the Raman shifts for this material in the liquid state have been measured by D. H. Rank and E. L. Pace [2]. In the present work, the data obtained for hexafluoroethane are in good agreement in the position of the bands with those given by Nielsen, et al. [1]. The study of the infrared absorption spectrum of chloropentafluoroethane in comparison with that of hexafluoroethane, from which it differs only slightly chemically, is of interest because, as a result of the symmetry of the latter, several of its fundamental vibrations are degenerate. Because of the asymetry of the former, however, all of the eighteen fundamental frequencies of chloropentafluoroethane are active in the infrared. Unfortunately, of the eighteen frequencies expected, seven were not observed, either because they were very low in intensity or existed in a region of long wavelengths not examined. A majority of the observed bands may be accounted for as combinations of the fundamental frequencies observed, although some difficulty in interpretation exists for three of those of lowest wave number.

II. Experimental Method

The materials used were of the group of "freons," supplied by duPont, and the spectra were obtained with these substances in the gaseous state. A gas cell of 5 cm in length with potassium bromide windows was used, except for the longest wavelengths. The initial pressure of the gas in the cell was 500 mm of mercury, but as this was too high for the observation of some of the absorption maxima, it was reduced in each case to the most suitable one. The pressure used is indicated on the curves. When measuring the long wavelength region with a thallium bromide-iodide prism, a 1-m cell with windows of polystyrene was used. On account of the lack of strength of the polystyrene windows, it was not possible to evacuate the cell. The cell was filled by allowing the gas to flow in slowly for several minutes. When the

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

bands were too intense for observing their structure, some of the gas was removed by flowing air slowly through the cell. When the amount of gas in the cell was reduced to a level that gave a good contrast in the different parts of the band, no further removal of the gas was made. By this method of reducing the quantity of the gas, it was not possible to determine the partial pressure.

The spectra of these two substances between 2 μ and 40 μ were recorded with Perkin-Elmer spectrometers, models 12A and 12B, using lithium fluoride, sodium chloride, potassium bromide, and thallium bromide-iodide prisms. With both spectrometers scanning and slit drive were automatic. Separate motor drives were used, one for the wavelength drum and the other to open the slit continuously to achieve approximately constant background energy at different wavelengths. Further details of these devices can be found in a paper by E. K. Plyler, R. Stair, and C. J. Humphreys [3].

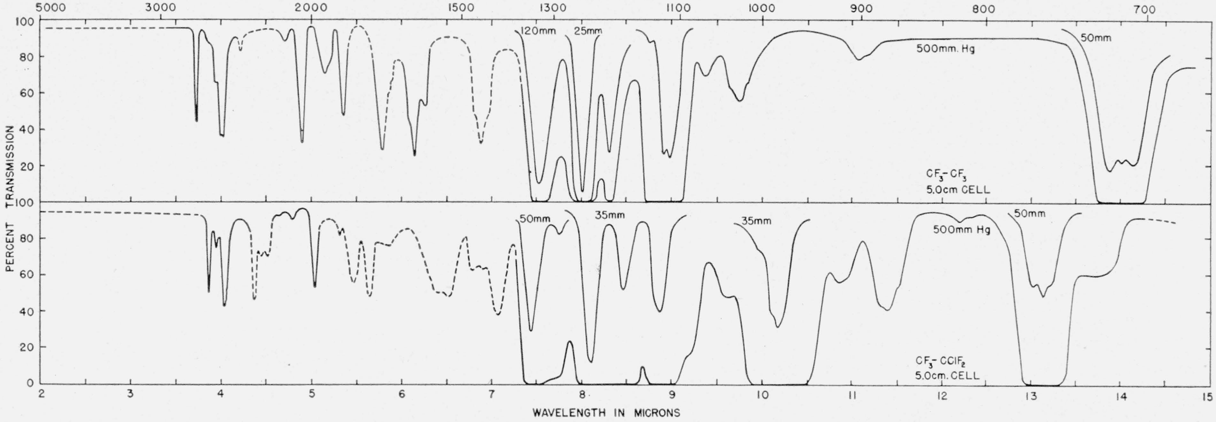

FIGURE 1. *Infrared absorption spectra of hexafluoroethane and chloropentafluoroethane in the gaseous state from 2 to 15 μ.*

The detector used for the regions observed with the lithium fluoride, sodium chloride, and potassium bromide prisms was a vacuum thermocouple with potassium bromide windows. In order to detect the weak radiation in the thallium bromide-iodide region, a Golay detector was used with a window and a lens of thallium bromide-iodide to focus the energy on the receiver. In both cases the signal from the receiver was amplified and recorded automatically.

