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VIBRATIONAL SPECTRA OF HEXAFLUOROBUTADIENE-1,3 AND 1-FLUORO-1-CHLOROETHYLENE

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VIBRATIONAL SPECTRA OF HEXAFLUOROBUTADIENE-1,3
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TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF ILLUSTRATIONS

VIBRATIONAL SPECTRA OF HEXAFLUOROBUTADIENE-1,3 AND 1-FLUORO-1-CHLOROETHYLENE

CHAPTER I

INTRODUCTION

Infrared and Raman spectroscopy provide valuable information in several fields of molecular physics and chemistry. One of the best known applications of infrared spectroscopy is in the field of chemical analysis. A comparison of the infrared spectrum of a substance with reference spectra of probable components will yield considerable information on the composition of the substance. If the substance contains an unknown compound for which no reference spectrum is available, a study of the absorption bands attributed to the compound will frequently yield suggestions regarding possible molecular structure.

While Raman spectroscopy is not yet used very much for chemical analysis, it is an important supplement to infrared spectroscopy in determining fundamental vibrational frequencies of molecules. If the spectra are not too complex, a comparison of observed infrared and Raman bands with the known fundamentals of related compounds will give all or most of the fundamentals of the compound under study. An analysis of overtones and combinations will frequently give any remaining fundamentals. Spectra of the gaseous phase and Raman polarization exposures give information on the symmetry species of many of the observed bands. The molecular configuration can frequently be determined by comparing the observed indications of symmetry species of the infrared and Raman bands with those predicted for various possible configurations.

When all the fundamental vibrational frequencies are known, it is possible to calculate the thermodynamic functions for the compound. A knowledge of fundamental vibrational frequencies, together with a knowledge of molecular geometry, makes possible, in the case of simple molecules and molecules of high symmetry, the determination of the force constants associated with the various chemical bonds.

The increased availability of fluorocarbons and fluorinated hydrocarbons during the past decade has made possible the study of their infrared and Raman spectra. These compounds are of particular interest because fluorine is the most electronegative of the elements, giving the compounds unique chemical and physical properties. At this University and in other laboratories, a considerable amount of research has been performed during the past few years to obtain and interpret infrared and Raman spectra of fluorocarbons and fluorinated hydrocarbons. The research reported in this dissertation is a study of the spectra of two such compounds, hexafluorobutadiene-1,3 and 1-fluoro-1-chloroethylene.

Investigations on the structure of ordinary butadiene-1,3, an important compound in the production of synthetic rubber, have been reviewed by Aston, Szasz, Woolley, and Brickwedde.[1] More recent studies of the molecular spectra have been made by Richards and Nielsen.[2] One of the conclusions of Aston, et al, and of Richards and Nielsen was that the most stable form of CH_2:CH-CH:CH_2 probably has a planar trans configuration. Here, and later in this dissertation, the terms trans and cis, as applied to CH_2:CH-CH:CH_2 and CF_2:CF-CF:CF_2, are used to indicate the relative orientation of the two vinyl groups with respect to the carbon carbon single bond. In the cis configuration, the vinyl groups are located symmetrically with respect to a reflection plane normal to the carbon carbon single bond, whereas in the trans configuration they are located symmetrically with respect to an inversion center at the center of mass. From the work of Aston, et al, the trans form of CH_2:CH-CH:CH_2 appears to be only a little more stable than the cis form. It may be

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[1] Aston, Szasz, Woolley, and Brickwedde, J. Chem. Phys. 14, 67 (1946).

[2] C. M. Richards and J. Rud Nielsen, J.O.S.A. 40, 438 (1950).

expected, therefore, that for CF_2:CF-CF:CF_2 there will not be a very great change in potential energy as the ethylene groups are rotated from the cis form to the trans form. This may be expected to lead to rather indefinite band contours in the infrared, adding to the difficulties of interpretation.

In contrast, the interpretation of the infrared and Raman spectra of CFCl:CH_2 should be comparatively simple. This compound has just half as many fundamental vibrational frequencies, and the infrared contours may be expected to be fairly definite. Previous work includes an infrared spectrum from 3 to 20 microns and a partial interpretation by Thompson and Torkington,[3] and an infrared spectrum from 1.6 to 52 microns and a complete interpretation by Mann, Acquista, and Plyler.[4] This last publication appeared after the completion of the work reported in this dissertation.

A number of related ethylenes have been studied previously. Results from the investigations of the vibrational spectra of ordinary ethylene are summarized by Herzberg.[5] The vibrational spectra of 1,1-difluoroethylene,[6] and tetra-

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[3] P. Torkington and H. W. Thompson, Trans. Faraday Soc. 41, 236 (1945).

[4] Mann, Acquista, and Plyler, J. Chem. Phys. 23, 2122 (1955).

[5] G. Herzberg, Infrared and Raman Spectra (D. Van Nostrand Co., New York, 1945), p. 325.

[6] Smith, Nielsen, and Claassen, J. Chem. Phys. 18, 326 (1950).

fluoroethylene[7] have been reported by Smith, Nielsen, and Claassen. Nielsen, Claassen, and Smith,[8] as well as Torkington and Thompson,[9] have reported results from 1,1-difluoro-2,2-dichloroethylene. Results for fluorotrichloroethylene have been given by Nielsen, Gullikson, and Woollett,[10] and by Mann and Plyler.[11] Mann, Acquista, and Plyler have given results for trifluoroethylene[12] and trifluorochloroethylene.[13] Nielsen, Liang, and Smith[14] have reported results for 1,1-difluoro-2-chloroethylene.

Statement of Problem

The objectives of the research reported in this dissertation were to obtain satisfactory infrared and Raman spectra of $CF_2{:}CF{-}CF{:}CF_2$ and $CFCl{:}CH_2$, to determine the fundamental

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[7] Nielsen, Claassen, and Smith, J. Chem. Phys. 18, 812 (1950).

[8] Nielsen, Claassen, and Smith, J. Chem. Phys. 18, 485 (1950).

[9] P. Torkington and H. W. Thompson, Trans. Faraday Soc. 41, 236 (1945).

[10] Nielsen, Gullikson and Woollett, J. Chem. Phys. 23, 1994 (1955).

[11] D. E. Mann, and E. K. Plyler, J. Chem. Phys. 23, 1989 (1955).

[12] Mann, Acquista, and Plyler, J. Chem. Phys. 22, 1586 (1954).

[13] Mann, Acquista, and Plyler, J. Chem. Phys. 21, 1949 (1953).

[14] Nielsen, Liang, and Smith, J. Chem. Phys. 20, 1090 (1952).

vibrational frequencies and their symmetry species for these compounds, to give a complete interpretation for the spectra on the basis of these fundamentals, and to determine the molecular configuration of CF_2:CF-CF:CF_2.

CHAPTER II

APPARATUS

Infrared

The infrared spectra were obtained with a Perkin-Elmer model 112 infrared spectrometer. This instrument consists of three units, a source unit, a monochromator, and a detection, amplification, and recording system.

The source unit includes a water cooled globar source, and mirrors to focus the source through the sample cell onto the entrance slit of the monochromator. A metal enclosure protects the mirrors. In the original design of the instrument the radiation enters and leaves this enclosure through windows of suitable material (sodium chloride or KRS-5). This feature has since been modified as will be discussed later.

The monochromator is a double pass unit. It utilizes a prism, in a Littrow arrangement, as the dispersing element. Because of the double pass feature combined with the Littrow arrangement, the radiation passes through the prism four times, giving the instrument better dispersion and better resolution than obtainable with a single pass instrument with a similar prism. The monochromator is also protected by a metal enclosure. In the original design the radiation enters this enclosure through a suitable window located immediately in front of the entrance slit. After passing through the slit the radiation is reflected by a collimating mirror into the prism. The Littrow mirror reflects the radiation back through the prism to the collimating mirror again. Reflection by this mirror brings the beam to a focus near a mechanical chopper operating at thirteen cycles per second. Several small plane mirrors serve to send the beam through the chopper and then back through the collimator-prism-Littrow-prism-collimator system again. This time the collimator focuses the beam via another small plane mirror on the exit slit. After passing through this slit the radiation is reflected by a plane mirror into an eliptical mirror which brings the beam to a focus on the thermocouple.

The spectrum is scanned by rotating the Littrow mirror. For this purpose, a long lever is attached to the Littrow mount. The end of this lever is attached to a block which moves in the screw threads of a shaft. Rotating this shaft results in a much slower rotation of the Littrow mirror. Fifteen to twenty revolutions of this shaft are required to scan the spectral range of the prism. The shaft is connected to a drum on the front of the base of the monochromator. This drum has two scales on it; one indicates the total number of revolutions of the shaft, and the other indicates the fractional part of a single revolution to a hundredth of a revolution. The wave length calibration of the monochromator is in terms of the readings of these scales. The shaft can be rotated either by hand or by a synchronous motor. The latter is always used to record a spectrum. A microswitch operated by a cam on the shaft makes a reference pip mark on the chart for each tenth of a revolution and an extra mark for each revolution.

The chopper causes the intensity of the radiation falling on the thermocouple to alternate with a frequency of thirteen cycles per second. The resulting A.C. signal from the thermocouple is amplified electronically. The A.C. output of the amplifier is rectified by contact points on the chopper assembly. This D.C. signal, which is proportional to the intensity of the radiation, is fed into a Leeds and Northrup recording potentiometer.

A lithium fluoride prism, a sodium chloride prism, and a cesium bromide prism are available for use in this instrument. When used to best advantage they cover the ranges from 2 to 6, from 6 to 14, and from 14 to 36 microns, respectively.

When prisms are changed, the Littrow mirror must be adjusted by means of a small Allen screw located on the base of the Littrow mount. Access to this screw is through a hole in the monochromator cover. This hole is normally plugged by a cork. The screw must be turned about 7.08 turns in a clockwise direction when changing from the NaCl prism to the CsBr prism. It must be turned about 3.55 turns in a counterclockwise direction when changing from the NaCl prism to the LiF prism. The final adjustment with each prism is made by setting some known sharp band to peak at the scale reading given by the calibration curves. Convenient bands to use are the NH_3 band at 3335.1 cm^{-1} with the LiF prism, one or more of the H_2O bands in the 1650 cm^{-1} region with the NaCl prism, and the CO_2 band at 668 cm^{-1} with the CsBr prism.

At the time a study of the spectra reported in the present work was undertaken, the instrument had been calibrated with the NaCl prism only. To calibrate the instrument for use with each of the other two prisms, spectra were taken of compounds with well-known bands. Atmospheric water vapor and carbon dioxide were used with the CsBr prism. Atmospheric water vapor and carbon dioxide, ammonia vapor, methane, hydrogen chloride vapor, hydrogen bromide vapor, and carbon monoxide were used with the LiF prism. The NH_3 vapor and the CH_4 were obtained from commercial cylinders. The HCl vapor was simply the vapor from aqueous hydrochloric acid. The HBr vapor was obtained by removing water from aqueous hydrobromic acid at low pressure with phosphorus pentoxide. The CO was obtained from the exhaust of a gasoline engine.

Several minor modifications have been made on the original instrument. A brass piece was machined to enclose the space between the globar and the source unit. This made it possible to remove the entrance window to the source unit and thus make the radiation path from the globar through the source unit relatively free of H_2O vapor and CO_2. A Plexiglas box was constructed to provide an enclosure between the source unit cover and the monochromator unit cover. When this box is in place, the exit window in the source unit cover, and the entrance window in the monochromator unit cover can be removed. The top and back of the box are removable to facilitate placing and removing sample cells. The box works best with cells for liquids. It can also be used with cells for gases up to 12 cm overall length. When a cell for gases is used, the inlet tube is brought into the box through a tight-fitting hole in the top. With this box in place, the entire path of the radiation from the globar to the thermocouple can be made relatively free of H_2O vapor and CO_2.

To help keep the enclosed region dry, dishes of drying material are placed in the monochromator and the source unit, and in the Plexiglas box when it is used. In addition, when spectra are being taken these spaces are flushed with oil-pumped dry nitrogen obtained from a commercial cylinder. The N_2 is admitted to the monochromator and source unit through holes provided for that purpose. It leaves through various leaks in these units. By passing about 1400 cc/min of N_2, the H_2O vapor can be reduced to a point where it is not objectionable, and the CO_2 can be reduced to a point where it is not detectable. The N_2 flow should be started several hours before the spectra are taken.

Only gaseous samples were studied in the present work. Three different cells were used to obtain the spectra. For use in the NaCl and LiF regions, a cell with NaCl windows was available. This cell consisted of a glass tube of about 40 mm diameter with the windows cemented to the ends. The gas was admitted to the cell by way of a small glass tube (about 8 mm) sealed to the side of the larger tube.

For use in all regions, a cell with KRS-5 (44% TlBr, 56% TlI) windows was constructed. This cell also consisted of glass tubing with the windows sealed to the ends. However for this cell, the size of the largest KRS-5 window available limited the size of the glass tubing to a diameter of about 35 mm. This window was used as the entrance window. The length of this cell was limited to 5.5 cm in order to make certain that the entrance window intersected all of the entrance cone of the monochromator. The exit window of the cell was smaller, and therefore the glass tubing had a taper near the small window. As in the case of the larger cell, the gas was admitted through a small glass tube sealed to the side of the large tube.

The third cell used is a Perkin Elmer one meter cell. This cell has a metal housing with KRS-5 windows. Inside are mirrors which reflect the radiation so that it traverses the length of the cell four times. This gives a one meter effective cell length in a relatively small cell.

For a given wavelength setting of the monochromator the signal which reaches the recorder is a function of a number of variables including: the output of the globar, the absorption and reflection by the windows and prism, the absorption by the sample, the absorption by the atmosphere along the path of the radiation, the slit width, the sensitivity of the thermocouple, and the gain of the amplifier. Several of these are dependent on the wavelength. Thus to determine the fraction of the energy absorbed by the sample it is necessary to obtain spectra both with and without the sample in the beam. The curve produced by the recorder without the sample in the beam is called the I_o curve. The same cell which is used for the sample, or a blank cell with very similar windows should be in place in the beam when the I_o curve is obtained. For gases the same cell can be used by evacuating it. After the I_o curve is obtained the sample is placed in the cell and another record is taken. It is convenient to turn the chart paper back so that this second curve is in alignment with the I_o curve. The percent transmission at any wavelength can be determined by taking the percent that the curve obtained with the sample in place is of the I_o curve at the wavelength in question.

The final results of infrared work on a compound are usually given in graphs of percent transmission vs wavelength, and in tables giving the wave numbers of the absorption peaks.

Raman

The Raman spectrograph used to obtain the spectra of liquid and crystalline samples has been described by Claassen.[1] It is a three prism instrument with a linear dispersion of 15 A/mm at 4358 A, now manufactured by the Applied Research Laboratories.

The irradiation apparatus used with liquid and crystalline samples has been described by Jackson.[2] A cross-section of this apparatus is shown in Figure 1. The source is a hairpin type mercury lamp which is normally operated at about 10 amperes. The filter is a glass tube filled with one fourth saturated sodium nitrite solution which effectively filters out radiation of wavelength less than 4300 A. This filter also serves as a cylindric lens to focus the radiation from the lamp onto the Raman tube. The 45° inclination of the plane of the lamp, filter, and Raman tube as shown in Figure 1 facilitates obtaining polarization data from a single exposure.

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[1] H. H. Claassen, Raman Spectra of Some Fluorinated Hydrocarbons, Ph.D. Thesis, University of Oklahoma, (1949) pp. 6-7.

[2] J. A. Jackson, Vibrational Spectra of Lead Alkyls, Ph.D. Thesis, University of Oklahoma, (1955) pp. 7-11.

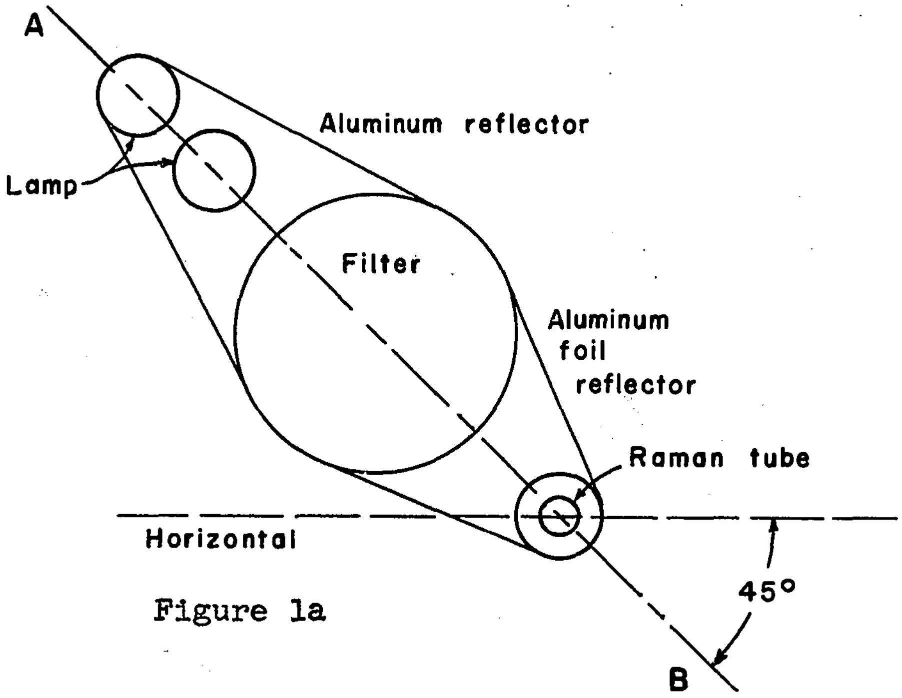

Figure 1a

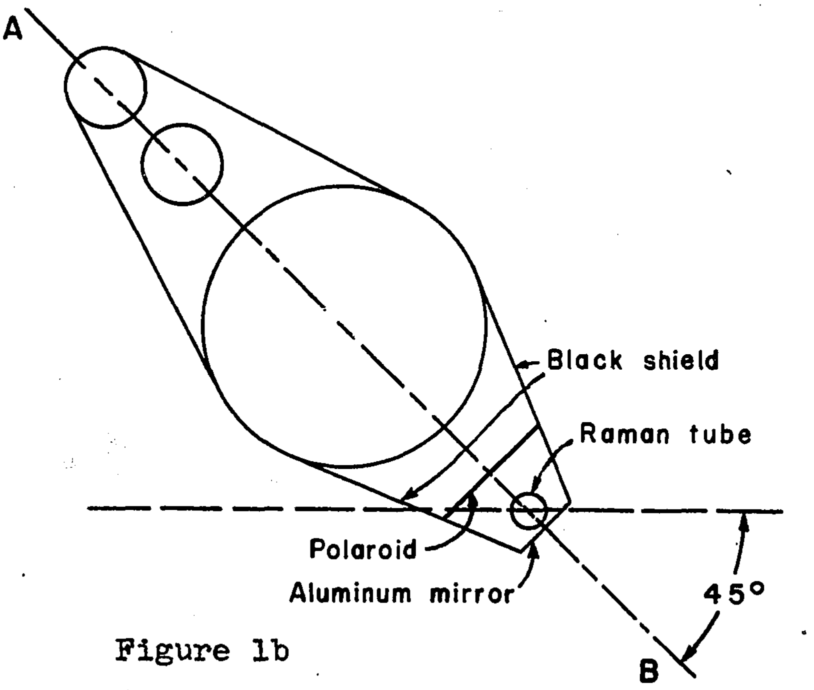

Figure 1b

Figure 1. Cross Section of Raman irradiation apparatus as used for ordinary exposures (a), and polarization exposures (b).

