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VIBRATIONAL SPECTRA OF CFCl:CHBr, C_2H_2FBr, CF_2Br-$CHBr_2$

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VIBRATIONAL SPECTRA OF CFCl:CHBr, C_2H_2FBr, CF_2Br-$CHBr_2$

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VIBRATIONAL SPECTRA OF CFCl:CHBr, C_2H_2FBr and CF_2Br-$CHBr_2$

CHAPTER I

INTRODUCTION

Fluorine chemistry has become of importance in recent years because of the increasing uses of fluorocarbons and fluorinated hydrocarbons in science and industry. The preparation and study of fluorinated hydrocarbons have received an added impetus since World War II, due in part to the production of atomic energy and the problems concerned with it, especially the separation of uranium isotopes. Their availability, together with their possible uses, led several researchers to a study of these compounds.

Fluorine is the most electronegative element and forms carbon compounds which possess unique physical and chemical properties. Most of these compounds are in general very inert and stable and are highly volatile. The fluorocarbons have in general about the same viscosity and temperature coefficient of viscosity as the corresponding hydrocarbons. They have very low surface tension and refractive index, and their dielectric constants are lower than those of hydrocarbons with the same carbon skeleton. By virtue of these interesting properties the fluorocarbons

have been put to innumerable uses in scientific research and industry, e.g., as lubricants, refrigerants and electrical insulators.

Many research workers have been engaged in the study of the molecular structure and properties of these compounds. Infrared spectroscopy is very useful to the analytical and structural chemist, for, in conjunction with the Raman effect, it provides an invaluable tool for the elucidation of molecular structure. There have been extensive spectroscopic investigations of fluorinated hydrocarbons and halogenated hydrocarbons at the University of Oklahoma and at other laboratories in this country as well as in England, Canada and Japan. With the availability of high speed electronic computers much work has also been done on the calculation of the fundamental vibrational frequencies of such compounds.

Much work has also been done on ethylenes and ethanes by means of electron diffraction and microwave spectroscopy. The former method of study has provided valuable information regarding the structural details of the molecules and the latter method gives accurate values for the potential barriers inhibiting internal rotation.

The present work, though not directly, forms part of a larger research project, supported by the Atomic Energy Commission, on the spectroscopic properties of fluorinated hydrocarbons. Since this research concerns the study of fluorinated ethylenes and ethanes, a brief survey of the

earlier work on these compounds is given in the following paragraphs.

Much work has been done in the past on the infrared and Raman spectra of other halogenated ethylenes.[1] Recently, Torkington and Thompson[2] studied six fluorinated ethylenes and gave complete assignments of fundamental vibrational frequencies for some compounds and partial assignments for others. Mann et al.[3] have studied several of the compounds experimentally. Recently, they have given a normal coordinate analysis of all the halogenated ethylenes[4] in which they have used a more general potential function of the Urey-Bradley[5] type than the one used earlier by Morino et al.[6] At the University of Oklahoma Prof. J. Rud Nielsen and his collaborators have been engaged in the study of fluorinated ethylenes and ethanes for more than a decade. They have studied the infrared and Raman spectra of more than ten ethylenes and

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[1]G. Herzberg, Infrared and Raman Spectra of Polyatomic molecules, D. Van Nostrand Co. Inc. N. Y. (1945).

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

[3]D. E. Mann et al., J. Res. National Bur. of Standards, 52, 67 (1954); J. Chem. Phys. 21, 1949 (1953); 22, 1586 (1954); 23, 1989, 2122 (1955).

[4]D. E. Mann et al., J. Chem. Phys. 27, 43 (1957).

[5]H. C. Urey and C. A. Bradley, Phys. Rev. 38, 1969 (1930).

[6]Y. Morino, K. Kuchitsu and T. Shinanouchi, J. Chem. Phys. 20, 726 (1952).

reported assignments for nine of these.[7] They have also calculated the thermodynamic properties of most of these compounds in the ideal-gaseous state. The symmetry species of the vibrational fundamentals were identified from the shapes of the infrared band contours and the separations of the P and R branches, as well as from polarization measurements of the Raman spectra or from Raman spectra of the compounds in the gaseous state.

Certain details of the spectra of these compounds throw much light on the structure of the molecules. For example, the band associated with C=C stretching is very intense in the Raman spectrum as well as in the infrared spectrum. The frequency of this band, which occurs at 1626 cm^{-1} in ethylene, is increased considerably by a substitution of one or more of the hydrogen atoms by fluorine atoms; whereas it is reduced, as might be expected, when substituted by chlorine or bromine atoms. It occurs around 1640 cm^{-1} when one fluorine atom is substituted and around 1749 cm^{-1} when two fluorine atoms are substituted. It reaches its highest value 1870 cm^{-1} in C_2F_4. Bands associated with CF stretching in all fluorinated hydrocarbons are weak and diffuse in the Raman effect and strong in the infrared. This is probably due to the highly ionic

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[7] J. Rud Nielsen et al., J. Chem. Phys., 16, 67 (1948); 18, 1471 (1950); 20, 473, 847 (1952); 21, 383, 1060, 1070 (1953); 23, 329 (1955); 27, 891 (1957); 27, 887 (1957).

character of the CF bond. The other fluorinated hydrocarbons likewise exhibit characteristic features.

Over twenty fluoro- and fluoro-chloroethanes with symmetrical end-group have been studied in this laboratory.[8] Substituted ethanes with no symmetrical end group are much more numerous. The spectra of some of these have been studied by Bernstein,[9] Kagarise[10] and Mizushima.[11] These workers have been mostly concerned with the problem of rotational isomerism. Rotational isomerism was first studied in organic compounds by Kohlrausch[12] who was led to believe in the existence of two isomeric forms by the large number of Raman lines observed in the spectrum of 1,2-dichloroethane in the liquid state.

The existence of two isomeric forms was definitely established by the later work of Kemp and Pitzer, Kistiakowsky, Lacher and Stitt and Wilson on the entropy and low temperature

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[8] J. Rud Nielsen et al., J. Chem. Phys. 16, 67 (1948); 18, 1471 (1950); 20, 473, 847 (1952); 21, 383, 1060, 1070 (1953); 23, 329 (1955); 27, 891 (1957); 27, 887 (1957).

[9] H. J. Bernstein et al., J. Chem. Phys. 8, 410 (1941); 17, 256, 358 (1949); 18, 897 (1950); J. Am. Chem. Soc. 73, 1815 (1951), 74, 1859 (1952).

[10] R. E. Kagarise et al., J. Chem. Phys. 17, 1354 (1949); Trans. Faraday Soc. 48, 394 (1952); J. Chem. Phys. 23, 207 (L), 113, 130 (1955); 24, 1264 (1956); 26, 380 (1957); 29, 680 (1958).

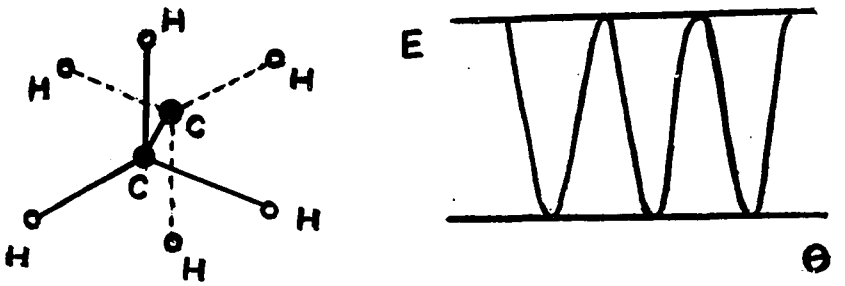
[11] S. Mizushima, Structure of Molecules, Academic Press Inc., Publishers, New York, N. Y. (1954).

[12] K. W. F. Kohlrausch, Z. physik. Chem. B, 1932, (18) 61.

heat capacity of C_2H_6 and C_2D_6.[1] They showed that the rotation of the two CH_3 groups in ethane relative to each other about the C-C axis is not free, as was long assumed by chemists. Measurements of the dipole moments of ethane and substituted ethanes, and the temperature variation of the dipole moments, have also confirmed this hypothesis. It is now believed that there are in general more than one potential minimum in one complete rotation of the end group about a single bond as axis, as shown in Figure 1 (b).

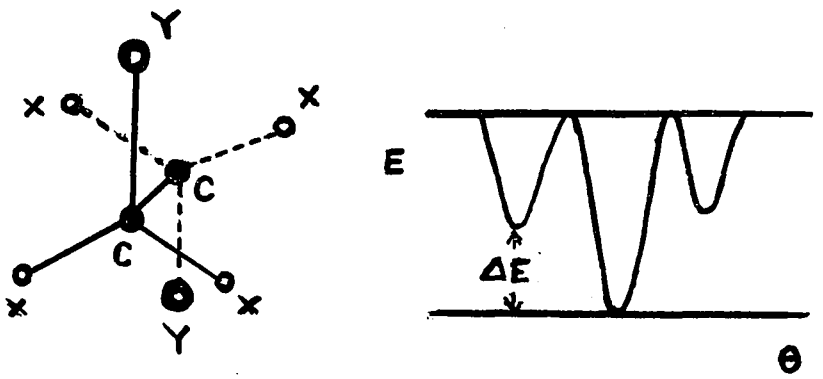
The minima correspond to the three identical stable configurations. They can be represented roughly by $\frac{1}{2} V_o(1-\cos 3\theta)$; however, the potential curve is not well known for any substituted ethane. In any case, the potential curve must of course by symmetrical around $\theta = 180^o$. Figures 2 (b) and (d) indicate possible potential curves for the trans and gauche forms of a molecule of type $CX_2Y-CX_2^1Y^1$ such as CH_2Cl-CH_2Cl or $CF_2Br-CBr_2H$. The spacing between two different minima may not be exactly 120°. If one minimum is deeper than the others, it corresponds to the more stable (i.e. less energetic) configuration; e.g. (a) represents the case where the trans form is more stable and (c) represents the case where the gauche form is more stable. In the liquid state the potential curve is generally different and the value of ΔE_o^o may not be the same as for the gas.

Although more than one stable configuration occurs in the liquid and gaseous phases of these compounds, cases

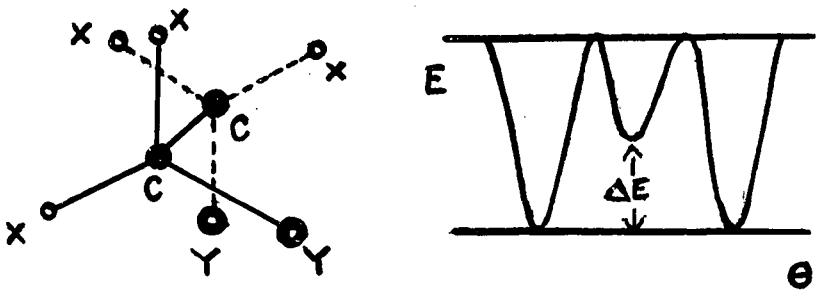


(a) (b)

Fig. 1. Molecular Configuration and Potential Curve of Ethane.



(a) (b)



(c) (d)

Fig. 2. Stable Configurations and Potential Curves of Molecule of Type CX_2Y-CX_2Y

are known in which only one form exists in the crystalline phase. Hence the spectrum of the crystalline solid may be simpler than those of the liquid and gas. This was first inferred by Mizushima and his coworkers[11] from the Raman spectra of 1,2-dihalogenoethanes.

In spite of the fact that these molecules exist in different isomeric forms, the great similarity in their physical and chemical properties makes their separation impossible. Nevertheless, the small differences in their heat functions and entropies can, in some cases, be obtained from the measurements of the temperature dependence of the intensities of Raman and infrared bands associated with the isomeric forms. This method of determining ΔE_o^o was first employed by Langseth and Bernstein[13] who measured the variation of intensities of infrared bands and later by Rank[14] and coworkers who made similar observations in the Raman effect. The energy difference has also been determined by measurements on the infrared bands in the liquid and vapor phase by Bernstein[15] and Mizushima.[16] The former has also determined these energy differences for several substituted ethanes from

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[13]A. Langseth and H. J. Bernstein, J. Chem. Phys. 8, 410 (1941).