For the recording of the absorption spectra in the region beyond 15 μ the technique described by Plyler [4, 5] was followed.

III. Experimental Results

In figures 1 and 2 are shown the plots of the percentage transmission of hexafluoroethane and chloropentafluoroethane as function of the wavelength. Figure 1 shows the short wavelength region for the two substances, and figure 2 the long wavelength region. The dotted parts correspond to regions in which absorptions of water vapor and carbon dioxide appear in the background energy, and the spectra in these regions have been established with the help of the recording spectrophotometer of Baird Associates, which cancels out the atmospheric bands.

In table 1 are shown the results for hexafluoroethane, first in brackets the intensities, then the frequencies observed, and in the next column, the values for the *P*, *Q*, and *R* branches when observed. The intensity scale is represented by numbers that are proportional to $\log_e I_0/I$. The bands that show no transmission with a given quantity of gas are assigned the intensity 10, and the intensity number of the weaker bands are relative to this band, except that (0,0) refers to bands that have between 2- and 5-percent absorption and (0,0,0) to bands of 2 percent or less of absorption.

The experimental results obtained by observing the infrared absorption spectra of hexafluoroethane in the present work show slight variations from those reported by Nielsen, et al. [1].

The intensities of the absorption bands depend on the cell length and the pressure of the gas. Except for small changes in the transmission pro-

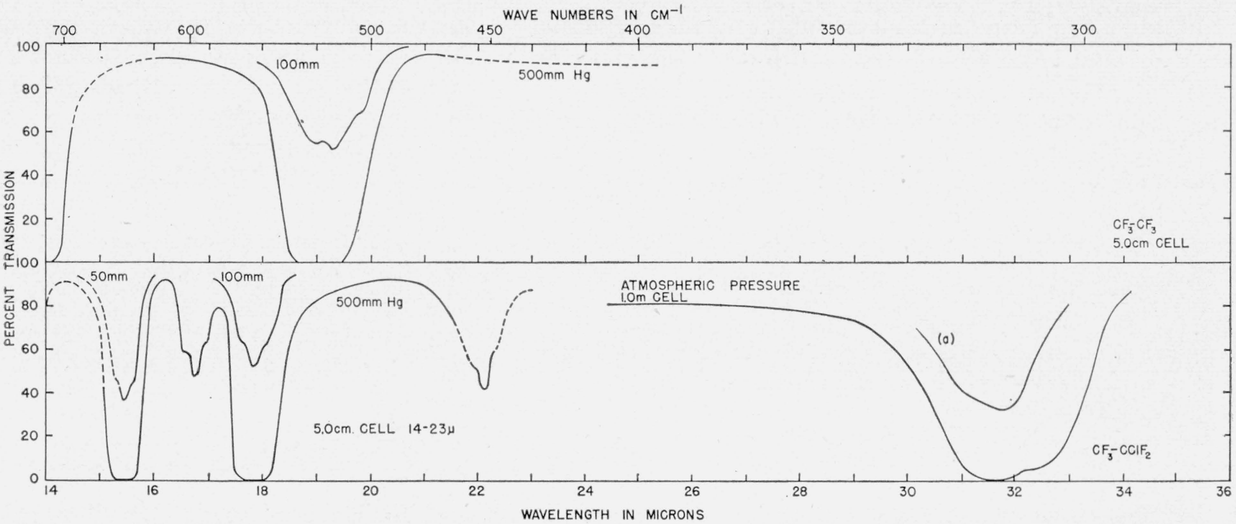

FIGURE 2. *Infrared absorption spectra of hexafluoroethane and of chloropentafluoroethane in the gaseous state from 15 to 36 μ.*

The chloropentafluoroethane insert (a) at 32 μ was observed by use of a 1-m cell with a partial pressure such that the transmittance was approximately 35 percent.