The spectrograph used to obtain the spectra of gases is the same make and model as that used for liquid and crystalline samples. The irradiation apparatus is of a type devised by H. L. Welsh[3] of the University of Toronto and will be described in a forthcoming Ph.D thesis by C. W. Gullikson. The source consists of two water-cooled mercury lamps which are normally operated at about 20 amperes each. The Raman tube is located between the lamps. It contains split spherical mirrors at each end which greatly increased the sample volume seen by the spectrograph. The lamps and Raman tube are surrounded by a box which has been painted with a white diffuse reflecting material. A filter jacket can be placed around the Raman tube and filled with saturated sodium nitrite solution to greatly reduce the intensity of mercury lines of wavelength less than 4300 A.

Before polarization exposures of the liquid were attempted, a check was made of the relative speed of two sets of irradiation apparatus. The first set uses the same irradiation arrangment as was used for ordinary exposures of liquids. The aluminum foil reflector around the Raman tube is removed, and a plane aluminum mirror is placed next to the Raman tube as shown in Figure 1b. A polaroid sheet that transmits the component of the electric vector normal to the

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[3] Welsh, Cumming, and Stansbury, J.O.S.A. 41, 712 (1951).

axis of the Raman tube is inserted between the filter and the Raman tube. The upper half of the spectrograph slit is covered by a polaroid which transmits the component of the elctric vector parallel to plane AB, while the lower half of the slit is covered by a polaroid which transmits the component of the electric vector normal to plane AB. The ratio of the intensity through the upper half of the slit to the intensity through the lower half of the slit should be 0.75 for non-totally symmetric bands and between 0 and 0.75 for totally symmetric bands.

The second set of polarization apparatus is similar to one described by Crawford and Horwitz.[4] The exciting light is collimated so as to enter the Raman tube in a direction nearly normal to its axis and therefore to the direction of observation. Two equal exposures are required. The exciting light is polarized in both exposures, but the direction of polarization is different. In the first exposure, the electric vector is parallel to the axis of the Raman tube while in the second it is normal to the axis. The ratio of a Raman band's intensity in the first exposure to its intensity in the second should be 6/7 for non-totally symmetric bands and between 0 and 6/7 for totally symmetric bands.

Test exposures with each set of apparatus using carbon tetrachloride showed that the second (two exposure) method

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[4] B. L. Crawford and W. Horwitz, J. Chem. Phys. 15, 268 (1947).

was about six times faster than the first (one exposure) method with respect to total exposure time. The Raman bands on a pair of 40 minute exposures with the second apparatus were of about the same density as the corresponding bands on an 8 hour exposure with the first apparatus. On the basis of this test, the second set of apparatus was chosen to make polarization exposures of CF_2:CF-CF:CF_2.

CHAPTER III

EXPERIMENTAL PROCEDURES

The infrared spectra of hexafluorobutadiene-1,3 and 1-fluoro-1-chloroethylene were obtained in the gaseous phase at room temperature over the region from 2.5 to 37 microns. The Raman spectrum was obtained of $CF_2:CF\text{-}CF:CF_2$ in the liquid phase at 20° C and -120° C. Weakly exposed Raman spectra were obtained of the crystalline phase at -160° C and of the gaseous phase at room temperature. The Raman spectrum of gaseous $CFCl:CH_2$ was obtained at room temperature.

The procedures for handling the samples and for obtaining the spectra are given in the following two sections.

Hexafluorobutadiene-1,3

Hexafluorobutadiene-1,3 has a normal boiling point of 5.8° C and a freezing point of -130° C.[1] Approximately 28 grams of this compound were received in a metal cylinder from the Naval Research Laboratory where it had been assigned serial number 503. It had been prepared by the M. W. Kellogg

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[1] W. T. Miller, Jr., Preparation of Fluorocarbons by Polymerization of Olefins. National Nuclear Energy Series Div. VII, 1, pp. 567-685 (Chem. Abstracts 46, 7988g, 1952).

Company. This sample was used for all the studies on this compound with the exception of the Raman polarization exposures.

Two infrared cells were used with this compound. An 11.7 cm cell, fitted with NaCl windows, was used in the LiF and NaCl regions, while a 5.5 cm cell fitted with KRS-5 windows was used in the CsBr region.

Both cells were provided with side arms for the purpose of controlling the pressure. After being evacuated they were filled with sample to a pressure of 60 cm of mercury and sealed off. The cell to be used was then placed in the sample area of the spectrometer and a bath of cold acetone was placed around the side arm as shown in Figure 2. The pressure in the cell could then be assumed to be equal to the vapor pressure of the sample at the temperature of the acetone, provided the temperature was low enough for a condensate to form. Dry ice was used to cool the acetone and to maintain the desired temperature. No vapor pressure data were found for CF_2:CF-CF:CF_2, but values were estimated from data on ordinary butadiene-1,3, and related molecules which have boiling points near 6° C.[2] The temperatures which were used when the spectra were obtained, and the corresponding vapor pressures as estimated from these data, are listed in Table 1.

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[2] T. E. Jordan, Vapor Pressure of Organic Compounds, (New York: Interscience Publishers, 1954).

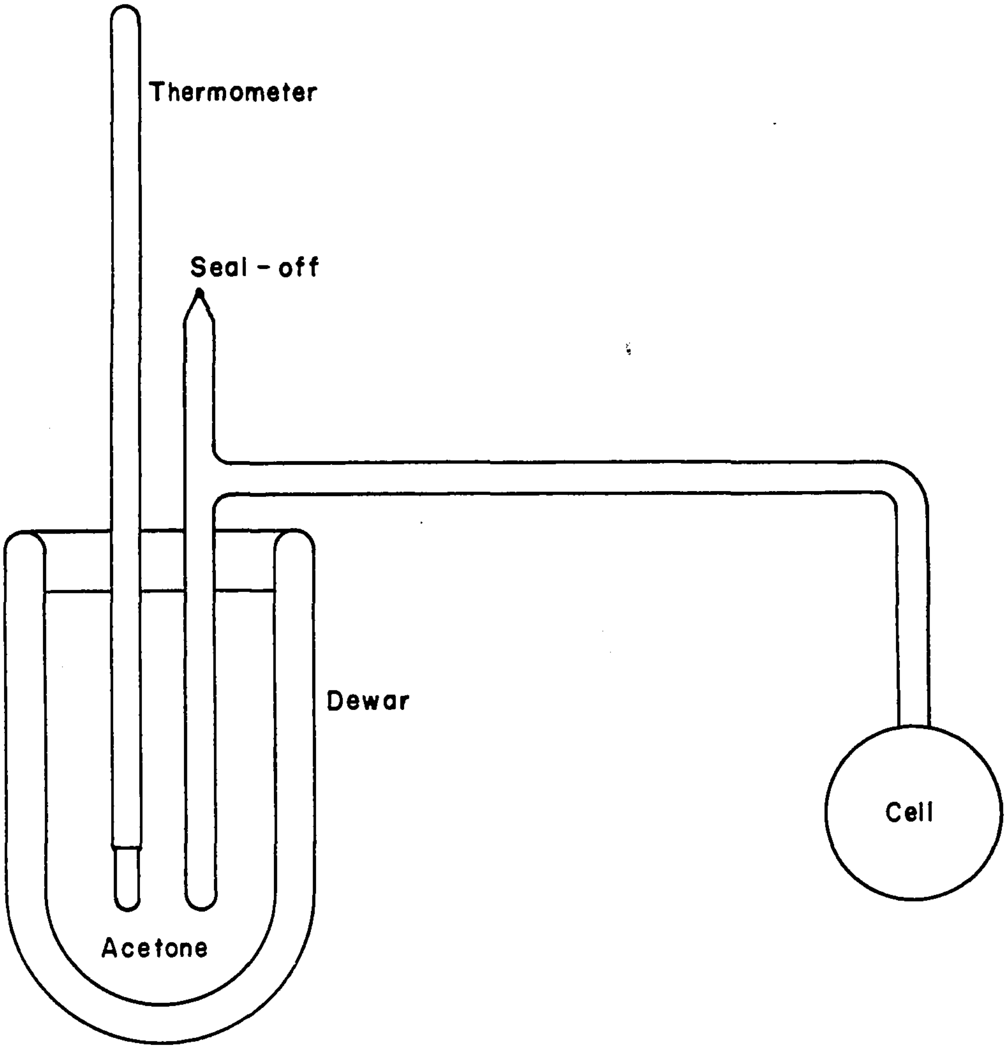

Figure 2. System for adjusting vapor pressure in the infrared gas cell.

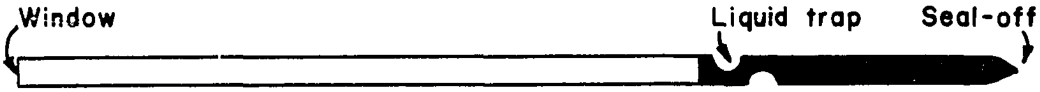

Figure 3. Raman tube used with liquid CF_2:CF-CF:CF_2.

TABLE 1

ACETONE BATH TEMPERATURES AND CORRESPONDING ESTIMATED VAPOR PRESSURES OF CF_2:CF-CF:CF_2

Bath Temperature °C	Estimated pressure cm of Hg
-80	1
-60	4
-41	10
-16.5	30
25 (no condensate)	60

With this method of handling the sample it was not possible to reduce the pressure to zero to obtain a true I_0 curve. The lowest pressure which could be reached with dry ice was about 1 cm of mercury. The record obtained with this pressure was satisfactory as an I_0 curve in all regions except those where the strongest absorption took place. An I_0 curve for most of these regions was obtained by extrapolation. For a few of the regions, however, the atmospheric absorption made it necessary to replace the sample cell with another cell having similar windows.

The 5.5 cm cell was used in the plastic box to reduce atmospheric absorption. The 11.7 cm cell was used prior to the completion of the plastic box. However, the length of this cell was such that only a few millimeters of atmosphere were in the radiation beam when the cell was placed in the sample area.

The Raman tube used for the liquid sample is shown in Figure 3. It was attached to the filling apparatus in a vertical position with the window down. The tube was then evacuated, filled to the liquid trap with sample by low temperature distillation, and sealed off. Unfortunately the vapor volume which was left between the liquid trap and the seal-off was not large enough to accommodate the expansion of the liquid from -80° C, the temperature of the distillation, to much higher than 30° C. It was decided to take the necessary precautions to keep the temperature below 30° C rather than risk contamination by opening the tube and adding to its length. For this purpose, a concentric glass tube was placed around the Raman tube in the irradiation apparatus and cold air was passed through the space between the two tubes. The air was obtained from the compressed air line and cooled by passing it through a copper coil immersed in ice water. The temperature of the sample was maintained at about 20° C in this way. Exposures of up to 33 hours were obtained. They are shown in Figure 11 of Chapter IV.

The low temperature apparatus was used as described by Jackson[3] to obtain exposures with the sample just above the freezing point. The Raman tube was placed in a clear vacuum jacket and cold nitrogen was passed around the Raman

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[1] J. A. Jackson, Jr., Vibrational Spectra of Lead Alkyls, Ph.D. Thesis, University of Oklahoma, (1955) pp. 14-15.

tube. The nitrogen was cooled by letting it flow through a copper coil immersed in liquid nitrogen. The temperature was controlled by adjusting the rate of flow of the nitrogen gas. The temperature of the sample was maintained at about -120° C. These exposures are shown in Figure 11 of Chapter IV.

Several attempts were made to crystallize the sample by slowly reducing the temperature below the freezing point. The result was a glass rather than a crystalline phase. On one occasion as this glass was allowed to warm rather rapidly through the freezing point, it started to form small crystals. The sample was immediately cooled again and took on an appearance very similar to a finely powdered snow. An exposure was taken with the sample in this condition, but the background was too high for the exposure to be of any value.

The Raman tube was allowed to come to room temperature, and was then moved slightly in the apparatus so that the sample would be illuminated nearer the window. Thus the Raman scattered light would not have to traverse as much crystalline material before leaving the Raman tube. The unexposed length adjacent to the window was reduced from about two or three millimeters to about one half of a millimeter. The sample was then cooled again below the freezing point and allowed to warm up rapidly through the freezing point. On this occasion the stresses were too great and the joint where the window was sealed onto the tube cracked. Bubbles of nitrogen started coming into the front of the Raman tube. The sample started to crystallize on these bubbles, and soon the entire sample was crystalline. It was maintained in the crystalline form and another exposure was obtained. In this exposure some of the strong Raman bands show up well enough for the exposure (see Figure 11, Chapter IV) to be of some interest. However, in the process it was contaminated with some CO_2 and probably some H_2O.

An attempt was made to obtain the Raman spectrum of the contaminated sample of $CF_2{:}CF\text{-}CF{:}CF_2$ in the gaseous phase. The cylinder was attached to the Raman tube and the system was evacuated to the cylinder valve. This valve was then opened to allow the sample to pass into the Raman tube. The total pressure reached was approximately two thirds of an atmosphere. A three hour exposure showed a very high background with signs of fluorescence.

The sample was removed from the apparatus by placing a bath of dry ice in acetone around the cylinder. The gas which remained in the apparatus was probably very rich in impurities. The Raman tube was evacuated, and the apparatus was checked by placing oxygen in it at one atmosphere pressure and taking a one hour exposure. The results of this exposure indicated that the system was in good alignment and that the mirrors were clean.

The sample was then put back in the apparatus, and a one hour exposure was taken. This time the pressure was about one half of an atmosphere. This one hour exposure showed a much lower background than the earlier three hour exposure. Exposures of 11½ and 76 hours were then taken. The intensities of most of the strong bands of the liquid spectrum are great enough on these exposures to be of assistance in determining their symmetry species. These exposures are shown in Figure 11 in Chapter IV.

After these spectra had been taken, the amount of $CF_2:CF-CF:CF_2$ which remained was not great enough to obtain polarization exposures. An additional sample was received from Professor J. D. Park of the University of Colorado, and polarization exposures were made of the sample in the liquid state at a temperature of about 30° C. A pair of three hour exposures are shown in Figure 11 of Chapter IV. A pair of 24 hour exposures were also made but the sample started to polymerize giving a higher background and weaker Raman bands in the second exposure than in the first. Thus the exposures could not be used for quantitative measurements. However, they provided a qualitative determination of the depolarization ratio of several bands.

1-Fluoro-1-chloroethylene

The sample of 1-fluoro-1-chloroethylene used in the present study was obtained from Peninsular ChemResearch Corporation, whose catalog lists the boiling point as 24° C.

The amount of the sample was about 100 g, and it was contained in a metal cylinder.

Two infrared cells, both with KRS-5 windows, were used for this compound. One was the 5.5 cm cell previously mentioned and the other was the one meter cell. Having KRS-5 windows, these cells were suitable for use over the entire spectral range studied.

In the CsBr region the 5.5 cm cell was used in the same arrangement as was used with CF_2:CF-CF:CF_2 (see Figure 2). The cell was evacuated, filled with sample to a pressure of 60 cm of mercury, and sealed off. The pressure could then be controlled by regulating the temperature of a cold bath around the side arm of the cell. In the case of CFCl:CH_2 only two pressures were used. One was the full 60 cm of mercury to which the cell was filled, and the other was the vapor pressure at -196° C (liquid nitrogen). This latter pressure was about 9 cm mercury. None of the bands showed strong enough absorption at 60 cm of mercury to require running the spectrum at a lower pressure. The curve obtained at the lower pressure was used as an I_o curve, except where the bands due the sample were strong enough to appear. For these regions the I_o curve was obtained by extrapolation. This procedure gave satisfactory results between 15 and 25 microns. Beyond 25 microns no absorption was observed.