[14]D. H. Rank et al., J. Chem. Phys. 16, 704 (1948); 17, 1354 (1949).

[15]H. J. Bernstein et al., J. Chem. Phys. 17, 258 (1949); 18, 897 (1950).

[16]S. Mizushima et al., J. Chem. Phys. 17, 591 (1949).

measurements made in solutions of the samples in dilute non-polar solvents.[17]

Recently work has been done in this laboratory by Klaboe[18] on CF_2H-CF_2H and a number of other substituted ethanes exhibiting rotational isomerism.

Some of the methods mentioned above have been employed in the present research in order to see if the bands occuring in the infrared and Raman spectra of the halogenated ethane CF_2Br-$CHBr_2$ are due to more than one isomer.

In this thesis a detailed study is made of the infrared and Raman spectra of the fluorinated ethylenes CFCl=CHBr and C_2H_2FBr and the ethane CF_2Br-$CHBr_2$. Since each of these compounds presents different problems, the work done on each compound and the results obtained are discussed in separate chapters.

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[17] H. J. Bernstein, J. Am. Chem. Soc., 73, 1815 (1951).

[18] P. Klaboe and J. Rud Nielsen (private communication).

CHAPTER II

EXPERIMENTAL

The infrared absorption spectra of the compounds in the gaseous state at room temperature were obtained with the aid of a Perkin-Elmer Model 112 double-pass spectrometer and an automatic recorder. A multiple-reflection cell of 1 m path length, fitted with KRS-5 windows was used.

The spectrometer was flushed with dry nitrogen to reduce absorption by atmospheric water vapor and carbon dioxide. Even so, the absorption due to the latter could not be completely eliminated. It is obvious that the amount of light incident on the detector for a particular wavelength setting depends on the number of molecules in the path of light, for a certain slit width and current through the globar. The absorbing molecules in the path of light also include traces of water vapor and carbon dioxide present in the instrument. Therefore, the actual transmittance due to the sample at any point in the transmission curve was obtained in the following way. The absorption curve (I_o curve) with the cell empty was obtained. Then the absorption curve I with the sample was recorded, superposed on the I_o curve. In order to do this, the recording paper was rolled

back and the latter curve started exactly at the same position as the I_o curve. The zero transmission line was carefully recorded with the slits closed. The percentage of energy transmitted for any wavelength was read off with the aid of a Gerber variable scale. When the zero and hundred percent transmission marks on this scale coincide with the zero and I_o, obtained as described above, the reading at any point on the absorption curve gives the per cent transmission directly.

In order to study the absorption spectra of the gases at higher temperatures, a cell constructed by Mr. C. J. Halley was used. This cell consists of a brass cylinder 10 cm long and of 5 cm external diameter provided with thick KBr windows. These windows lie inside screw caps which press them tightly against the plane ends of the brass cylinder from which they are separated by rubber gaskets. The seals are made air tight by means of glyptal. A coil of chromel wire is wound around the cell which is heated by passing a suitable current through the wire. The temperature of the gas inside is measured around the midpoint of the cell with a calibrated constantan-iron thermocouple placed in contact with the metal part. The cell is connected to a vacuum line by means of a short capillary tube attached to its side with the aid of a glass metal joint. The capillary tube is used in order to keep the number of absorbing molecules inside the cell nearly constant.

The absorption spectra of the liquids were obtained

with sealed and demountable cells constructed in this laboratory.[19] Sealed cells of thickness 90 μ and 50 μ were used. For the very intense bands a demountable cell with sufficiently thin spaces was used.

For the study of the liquids at different temperatures, the sealed cell is provided with a heating coil. The temperature was measured by means of a calibrated iron-constantan thermocouple placed in contact with a piece of aluminum foil wrapped around the side of the cell and in good contact with the windows.

The infrared absorption spectra of the samples in the solid state were obtained with the aid of a low-temperature cell designed by Mr. C. J. Halley. It is somewhat similar to the cell described by Lord, McDonald and Miller.[20] The cell constructed in this laboratory, consists of two parts as shown in Fig. 3. The upper part is a dewar, 20 cm high and of 6 cm internal diameter, with a Kovar glass metal seal at the bottom. To the metal seal is attached a small hollow metal cap with a screw thread in which fits a copper cylinder carrying a rectangular copper frame. A silver chloride or KBr plate is attached firmly to the copper frame by means of screws. The metal joint and the copper cylinder ensure good

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[19] D. C. Smith and F. C. Miller, J. Opt. Soc. Am. 34, 130 (1944).

[20] R. C. Lord, R. S. McDonald and F. A. Miller, J. Opt. Soc. Am., 42, 149 (1951).

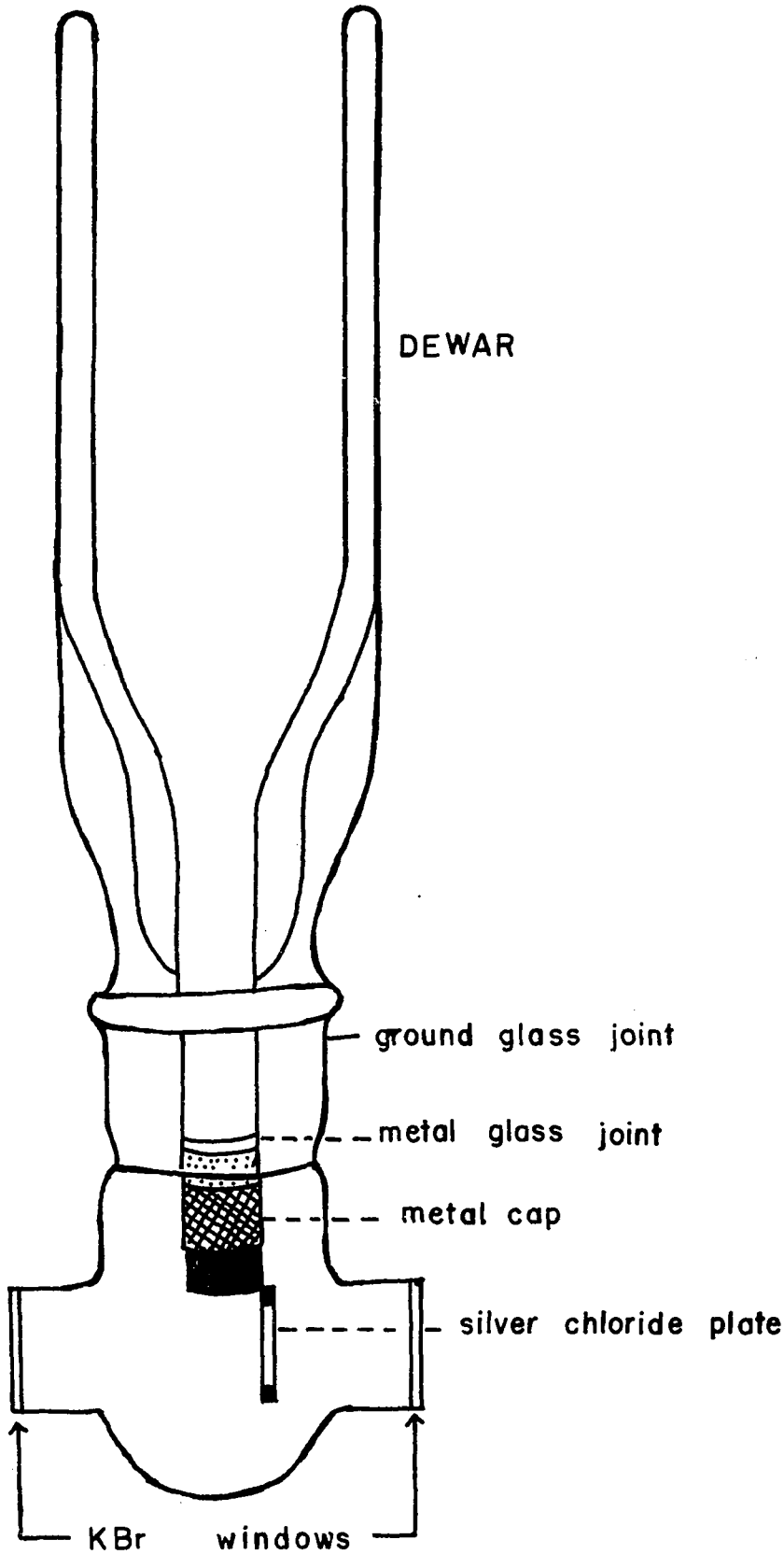


Fig. 3. Low Temperature Cell For Infrared Work.

thermal contact between the refrigerant in the dewar and the silver chloride (or KBr) plate. The dewar is provided with a ground joint which fits over the lower part. The ground joint must be greased well so that there will not be any difficulty in separating the dewar from the cell.

The lower part is a glass bulb, as shown in Fig. 3, fitted with thick KBr windows, attached firmly to the cell with the aid of glyptal. The windows are 5 cm in diameter and fit exactly in front of the condensing system and the entrance slit of the spectrometer. The silver chloride (or KBr) plate mentioned above is in line with the windows of the cell. The latter is provided with a narrow side tube, at the end of which is a ground joint connecting the cell to a vacuum line and a manometer.

The cell is evacuated carefully and the dewar is filled with liquid air which cools the copper cylinder below, and this in turn cools the silver chloride (or KBr) plate. When the stop cock in the side tube attached to the container of the sample under investigation is opened, the sample passes into the cell and condenses on the cooler parts of the latter, in particular on the silver chloride (or KBr) plate. Care must be taken to see that the cell is evacuated thoroughly and also that there are no traces of air inside the dewar. For if there is any moisture over the metal part in the dewar, it freezes and forms a good insulation between the refrigerant and the metal part, thus making it difficult to produce a low

temperature inside the cell. To improve thermal contact a piece of aluminum foil is wrapped along the edges of the silver chloride (or KBr) plate.

It is very important that the solid formed be in the crystalline state; for if it is in the form of a glass its spectrum is more or less the same as that of the liquid. To insure that the solid is in the crystalline form the vapor must be let in very slowly. The temperature at which the condensation takes place is also important. However, in the cell used here there is no provision for varying the temperature except by varying the nature and the amount of the refrigerant. Unfortunately, even when the vapor is admitted as slowly as practicable, one cannot be absolutely certain that the solid formed is in the crystalline state.

The Raman spectra of the compounds were obtained with the spectrograph described by Classen[21] and Hudson.[22] The linear dispersion is 15 A/mm near 4358 A and 34 A/mm at 5000 A. Eastman Kodak Royal Pan sheet film was used for the photographic recording of most of the spectra. The films were developed for 12 minutes in Kodak DK-60a developer at 20°C. Much faster but more coarse-grained films, SO 1177 and Royal X Pan, manufactured by Eastman Kodak were used for

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[21] H. H. Classen, "Raman Spectra of Some Fluorinated Hydrocarbons" (Unpublished Ph.D. dissertation, Dept. of Physics, Oklahoma University).

[22] R. L. Hudson, "Raman Spectra of Some Fluorinated Aromatics" (Unpublished Ph.D. dissertation, Dept. of Physics, Oklahoma University).

the strongest exposures. They reduced the times of exposure by a factor of 6 or 8. An iron arc comparison spectrum was photographed adjacent to the Raman spectrum. The film was enlarged 22.5 times and the frequencies of the Raman bands were determined by interpolation using close iron lines for reference and a large-scale calibration curve.[21,22]

In the tables listing the Raman data the following abbreviations were used to describe roughly the relative intensities and the general appearance of the bands; s strong, vs very strong, vvs very very strong, m medium, w weak, vw very weak, vvw very very weak, sh sharp, d diffuse and b broad.