TABLE 1. *Wave numbers and relative intensities of the observed bands of hexafluoroethane*

Intensity	Observed bands		Intensity	Observed bands	
	Center	Branches		Center	Branches
	cm^{-1}	*cm*$^{-1}$		*cm*$^{-1}$	*cm*$^{-1}$
[5]	518	505	[10]	1, 247	--------
		518	[6]	1, 324	--------
		526	[3]	(1, 453)	--------
[8]	714	707	[2]	1, 595	--------
		714	[3]	1, 626	--------
		720	[3]	1, 727	--------
[0]	896	895	[2]	1, 866	--------
		903	[1]	1, 938	--------
[2]	1, 025	--------	[3]	2, 041	--------
[1]	1, 065	1, 063	[00]	2, 115	--------
		1, 067	[3]	2, 483	2, 475
[8]	1, 117	1, 112			2, 493
		1, 121	[1]	2, 534	--------
[00]	1, 142	--------	[3]	2, 667	--------
[6]	1, 203	--------			

duced by pressure alone when the number of molecules in the path of the radiant energy is the same, the intensities of the bands are proportional to the total number of molecules in the path. In the work of Nielsen, et al., greater absorption was obtained in the bands because they used a larger quantity of gas in the absorption path for their measurements. This may, in part, account for the differences in experimental results in the region from 10 to 13.5 μ between these two sets of data. In the present work only one band is observed in this region at 894 cm^{-1}, while several small bands are listed in the tables of Nielsen, et al. with values between 750 and 1,000 cm^{-1}.

A scanning of the region from 25 to 40 μ did not reveal any bands of sufficient intensity for detection. The absence in the 25- to 40-μ region of any bands of appreciable intensity supports the assignment of Nielsen that ν_9 is less than 250 cm^{-1}, the value 216 cm^{-1} being used.

The band at 518 cm^{-1} appears to have P, Q, and R branches when it is observed at a pressure of 100 mm Hg (see fig. 2). With larger amounts of gas the structure of the band is not observable, and the region of greatest absorption is at 522 cm^{-1}. The experimental results for this region are not shown by Nielsen, and it is not possible to determine the part of the band that he used in determining the value of 522 cm^{-1}.

The combination band, $\nu_1+\nu_5$, was forecast by Nielsen, et al. but does not appear in his graph of the experimental results. This band is of medium intensity and, as observed in this work, has a transmission of 40 percent at its maximum when the gas is measured with a pressure of 500 mm Hg in the 5-cm cell.

In general the two sets of data correspond closely, and in some bands the results of Nielsen, et al. show better detail. These slight differences in several parts of the spectrum are caused by observations being carried out with different amounts of hexafluoroethane in the cell.

In table 2 the values of the absorption maxima found for chloropentafluoroethane are given; the order of the wave numbers of the bands is the same as in table 1. As this substance had not been previously measured, a comparison with other experimental results is not possible. Neither in table 1 nor in table 2 are given those lateral branches not completely resolved.

TABLE 2. *Wave numbers and relative intensities of the observed bands of chloropentafluoroethane*

Intensity	Observed bands		Intensity	Observed bands		Intensity	γ
	Center	Branches		Center	Branches		
	cm^{-1}	*cm*$^{-1}$		*cm*$^{-1}$	*cm*$^{-1}$		*cm*$^{-1}$
[4]	314	-------	[6]	982	-------	[2]	(1, 828)
[3]	452	-------	[2]	1, 044	-------	[1]	(1, 883)
[5]	560	-------	[6]	1, 129	-------	[2]	1, 984
[3]	596	-------	[8]	1, 182	-------	[00]	2, 096
[8]	647	-------	[10]	1, 233	-------	[000]	2, 151
[2]	372	-------	[4]	1, 290	-------	[1]	(2, 212)
[8]	762	756 762 768	[7]	1, 346	-------	[1]	2, 252
			[2]	1, 414	-------	[2]	2, 309
[00]	808	-------	[1]	(1, 453)	-------	[2]	2, 476
[0]	820	-------	[1]	1, 473	-------	[1]	2, 531
[3]	876	868 876 884	[4]	1, 553	1, 536 1, 567	[2]	2, 591
			[00]	(1, 709)	-------	--------	-------
[2]	922	-------	[2]	(1, 776)	-------	--------	-------