This region, from 25 to 37 microns, was therefore ex-

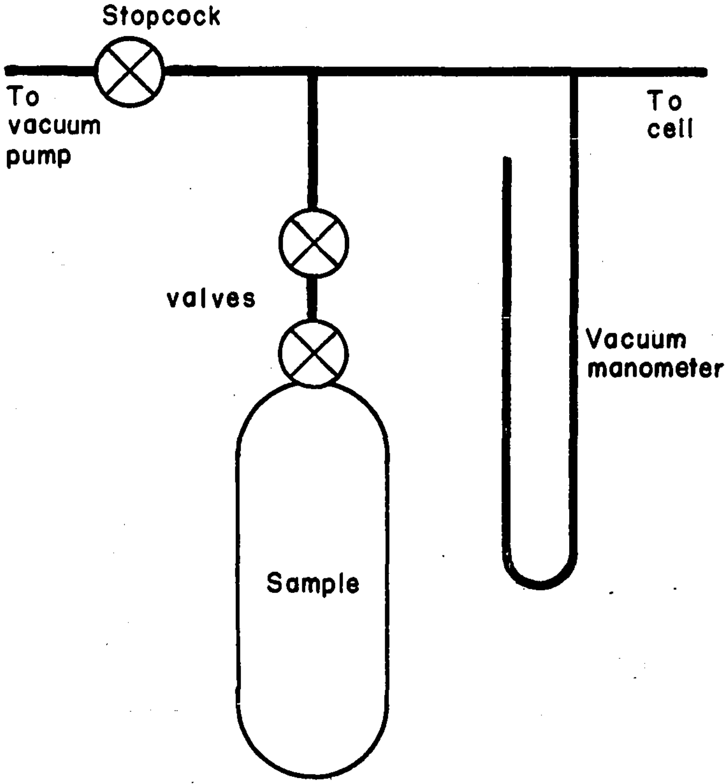


Figure 4. System for letting sample into 1 meter cell.

amined by means of the one-meter cell. A filling system was arranged for this cell which could be used while the cell was in position for taking spectra. Figure 4 shows this system schematically. The system was evacuated, and an I_0 curve was obtained. Then the sample was allowed to enter the cell until the pressure was about 60 cm of mercury. The spectrum was then taken. This curve showed clearly two bands which did not appear with the shorter cell. One of these bands is believed to be caused by an impurity, but the other has been interpreted as one of the fundamentals of $CFCl{:}CH_2$.

Thus, the one meter cell was helpful in obtaining the data necessary for assigning all fundamentals.

In the NaCl region, the 5.5 cm cell was used. However, for this region, the cell was connected to a filling system of the same type as was used with the one meter cell (see Figure 4). The cell was evacuated to obtain an I_0 curve. Then the sample was allowed to enter the cell to a pressure of 5 cm of mercury and a spectrum was run. The pressure was increased to 20 cm of mercury for another run, and to 60 cm for the last run. The last run gave high absorption over the entire range from 6 to 15 microns so that there was no need to use the longer cell.

In the LiF region, the one meter cell was used. The same filling system was used as before. The spectrum was run with the following pressures in the cell: 0 (for an I_0 curve), 0.5, 3.0, and 20 cm of mercury. In addition, a pressure of 0.1 cm of mercury was used for one band which was strongly absorbed at the higher pressures.

The Raman spectrum of $CFCl{:}CH_2$ was obtained in the gaseous phase only. The cell was filled to a pressure of approximately three atmospheres. Exposures of 24½ and 99 hours, shown in Figure 16 in Chapter V were obtained.

When an interpretation of these spectra of $CFCl{:}CH_2$ was attempted, an infrared band of medium intensity with branches at 3330 and 3347 cm^{-1} could not be interpreted as a band of this compound. In an effort to check the possibility that the band might be due to an impurity, this part of the spectrum was run again with the following difference in procedure. The sample was not taken from vapor phase in the top of the cylinder as had been done previously, but was taken from the liquid phase by inverting the cylinder. The cell was filled to 3.0 cm of mercury pressure, and the spectrum was run between about 2900 and 3500 cm^{-1}. The intensity of the band in question was compared in both this and the original spectrum with that of a band with branches at 3062 and 3077 cm^{-1} which is believed to be due primarily to C-H stretching in $CFCl:CH_2$. The results were not conclusive, but indicated that the band in question might result from an impurity with lower boiling point than the sample.

The intensity of this band was as great as that of the band at 3070 cm^{-1}. Thus, if it were due to an impurity, it must be a fundamental of that impurity. Its wave number suggests that the impurity might have a C⁝C-H, an N-H, or an O-H group. The spectra of acetylene, methylacetylene, ammonia, methanol, ethanol, and a number of other common organic compounds were checked in this region. None of them were the observed impurity. The possibility of an O-H or N-H group suggested washing the sample with water to remove the impurity. The apparatus used for this purpose is shown schematically in Figure 5. The system was evacuated, and an I_0 curve was run,

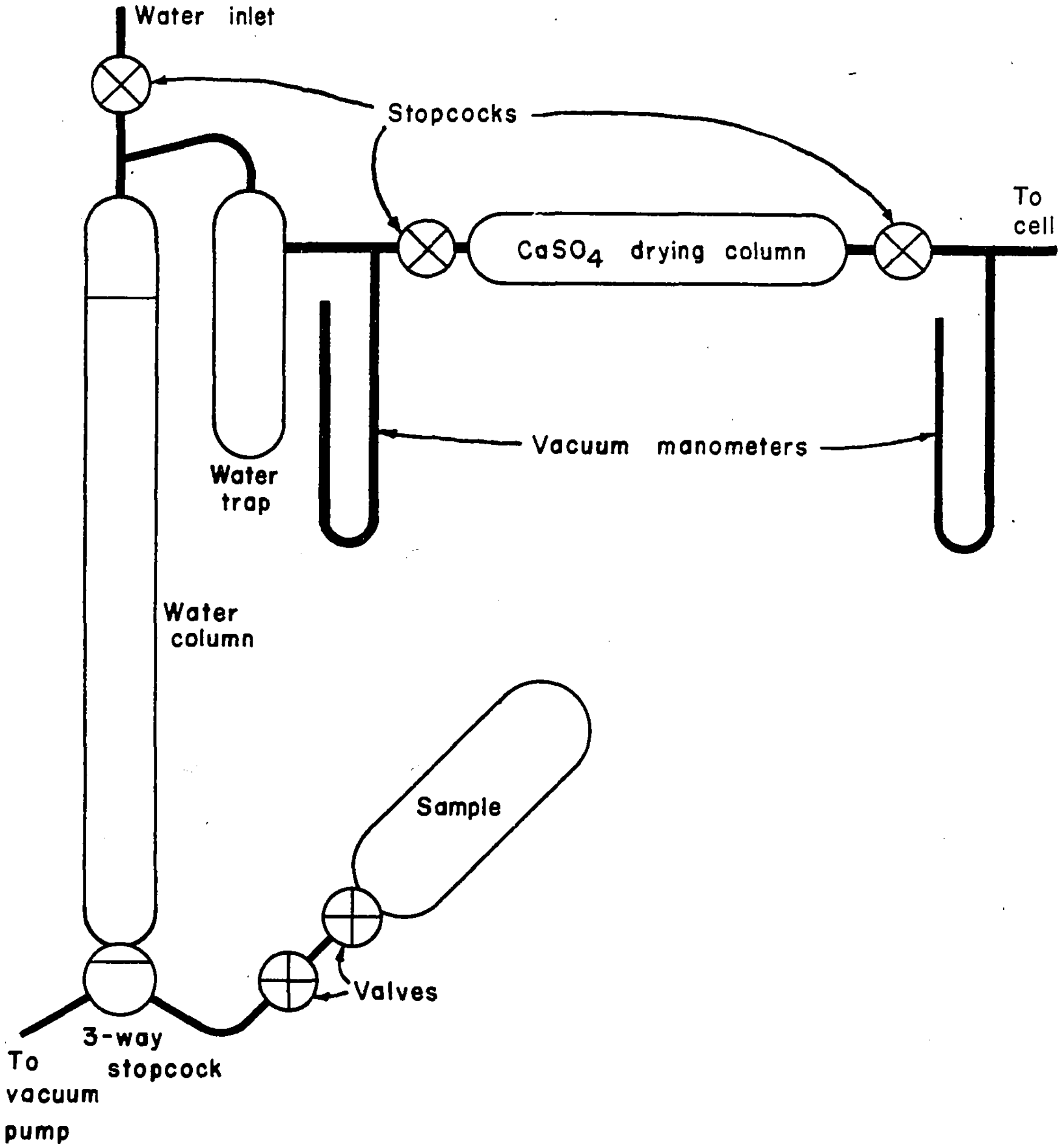


Figure 5. System for washing sample with water.

then air free water was allowed to flow into the washing column. The sample was allowed to bubble slowly through the water, after which it passed through the $CaSO_4$ drying column and into the cell. No noticeable difference in the intensity of the band in question was observed. Attempts to use alumina and magnesol to remove either the impurity or the sample preferentially were equally unsuccessful.

After these attempts to determine whether or not the band in question was due to an impurity, the cylinder containing the sample was sent to the Chemical Engineering Department of this University to be divided into fractions with their low temperature Podbielniak distillation column. The results of this distillation showed a constant boiling point of -27° C, and therefore apparently one compound. However, the first, middle, and last fractions were collected separately. These would correspond to low, intermediate, and high boiling fractions respectively.

A spectrum of the high boiling portion was taken from 2900 to 3500 cm^{-1}. This spectrum showed a more definite reduction in the intensity of the 3340 cm^{-1} band. However, the reduction of intensity was not considered great enough to be conclusive evidence.

Next, a spectrum of the same region was taken of the low boiling fraction. In this spectrum the band at 3340 cm^{-1} showed a very definite increase in intensity, verifying that it was due to an impurity. This increase in intensity corresponded to approximately a two-fold increase in the partial pressure of the impurity. The band at 3070 cm^{-1} showed no measurable decrease in intensity. Since a change of 10% or more in the partial pressure of $CFCl:CH_2$ should give a measurable change in intensity, the partial pressure of the impurity in the original sample was probably not over 10% of the total pressure. The infrared spectrum of this low boiling fraction was studied from 2.5 to 37 microns. The bands which were enhanced in this spectrum are listed in Table 8 of Chapter V.

CHAPTER IV

VIBRATIONAL SPECTRA OF HEXAFLUOROBUTADIENE-1,3

The infrared spectrum of gaseous hexafluorobutadiene-1,3 was obtained in the 2.5 to 6 micron range with the lithium fluoride prism, in the 6 to 14 micron range with the sodium chloride prism, and in the 14 to 36 micron range with the cesium bromide prism. This spectrum is shown in Figures 6, 7, and 8. After this spectrum was obtained an infrared spectrum of this compound in the gaseous phase, shown in Figures 9 and 10, was received from the Naval Research Laboratory. A careful comparison of the two spectra shows general agreement with respect to wave numbers and band contours. In a few regions, the NRL spectrum shows better resolution than that obtained here. In a few other regions the reverse situation exists. Table 2 lists the wave numbers of all the observed infrared bands. A few of the values are taken from the NRL spectrum where its resolution is better.

The Raman spectrum of liquid $CF_2:CF-CF:CF_2$ was obtained at room temperature and -120° C. A weak spectrum of crystalline $CF_2:CF-CF:CF_2$ was obtained at -160° C. A weak spectrum of the gas was obtained at room temperature and a pressure of

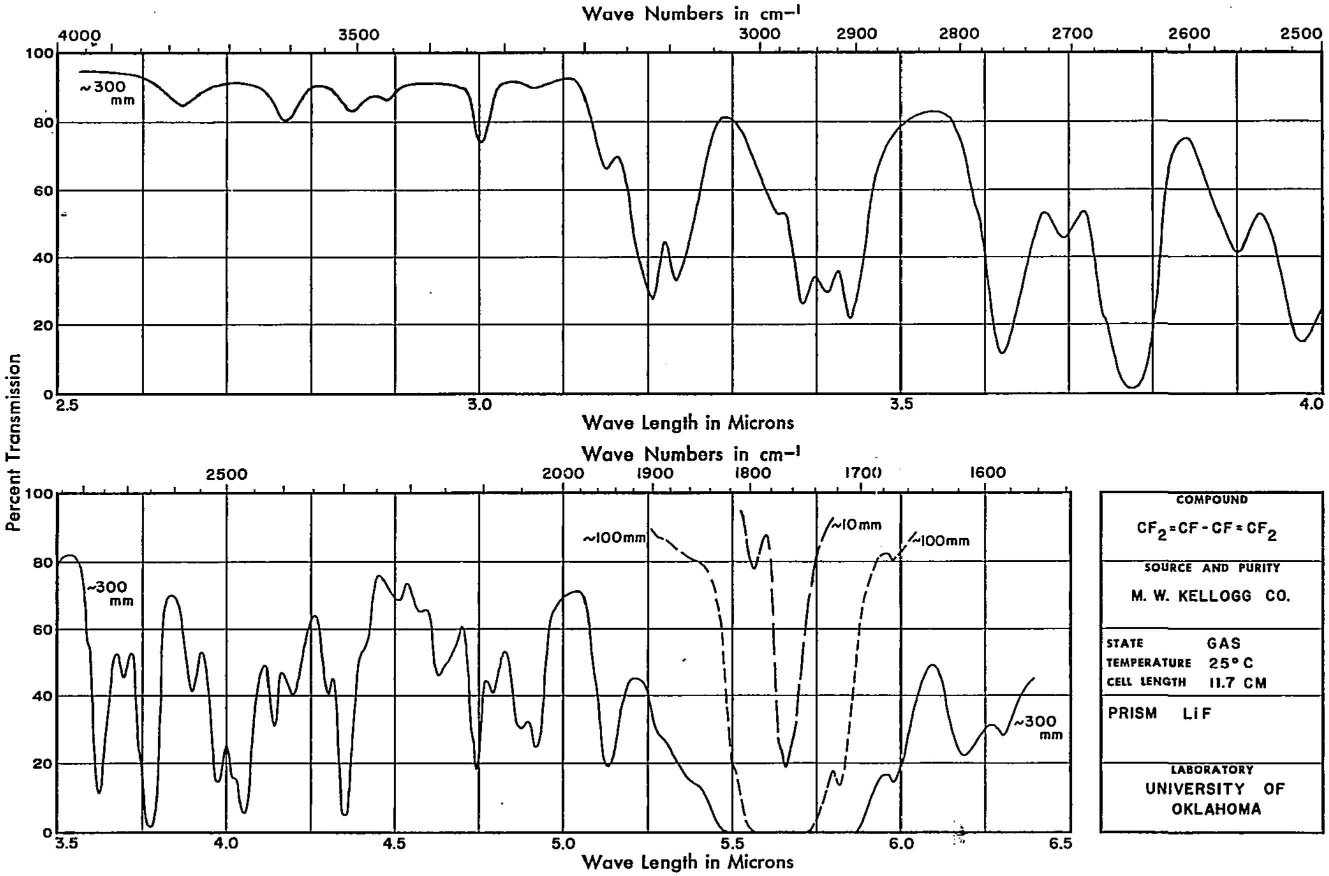


Figure 6. Infrared Spectrum of CF_2:CF-CF:CF_2, LiF Region.

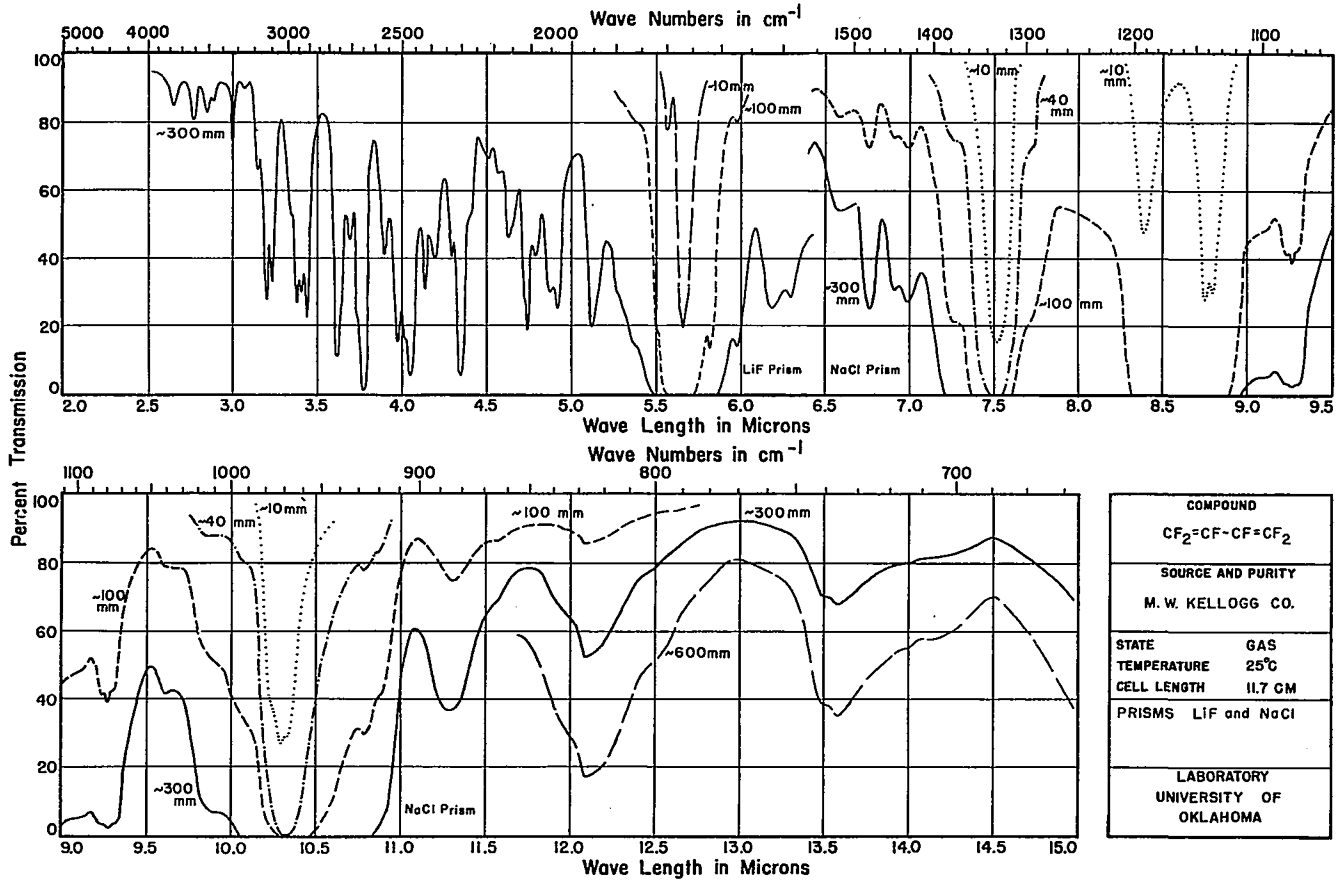


Figure 7. Infrared Spectrum of CF_2:CF-CF:CF_2, NaCl Region.