The Raman exposures intended for polarization measurements were obtained by an apparatus similar to that developed by Crawford and Horwitz.[23] It is described in detail in the thesis of Classen.[21]

The Raman spectra of the compound in the liquid state at low temperatures (-50°C to -70°C) were obtained by a method developed by Jackson.[24] The Raman tube was enclosed in a double-walled vacuum jacket through the interior of which was maintained a continuous flow of nitrogen gas cooled by passing it through a coil immersed in liquid air. The

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[23]B. L. Crawford Jr. and W. Horwitz, J. Chem. Phys. 15, 882 (1947).

[24]Jasper A. Jackson Jr.: Vibrational Spectra of Lead Alkyls (Unpublished Ph.D. dissertation, Dept. of Physics, Oklahoma University).

temperature inside the jacket could be varied by adjusting the flow of nitrogen and was measured by means of a calibrated thermocouple.

CHAPTER III

INFRARED AND RAMAN SPECTRA OF CFCl:CHBr

Introduction

Much work has been done on the study of infrared and Raman spectra of substituted ethylenes. Nevertheless, very few compounds with three of the hydrogen atoms substituted have been previously studied.[25,26,27] In this chapter is given an account of the results obtained in a study of the infrared and Raman spectra of CFCl:CHBr. It appears that no previous spectroscopic work has been done on this compound. Moreover, no data are available on this compound from other fields of investigation, such as electron diffraction or microwave spectroscopy.

Experimental Results

The sample (b.p.68°C at 630 mm pressure) was prepared in the laboratory of Professor J. D. Park at the University of Colorado. No information was given regarding its purity

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[25] D. E. Mann, N. Acquista and E. K. Plyler, J. Chem. Phys. 22, 1586 (1954).

[26] J. Rud Nielsen, C. Y. Liang and D. C. Smith, J. Chem. Phys. 20, 1090 (1952).

[27] J. Rud Nielsen and Rose Theimer, J. Chem. Phys. 27, 264 (1957).

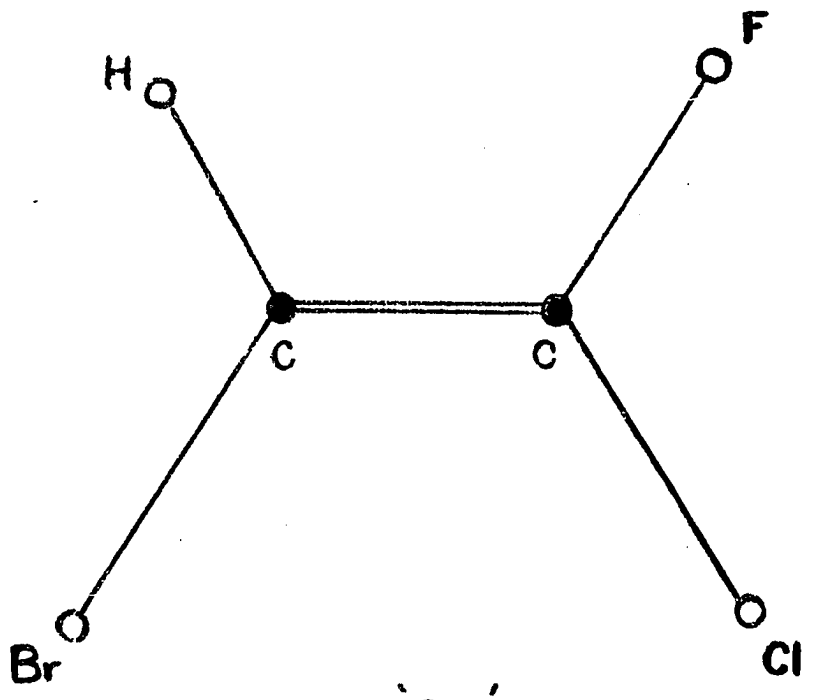
nor as to which isomer was present. However, the spectra indicate the presence of two isomers.

The infrared absorption spectrum of the gas at room temperature was obtained with a Perkin-Elmer Model 112 double-pass spectrometer equipped with CsBr, NaCl and LiF prisms and with a 1-m cell. The wave numbers of the observed absorption maxima (or in some cases "shoulders") are listed in Table I and the spectra are shown in Figs. 5-7. The spectrum of the liquid was obtained with the sealed and demountable cells mentioned in Chapter II. The spectra are shown in Figs. 8-10, and the data are listed in Table II.

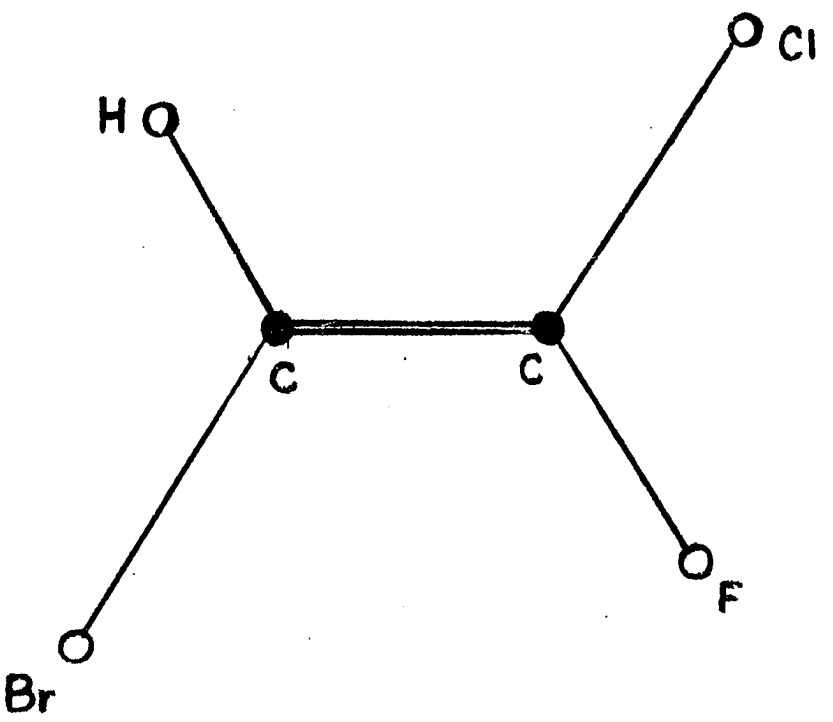
The Raman spectrum of the liquid sealed in a Pyrex glass tube was obtained at room temperature. Spectra intended for polarization measurements were photographed but no quantitative measurements could be made because of a pronounced background which probably was due to the photosensitivity of the sample. The Raman spectrum of the liquid was also observed at a temperature of -50°C. Apart from the fact that the Raman bands were sharper and better defined, as expected, the latter spectrum did not provide additional information. The Raman spectral data are listed in Table III.

Interpretation

The structural formula CFCl:CHBr can represent either of the two isomeric forms pictured in Fig. 4: (a) a form in which the Cl and Br atoms are in the cis position relative to each other, and (b) a form in which the Cl atom



a - 'Cis'



b - 'Trans'

Fig. 4. Molecular Configurations of CFCl=CHBr

is in the trans position relative to the Br atom. For brevity, these forms will henceforth be referred to as the cis and trans forms. In either form the molecule has the symmetry C_S, so that the 12 normal vibrations divide into nine of species a' (in-plane) and three of species a" (out-of-plane).

As already mentioned the observed spectra contain almost twice the number of intense bands expected of a single isomer. This indicates that both isomeric forms are present in the sample. However, one of them appears to be considerably more abundant than the other. The sample was tested with a gas chromatograph, and the result confirmed the presence of two isomeric forms of considerably different abundance.

The moments of inertia of the two molecular species have been calculated. In the absence of electron diffraction data for this compound, the following structural parameters taken from previous work on related compounds[28] were used: the C:C, C-F, C-Cl C-Br distances as 1.31, 1.31, 1.72, 1.90 A, respectively, and the C=C-halogen angles as 123°. The calculated moments of inertia for the cis form are: 166.4, 654.9, and 821.3×10^{-40} g.cm.^{2} The moments of inertia obtained for the trans form are: 125.0, 911.3 and 1036.3×10^{-40} g. cm.^{2} The axes corresponding to the smallest moments of inertia make angles, with the C=C bonds, of 21°26' in the cis and 40°43' in the trans molecule.

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[28] D. E. Mann et al., J. Chem. Phys. 27, 52 (1957).

Since the axes belonging to the largest moments of inertia are perpendicular to the symmetry planes or planes of the molecules, the a" bands in both cases are of type C. On the other hand, the a' bands will generally be hybrids between types A and B. From the calculated values of the moments of inertia the Badger-Zumwalt[29] parameters, $\rho=(a-c)/b$ and $s=(2b-a-c)/(a-c)$ were determined; a,b,c, are the reciprocals of the moments of inertia, $A<B<C$, respectively. From these parameters and the curves given in the paper of Badger and Zumwalt,[29] approximate information regarding the contours of type A, B and C bands can be obtained. In the present cases, it was found necessary to extrapolate from the Badger-Zumwalt curves to such an extent that the results were not very useful.

The calculated moments of inertia show that both molecules are fairly nearly symmetric tops with the axes of smallest moments of inertia lying in the symmetry plane. Therefore the a" fundamentals can also be described roughly as perpendicular bands and the a' fundamental hybrids between perpendicular and parallel. Some information regarding the contours can therefore be obtained from a paper by Gerhard and Dennison.[30] From the parameter $\beta=(A/C)-1$, where $A=B\neq C$, the doublet separation for the "parallel" bands are found to be

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

[30]S. L. Gerhard and D. M. Dennison, Phys. Rev. 43, 197 (1933).

9 cm^{-1} and 10 cm^{-1} for the cis and trans molecules, respectively. The ratio of the Q branch to the entire parallel band is found to be 0.2 for the cis and 0.1 for the trans. The perpendicular bands including the a" fundamentals should be broad in both cases, and more so for the trans than for the cis molecule. The a" bands of the cis form should have a more pronounced zero branch than for the trans form. Unfortunately, the contours of most of the bands in the infrared spectrum of the gas are not well defined due to overlapping. However the presence of more than one band if they are close together is ascertained with the aid of the infrared spectrum of the liquid and the Raman spectrum.

In certain spectral regions the bands seem to occur in pairs, one band of the pair being more intense than the other. In such cases it is natural to assume that the stronger of the two belongs to the more abundant isomeric form. Thus two intense bands are present in the Raman spectrum at 3115 cm^{-1} and 3092 cm^{-1}, the former being the stronger of the two. These are undoubtedly the two expected fundamentals associated with C-H stretching motions. The corresponding bands in the infrared spectrum of the gas occur at 3108 cm^{-1} and 3107 cm^{-1}; and in the infrared spectrum of the liquid at 3113 cm^{-1} and 3089 cm^{-1}. Again the band of higher wave number is the more intense. It will be ascribed to the more abundant isomer which will be denoted by I, while the band at 3107 cm^{-1} is ascribed to the less abundant isomer which

will be designated as II. The question whether I is cis or trans (in the sense described above) will be discussed later.

There are two strong bands at 1650 and 1640 cm^{-1} in the infrared spectrum of the gas. The corresponding bands occur with high intensity at 1650 cm^{-1} and 1632 cm^{-1} in the Raman spectrum of the liquid. These undoubtedly represent a' fundamentals due to C=C stretching, one for each isomer. This is in accord with the observations made by previous workers,[31] and with the calculations made by Mann and others,[32] that the wave number of this fundamental is about 1640 in ethylenes with only one fluorine atom substituted. In both the infrared and the Raman spectrum the band at higher frequency is more intense than the other. It is, therefore, attributed to isomer I and the other to II.

Two bands at 1125 cm^{-1} and 1250 cm^{-1} are very strong in the infrared spectrum but have rather weak counterparts at 1125 cm^{-1} and 1242 cm^{-1} in the Raman spectrum; especially the Raman band at 1125 cm^{-1} is very diffuse. These bands are assigned as a' fundamentals. They are probably associated with C-F stretching motions which usually exhibit the above spectral features. The stronger band at 1125 cm^{-1} in the infrared spectrum of the gas is ascribed to I and the weaker band near 1250 cm^{-1} to II.