IV. Discussion

1. Hexafluoroethane

The substances of this type admit two possible configurations, the alternate one with the symmetry model D_{3d} and the eclipsed one with the model D_{3h}. Nielsen, et al. [1], after a detailed discussion, preferred the alternate form, which is in accordance with the hypothesis of D. T. Hamilton and F. F. Cleveland [6] for the case of hexafluoroethane. Their analysis was made from the study of the Raman spectra.

Adopting this hypothesis, and taking into consideration the Raman data given by Rank and Pace [2], the fundamental vibrations will be those that are indicated in table 3, in which are shown the term, the wave number (cm^{-1}), the activity, and the group from which they originate.

The values given, as far as the frequencies active in the infrared are concerned, differ only from those by Nielsen, et al. [1] by a very few units for the frequencies ν_7 and ν_8. On the other hand the frequency ν_9 must be less than 250 cm^{-1}. In Nielsen's work it is supposed to be 216 cm^{-1}, and with this value concordant, numbers for the combination bands can be obtained. The region of low frequencies was examined and no absorption maximum was found, thus giving the impression that any possible absorption band must be in a region of an even lower frequency in accordance with the assumption by Nielsen, et al.

TABLE 3. *Fundamental bands of hexafluoroethane with listing of band designation, activity, wave number, and type of vibration*

Term	ν	Activity	Type of vibration	Term	ν	Activity	Type of vibration
	cm^{-1}				*cm*$^{-1}$		
ν_1	1, 420	R	ν_{CF}	ν_7	1, 247	I	ν_{CF}
ν_2	809	R	ν_{CC}	ν_8	518	I	δ_{FCF}
ν_3	349	R	δ_{FCF}	ν_9	(216)	I	δ_{CCF}
ν_4	-----	Inactive	Twist	ν_{10}	1, 237	R	ν_{CF}
ν_5	1, 117	I	ν_{CF}	ν_{11}	620	R	δ_{FCF}
ν_6	714	I	δ_{FCF}	ν_{12}	380	R	δ_{CCF}

Considering the data obtained here, the present interpretation of the nonfundamental frequencies as combination tones has been made following the indications of Nielsen, et al. [1], and the differences between the observed and calculated values are of the same order as those of the authors mentioned, except in two cases where these values were a little larger. The combination tone corresponding to $\nu_1+\nu_5$, forecast but not found by these authors, is observed with the lithium fluoride prism at 2,534 cm^{-1}. These observed and calculated frequencies are to be found in table 4.

TABLE 4. *Observed and calculated wave numbers of the combination bands of hexafluoroethane*

ν (observed)	Term	ν (calculated)	ν (observed)	Term	ν (calculated)
cm^{-1}		*cm*$^{-1}$	*cm*$^{-1}$		*cm*$^{-1}$
896	$\nu_1-\nu_8$	902	1, 727	$\nu_5+\nu_{11}$	1, 737
1, 025	$\nu_2+\nu_9$	1, 025	1, 866	$\nu_7+\nu_{11}$	1, 867
1, 065	$\nu_3+\nu_6$	1, 063	1, 938	$\nu_1+\nu_8$	1, 938
1, 142	$\nu_8+\nu_{11}$	1, 138	2, 041	$\nu_2+\nu_7$	2, 056
1, 203	$\nu_1-\nu_9$	1, 204	2, 115	$\nu_1+\nu_6$	2, 134
1, 324	$\nu_2+\nu_8$	1, 327	2, 483	$\nu_7+\nu_{10}$	2, 484
1, 453	$\nu_9+\nu_{10}$	1, 453	2, 534	$\nu_1+\nu_5$	2, 537
1, 595	$\nu_3+\nu_7$	1, 596	2, 667	$\nu_1+\nu_7$	2, 667
1, 626	$\nu_7+\nu_{12}$	1, 627	-----	-----	-----