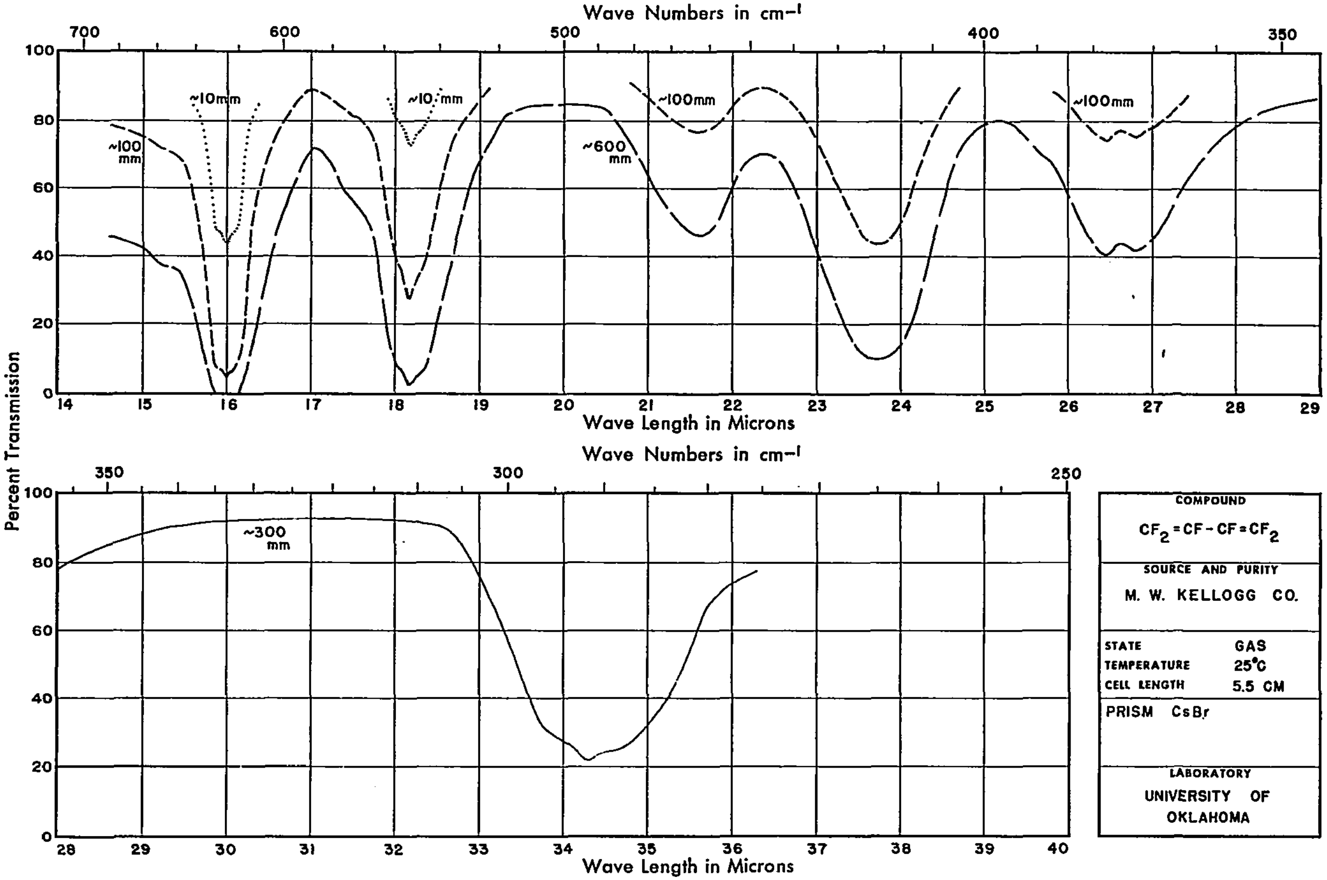
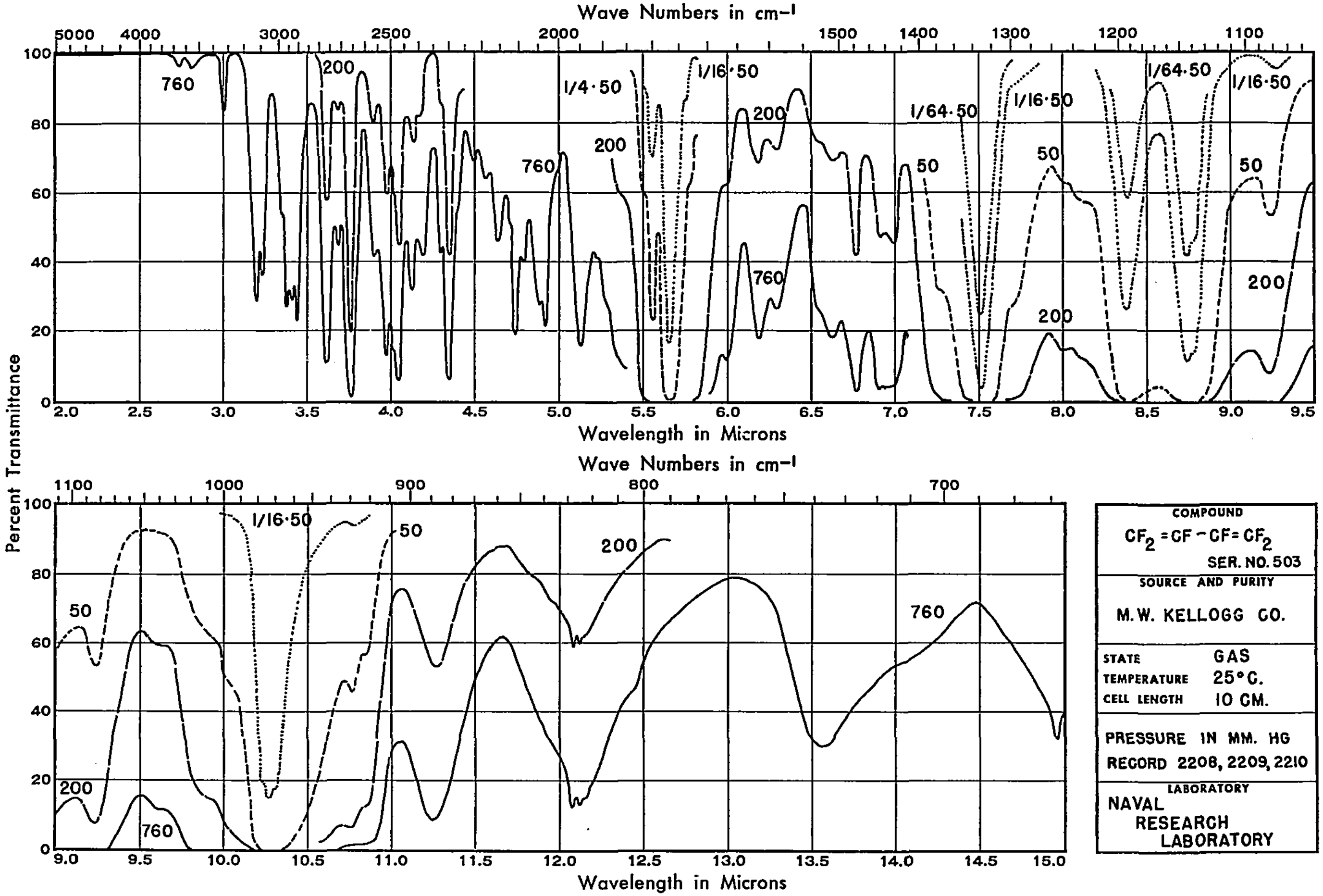


Figure 8. Infrared Spectrum of $CF_2:CF-CF:CF_2$, CsBr Region.



COMPOUND
$CF_2=CF-CF=CF_2$
SER. NO. 503

SOURCE AND PURITY
M. W. KELLOGG CO.

STATE	GAS
TEMPERATURE	25°C.
CELL LENGTH	10 CM.

PRESSURE IN MM. HG
RECORD 2208, 2209, 2210

LABORATORY
NAVAL
RESEARCH
LABORATORY

Figure 9. Naval Research Lab Inrared Spectrum of CF_2:CF-CF:CF_2, NaCl Region.

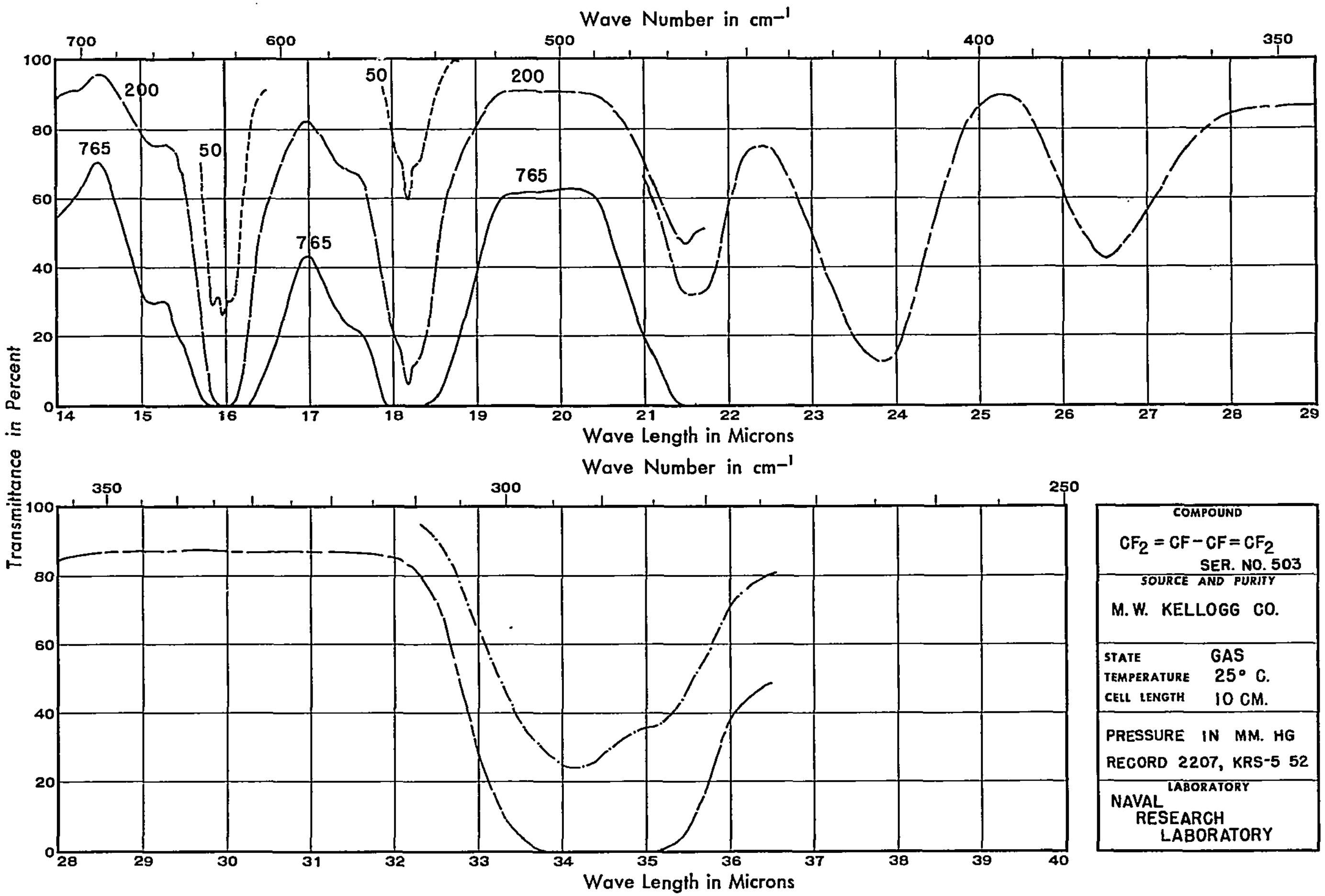


Figure 10. Naval Research Lab Infrared Spectrum of CF_2:CF-CF:CF_2, CsBr Region.

approximately one third of an atmosphere. Polarization exposures were made of the liquid phase at room temperature. These spectra are shown in Figure 11. In the spectrum of the liquid many of the bands are much sharper at low temperature than at room temperature. For this reason the wave numbers for the liquid phase listed in Table 3 are taken from exposures obtained at low temperature.

From the fact that tetrafluoroethylene[1] is undoubtedly planar one would expect each fluorinated vinyl group of CF_2:CF-CF:CF_2 to be planar. If this is the case, the molecule could belong to any of the three following symmetry point groups: C_{2h}, C_{2v}, or C_2. In the case of C_{2h} symmetry the molecule will have a planar <u>trans</u> configuration for which the 24 fundamental vibrations divide into $9\ a_g + 4\ a_u + 3\ b_g + 8\ b_u$. Species a_g and b_g are Raman-active (12 fundamentals), while species a_u and b_u are infrared-active (12 fundamentals). In the case of C_{2v} symmetry the molecule will have a planar <u>cis</u> configuration for which the 24 fundamental vibrations divide into $9\ a_1 + 4\ a_2 + 8\ b_1 + 3\ b_2$. All four species are Raman-active (24 fundamentals), and all except species a_2 are infrared-active (20 fundamentals). In the case of symmetry C_2, the planes of the two fluorinated vinyl groups will not coincide. For this symmetry the 24 fundamental vibrations divide into 13 <u>a</u> + 11 <u>b</u> where both species are Raman-active and infrared-

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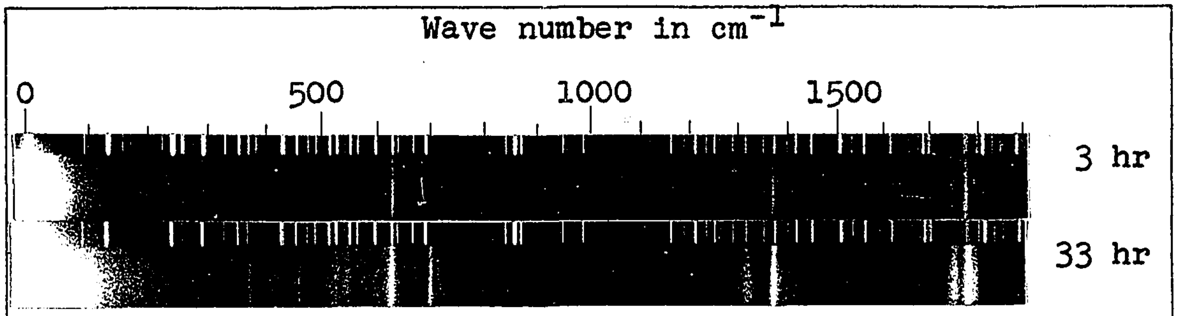
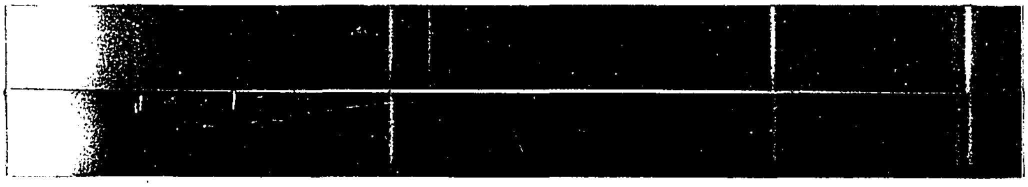
[1] Nielsen, Claassen, and Smith, J. Chem. Phys. 18, 812 (1950).



Liquid, 20°C

Liquid, -120°C



2 Hr Polarization Exposures

Solid

Gas

Figure 11.

Raman Spectra of $CF_2:CF-CF:CF_2$.

active.

Previous work on ordinary butadiene-1,3[2] indicates that in its most stable form it has planar trans configuration with C_{2h} symmetry. In the spectra of CF_2:CF-CF:CF_2 there are 17 Raman bands with medium and stronger intensities, and 18 infrared bands with medium and stronger intensities. The wave numbers of 8 of these Raman bands coincide very well with wave numbers of 8 of these infrared bands. It is probable that most of these medium and stronger bands are fundamentals. If so, there are too many Raman-active fundamentals, and too many infrared active fundamentals to be explained on the basis of a trans configuration.

On the other hand, the spectra can be explained satisfactorily on the assumption of a planar cis configuration (C_{2v}). The following interpretation is based on this assumption. The evidence, however, does not exclude the possibility of the C_2 configuration mentioned above, or the possibility of two of the three possible forms existing together.

The principal moments of inertia have been calculated for CF_2:CF-CF:CF_2 molecules of C_{2v} symmetry on the basis of the following values of bond lengths and angles obtained from similar molecules:[3] 1.54, 1.31, and 1.31 A for the C-C,

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[2] C. M. Richards and J. Rud Nielsen, J.O.S.A. 40, 438 (1950).