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[31] J. B. Hatcher and D. M. Yost, J. Chem. Phys., 5, 992 (1937).

[32] D. E. Mann et al., J. Chem. Phys., 27, 51 (1957).

In the infrared spectrum of the gas two bands are observed at 1060 cm^{-1} and 1082 cm^{-1} and in the infrared spectrum of the liquid at 1057 cm^{-1} and 1079 cm^{-1}. There does not seem to be any doubt that these are a' fundamentals of the two isomers; the stronger band of higher frequency is ascribed to I and the weaker band to II. In the Raman spectrum there are two bands of medium intensity at 1072 cm^{-1} and 1083 cm^{-1}. In addition there is a very weak and diffuse band at 1062 cm^{-1}. There can be no doubt that the band at 1083 cm^{-1} corresponding to the band at 1082 cm^{-1} in the infrared spectrum of the gas and to the band at 1079 cm^{-1} in the infrared spectrum of the liquid, is the a' fundamental of I. In view of its intensity the band at 1072 cm^{-1} might be interpreted as the corresponding a' fundamental of II. However, the frequency of the weak band at 1062 cm^{-1} agrees fairly well with that of the band at 1057 cm^{-1} in the infrared spectrum of the liquid. It is therefore assigned as the a' fundamental of II and the band at 1079 cm^{-1} is believed to be the overtone of the fundamental at 532 cm^{-1}. The peculiarities in the intensities of these bands are discussed later.

The Raman bands at 831 cm^{-1} and 801 cm^{-1} are undoubtedly a' fundamentals of the two isomers. The former is very weak but has very strong counterparts at 833 cm^{-1} in the infrared spectrum of the gas, and at 829 cm^{-1} in the infrared spectrum of the liquid. The bands near 801 cm^{-1} are strong in all these spectra. These fundamentals are probably

associated largely with C-Cl stretching. The fundamental of lower frequency which is the stronger of the two in the infrared spectra of both gas and liquid is ascribed to I and the other to II. Other spectral features supporting this choice will be discussed later. Likewise, the two Raman bands at 647 cm^{-1} and 532 cm^{-1} are assigned as a' fundamentals associated with C-Br stretching. The corresponding bands in the infrared spectrum of the gas and the liquid appear at 647 cm^{-1} and 546 cm^{-1}, and at 641 cm^{-1} and 532 cm^{-1}, respectively. The fundamental of higher frequency which is strong in all three spectra is ascribed to I, while that of lower frequency which is weaker in all spectra is ascribed to II.

In the infrared spectrum of the gas a very strong absorption maximum is found at 753 cm^{-1} surrounded by shoulders on both sides. The contour, although not clear cut, indicates that it may be a type C band. In the infrared spectrum of the liquid two maxima are found, one at 755 cm^{-1} and a weaker one at 746 cm^{-1}. In the Raman spectrum a strong band is observed at 748 cm^{-1} and a much weaker and more diffuse band at 759 cm^{-1}. The infrared band at 753 cm^{-1} in the gas, and the Raman and infrared bands in the liquid near 747 cm^{-1} are assigned as an a" fundamental of I. The bands near 757 cm^{-1} in the liquid and the shoulder at 759 cm^{-1} in the gas are assigned as the corresponding a" fundamental of II. The motion associated with these fundamentals may be

described roughly as CHBr wagging.

In the Raman spectrum a weak band is found at 490 cm^{-1}. The corresponding infrared band in the gas at 493 cm^{-1} has definitely type C contour. It is interpreted as an a" fundamental and is ascribed to I. The bands at 434 cm^{-1} which are rather more intense in the infrared and Raman spectra, are assigned as the corresponding a" fundamental of II.

Although the main criterion for ascribing the fundamentals to the two molecules has been the relative intensities of the bands, the interpretation of many of the weaker bands as binary combinations in terms of the fundamentals has also been considered. The assignment which explains the largest number of combination bands has been taken as the most probable one. On this basis, the more intense bands at 434 cm^{-1} are ascribed to the less abundant molecule II and the less intense bands at 490 cm^{-1} to I. For similar reasons the very strong Raman band at 272 cm^{-1} is assigned to II and the weaker band near 225 cm^{-1} to I. These are a' fundamentals probably involving mainly CHBr rocking.

The fact that the number of intense bands in both the infrared and Raman spectra is less than 24 shows that there must be some fundamentals which are common to both molecular species. The strong Raman band at 354 cm^{-1}, the medium intensity infrared band at 352 cm^{-1} in the gas, and the strong infrared band observed at 350 cm^{-1} in the liquid are

assigned as an a' fundamental common to both isomers. It is probably associated mainly with CFCl deformation. The intense Raman band of wave number 167 is also assigned as an a" fundamental common to both molecular species; the motion involved is perhaps largely CFCl rocking.

The bands of wave numbers below 350 were observed only in the Raman spectrum. The Raman bands at 146 cm^{-1} and 176 cm^{-1} are assigned as the lowest a" fundamentals; the more intense band at 146 cm^{-1} is ascribed to I and the less intense band of higher wave number to II. The motions probably consist largely of twisting.

Discussion

As has already been mentioned, the Raman band at 1060 cm^{-1} is very weak and diffuse. It is identified with the a' fundamental corresponding to the strong infrared band of the liquid near 1057 cm^{-1}. The Raman band of wave number 1072 is very strong and is interpreted as the overtone of the fundamental at 532 cm^{-1}. The enhancement of the intensity of the overtone may be due to Fermi resonance. There are certain other bands which exhibit similar pecularities of enhancements of intensities and also frequency shifts; these are designated by (F) in the tables.

In the absence of calculated frequencies of the fundamentals for the molecules in question, the fundamental vibrational frequencies of trans and cis CFCl:CFBr (which appears to be most similar to the compounds under investigation)

from the paper by Mann[32] et al. are given for comparison along with the assigned fundamentals of CFCl:CHBr in Table VI.

The above assignment of fundamentals can be tested by certain sum rules proposed by Bernstein[33] and Mizushima.[34] According to the former, the sum of in-plane and out-of-plane fundamentals for the two molecular species must be the same. These sums are found to be 1392 cm^{-1} and 1369 cm^{-1} for the a" fundamentals, and 9181 cm^{-1} and 9227 cm^{-1} for the a' fundamentals of I and II, respectively. Thus this sum rule is satisfied fairly accurately.

It has been formerly shown by Mizushima[35] that $\Sigma_i \nu_i^2$ is constant for rotational isomers of ethanes. This is derived from the well known relation[36] $|FG-4\pi^2\nu^2E|=0$ for the case of rotational isomers having force constants that are approximately the same. It has been shown that this rule also holds well for the cis and trans isomers of ethylenes (1,2 dichloroethylene and the deuterated compounds of the same). In the present case, the sums of the squares of the assigned wave numbers are 17045 x 10^3 and 17042 x 10^3 for molecules I and II respectively. This close agreement lends considerable support to the assignments made.

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[33]H. J. Bernstein, J. Chem. Phys. 20, 263 (1952).

[34]S. Mizushima et al., J. Chem. Phys. 21, 215 (1953).

[35]S. Mizushima, Structure of Molecules (Academic Press Inc. Publishers, N. Y., 1954).

[36]E. B. Wilson, J. C. Decins and P. C. Cross, Molecular Vibrations (Mc Graw-Hill Book Co. Inc., N. Y., 1955).

It does not seem to be possible to definitely identify molecule I and II with either the cis or the trans forms as defined previously. One difficulty, is that, as has already been mentioned, many of the bands overlap so that the contours are not quite clear. However, there are a few bands with well-defined contours of which the one at 493 cm^{-1} is certainly an a" band. This may be due to the cis form which, as mentioned earlier, should have more intense zero branches than those of the trans form. This band has already been assigned to molecule I. Therefore it appears that molecule I can be identified with the cis form. Again, for the cis isomer, the C-F and C-Br stretching motions are approximately in the direction of the axis of least moment. The bands representing these modes of vibration should be parallel, as the observed bands near 1125 cm^{-1} and 801 cm^{-1} which are assigned as fundamentals of molecule I, appear to be. This assignment of a particular set of bands to one of the two molecular species in question cannot be taken as conclusive evidence, but needs to be confirmed by other experimental and theoretical facts, such as an observation of the spectrum with better resolution or calculation of the fundamental vibrational frequencies by a normal coordinate analysis. Though it would be desirable to separate the two molecular species this may be very difficult, for it is likely that the two form an azeotropic mixture.

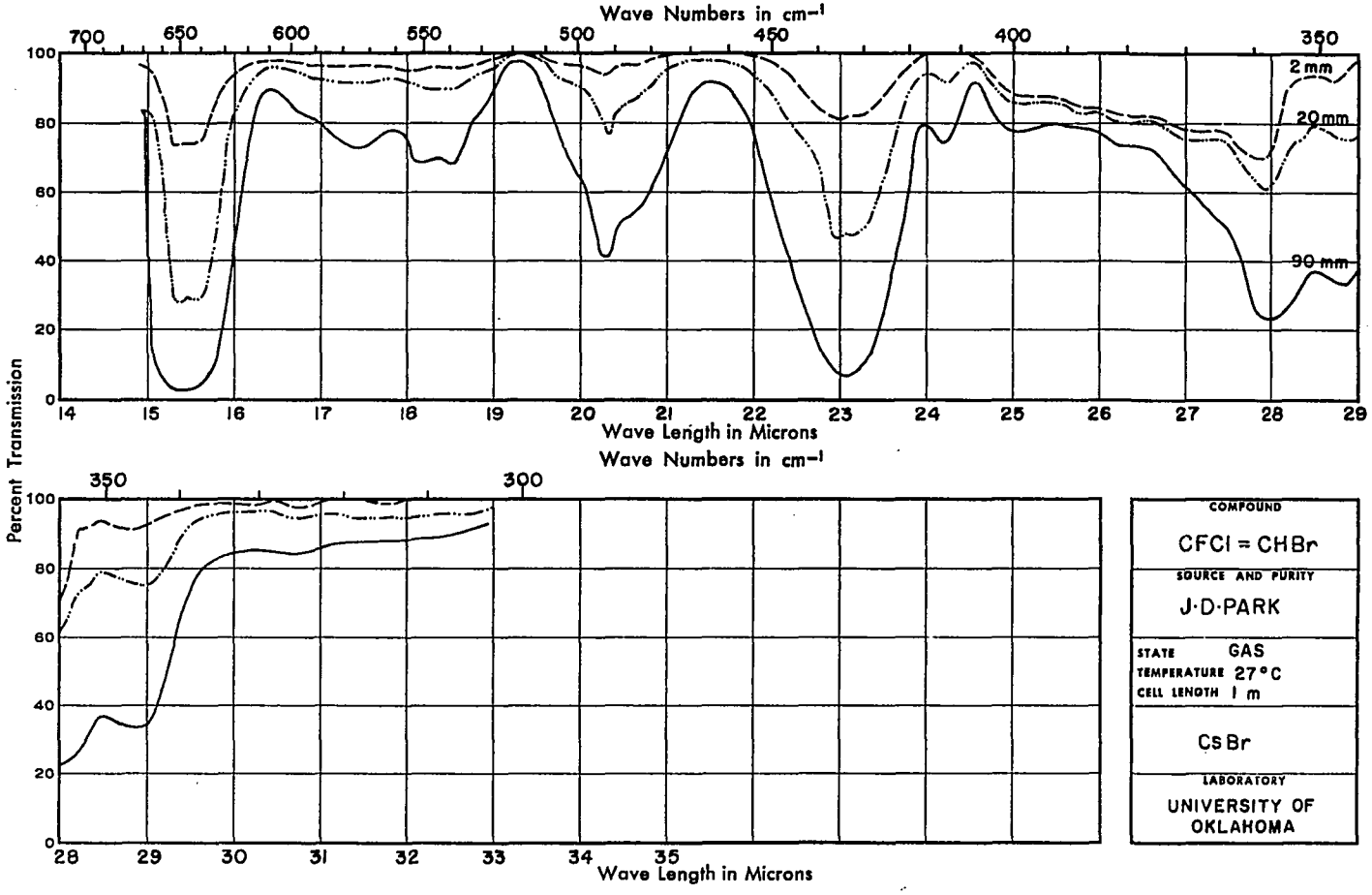


Fig. 5. Infrared Spectrum of Gaseous CFCl-CHBr (CsBr Region).