2. Chloropentafluoroethane

The presence of the chlorine atom destroys the symmetry, which permits the eighteen fundamental modes of vibration, all active in the infrared, to appear. Unfortunately, some frequencies are predicted to be so low that they are not in the region studied, which extends to 250 cm^{-1}. Others, which were supposed to be in the region of lowest frequencies studied, have not appeared as can be seen in the curve. The region from 25 to 40 μ shows only one absorption maximum where five were supposed to be.

With the data obtained, 11 of the 18 fundamental frequencies, which are indicated in table 5, have been established. To assign the fundamental bands, the intensities and the regions in which they appear were taken into consideration. To classify them, bringing them in relation with hexafluoroethane, "prime" frequencies have been introduced where the double degenerates of hexafluoroethane give way to two different frequencies in the chloropentafluoroethane. In table 5 the term, the value of the frequency if found, and the group from which it originates, are indicated.

TABLE 5. *Fundamental bands of chloropentafluoroethane with listing of band designation, activity, wave number, and type of vibration*

Term	ν	Type of vibration	Term	ν	Type of vibration
	cm^{-1}			*cm*$^{-1}$	
ν_1	1, 346	ν_{CF}	ν_9	-----	δ_{CCF}
ν_2	762	ν_{CC}	ν'_9	-----	δ_{CCCl}
ν_3	314	δ_{FCF}	ν_{10}	1, 182	ν_{CF}
ν_4	-----	Twist	ν'_{10}	647	ν_{CCl}
ν_5	982	ν_{CF}	ν_{11}	-----	δ_{FCCl}
ν_6	596	δ_{FCF}	ν'_{11}	560	δ_{FCF}
ν_7	1, 129	ν_{CF}	ν_{12}	-----	δ_{CCF}
ν'_7	1, 233	ν_{CF}	ν'_{12}	-----	δ_{CCF}
ν_8	-----	δ_{FCCl}			
ν'_8	452	δ_{FCF}			

Although only a few of the fundamental frequencies are known, the remaining bands can be explained as harmonic or combination tones, with the exception of the three with lowest wave numbers. For these, surely the lowest fundamental frequencies, which have not been found, must be taken into consideration. These are given in table 6.

TABLE 6. *Observed and calculated wave numbers of the combination and overtone bands of chloropentafluoroethane*

ν (observed)	Term	ν (calculated)	ν (observed)	Term	ν (calculated)
cm^{-1}		*cm*$^{-1}$			
732	-----------	---------	1, 776	$\nu'_{10}+\nu_7$	1, 776
808	-----------	---------	1, 828	$\nu'_{10}+\nu_{10}$	1, 829
820	-----------	---------	1, 883	$\nu_2+\nu_7$	1, 891
876	$\nu'_{11}+\nu_3$	874	1, 984	$\nu_2+\nu'_7$	1, 995
922	$\nu_6+\nu_3$	910	2, 096	$\nu_2+\nu_1$	2, 108
1, 044	$\nu'_8+\nu_6$	1, 048	2, 155	$\nu_5+\nu_{10}$	2, 164
1, 290	$2\nu'_{10}$	1, 294	2, 212	$\nu_5+\nu'_7$	2, 215
1, 414	$\nu'_{10}+\nu_2$	1, 409	2, 252	$2\nu_7$	2, 258
1, 453	$\nu_3+\nu_7$	1, 443	2, 309	$\nu_7+\nu_{10}$	2, 311
1, 553	$\nu'_{11}+\nu_5$	1, 542	2, 476	$\nu_7+\nu_1$	2, 475
1, 709	$\nu_6+\nu_7$	1, 725	2, 531	$\nu_{10}+\nu_1$	2, 528
			2, 591	$\nu'_7+\nu_1$	2, 579

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