[3] Landolt-Börnstein, Zahlenwerte und Funktionen (Springer Verlag, Berlin-Gottingen-Heidelberg, 1951), 6th ed., Vol. 1, part 3, pp. 12-14.

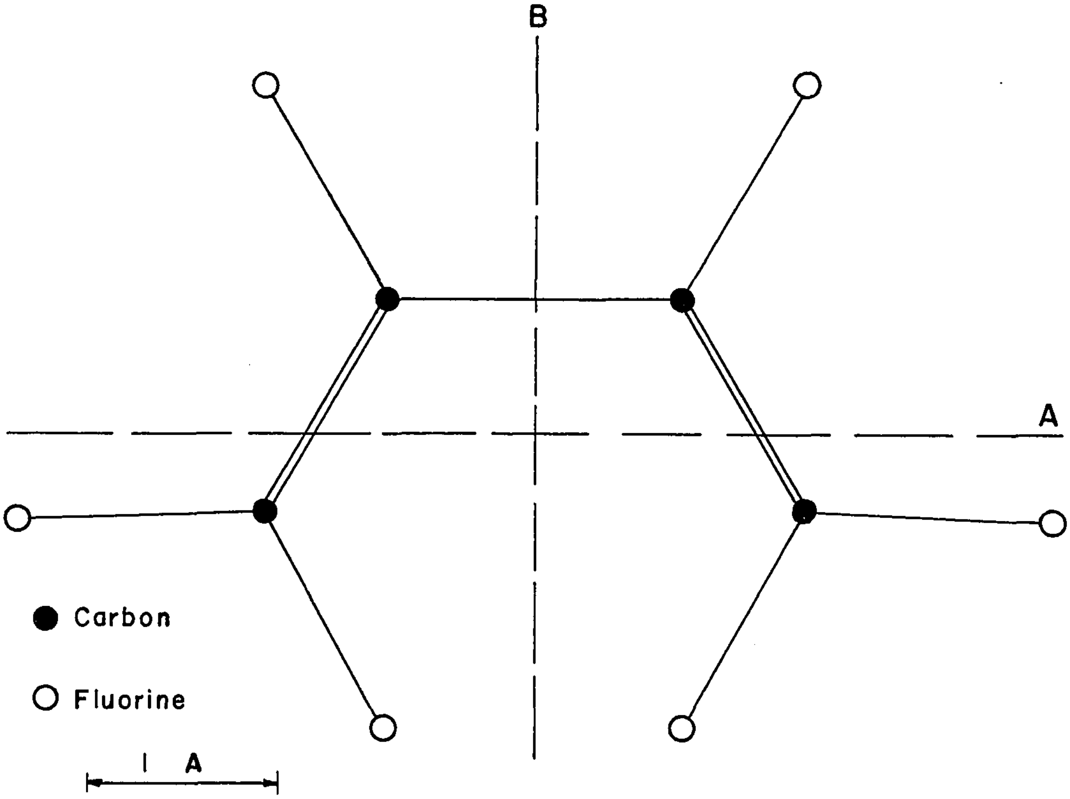

Figure 12. Molecular configuration of cis CF_2:CF-CF:CF_2.

C:C, and C-F bonds, respectively; and 120°, 120°, and 123° for the C-C:C, C-C-F, and C:C-F angles, respectively. The values obtained for the principal moments of inertia are 418, 753, and 1171 x 10^{-40} g cm^2. The configuration of the molecule, and the locations of the axes of least moment (A) and intermediate moment (B) are shown in Figure 12. The center of mass is located 0.72 A from the C-C bond.

The contours of the infrared bands should be of type B for species a_1, type A for species b_1, and type C for species b_2. From the curves of Badger and Zumwalt,[4] the P-R separations of type A and type C bands have been estimated to be 9 and approximately 10 cm^{-1}, respectively, while the Q-Q separation for type B bands has been estimated to be 7 cm^{-1}.

In order to use data from related molecules as an aid in assigning the fundamentals it is helpful to consider classically the general nature of the motions of the nuclei for the various normal vibrations. The designation of each vibration will in general mention only the motions that have the greatest amplitudes. For example, in a "C-F stretching" vibration the motions of greatest amplitudes are the stretching of the carbon fluorine bonds, but it should be understood that all the nuclei are moving and that the C-F bonds may suffer some bending in addition to stretching.

Two normal vibrations, one of species a_1 and one of species b_1, should consist primarily of carbon carbon double bond stretching. $CF_2{:}CF_2$ and $CF_2{:}CF\text{-}CF_3$[5] each have one vibration of this type, at 1872 and 1797 cm^{-1} respectively. The infrared spectrum of gaseous $CF_2{:}CF\text{-}CF{:}CF_2$ has a very strong band at 1766 cm^{-1} and a strong band at 1799 cm^{-1}. The Raman spectrum of the liquid has a very strong polarized

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[4] R. M. Badger and L. R. Zumwalt, J. Chem. Phys. 6, 711 (1938).

[5] Nielsen, Claassen, and Smith, J. Chem. Phys. 20, 1916 (1952).

band at 1796 cm^{-1} and strong bands at 1769 and 1810 cm^{-1}. The band at 1769 cm^{-1} is depolarized in the liquid and diffuse in the gas. Because of its polarization, the Raman band at 1796 cm^{-1} must be of species a_1. It is interpreted as a C:C stretching fundamental. On the basis of its strength in the infrared, the band at 1766 cm^{-1} and the corresponding Raman band at 1769 cm^{-1} is interpreted as a C:C stretching fundamental of species b_1.

Six of the fundamental vibrations may be expected to consist largely of carbon fluorine bond stretching. Three of these will be of species a_1 and three will be of species b_1. In each of the a_1 fundamentals, the motions of the nuclei in one fluorinated vinyl group will be in phase with the motions of the nuclei in the other fluorinated vinyl group. Corresponding to each a_1 vibration, there will be a b_1 vibration in which the nuclei in each fluorinated vinyl group move much as they do in the a_1 vibration, except that the motions of the nuclei in one fluorinated vinyl group will be out of phase with the motions of the nuclei of the other fluorinated vinyl group. For the C-F stretching modes, these two fundamentals may be expected to be in pairs of one of species a_1 and one of species b_1. The corresponding fundamentals in CF_2:CF_2 lie at 1338, 1337, 1186, and 778 cm^{-1}; while those in CF_2:CF-CF_3 lie at 1398, 1336, 1211, 1179, 1122, and 1037 cm^{-1}. From these values, it may be concluded that the C-F stretching fundamentals in CF_2:CF-CF:CF_2 lie between 750 and 1400 cm^{-1}. The very strong polarized Raman band at 1381 in the liquid and 1378 in the gas, and the medium infrared band at about 1377 cm^{-1}, are interpreted as C-F stretching fundamental of species a_1. Near this wave number, at 1330 cm^{-1}, is a medium diffuse Raman band and a very strong infrared band. Since this band was very weak on the polarization exposures from which the estimated depolarization ratio of 0.7 was obtained, the value is probably within experimental error of being 0.86. Thus the band could be depolarized. It is interpreted as a C-F stretching fundamental of species b_1. The very strong type B infrared band and the weak Raman band at 1140 cm^{-1} must be another of the C-F stretching fundamentals of species a_1. The strongest band in both spectra near this value is the very strong infrared band and weak depolarized Raman band at 1193 cm^{-1}. It is interpreted as the corresponding b_1 C-F stretching fundamental. The band at 972 cm^{-1} is very strong in the infrared with a type A contour, and is very weak and depolarized in the Raman spectrum. It is interpreted as the other b_1 C-F stretching fundamental. There now remains one a_1 C-F stretching fundamental to be assigned. Its wave number should lie near 972 cm^{-1}. In the Raman spectrum, the only band near 972 cm^{-1} is a very very weak band at about 939 cm^{-1}. It appears as a medium band in the infrared at 928 cm^{-1}. It is interpreted as the remaining

a_1 C-F stretching fundamental.

The last bond stretching fundamental to be assigned is of species a_1 and should involve largely carbon carbon single bond stretching. The corresponding fundamental in CF_2:CF-CF_3 lies at 767 cm^{-1} and is very strong in the Raman effect. In CF_2:CF-CF:CF_2 this vibration probably involves very little change in dipole moment and therefore should be weak in the infrared. In the Raman spectrum of CF_2:CF-CF:CF_2 the highest strong band below the C-F stretching fundamentals is polarized and lies at 699 cm^{-1} in the gas and at 705 cm^{-1} in the liquid. In the infrared spectrum there is a very weak band at this wave number. Thus, 699 cm^{-1} is interpreted as an a_1 fundamental involving largely C-C stretching.

Of the fifteen bending fundamentals, two consisting largely of CF_2 deformation may be expected to have the highest wave numbers. Their species are a_1 and b_1. They may be expected to lie close together because of the large separation of the CF_2 groups in CF_2:CF-CF:CF_2. The corresponding wave numbers in CF_2:CF_2 are 558 and 394 cm^{-1}, while that in CF_2:CF-CF_3 is 655 cm^{-1}. In the Raman spectrum of liquid CF_2:CF-CF:CF_2 there is a very strong depolarized band at 633 cm^{-1} and a medium band at 624 cm^{-1}. In the Raman spectrum of gaseous CF_2:CF-CF:CF_2 there is a diffuse weak band with a center around 630 cm^{-1}. In the infrared spectrum of gaseous CF_2:CF-CF:CF_2 there is a very strong band with branches measured on the NRL spectrum at 621, 625, and 630 cm^{-1}. The appearance of this band suggests that it may be a superposition of a type A band with central maximum at 625 cm^{-1} and a weaker type B band with maxima around 623 and 630 cm^{-1}. It is thus interpreted as an overlapping of the two CF_2 deformation fundamentals with the b_1 fundamental at 625 cm^{-1}, and the a_1 fundamental around 627 cm^{-1}. In the Raman spectrum of the liquid, the band at 624 cm^{-1} is interpreted as the b_1 fundamental, and the band at 633 cm^{-1} is interpreted as the a_1 fundamental. Part of the intensity at the latter wave number undoubtedly results from the combinations: $170 + 463 = 633$ A_2, $210 + 422 = 632$ B_2, and $260 + 375 = 635$ B_2, which helps account for the high depolarization ratio.

Eight of the bending fundamentals may be expected to involve primarily CF and CF_2 rocking and wagging. Four of these, two of species a_1 and two of species b_1 may be characterized as rocking (in plane). The other four, two of species a_2 and two of species b_2 may be termed wagging (out of plane). In CF_2:CF_2 the CF_2 rocking fundamentals are at 503 and 210 cm^{-1}, and the CF_2 wagging fundamentals are at 517 and 407 cm^{-1}. In CF_2:CF-CF_3 the CF_2 rocking fundamental is believed to be at 513 cm^{-1}, the CF rocking fundamental is uncertain, but it probably is below 370 cm^{-1}, the CF_2 wagging fundamental is believed to be at 462 cm^{-1}, and the CF wagging fundamental is believed to be at 370 cm^{-1}. From these values and the fact that there should be less interaction between the CF_2 groups in CF_2:CF-CF:CF_2 than in CF_2:CF_2 due to their greater separation, the eight CF and CF_2 rocking and wagging fundamentals may be expected to lie between 300 and 550 cm^{-1}. There are only two strong polarized Raman bands in this range, at 468 and 374 cm^{-1}. Both are weak in the infrared, 374 having a type B contour, and 468 an indefinite contour. These are interpreted as the a_1 fundamentals involving CF and CF_2 rocking. Near these in the Raman spectrum of the liquid are two diffuse depolarized bands of medium intensity whose wave numbers are 530 and 418 cm^{-1}. The similar appearance of these bands indicate they are probably of the same species. In the infrared spectrum they appear as a very weak shoulder at 524 cm^{-1} and as a medium band of indefinite contour at 422 cm^{-1}. Their close proximities to the fundamentals of species a_1 indicate that they are probably CF and CF_2 rocking fundamentals of species b_1. Since 378 and 418 cm^{-1} are closer together than 468 and 530 cm^{-1}, indicating less interaction, the former are believed to involve mainly CF_2 rocking and the latter CF rocking.

The strong type C infrared band and the strong depolarized Raman band at 550 cm^{-1} in the gas and at 552 cm^{-1} in the liquid must be of species b_2. They probably correspond to one of the wagging modes. Near this wave number, at 576 cm^{-1}, is a very weak Raman band. In the infrared spectrum a very weak shoulder is observed at 574 cm^{-1}. On the basis of its close proximity to 552 cm^{-1}, the Raman band at 576 cm^{-1} is interpreted as a fundamental of species a_2 corresponding to one of the wagging modes. The shoulder at 574 cm^{-1} in the infrared spectrum can be explained as a combination band.

The only remaining Raman bands in the range from 300 to 550 cm^{-1} are two very very weak bands at 330 and 321 cm^{-1}. Neither is observed in the infrared spectrum. They are interpreted as the remaining wagging fundamentals. One is of species a_2 and one is of species b_2. The interpretation of combination bands favors assigning 321 cm^{-1} as the a_2 fundamental and 330 cm^{-1} as the b_2 fundamental, but the evidence is not conclusive.

There remain five fundamentals to be assigned. Two should involve largely CF_2 twisting. One of these should be of species a_2 and the other of species b_2. The other three fundamentals should involve primarily skeletal deformation. One of these should be of species a_1, another of species a_2, and the third of species b_1. The strong type A infrared band at 291 cm^{-1} and the medium depolarized Raman band at 295 cm^{-1} are interpreted on the basis of the infrared contour as a fundamental of species b_1. It must involve largely skeletal deformation. The strong polarized Raman band at 190 cm^{-1} is interpreted as a fundamental of species a_1 involving skeletal deformation. The only remaining unassigned Raman bands of low wave number are at 260, 210, and 170 cm^{-1}. The band at 260 cm^{-1} is of medium intensity, and is depolarized, the band at 210 cm^{-1} is weak, and the band at 170 cm^{-1} is weak and may be spurious. The bands at 260 and 210 cm^{-1} are interpreted as fundamentals of species b_2 and a_2 involving CF_2 twisting. The interpretation of combination bands very slightly favors assigning 210 as the fundamental of species a_2 and 260 as the fundamental of species b_2. The band at 170 cm^{-1} is interpreted as the remaining fundamental of species a_2 which involves largely skeletal deformation.

The assigned fundamentals are listed in Table 4. On the basis of these fundamentals, it has been possible to explain satisfactorily practically all of the remaining infrared and Raman bands as overtones or combinations. These interpretations are listed in Tables 2 and 3. All wave numbers of fundamentals used in the interpretations were determined from the spectra of the gaseous phase except 633 a_1, 530 b_1, 330 b_2, 260 b_2, and the four a_2 fundamentals. The wave numbers given for these fundamentals were determined from the Raman spectrum of the liquid phase.

Of particular interest among the bands not assigned as fundamentals is the strong Raman band at 1810 cm^{-1} which is almost as intense as the b_1 fundamental at 1768 cm^{-1}. It probably represents one, or both, of the combinations 422 +

1378 = 1800 B_1 and 463 + 1330 = 1793 B_1 in Fermi resonance with the b_1 fundamental at 1768 cm^{-1}. Another band of interest is the medium type A infrared band at 1080 cm^{-1}. It is interpreted as the combination 463 + 633 = 1096 B_1 in Fermi resonance with the b_1 fundamental at 1193 cm^{-1}, with some contribution from the combination 463 + 625 = 1088 A_1.

The infrared bands at 2788, 3330, and 3781 cm^{-1} cannot be explained as binary combinations, however they can be readily explained as ternary combinations. In the process of finding suitable ternary combinations, only a few possibilities were considered and thus there may be ternary combinations other than the ones listed in Table 2 which contribute to these bands.

There is no evidence from the spectra to exclude the possibility that the molecules have a form with symmetry C_2 instead of C_{2v}. If this is the case the bands that have been interpreted as belonging to species a_1 and a_2 of group C_{2v} would belong to species <u>a</u> of group C_2. The bands interpreted as belonging to species b_1 and b_2 of group C_{2v} would belong to species <u>b</u> of group C_2.

Also it is possible that CF_2:CF-CF:CF_2 may have two molecular forms existing together, at least in the liquid and gaseous phases. The Raman spectrum of the crystal shows some evidence in support of this possibility. The very strong band at 1796 cm^{-1} in the Raman spectrum of the liquid apparently does not appear in the spectrum of the crystal, while the strong band at 1810 cm^{-1} in the liquid appears in the crystal at 1809 cm^{-1}. The strong band at 1768 cm^{-1} in the liquid probably also appears in the crystal, although the band observed in the crystal could be a mercury line located 1770 cm^{-1} from 4358 A. However, it seems too intense, and is probably an overlapping of the mercury line and a Raman band. If two forms exist in the liquid and gaseous phases, four fundamentals (two for each form) may be expected near 1800 cm^{-1}. The band at 1796 cm^{-1} in the Raman spectrum of the liquid must then be a fundamental of the form that is absent in the crystal. Furthermore, since it appears in both the infrared and Raman spectra of the gaseous phase, it must be due to some form other than trans. If the bands measured at 1769 and 1810 cm^{-1} in the Raman spectrum of the liquid are both fundamentals, they must be fundamentals of the same molecular form since both appear in the Raman spectrum of the crystalline phase. Furthermore, this molecular form cannot be the trans form since for the trans form only one Raman-active fundamental is expected in this region. Thus, if two forms are present in the liquid and gaseous phases, they are probably the cis form and a form of symmetry C_2. While the spectrum of the crystalline phase does indicate the possibility of two forms, the spectrum is too weak to be considered as important evidence.