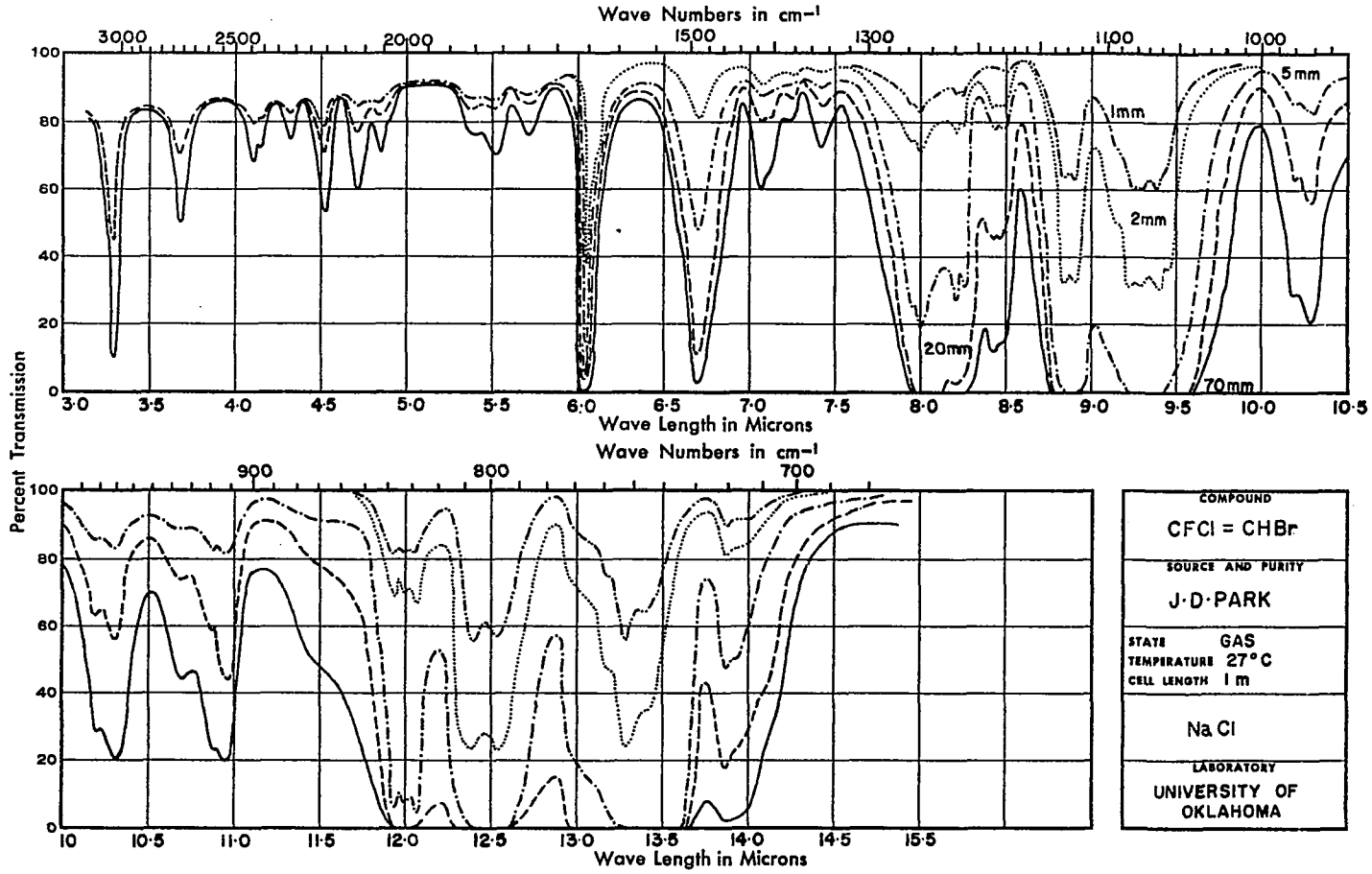


Fig. 6. Infrared Spectrum of Gaseous CFCl:CHBr (NaCl Region).

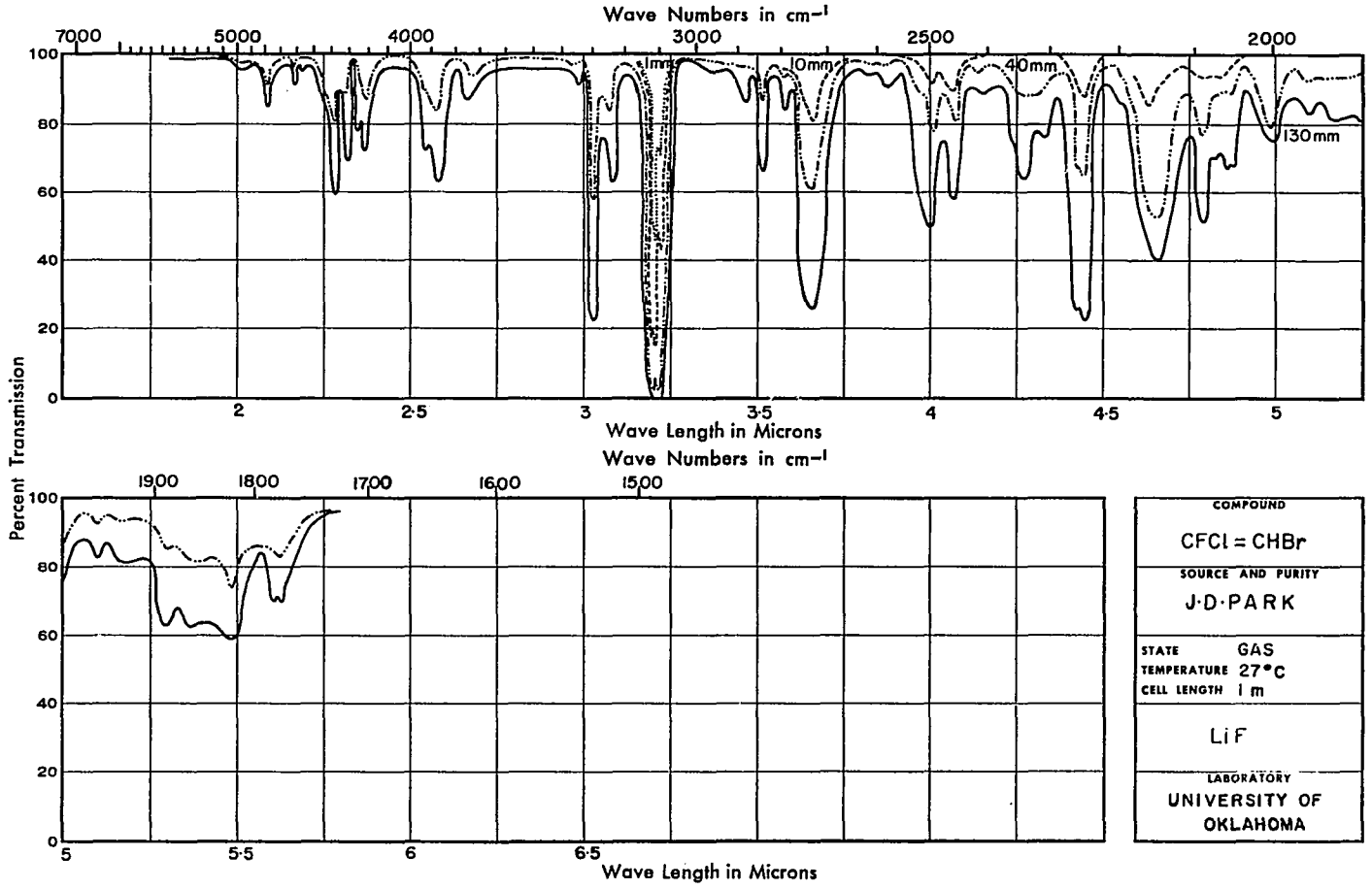


Fig. 7. Infrared Spectrum of Gaseous CFCl:CHBr (LiF Region).

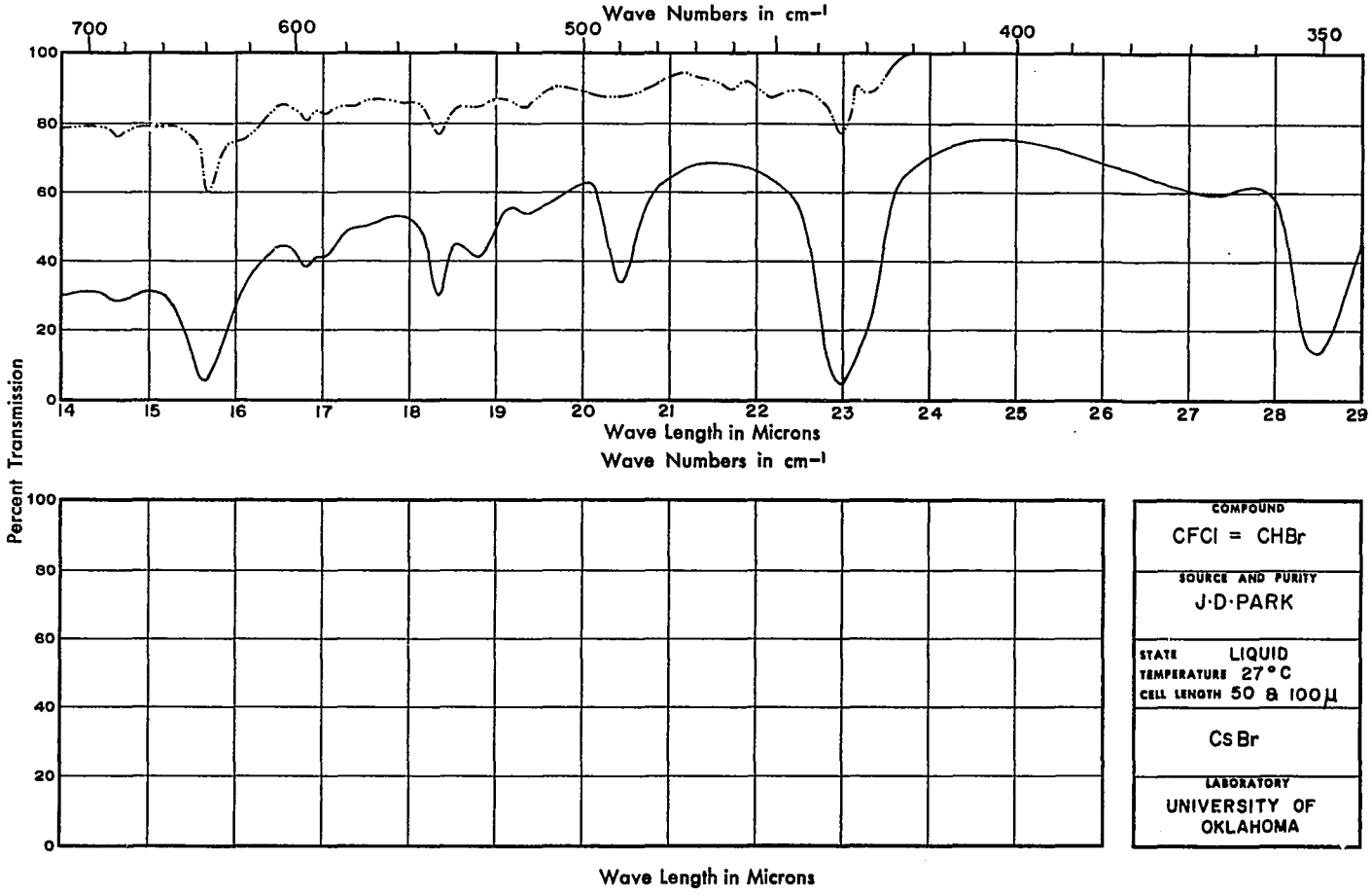


Fig. 8. Infrared Spectrum of Liquid CFCl:CHBr (CsBr Region).

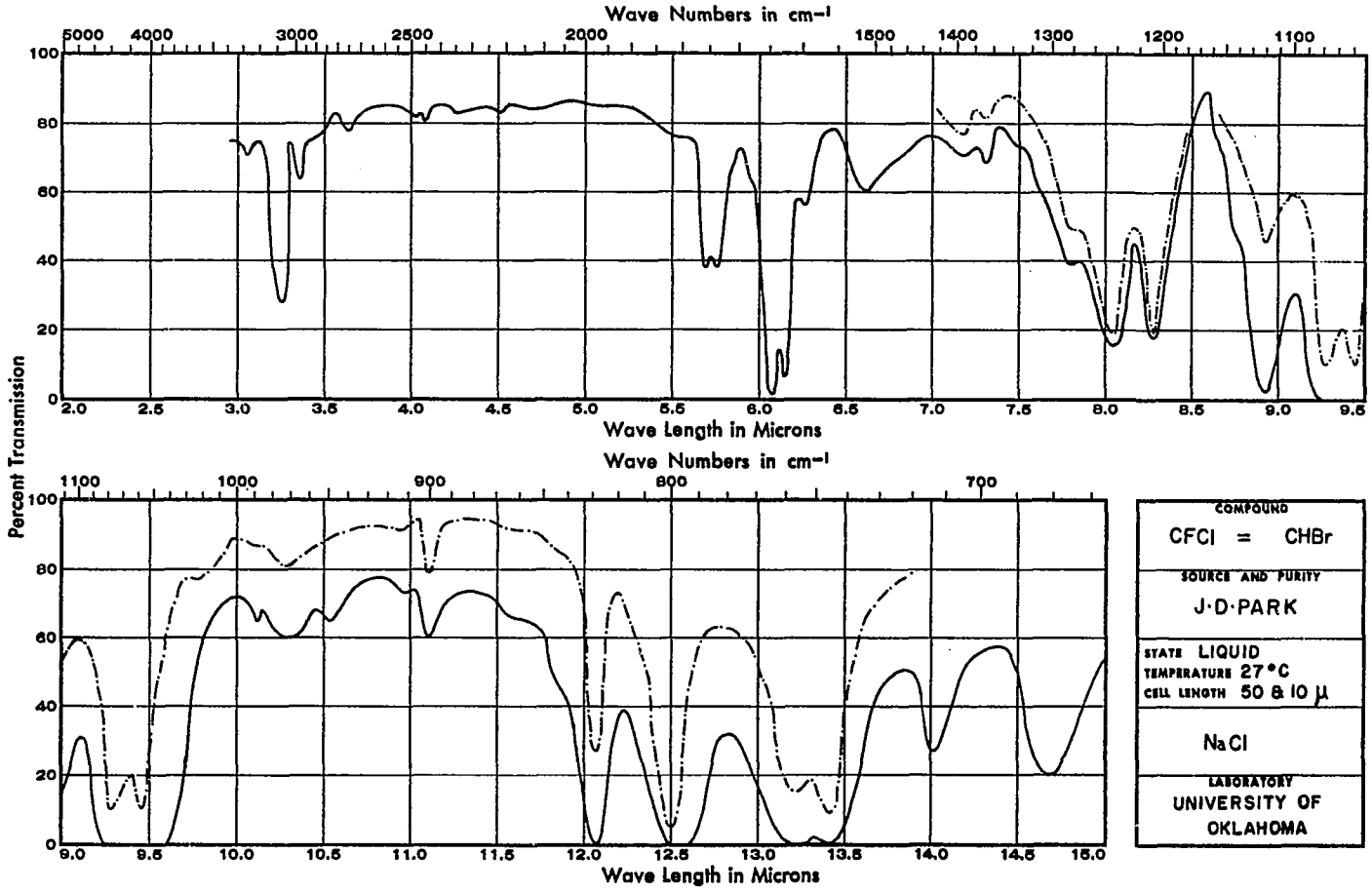


Fig. 9. Infrared Spectrum of Liquid CFCl:CHBr (NaCl Region).

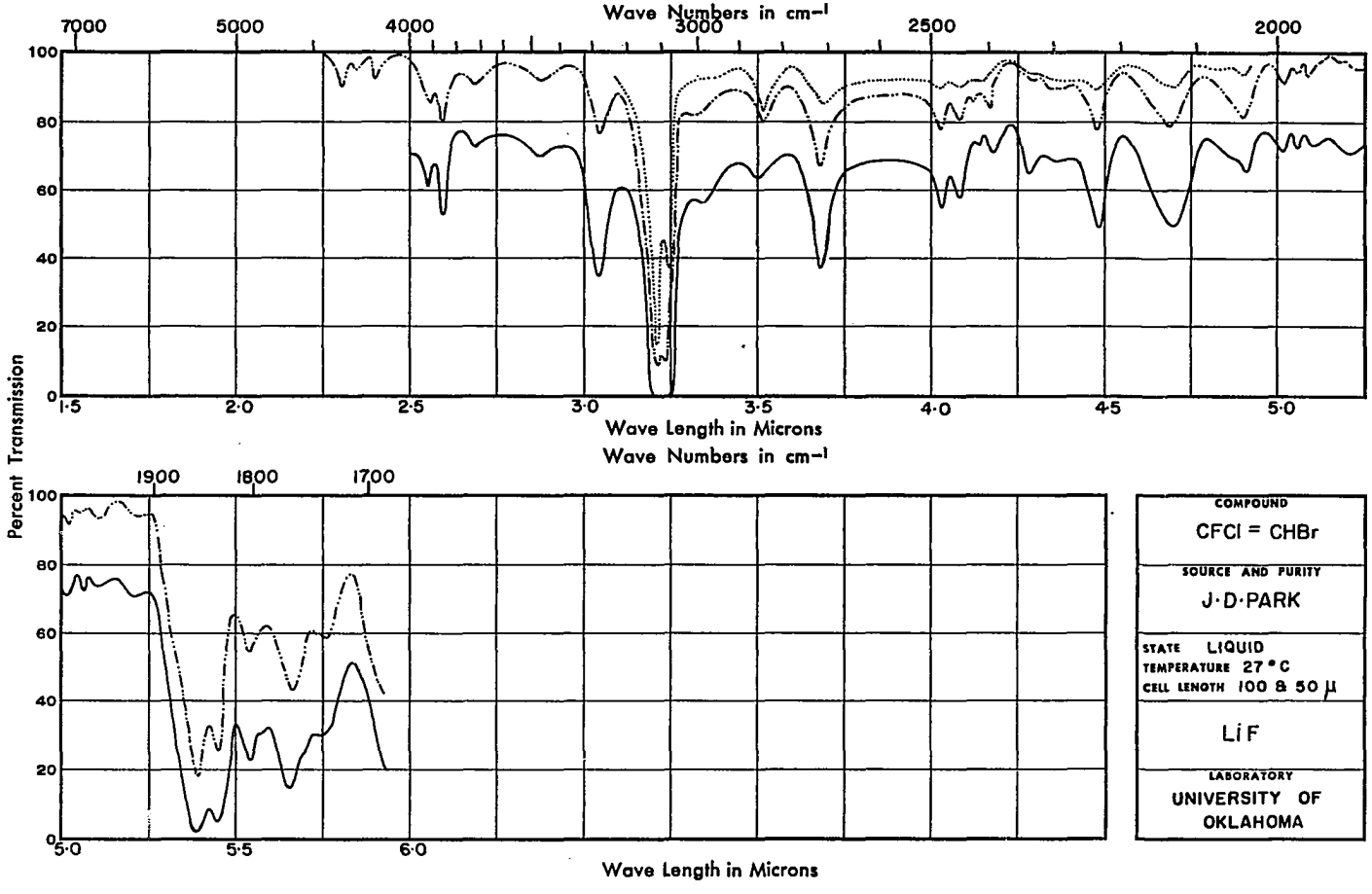


Fig. 10. Infrared Spectrum of Liquid CFCl=CHBr (LiF Region).

TABLE I

INFRARED SPECTRAL DATA FOR GASEOUS CFCl:CHBr

Wave number	Description	Interpretation
346	m	a' fundamental (352) I,II
358	m	
369	vvw	146 + 225 = 371
380	vvw	546 - 167 = 379
390	vvw	167 + 225 = 392
399	vw	753 - 352 = 401
413	vw	759 - 352 = 407
432	s	a" fundamental (434) II
435	s	
488	vw	
493	w	a" fundamental I
500	vw	
533	vvw	176 + 352 = 528
540	vw	a' fundamental (546) II
551	vw	
575	vw	225 + 352 = 577
641	s	a' fundamental (647) I
652	s	
709	m	2 x 352 = 704; 272 + 434 = 706; 167 + 546 = 713
719	s	225 + 493 = 718
721	s	

TABLE I--Continued

Wave number	Description	Interpretation
747	vs	
753	vs	a" fundamental (753) I
759	vs	a" fundamental II
765	m	
798	vs	a' fundamental (803) I
808	vs	
829	vs	
833	vs	a' fundamental II
838	vs	
870	w	2 x 434 = 868
912	m	167 + 759 = 926
919	m	
935	w	176 + 759 = 935
969	m	167 + 803 = 970
980	m	434 + 546 = 980 2 x 493 = 986
1022	vw	272 + 759 = 1031
1056	vs	a' fundamental (1060) II
1064	vs	
1078	vs	a' fundamental (1082) I
1086	vs	
1092	m	272 + 833 = 1105

TABLE I--Continued

Wave number	Description	Interpretation
1122 }	vs	a' fundamental (1127) I
1131 }	vs	
1181	s	352 + 833 = 1185
1185	s	434 + 759 = 1193
1210 }	s	167 + 1060 = 1227 (F) 146 + 1082 = 1228
1217 }	s	
1250 }	vs	a' fundamental (1250) II
1256 }	vs	
1348	vw	225 + 1127 = 1352
1381	vvw	546 + 833 = 1379
1405 }	vw	647 + 753 = 1400
1414 }	w	352 + 1060 = 1412 167 + 1250 = 1417
1493	s	434 + 1060 = 1494 2 x 759 = 1518 2 x 753 = 1506
ca1640	s	a' fundamental II
1650	vs	a' fundamental I
1748	vw	647 + 1082 = 1729
1778	vw	647 + 1127 = 1774
1784	vw	546 + 1250 = 1796 146 + 1650 = 1796
1820	w	759 + 1060 = 1819 753 + 1082 = 1835
1866	vw	753 + 1127 = 1880

TABLE I--Continued

Wave number	Description	Interpretation
1887	vw	833 + 1060 = 1893 803 + 1082 = 1885 753 + 1127 = 1880
1938	vvw	803 + 1127 = 1930
1962	vvw	
2004	vw	352 + 1650 = 2002 759 + 1250 = 2009
2051	vw	
2058	vw	434 + 1640 = 2074
2060	vvvw	
2088	w	833 + 1250 = 2083
2146	m	2 x 1082 = 2164
2198	vvvw	1082 + 1127 = 2209
2250	m	2 x 1127 = 2254
2262	m	
2309	vvw	1060 + 1250 = 2310
2338	vw	
2350	vw	
2410	vvvw	753 + 1650 = 2403
2457	w	803 + 1650 = 2453
2500	w	2 x 1250 = 2500
2732	m	1082 + 1650 = 2732
2793	vvw	1127 + 1650 = 2777
2845	vw	