If two forms are present, it may be expected that at low temperatures the bands of the more stable form should be enhanced, while the bands of the less stable form should be weakened. A careful study of the Raman spectrum of the liquid at 20° C and at -120° C shows no differences in relative intensities that cannot be explained by the greater sharpness of many of the bands in the spectrum taken at -120° C.

The fundamentals assigned in Table 4 are based on the assumption of a cis form. They give a reasonable interpretation of each band of the infrared and Raman spectra. If two molecular forms are present, a number of bands may be expected that cannot be interpreted on the assumption of one form. Thus the results of the present study indicate that the molecules of $CF_2:CF-CF:CF_2$ exist in only one form, and that this form has the symmetry either of point group C_{2v} (cis form) or of point group C_2 (non-planar).

The important uncertainties in the interpretation given here are the molecular configuration, the symmetry species of the CF_2 deformation fundamentals at 625 and 633 cm^{-1}, the symmetry species of the CF_2 wagging fundamentals at 321 and 330 cm^{-1}, and the symmetry species of the CF_2 twisting fundamentals at 210 and 260 cm^{-1}. Additional information on molecular configuration, and on the symmetry species of the CF_2 deformation fundamentals could be obtained from well exposed polarization spectra with the sample at low temperature. From such exposures it should be possible to determine the depolarization ratio for the band at 1810 cm^{-1} and thus establish whether it is a non-totally symmetric conbination band as interpreted here, or a totally symmetric fundamental which would imply the existence of two molecular forms. If only one form is present, the total number of polarized Raman bands should indicate whether the form has symmetry C_{2v} (cis) or C_2 (non-planar). From polarization exposures taken with the sample at low temperature it should also be possible to determine the depolarization ratio for the band at 624 cm^{-1} and thus check the assignments given here for the symmetry species of this band and the other CF_2 deformation fundamental at 633 cm^{-1}.

An infrared spectrum of the liquid phase would help check the assumption given here that the observed infrared band of the gaseous phase at 625 cm^{-1} is a superposition of two bands. Since fundamentals of species a_2 are infrared-inactive, the symmetry species of the fundamentals at 321 and 330 cm^{-1} could be determined if one of them appeared in the infrared spectrum of the liquid phase. Similarly, an infrared spectrum of either the liquid or gaseous phase from 37 to 50 microns would help check the assignment given here for the symmetry species of the CF_2 twisting fundamentals at 210 and 260 cm^{-1}.

A better Raman spectrum of the gaseous phase would supplement polarization exposures as an aid in checking which bands are totally symmetric. Thus, most of the remaining uncertainties could be resolved with the aid of Raman polarization exposures obtained with the sample at low temperature, an infrared spectrum extended to 50 microns, and a better Raman spectrum of the gaseous phase.

TABLE 2

INFRARED SPECTRUM OF GASEOUS HEXAFLUOROBUTADIENE-1,3

Wave number	Description[a]	Band type	Interpretation (based on C_{2v} symmetry)
285 291 296	s	A	b_1 fundamental
372 378	w	B	a_1 fundamental
422	m		b_1 fundamental
463	w		a_1 fundamental
~524	vw		b_1 fundamental; 2 x 260 = 520 A_1
~545 550 ~554	s	C	b_2 fundamental
~574	vw		260 + 321 = 581 B_1; 3 x 190 570 A_1
~621[b] 625[b] 630[b]	vs	A	b_1 + a_1 fundamentals
658	vw		2 x 330 = 660 A_1; 192 + 463 = 655 A_1
~707	vw		a_1 fundamental
~714	vw		291 + 422 = 713 A_1
736	w		210 + 530 = 740 B_2

TABLE 2--Continued

Wave number	Description	Band type	Interpretation (based on C_{2v} symmetry)
~741	w		321 + 422 = 743 B_2; 170 + 576 = 746 A_1
~800	vw		170 + 633 = 803 B_2; 375 + 422 = 797 B_1
~823^b 825^b 829^b	w		192 + 633 = 825 B_1; 291 + 530 = 821 A_1
~838	vw		210 + 633 = 843 B_2; 2 x 422 = 844 A_1; 260 + 576 = 836 B_1
~864	vw		291 + 576 = 867 B_2
885	w		422 + 463 = 885 B_1; 260 + 625 = 885 B_2
~918	w		375 + 550 = 925 B_2
928	m		a_1 fundamental
968 972 ~977	vs	A	b_1 fundamental
~995	m		422 + 576 = 998 B_2; 463 + 530 = 993 B_1; 375 + 625 = 1000 A_1
~1015	m		463 + 550 = 1013 B_2
1041	w		422 + 625 = 1047 B_1
1075 1080 1083	m	A	463 + 633 = 1096 B_1; 463 + 625 = 1088 A_1

TABLE 2--Continued

Wave number	Descrip- tion	Band type	Interpretation (based on C_{2v} symmetry)
1096	vw		$2 \times 550 = 1100$ A_1
1137 1142	vs	B	a_1 fundamental
1193	vs		b_1 fundamental
~1292	m		$321 + 972 = 1293$ B_2
1330	vs		b_1 fundamental
~1377	m		a_1 fundamental
1431	w		$291 + 1140 = 1431$ B_1; $463 + 972 = 1435$ B_1
1447	w		$530 + 928 = 1458$ B_1
1479	w		$550 + 928 = 1478$ B_2; $291 + 1193 = 1484$ A_1
1518	w		$192 + 1330 = 1522$ B_1; $375 + 1140 = 1515$ A_1
1590	w		$625 + 972 = 1597$ B_1
1617	w		$422 + 1193 = 1615$ A_1; $291 + 1330 = 1621$ A_1
1670	w		$530 + 1140 = 1670$ B_1; $699 + 972 = 1671$ B_1; $291 + 1378 = 1669$ B_1
1718	m		$530 + 1193 = 1723$ A_1
1766	vs		b_1 fundamental
1799	s		a_1 fundamental
~1818	m		$625 + 1193 = 1818$ B_1

TABLE 2--Continued

Wave number	Description	Band type	Interpretation (based on C_{2v} symmetry)
~1858	w		$530 + 1330 = 1860\ A_1$; $2 \times 928 = 1856\ A_1$
~1895	w		$699+1193 = 1892\ B_1$; $928 + 972 = 1900\ B_1$
1947	w		$2 \times 972 = 1944\ A_1$; $625 + 1330 = 1955\ B_1$
2033	w		$699 + 1330 = 2029\ B_1$
2051	w		$260 + 1796 = 2056\ B_2$; $291 + 1766 = 2057\ A_1$
2087	w		$291 + 1796 = 2087\ B_1$; $321 + 1766 = 2087\ B_2$; $699 + 1378 = 2077\ A_1$
~2104 2108 ~2112	w		$972 + 1140 = 2112\ B_1$; $928 + 1193 = 2121\ B_1$
2158	w		$972 + 1193 = 2165\ A_1$
2186	vw		$422 + 1766 = 2188\ A_1$
2215	vw		$422 + 1796 = 2218\ B_1$
~2261	vw		$463 + 1796 = 2259\ A_1$; $928 + 1330 = 2258\ B_1$
2300	w		$972 + 1330 = 2302\ A_1$; $530 + 1766 = 2296\ A_1$
2321	w		$530 + 1796 = 2326\ B_1$;
2383	w		$2 \times 1193 = 2386\ A_1$; $625 + 1766=2391\ B_1$
2415	w		$625 + 1796 = 2421\ A_1$

TABLE 2--Continued

Wave number	Description	Band type	Interpretation (based on C_{2v} symmetry)
2467	w		699 + 1766 = 2465 B_1; 1140 + 1330 = 2470 B_1
~2489	w		699 + 1796 = 2495 A_1
2516	w		1140 + 1378 = 2518 A_1; 1193 + 1330 = 2523 A_1
2564	w		1193 + 1378 = 2571 B_1
2649	m		2 x 1330 = 2660 A_1
~2673	w		928 + 1766 = 2694 B_1; 190 + 699 + 1796 = 2685 A_1
2708	w		1330 + 1378 = 2708 B_1
2762	w		972 + 1796 = 2768 B_1; 2 x 1378 = 2756 A_1
~2788	w		321 + 1140 + 1330 = 2791 B_2; 421 + 2 x 1193 = 2808 B_1
2907	w		1140 + 1766 = 2906 B_1
2931	w		1140 + 1796 = 2936 A_1
2955	w		1193 + 1766 = 2959 A_1
2982	vw		1193 + 1796 = 2989 B_1
3094	w		1330 + 1766 = 3096 A_1
3120	w		1330 + 1796 = 3126 B_1
~3158	w		1378 + 1766 = 3144 B_1
3173	vw		1378 + 1796 = 3174 A_1
3330	vw		210 + 1378 + 1766 = 3354 B_2
3510	vw		2 x 1766 = 3532 A_1

TABLE 2--Continued

Wave number	Description	Band type	Interpretation (based on C_{2v} symmetry)
3614	vw		$2 \times 1796 = 3592$ A_1
3781	vw		$699 + 1330 + 1766 = 3795$ A_1

[a] The following abbreviations are used: s strong, m medium, w weak, and v very.

[b] Wave numbers taken from spectrum obtained at the Naval Research Laboratory.

TABLE 3

RAMAN SPECTRA OF HEXAFLUOROBUTADIENE-1,3

Gas		Liquid			Crystal		Interpretation (based on C_{2v} symmetry)
Wave number	Description [a]	Wave number	Description [a]	Depolarization	Wave number	Description [a]	
176?	w,b	170?	m		172?	m	a_2 fundamental[b]
192	w	190	m	p			a_1 fundamental
		210	w				a_2 fundamental[c]
		260	m	dp			b_2 fundamental[c]
		295	m	dp			b_1 fundamental
		321	vvw				a_2 fundamental[c]
		330	vvw				b_2 fundamental[c]
374	w	378	s	0.36			a_1 fundamental
		418	m,d	dp			b_1 fundamental
		468	s	p			a_1 fundamental
		530	m,b	dp			b_1 fundamental
		552	s	dp			b_2 fundamental
		576	vw				a_2 fundamental

TABLE 3--Continued

Gas		Liquid			Crystal		Interpretation
Wave number	Description	Wave number	Description	Depolarization	Wave number	Description	(based on C_{2v} symmetry)
		609	vw,b	dp			$291 + 321 = 612$ B_2; $192 + 422 = 614$ B_1
		624	m				b_1 fundamental
~630	w,vd	633	vs	0.9	636	m	a_1 fundamental; $170 + 463 = 633$ A_2; $210 + 422 = 632$ B_2; $260 + 375 = 635$ B_2
699	m	705	s	0.46	707	w	a_1 fundamental
		718	w	p			$219 + 422 = 713$ A_1
		730	vw				$210 + 530 = 740$ B_2
		939	vvw,b				a_1 fundamental
		968	vw,b	dp			b_1 fundamental
		1130	w,b				a_1 fundamental
		1184	w,d	dp			b_1 fundamental
1325	m	1329	m,d	0.7			b_1 fundamental
1378	m	1381	vs	0.56	1376	m	a_1 fundamental

TABLE 3--Continued

Gas		Liquid			Crystal		Interpretation
Wave number	Description	Wave number	Description	Depolarization	Wave number	Description	(based on C_{2v} symmetry)
1769	w,d	1768	s	0.8	1768[d]	m	b_1 fundamental
1793	s	1796	vs	0.45			a_1 fundamental
1810	w	1810	s		1809	m	$422 + 1378 = 1800$ B_1; $463 + 1330 = 1793$ B_1

[a] The following abbreviations are used: s strong, m medium, w weak, b broad, d diffuse, and v very.

[b] May be spurious.

[c] Species uncertain (see text).

[d] Overlaps faint Hg line at 4722.8 A.

TABLE 4

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF HEXAFLUOROBUTADIENE-1,3 (C_{2v})

Species	Wave number I.R.(g)	Ra.(g)	Ra.(liq)	Approximate character
a_1		192 w	190 m	Skeletal deformation
	375 w	374 w	378 s	CF_2 rocking
	463 w		468 s	CF rocking
	~630 vw		633 vs	CF_2 deformation
	~707 vw	699 m	705 s	C-C stretching
	928 m		939 vvw,b	C-F stretching
	1140 vs		1130 w,b	C-F stretching
	1377 m	1378 m	1381 vs	C-F stretching
	1799 s	1793 s	1796 vs	C:C stretching
a_2		176 w,b	170 m	Skeletal deformation
			210 w	CF_2 twisting
			321 vvw	CF_2 wagging
			576 vw	CF wagging
b_1	291 s		295 m	Skeletal deformation
	422 m		418 m,d	CF_2 rocking
	~524 vw		530 m,b	CF rocking
	625 vs	~630 w,vd	624 m	CF_2 deformation
	972 vs		968 vw,b	C-F stretching
	1193 vs		1184 w,d	C-F stretching
	1330 vs	1325 m	~1329 m,d	C-F stretching

TABLE 4--Continued

Species	Wave number I.R.(g)	Ra.(g)	Ra.(liq)	Approximate character
	1766 vs	1769 w,d	1768 s	C:C stretching
b_2			260 m	CF_2 twisting
			330 vvw	CF_2 wagging
	550 s		552 s	CF wagging

CHAPTER V

VIBRATIONAL SPECTRA OF 1-FLUORO-1-CHLOROETHYLENE

Torkington and Thompson[1] obtained an infrared spectrum of gaseous 1-fluoro-1-chloroethylene in the 3 to 20 micron range with fairly low resolution, and assigned most of the fundamental vibrational frequencies. After completion of the work described in the present dissertation, Mann, Acquista, and Plyler[2] have reported infrared data for gaseous $CFCl{:}CH_2$ covering the region from 1.6 to 52 microns. They have given an assignment of all the fundamental vibrational frequencies in complete agreement with that of the present work. They have calculated thermodynamic functions for the compound.

In the present work, the infrared and Raman spectra of 1-fluoro-1-chloroethylene have been obtained in the gaseous phase. Figures 13, 14, and 15 show the infrared spectrum over the region from 2.5 to 37 microns. The spectrum from 2.5 to 6.3 microns, obtained with the LiF prism, is shown in Figure 13. Figure 14 repeats this portion of the spectrum

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[1] P. Torkington and H. W. Thompson, Trans. Faraday Soc. 41, 236 (1945).

[2] Mann, Acquista, and Plyler, J. Chem. Phys. 23, 2122 (1955).

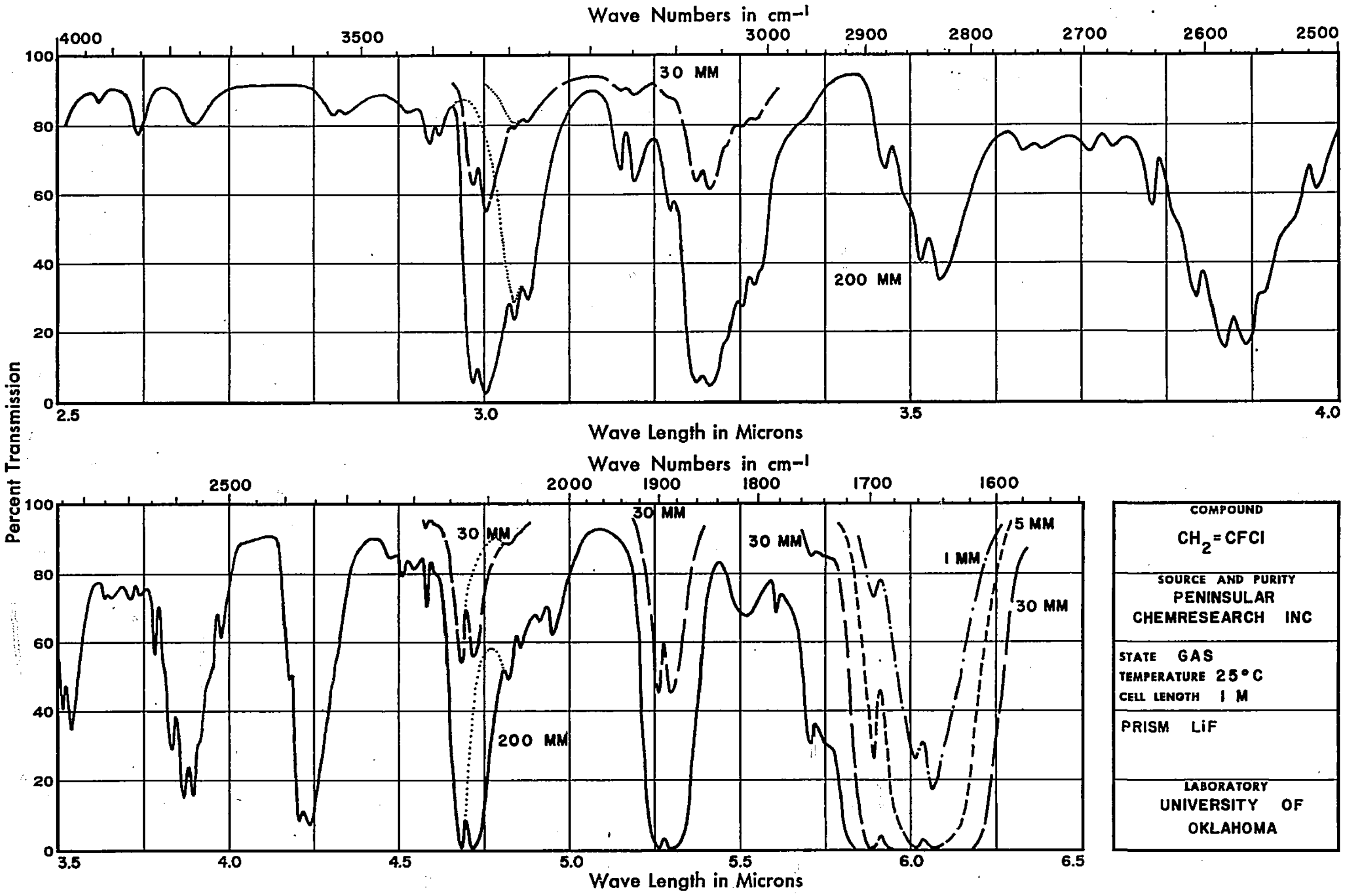

Figure 13. Infrared spectrum of CFCl:CH$_2$, LiF region.