TABLE I--Continued

Wave number	Description	Interpretation
2886	vvw	1250 + 1640 = 2890
3101	m	
3107	m	a' fundamental II
3110	m	
3123	vs	a' fundamental (3128) I
3131	vs	
3241	vw	2 x 1640 = 3280
3300	m	2 x 1650 = 3300
3356	vvw	272 + 3107 = 3379
3876	vw	753 + 3128 = 3881
3929	vw	803 + 3128 = 3931 833 + 3107 = 3940
4237	vw	1127 + 3128 = 4255
4338	vw	1250 + 3107 = 4357
4396	w	
4785	vvw	1650 + 3128 = 4778

TABLE II

INFRARED SPECTRAL DATA FOR LIQUID CFCl:CHBr

Wave number	Description	Interpretation
350	s	a' fundamental I, II
365	vw	146 + 225 = 371
430	m	167 + 272 = 439
435	s	a' fundamental II
489	m	a" fundamental I
517	m	167 + 350 = 517
532	m	a" fundamental II
545	m	2 x 272 = 544
588	m	225 + 350 = 575 (F)
595	m	167 + 435 = 602
641	s	a' fundamental I
680	w	2 x 350 = 700
712	s	225 + 489 = 714 272 + 435 = 707
746	vs	a" fundamental I
755	vs	a" fundamental II
800	vs	a' fundamental II
829	vs	a' fundamental I
844	m	350 + 489 = 839
861	m	2 x 435 = 870 225 + 641 = 866
900	s	146 + 746 = 892

TABLE II--Continued

Wave number	Description	Interpretation
906	m	167 + 746 = 913 167 + 755 = 922
949	s	146 + 800 = 946
970	s	167 + 800 = 967 435 + 532 = 967 225 + 746 = 971
991	s	350 + 641 = 991
1020	s	272 + 755 = 1027
1057	vs	a' fundamental II
1079	vs	a' fundamental I
1120	vs	a' fundamental I
1192	s	435 + 755 = 1190
1211	vs	146 + 1079 = 1225 (F) 167 + 1057 = 1224
1242	vs	a' fundamental II
1252	vs	435 + 829 = 1264 146 + 1120 = 1266
1279	m	2 x 641 = 1282
1332	m	272 + 1057 = 1329
1350	w	225 + 1120 = 1345
1402	m	350 + 1057 = 1407
1413	w	176 + 1242 = 1418
1504	w	272 + 1242 = 1514 2 x 755 = 1510
1597	w	350 + 1242 = 1592 2 x 800 = 1600

TABLE II--Continued

Wave number	Description	Interpretation
1629	vs	a' fundamental II
1649	vs	a' fundamental I
1730	m	641 + 1079 = 1720
1757	m	641 + 1120 = 1761
1802	m	176 + 1629 = 1805 755 + 1057 = 1812
1832	s	746 + 1079 = 1825
1858	s	800 + 1079 = 1879
1926	vvvw	800 + 1120 = 1920
2040	vvw	435 + 1629 = 2064
2062	vvw	829 + 1242 = 2071
2085	w	2 x 1057 = 2114
2130	m	489 + 1649 = 2138
2151	vw	2 x 1079 = 2158
2234	m	2 x 1120 = 2240
2452	w	829 + 1629 = 2458
2698	vw	1057 + 1629 = 2686
2716	m	1079 + 1649 = 2728
2780	vvw	1120 + 1649 = 2769 1242 + 1629 = 2871
3089	s	a' fundamental II
3113	s	a' fundamental I
3289	m	2 x 1649 = 3298 167 + 3113 = 3280

TABLE II--Continued

Wave number	Description	Interpretation
3465	vvw	350 + 3113 = 3463
3730	vvw	641 + 3113 = 3754
3847	m	746 + 3113 = 3859
3913	vvw	800 + 3113 - 3913
4172	vvw	1079 + 3113 = 4192
4284	vvw	
4338	vvw	1242 + 3089 = 4331

TABLE III

RAMAN SPECTRAL DATA FOR LIQUID CFCl:CHBr

Wave number	Description	Exciting* Hg lines	Interpretation
146	s sh	±e	a" fundamental I
167	m sh	±e	a' fundamental I II
176	vw d	e	a" fundamental II
225	vw d	±e	a' fundamental I
272	vs sh	±e,f,i	a' fundamental I
354	s sh	±e,k,i	a' fundamental I II
365	vvw	e	146 + 225 = 371
395	vvvw	e	167 + 225 = 392
430	w	e,k	167 + 272 = 439
434	s sh	±e,k,i	a" fundamental II
490	w sh	e,k	a" fundamental I
532	m sh	e,k	a' fundamental II
637	m	±e,k	146 + 490 = 636
643	s sh	e,k	a' fundamental I
748	s sh	±e,k,i	a" fundamental I
759	w	e,k	a" fundamental II
766	w	e,k	354 + 434 = 788 (F)
801	s	e,k,i	a' fundamental I
831	vvw	e,k,i	a' fundamental I
979	vvw	e	2 x 490 = 980
995	vvvw	e	354 + 643 = 997
ca1062	vvvw d	e	a' fundamental II

TABLE III--Continued

Wave number	Description	Exciting* Hg lines	Interpretation
1072	m d	e,k	2 x 532 = 1064 (F)
1083	m	e,k,i	a' fundamental I
1125	vvw	e	a' fundamental I
1186	vvvw	e	434 + 759 = 1193
1213	m	e,k,i	146 + 1083 = 1229
1240	vw d	e,k	a' fundamental II
1254	vvw d	e	434 + 831 = 1265 146 + 1125 = 1271
1296	vvw	e	532 + 759 = 1291 490 + 801 = 1291 2 x 643 = 1286 167 + 1125 = 1292
1596	vvw	e	354 + 1240 = 1594 2x801 = 1602
1632	s sh	e,k	a' fundamental II
1650	vs	e,k	a' fundamental I
1666	m	e	2 x 833 = 1666
3092	s	e,k,i	a' fundamental II
3115	s	e,k,i	a' fundamental I

*d = 4916 A, e = 4358 A, f = 4347 A, g = 4339 A, k = 4047 A; - = anti-Stokes lines, + = Stokes lines.

TABLE IV

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF CFCl:CHBr (I)
(in cm^{-1})

Species	Infrared		Raman	Approximate
	Gas	Liquid	Liquid	motion
a"			146 s	Twisting
a'			167 m sh	CFCl rocking
a'			225 vw d	CHBr rocking
a'	352 m	350 s	354 s sh	CFCl deformation
a"	493 w	489 m	490 w	CFCl wagging
a'	647 s	641 s	643 s sh	CBr stretching
a"	753 vs	746 vs	748 s	CHBr wagging
a'	803 vs	800 vs	801 s sh	CCl stretching
a'	1082 vs	1079 vs	1083 m	CHBr deformation
a'	1127 vs	1120 vs	1125 vvw	CF stretching
a'	1650 vs	1649 vs	1650 vs	C=C stretching
a'	3128 vs	3113 s	3115 s	CH stretching

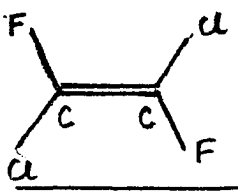
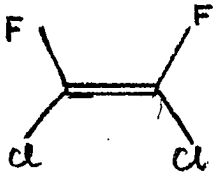
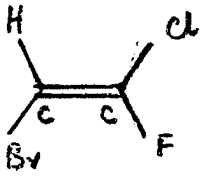
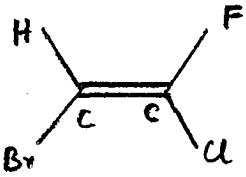
TABLE V

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF CFCl:CHBr (II)
(in cm^{-1})

Species	Infrared Gas	Infrared Liquid	Raman Liquid	Approximate motion
a'			167 m sh	CFCl rocking
a"			176 vw d	twisting
a'			272 vs sh	CHBr rocking
a'	352 m	350 s	354 s sh	CFCl deformation
a"	434 s	435 s	434 s	CFCl wagging
a'	546 vw	532 m	532 m sh	CBr stretching
a"	759 vs	755 vs	759 w	CHBr wagging
a'	833 vs	829 vs	831 vvw	CCl stretching
a'	1060 vs	1057 vs	1072 m d	CHBr deformation
a'	1250 vs	1242 vs	1240 vw d	CF stretching
a'	1640 s	1629 vs	1632 s sh	C=C stretching
a'	3107 m	3089 s	3092 s	CH stretching

TABLE VI

VIBRATIONAL FUNDAMENTALS OF CIS AND TRANS
CFCl:CFBr and CFCl=CHBr
(in cm^{-1})

Mann et al.[32]			Present work		
					
Wave number	Species	Wave number	Wave number	Species	Wave number
1727	a'	1725	3092	a'	3128
1232	a'	1248	1640	a'	1650
1187	a'	1127	1250	a'	1127
829	a'	941	833	a'	803
626	a'	520	546	a'	647
426	a'	417	1060	a'	1082
345	a'	340	354	a'	354
266	a'	325	272	a'	225
165	a'	157	167	a'	167
502	a"	507	759	a"	753
351	a"	339	434	a"	493
127	a"	141	176	a"	146

CHAPTER IV

INFRARED AND RAMAN SPECTRA OF C_2H_2FBr

Introduction

The Raman and infrared spectra of doubly substituted ethylenes, especially of cis and trans CHCl:CHCl, were extensively investigated in the past.[1] Also several reports have been published on the Raman and infrared spectra of vinylidene chloride, $CH_2:CCl_2$.[37,38,39] Edgell, Roberts and Byrd[40] have studied the Raman and microwave spectra of vinylidene fluoride, and Nielsen et al.[41] have made a detailed study of its infrared and Raman spectra. Vinylidene bromide and its deutero derivatives were studied by Hemptinne, Velghe and Van Riet.[42] Normal coordinate analyses of some of these

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[37] J. Cabannes, J. Chim. Phys., 35, 9 (1938).

[38] V. M. Tatevski and A. V. Frost, Vestrik, Moscow Univ., No. 3, 65 (1947).

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

[40] W. Byrd, Ph.D. Thesis, State University of Iowa (1949); W. F. Edgell and W. Byrd, J. Chem. Phys., 17, 1740 (1949); W. F. Edgell and A. Roberts, Phys. Rev., 76, 178 (1949); W. F. Edgell and A. Roberts, J. Chem. Phys., 17, 742 (1949).

[41] J. Rud Nielsen et al., J. Chem. Phys., 18, 326 (1950).

[42] Hemptinne, Velghe and Van Riet, "Recueil de travaux

compounds also have been published.[43,6] Torkington and Thompson[2] have made a partial analysis of CH_2:CFCl. More recently Mann, Acquista and Plyler[44] have given a more complete interpretation of its infrared spectrum. The compound CH_2:CFCl is very similar to the one which is the subject of the present study, namely C_2H_2FBr. An account of the infrared and Raman spectra of C_2H_2FBr is given in this chapter. No similar work has been done on this compound previously; and there are no data either from electron diffraction measurements or from microwave spectroscopic studies.