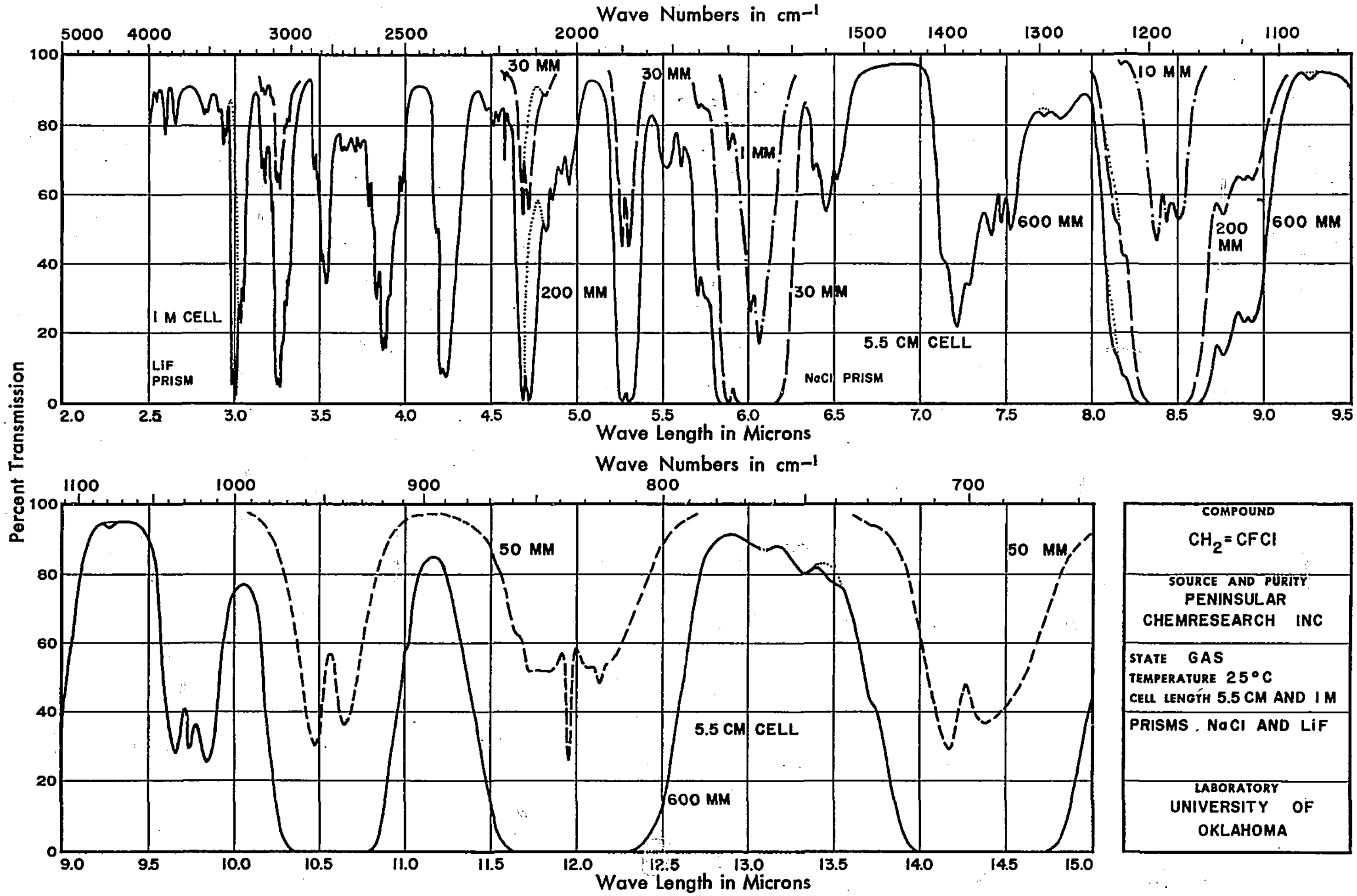

Figure 14. Infrared spectrum of $CFCl:CH_2$, NaCl region.

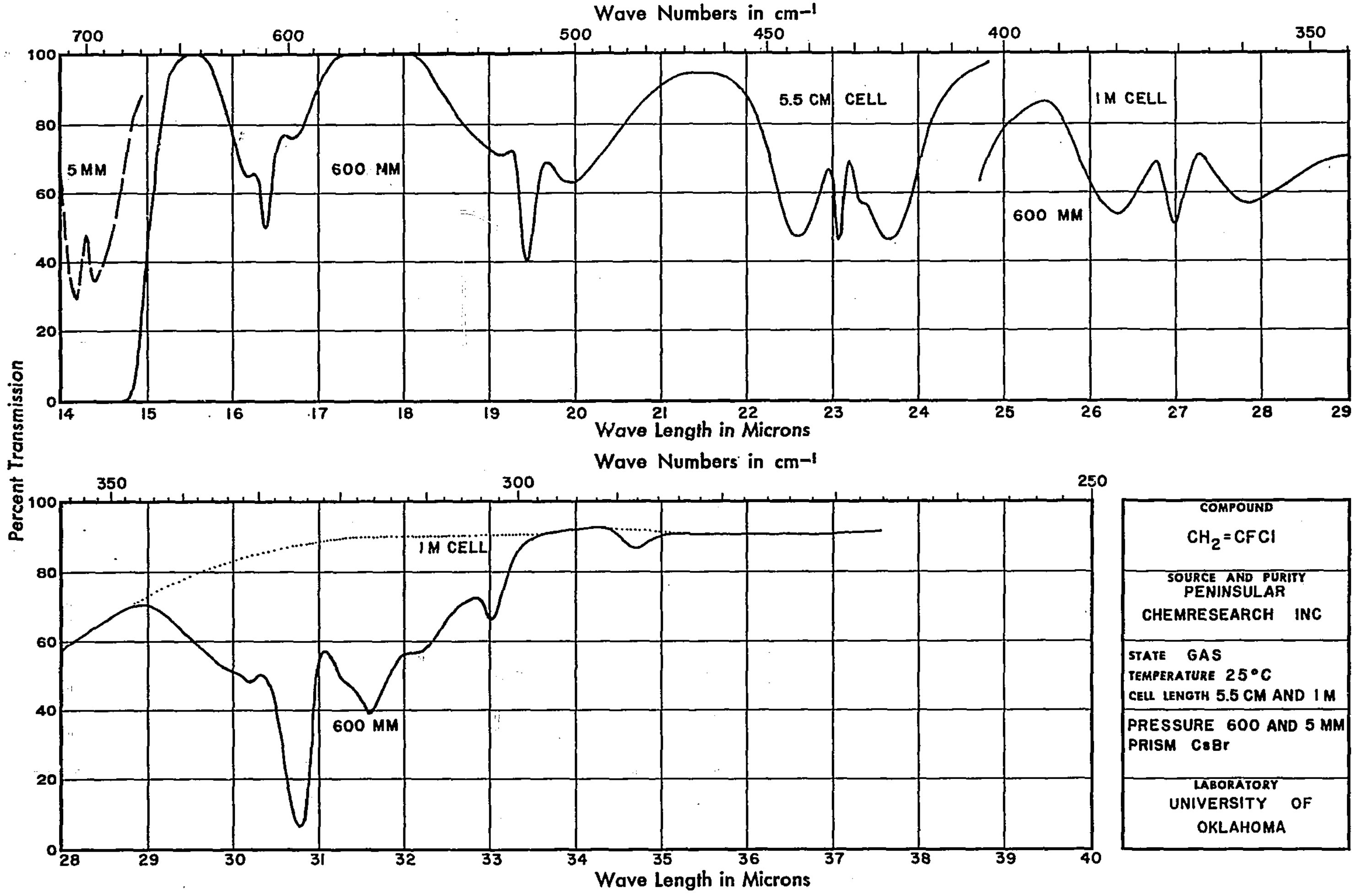

Figure 15. Infrared spectrum of CFCl:CH_2, CsBr region.

on a smaller scale and also shows the spectrum to 15 microns as obtained with the NaCl prism. The spectrum from 15 to 37 microns, obtained with the CsBr prism, is shown in Figure 15. These figures include bands which have definitely been identified as impurity bands. The dotted portions of the curves are estimates of the spectrum of pure $CFCl{:}CH_2$. The wave numbers of the observed infrared absorption maxima, with the exception of those of the impurity, are listed in Table 5.

The Raman spectrum of gaseous $CFCl{:}CH_2$ was obtained with the multi-reflection irradiation apparatus. Figure 16 shows 24 and 99 hour exposures of this spectrum. The wave numbers of the observed Raman bands are listed in Table 6.

Previous investigations of ordinary ethylene,[3] 1,1-dichloroethylene,[4] and 1,1-difluoroethylene[5] show that these molecules are planar. Thus a molecule of $CFCl{:}CH_2$ is undoubtedly also planar. Its symmetry will therefore be that of point group C_s, and the twelve normal vibrations will divide into $9\ a' + 3\ a''$. Both species are infrared and Raman active. An infrared band of species a' should have a contour which is a hybrid of type A and type B contours. An infrared band of species a" should have a type C contour.

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[3] G. Herzberg, Infrared and Raman Spectra (D. Van Nostrand Co., New York, 1945) p. 325.

[4] P. Joyner and G. Glockler, J. Chem. Phys. 20, 302 (1952).

[5] Smith, Nielsen, and Claassen, J. Chem. Phys. 18, 326 (1950).

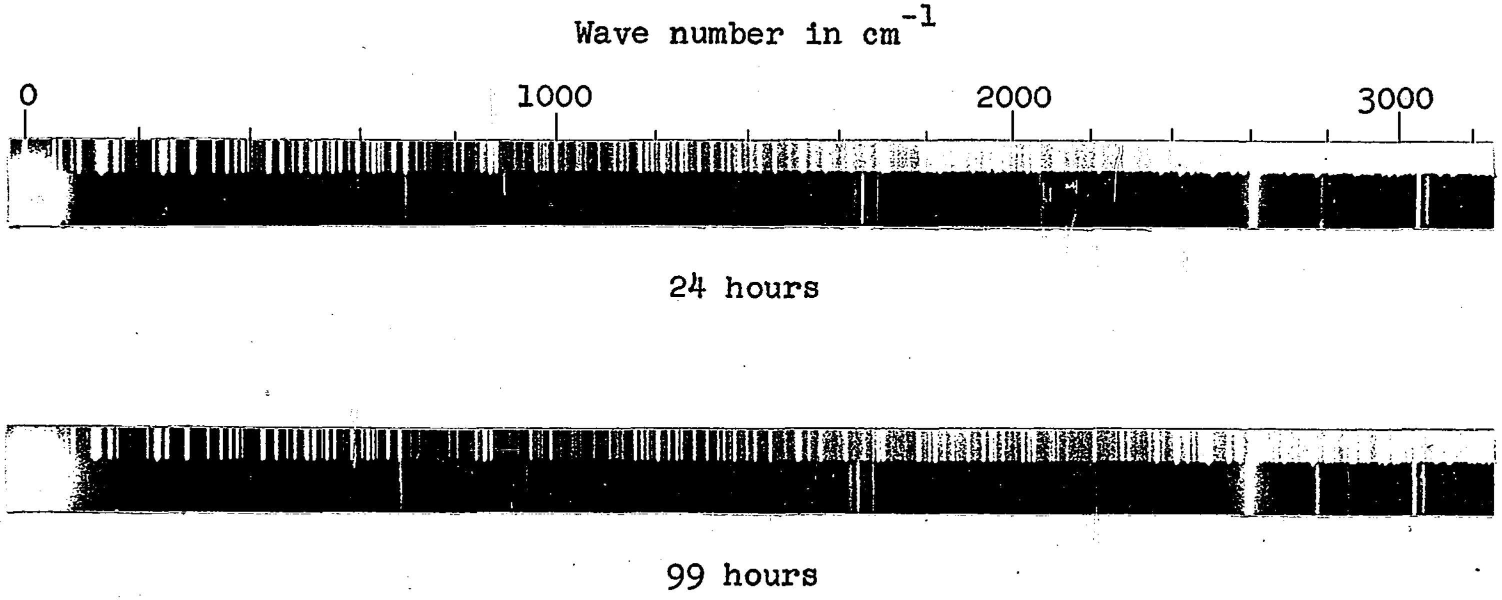

Figure 16.

Raman spectrum of gaseous $CFCl:CH_2$.

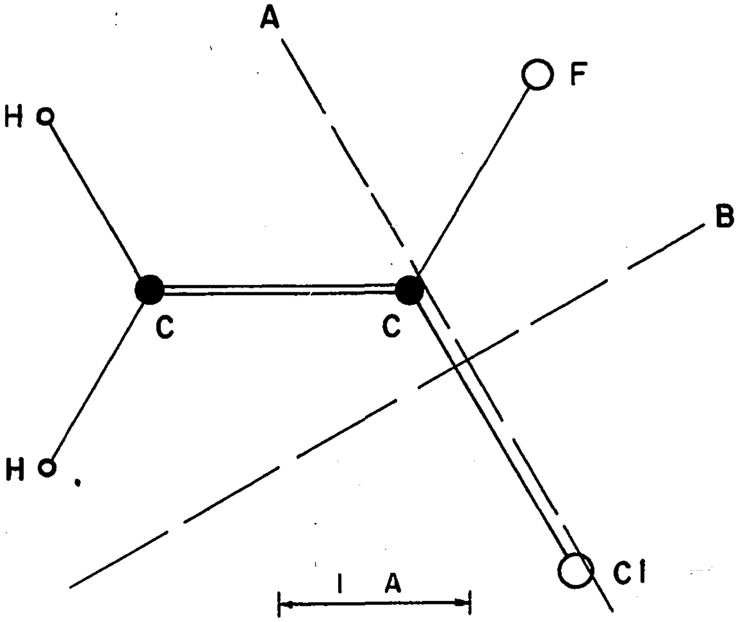

Figure 17. Molecular configuration of $CFCl:CH_2$.

The following bond lengths and angles for related molecules[6] have been used to calculate the principal moments of inertia of the $CFCl:CH_2$ molecule: C-H distance 1.07 A, C:C distance 1.36 A, C-F distance 1.32 A, C-Cl distance 1.69 A, C:C-H angle 122°, C:C-F angle 122°, and C:C-Cl angle 122°. The resulting values for the principal moments of inertia are 79.6, 163.4, and 243.0 x 10^{-40} g cm^2. The molecular configuration along with the locations of the axes of least moment (A), and of intermediate moment (B) are shown in Figure 17. The center of mass is 0.36 A from the line of the C:C bond, and 0.31 A from a normal to the C:C bond through

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[6] Landolt-Börnstein, Zahlenwerte und Funktionen (Springer Verlag, Berlin-Gottingen-Heidelberg, 1951), 6th ed., Vol. 1, part 3, pp. 12-13.

the nearest carbon atom. The axis of the least moment makes an angle of 61° with the line of the C:C bond. From the curves of Badger and Zumwalt,[7] the P-R separations of type A and C infrared bands have been estimated to be about 18 and 15 cm^{-1}, respectively, while the Q-Q separation of type B infrared bands has been estimated to be about 15 cm^{-1}.

Two of the fundamentals of species a' may be expected to have wave numbers near 3000. They may be characterized as resulting primarily from carbon hydrogen bond stretching motions. The corresponding fundamentals in $CCl_2:CH_2$ lie at 3035 and 3130 cm^{-1}. Those in $CF_2:CH_2$ lie at 3059 and 3100 cm^{-1}. Torkington and Thompson measured infrared bands of $CFCl:CH_2$ at 3015, 3055, and 3140 cm^{-1}. They tentatively assigned 3055 and 3140 as C-H stretching fundamentals. The strongest infrared band in this region of the spectrum of $CFCl:CH_2$ obtained here is a medium type B band with maxima at 3062 and 3077 cm^{-1}. The strongest Raman band in this region is a strong band at 3071 cm^{-1}. These bands must represent one of the C-H stretching fundamentals. Other infrared bands in this region are a weak type B band with maxima at 3013 and 3027 cm^{-1}, a weak shoulder at about 3043 cm^{-1}, a weak band at 3106 cm^{-1}, and a very weak type B band with maxima at 3150 and 3164 cm^{-1}. Other Raman bands in this region are a medium band at 3062 cm^{-1}, weak bands at 3018

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[7] R. M. Badger and L. R. Zumwalt, J. Chem. Phys. 6, 711 (1938).

and 3158 cm^{-1}, and a very weak band at 3102 cm^{-1}. On the basis of its appearance in the infrared and its ability to explain several combination bands, the infrared band with maxima at 3013 and 3027 cm^{-1} and corresponding Raman band at 3018 cm^{-1} are interpreted as the other C-H stretching fundamental.

The highest of the remaining seven fundamentals of species a' may be expected to lie near 1700 cm^{-1}. It should consist primarily of carbon carbon double bond stretching. The C:C stretching fundamental of $CCl_2:CH_2$ lies at 1616 cm^{-1}, and the corresponding fundamental of $CF_2:CH_2$ is believed to lie at 1728 cm^{-1}. The strongest infrared band of $CFCl:CH_2$ in this region is a very intense type B band with maxima at 1649 and 1663 cm^{-1}. Corresponding to this is a strong Raman band at 1654 cm^{-1} which is the strongest Raman band of $CFCl:CH_2$ in this region. These bands have been interpreted as being due to the C:C stretching fundamental of species a'. This is essentially in agreement with Torkington and Thompson who give 1645 cm^{-1} as the wave number of this fundamental.

The next lower fundamental of species a' should involve largely CH_2 deformation. The corresponding fundamentals of $CF_2:CH_2$ and of $CCl_2:CH_2$ lie at 1414 and 1391 cm^{-1} respectively. Thus this fundamental of $CFCl:CH_2$ may be expected to lie near 1400 cm^{-1}. In this region of the infrared spectrum of $CFCl:CH_2$ are three strong maxima at 1370, 1385, and 1405 cm^{-1}, with 1385 cm^{-1} stronger than the other two. The separations are too large for these maxima to constitute either a type C or a type A band. Corresponding to these wave numbers are two weak Raman bands at 1375 and 1380 cm^{-1}. These infrared and Raman bands are probably an overlapping and a mixing of the fundamental level of species a' with the overtone level 2 x 700 = 1400 A'. The wave number of the fundamental has been taken as approximately 1385 cm^{-1}, corresponding to the maximum absorption in the infrared spectrum.

Continuing toward lower wave numbers, the next fundamental of species a' will probably be one involving largely C-F stretching. The corresponding two fundamentals of CF_2:CH_2 lie at 1302 and 926 cm^{-1}; and the corresponding fundamental of CFCl:CCl_2[8,9] lies at 1181 cm^{-1}. The strongest infrared band of CFCl:CH_2 in this region is a very intense type A band with maxima at 1175, 1185, and 1193 cm^{-1}. That no band is observed near this wave number in the Raman spectrum is not unreasonable for a C-F stretching vibration. Thus this band is interpreted as the fundamental of species a' involving mainly C-F stretching. This interpretation is in agreement with that of Torkington and Thompson.

The next fundamental of species a' is probably one

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[8] Nielsen, Gullikson, and Woollett, J. Chem. Phys. 23, 1994 (1955).

[9] D. E. Mann and E. K. Plyler, J. Chem. Phys. 23, 1989 (1955).

which involves CH_2 rocking. $CF_2:CH_2$ has a fundamental of this nature at 955 cm^{-1}, and $CCl_2:CH_2$ has one at 1088 cm^{-1}. The only observed Raman band of $CFCl:CH_2$ near these wave numbers is a medium band at 946 cm^{-1}. Corresponding to this in the infrared spectrum is a strong type B band with maxima at 939 and 954 cm^{-1}. These bands have been interpreted as being due to the CH_2 rocking fundamental of species a'. This interpretation is in agreement with that of Torkington and Thompson.

It may be expected that the next lower fundamental of species a' should involve a large amount of C-Cl stretching. The two fundamentals of this nature in $CCl_2:CH_2$ lie at 601 and 788 cm^{-1}, and the corresponding wave number in $CF_2:CFCl$[10] is 689. The strongest infrared band of $CFCl:CH_2$ in this region is a very strong type B band with maxima at 695 and 705 cm^{-1}. Corresponding to this in the Raman spectrum is a medium, broad band at 698 cm^{-1}. The maximum intensity of this Raman band appears to be near the high wave number side. Thus its broad appearance probably results from an overlapping of two bands, the higher band resulting from $CFCl:CH_2$ molecules containing Cl_{35} and the lower, weaker band resulting from $CFCl:CH_2$ molecules containing Cl_{37}. These bands have been interpreted as the C-Cl stretching fundamental of species a'. This interpretation is in agreement with that

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[10] Mann, Acquista, and Plyler, J. Chem. Phys. 21, 1949 (1953).

of Torkington and Thompson.

There remain two fundamentals of species a' to be assigned. They should involve largely planar CFCl bending. In $CCl_2:CH_2$ the corresponding fundamentals are believed to lie at 299 and 375 cm^{-1} and in $CF_2:CH_2$ they are believed to lie at 438 and 550 cm^{-1}. Torkington and Thompson assigned a band at 516 cm^{-1} as one of these fundamentals. In the infrared spectrum of $CFCl:CH_2$ obtained here, a band with a central maximum at 514 cm^{-1} has a definite type C contour and therefore cannot be of species a'. However, there are two remaining bands with appropriate contours. They are a medium type A band with maxima at 422, 433, and 442 cm^{-1} and a very weak type A band with maxima at 359, 370, and 380 cm^{-1}. In the Raman spectrum of $CFCl:CH_2$ only two sharp bands appear in this region. They are both weak and lie at 370 and 432 cm^{-1}. These wave numbers coincide very well with the infrared values just given. Thus these bands are interpreted as the remaining a' fundamentals.

There should be three fundamentals of species a". The highest should involve largely CH_2 wagging. The corresponding fundamental of $CF_2:CH_2$ lies at 803 cm^{-1} and the corresponding fundamental of $CCl_2:CH_2$ lies at 874 cm^{-1}. Torkington and Thompson interpreted a band of $CFCl:CH_2$ at 835 cm^{-1} as this fundamental. In the spectrum obtained here this appears as a very strong type C infrared band with a central maximum at

835 cm^{-1}. The corresponding Raman band is very very weak with two diffuse maxima at about 823 and 844 cm^{-1}. The present work is in agreement with the interpretation of Torkington and Thompson.

The remaining two fundamentals of species a" should involve mostly CFCl wagging and twisting. In $CF_2:CH_2$ the corresponding fundamentals lie at 590 and 611 cm^{-1}, while in $CCl_2:CH_2$ they lie at 458 and 686 cm^{-1}. A medium type C band in the infrared spectrum of $CFCl:CH_2$ with a central maximum at 514 cm^{-1} must be one of these fundamentals. Corresponding to this in the Raman spectrum of $CFCl:CH_2$ is a very faint diffuse band with two maxima at about 505 and 533 cm^{-1}.

In the infrared spectrum of $CFCl:CH_2$ there appear two other type C bands in the low wave number region. They are a medium band with a central maximum at 610 cm^{-1} and a weak band with a central maximum at 325 cm^{-1}. Both of these bands show evidence of resulting from an impurity. Neither of them appear in the Raman spectrum. Because these are the only two bands which could be interpreted as the remaining fundamental, it is believed that one is probably an overlapping of the fundamental of $CFCl:CH_2$ and an impurity band, and that the other results entirely from the impurity. The band at 610 cm^{-1} is the stronger of the two, and it helps explain more combination bands. It is in better agreement with the wave numbers of the corresponding fundamentals of related compounds. Thus the band at 610 cm^{-1} is interpreted as the fundamental of species a", and the band at 325 cm^{-1} is interpreted as an impurity band. Torkington and Thompson observed a band at 621 cm^{-1}.

The assigned fundamentals are listed in Table 7. As stated previously, they agree with the fundamentals listed by Mann, <u>et</u> <u>al</u>. The greatest discrepancy in the wave numbers listed for the fundamentals is found in the case of the a" fundamental measured by Mann, <u>et</u> <u>al</u>, at 607 cm^{-1} and here at 610 cm^{-1}. As stated earlier, this band seems to overlap an impurity band, which may account for the discrepancy.

On the basis of these fundamentals, most of the remaining bands can be interpreted as overtones, binary combinations, or ternary combinations. Of particular interest are the medium type A infrared band at 1339 cm^{-1} and the corresponding weak Raman band at 1338 cm^{-1}. These bands are interpreted as the combination $514 + 835 = 1349$ of species A' in Fermi resonance with the a' fundamental at about 1385 cm^{-1}.

Also of interest in the infrared spectrum are the weak absorption maxima at 751 and 762 cm^{-1}. They are interpreted as the central branch and one of the side branches, respectively, of the difference band $1185 - 433 = 752$ A'. The other side branch is masked by the very strong band at 700 cm^{-1}. The side branches of the infrared bands at 433 and

835 cm^{-1} show structure which cannot be explained as resulting from combinations, overtones, or difference bands. This structure may result from upper stage bands of the fundamentals or from impurities. Two infrared bands have not been interpreted. One is a weak shoulder at 907 cm^{-1}, and the other is a medium band at 1140 cm^{-1}. They may result from impurities although no evidence for this was found when the spectrum was checked for impurity bands.

In the Raman spectrum only the very faint band at 709 cm^{-1} cannot be explained as an overtone, combination, or difference band. It may be an upper stage band corresponding to the fundamental at 700 cm^{-1}, or it may result from an impurity.

Infrared bands which have been identified with the impurity mentioned in Chapter III are listed in Table 8. Although the impurity has not been identified, the following remarks can be made. It is not a common organic compound. It has a boiling point a little below -24° C. It is probably composed of six or more atoms to account for the twelve observed bands. It probably has two C-H bonds to account for the bands at 2930 and 2964 cm^{-1}. A C⋮C bond may be responsible for the band at 2119 cm^{-1}. This indicates the posibility that the impurity may be CH_2F-C⋮C-H, or something similar. Another possibility might be CH_2FOH, although this compound would probably not have a fundamental near 2100 cm^{-1}.

The spectrum shown by Mann, et al. shows most of the bands of the impurity which were observed on the original spectrum obtained here. They have attempted to interpret these bands as bands of $CFCl{:}CH_2$.

The greatest uncertainties in the interpretation given here are concerned with the a' fundamental at about 1385 cm^{-1}, the a" fundamental at 610 cm^{-1}, and the medium infrared band at 1140 cm^{-1}. In the case of the 1385 fundamental it is primarily a question of obtaining a better value for its wave number. Infrared and Raman spectra of the liquid phase should help sort out the fundamental and the neighboring combinations, and a high resolution infrared spectrum might help determine a better value for the fundamental. In the case of the fundamental at 610 cm^{-1} and the band at 1140 cm^{-1} it is a question of whether or not they are bands of impurities. An infrared spectrum of a pure sample of $CFCl{:}CH_2$ would give the answer to this. Except for these three bands and the weak bands mentioned previously, the interpretation of the spectra is satisfactory.

TABLE 5

INFRARED SPECTRUM OF GASEOUS 1-FLUORO-1-CHLOROETHYLENE

Wave number	Description[a]	Band type	Interpretation
359 370 380	vw	A	a' fundamental
422 ~ 426 433 442	m	A	a' fundamental
503 514 524	m	C	a" fundamental
599 610 617	m	C	a" fundamental
695 705	vs	B	a' fundamental
~729	m		2 x 370 = 740 A'
751 762	w	A	1185 - 433 = 752 A'

TABLE 5--Continued

Wave number	Description	Band type	Interpretation
819 824 828 835 843 854 ~858	vs	C	a" fundamental
~865	m		2 x 433 = 866 A'
~907	w		
939 954	vs	B	a' fundamental
1016 1027 1035	m	A	2 x 514 = 1028 A'
1119	m		514 + 610 = 1124 A'
1126	m		433 + 700 = 1133 A'
1140	m		
1175 1185 1193	vvs	A	a' fundamental
~1222	s		2 x 610 = 1220 A'

TABLE 5--Continued

Wave number	Description	Band type	Interpretation
1279	vw		433 + 835 = 1268 A"
1330 1339 1348	m	A	514 + 835 = 1349 A'
1370	m		433 + 946 = 1379 A'
1385	s		a' fundamental
1405	m		2 x 700 = 1400 A'
1535	w		700 + 835 = 1535 A"
1550	m		610 + 946 = 1556 A"; 370 + 1185 = 1555 A'
1567	w		370 + 514 + 700 = 1584 A"
1649 1663	vvs	B	a' fundamental
1697	s		514 + 1185 = 1699 A"
~1738	w		433 + 610 + 700 = 1743 A"; 370 + 433 + 946 = 1749 A'
1751	w		370 + 1385 = 1755 A'
1784	vw		835 + 946 = 1781 A"; 610 + 1185 = 1795 A"
1810	vw		433 + 1385 = 1818 A'
1887 1900	m	B	2 x 946 = 1892 A'; 514 + 1385 = 1899 A"; 700 + 1185 = 1885 A'

TABLE 5--Continued

Wave number	Description	Band type	Interpretation
2020	vw		835 + 1185 = 2020 A"; 370 + 1654 = 2024 A'
2035	vw		2 x 433 + 1185 = 2051 A'; 2 x 610 + 835 = 2055 A"
2059	w		514 + 610 + 946 = 2070 A'; 433 + 700 + 946 = 2079 A'
2074	w		700 + 1385 ≐ 2085 A'; 433 + 1654 ≐ 2087 A'
2135	m		946 + 1185 = 2131 A'
~2172	vvw		514 + 1654 = 2168 A"
2183	vvw		514 + 2 x 835 = 2184 A"; 370 + 433 + 1385 = 2188 A'
2201	vvw		2 x 514 + 1185 = 2213 A'; 433 + 835 + 946 = 2214 A"
2215	vvw		835 + 1385 = 2220 A"
2219	vvw		2 x 700 + 835 = 2235 A"
2237	vvw		2 x 433 + 1385 = 2251 A'; 370 + 700 + 1185 = 2255 A'
2359 2376	m	B	2 x 1185 = 2370 A'
2391	w		514 + 700 + 1185 = 2399 A"; 2 x 610 + 1185 = 2405 A'
2514 ~2530	vw	B	514 + 835 + 1185 = 2534 A'
2554	w		433 + 946 + 1185 = 2564 A'

TABLE 5--Continued

Wave number	Description	Band type	Interpretation
2564	w		1185 + 1385 = 2570 A'
2585	w		514 + 700 + 1385 = 2599 A"; 433 + 514 + 1654 = 2601 A"; 2 x 610 + 1385 = 2605 A'
2607	w		946 + 1654 = 2600 A'
~2625	w		610 + 835 + 1185 = 2630 A'
2642	w		433 + 835 + 1385 = 2653 A"
2676	vw	B	370 + 946 + 1385 = 2697 A'
2695			
2737	vw	B	2 x 1385 = 2770 A'
2753			
2828	w	B	1185 + 1654 = 2839 A'
2847			
~2865	vw		514 + 700 + 1654 = 2868 A"
2881	vw		514 + 2 x 1185 = 2884 A"; 700 + 835 + 1385 = 2920 A"
~3006	w		700 + 946 + 1385 = 3031 A'
3013	w	B	a' fundamental
3027			
~3043	w		1385 + 1654 = 3039 A'
3062	m	B	a' fundamental
3077			
3106	w		370 + 2 x 1385 = 3140 A'

TABLE 5--Continued

Wave number	Description	Band type	Interpretation
3150	vw		835 + 946 + 1385 = 3166 A"
3164	vw		610 + 1185 + 1385 = 3180 A"; 700 + 835 + 1654 = 3189 A"
3275 3293	w	B	2 x 1654 = 3308 A'
3389 3404	vw	B	370 + 3018 = 3388 A'
3436	vvw		370 + 3071 = 3441 A'; 433 + 3018 = 3451 A'
3524 3539	vvw	B	514 + 3018 = 3532 A"; 514 + 3071 = 3585 A"
3762	vvw		700 + 3071 = 3771 A'
3855	vw		835 + 3018 = 3853 A"; 835 + 3071 = 3906 A"
3925	vvw		946 + 3018 = 3964 A'; 946 + 3071 = 4017 A'

[a] The following abbreviations are used: s strong, m medium, w weak, and v very.

TABLE 6

RAMAN SPECTRUM OF GASEOUS 1-FLUORO-1-CHLOROETHYLENE

Wave number	Description[a]	Interpretation
370	w,sh	a' fundamental
432	w,sh	a' fundamental
505	vvw,d	a" fundamental
533		
698	m,b	a' fundamental
709	vvw	
823	vvw,d	a" fundamental
844		
946	m,sh	a' fundamental
1338	w,sh	514 + 835 = 1349 A'
1375	w,sh	433 + 946 = 1379 A'
1380	w,sh	a' fundamental
1400	vvw	2 x 700 = 1400 A'
1422	vvw	610 + 835 = 1445 A'
1637	m,b	700 + 946 = 1646 A'
1654	s,sh	a' fundamental
1670	w,sh	370 + 610 + 700 = 1680 A'?
1689	m,sh	2 x 835 = 1670 A'
3018	w,sh	a' fundamental
3062	m	1385 + 1654 = 3039 A'?

TABLE 6--Continued

Wave number	Description	Interpretation
3071	s,sh	a' fundamental
3102	vw	370 + 2 x 1385 = 3140 A'?
3160	w,d	433 + 2 x 1385 = 3203 A'; 370 + 1185 + 1654 = 3209 A'

[a] The following abbreviations have been used: s strong, m medium, w weak, v very, sh sharp, b broad, and d diffuse.

TABLE 7

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF 1-FLUORO-1-CHLOROETHYLENE

Species	Wave number I.R.(g)	Wave number Ra.(g)	Approximate character
a'	370 vw	370 w	CFCl bending
	433 m	432 w	CFCl bending
	700 vs	698 m,b	C-Cl stretching
	946 vs	946 m	CH_2 rocking
	1185 vvs		C-F stretching
	~1385 s	~1380 w	CH_2 deformation
	1656 vvs	1654 s	C:C stretching
	3020 w	3018 w	C-H stretching
	3070 m	3071 s	C-H stretching
a"	514 m	519 vvw,d	CFCl bending
	610 m		CFCl bending
	835 vs	834 vvw,d	CH_2 wagging

TABLE 8

INFRARED BANDS ASCRIBED TO AN IMPURITY IN THE SAMPLE OF CFCl:CH$_2$

Wave number	Description [a]	Band type
311	w	C
317		
320		
325		
330		
334		
~600[b]	m	
741	w	
773	w	
~796	m	
1078	vw	
~1229	m	
1295	w	
2080	vvw	
2119	m	
2930	vvw	
2964	vvw	
3330	m	B
3347		

[a] The following abbreviations are used: s strong, m medium, w weak, v very.

[b] Masked by the CFCl:CH$_2$ fundamental at 610 cm^{-1}.

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