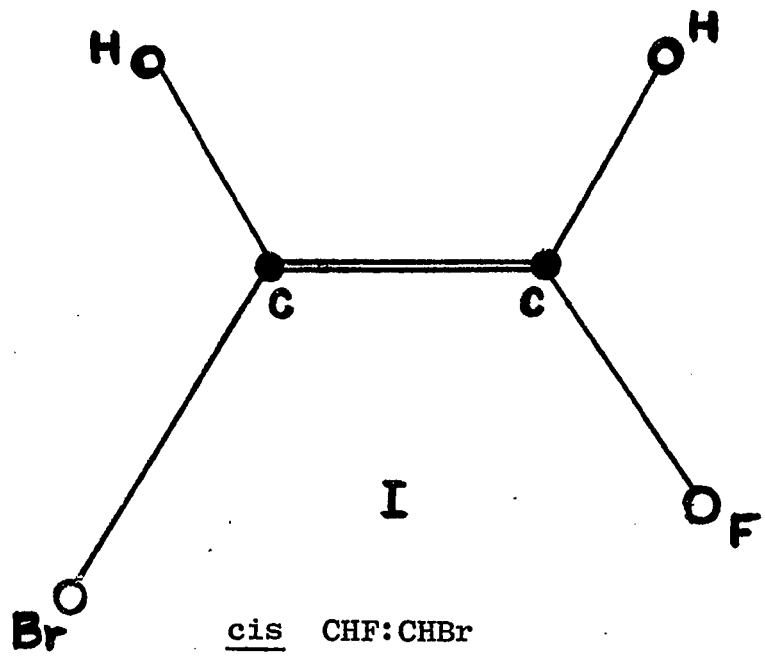
The sample was prepared by Prof. J. D. Park at the University of Colorado. As stated by him, it is very unstable. Because of its tendency to polymerize, a small amount of hydroquinone was added as an inhibitor. When the sample was distilled it seemed to polymerize under the action of heat and light. It turned milky when the bulb was agitated but became clear again when allowed to stand. The structural formula of the sample is not known. In fact Prof. Park did not claim more than is expressed by the formula C_2H_2FBr. It can be any of three possible forms shown in Figs. 11 and 12 or a mixture of two or all of these molecular species.

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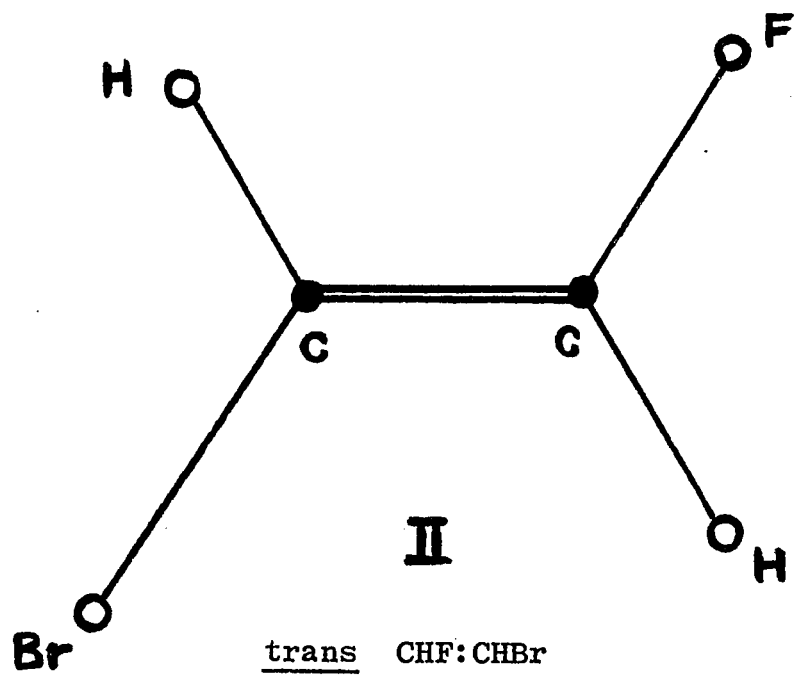
du laboratoire de Physique (University de Louvain, 1945). Reprinted from Bulletin de l'academie Royale de Belgique (classe de sciences) 30, 40 (1944).

[43] P. Torkington, Proc. Roy. Soc. 206, 17 (1951).

[44] D. E. Mann, N. Acquista and E. K. Plyler, J. Chem. Phys. 23, 2122 (1955).

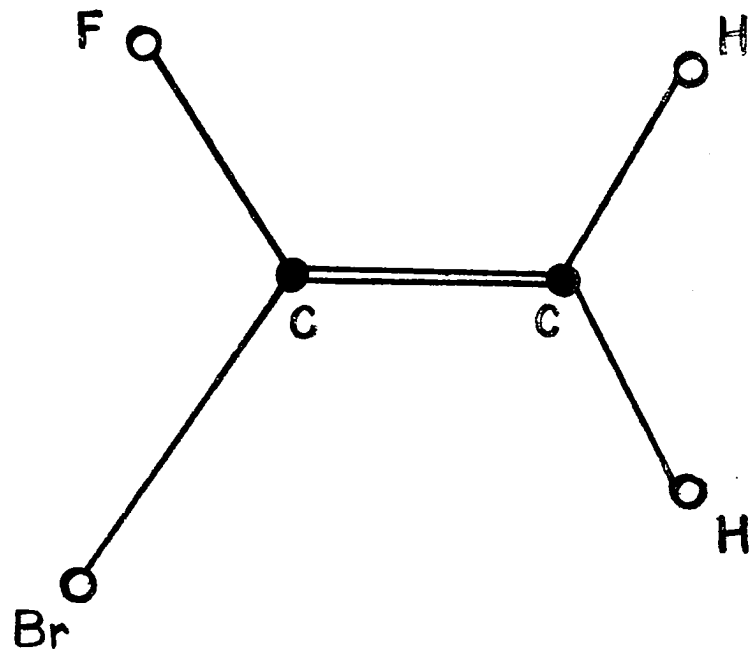


cis CHF:CHBr



trans CHF:CHBr

Fig. 11. Molecular Configurations of CHF:CHBr



III

Fig. 12. Molecular Configuration of CH_2:CFBr

Experimental Results

The infrared absorption spectrum of the gas at room temperature was obtained with a Perkin-Elmer Model 112 double-pass spectrometer in the region 2 μ to 40 μ. The spectra are shown in Figs. 13-15. The wave numbers of the observed absorption maxima (or in some cases "shoulders") are listed in the first column of Table VII.

The Raman spectrum of the liquid contained under pressure in a sealed Raman tube was photographed in the usual way at room temperature. The liquid became milky on exposure probably due to partial polymerization. However, when it was set aside it became clear again. In order to prevent polymerization the Raman spectrum was obtained at a temperature of -70°C with the aid of the arrangement described in Chapter II. Even so, after long exposure the sample appeared to turn milky; therefore no polarization measurements were made. However, fairly complete Raman spectra were obtained with exposures ranging from 15 minutes to 6 hours. The Raman spectral data are given in Table VIII.

Interpretation

As has already been mentioned the sample C_2H_2FBr may consist of any one of the molecular species shown in Figs. 11 and 12 or it may be a mixture of two or all of them. All three forms have the symmetry C_s. The 12 normal vibrations belonging to any one of the three molecules therefore divide into 9 of species a' (in-plane) and 3 of species a"

(out-of-plane). The latter have type C contours in the infrared spectrum and the a' fundamental have contours that are hybrids between types A and B. As it is not known which of the molecular species is present, the moments of inertia of all the three possible structures were calculated, assuming the following atomic distances and angles[28] C=C=1.31 A, C-H=1.08 A, C-F 1.31 A, C-Br 1.90 A, C C-halogen angle 123°. From the values of the moments of inertia, the Badger-Zumwalt[29] parameters listed below for the three different molecular species were calculated. I refers to the form in which the hydrogen atoms are in cis positions, II refers to the form in which they are in the trans positions and III to the molecular species in which the two hydrogen atoms are attached to the same carbon atom.

Molecule	Moments of Inertia			Badger-Zumwalt parameters	
	A	B	C	s	ς
I	188.6	206.6	395.2 x 10^{-40} gcm^2	0.7	0.57
II	15.1	514.0	529.0	0.1	32.00
III	123.3	229.4	352.7	-0.43	1.20

$s=(2b-a-c)/(a-c)$ and $\varsigma=(a-c)/b$ where a, b and c are the reciprocals of the moments of inertia A, B and C, respectively (A<B<C). The angle that the axis belonging to the smallest moment of inertia makes with the C=C bond in form I

is 31°26'; in form II it is 49°18' and in form III it is 81°50'.

For molecule II, as can be seen from the calculated parameters, a wide extrapolation is required from Badger-Zumwalt curves so they are of little value. However, it is obvious that II is almost a symmetric top with the axis of symmetry in the plane of the molecule. Therefore, the a" infrared bands are almost perpendicular and the a' bands hybrids between parallel and perpendicular bands. Some information regarding the contours can be obtained from the paper of Gerhard and Dennison[30] mentioned in the previous chapter. From an extrapolation of the curves given therein, the separation of the P and R branches is predicted to be approximately 10 cm^{-1}. The perpendicular bands should be broad without any definite PQR structure if the value of is greater than 4, where $\beta = (C/A)-1 \simeq (B/A)-1$. However, in this case the molecule is nearly linear with $\beta = 35$. If it were completely linear the parallel bands would have simple PR branches and no zero branch. In this particular case, the zero branch may be expected to be very weak. The perpendicular bands will have about the same PR separations as the parallel bands and will have a Q branch.

From an extrapolation of Badger and Zumwalt curves the PR separations of the A and C type bands of species I are found to be 18 and 24 cm^{-1} respectively, and the QQ separations for type B bands are 4 cm^{-1}. However, species I can

also be regarded as a nearly symmetric top with the axis of largest moment of inertia being the approximate symmetry axis of the molecule. From this point of view the a" bands will be nearly parallel and the a' bands nearly perpendicular. From the paper of Gerhard and Dennison it is seen that the parallel bands have an intense zero branch, the intensity of which is half the intensity of the whole band; since the QQ separations are extremely small it appears like a single branch. The perpendicular bands also have a zero branch and have a separation approximately equal to 13 cm^{-1}.

For the molecular species III the Badger-Zumwalt parameters are well within the limits for which the curves are given. Therefore the separations of the PR branches and QQ branches are obtained without any extrapolation. The PR separations are found as 16 and 12 cm^{-1} respectively for the A and C type bands and the QQ separations as 10 cm^{-1} for the type B bands.

The observed separations for some of the bands, which appear to be of type C, seem to indicate that they belong to I. On the other hand, the QQ separations of what appear to be type B bands indicate that they belong to III. Although the a" bands of I seem to have the contours predicted by the Gerhard and Dennison curves the fact that the a' bands also must have zero branches seems to rule out the possibility that species I is the component responsible for most of the intense observed bands.

The abundance of bands in both the infrared and Raman spectra indicates that there is more than one type of molecule present. One might assume that the sample is a mixture of the cis and trans forms of CHF:CHBr. However, certain spectral features, described in the following paragraphs, show that the most abundant molecular species present in the sample is probably H_2C:CFBr. The observed bands which cannot be ascribed to III may be due to one of the other molecular species or to dimers or polymers of CH_2:CFBr present as impurities.

In the Raman spectrum of the liquid there are two bands at 2992 cm^{-1} and 3143 cm^{-1} of medium intensity, and in the infrared spectrum two bands are found at 3060 cm^{-1} and 3109 cm^{-1}. These are undoubtedly caused by the most abundant molecular species present in the sample and may be assigned as fundamentals associated with C-H stretching. The Raman band at 3143 cm^{-1} is so close to the mercury line of wavelength 5026 A that an accurate determination of its frequency is not possible.

The very intense Raman and infrared bands at 1640 cm^{-1} obviously represent an a' fundamental associated with C=C stretching.

In the Raman spectrum an intense band is observed at 1367 cm^{-1}. The corresponding infrared band is not very strong. These bands are assigned as an a' fundamental. If this fundamental were ascribed to molecule I or II, it should

be associated largely with C-F stretching or C-H bending or with a mixture of these two motions. However, because of its high intensity and sharpness in the Raman spectrum it can hardly be ascribed to C-F stretching; moreover its frequency is rather too high for it to be associated with C-H bending in a molecule in which one of the hydrogens in a methylene group is substituted by either fluorine or bromine. On the other hand, it can be readily explained as the CH_2 planar deformation mode of CH_2:CFBr. In fact, its wave number is in accord with those of similar fundamentals in related molecules such as CH_2:CF_2, CH_2:CCl_2, CH_2:CBr_2, etc. These fundamentals are observed in the region from 1379 to 1414 cm^{-1} and their wave numbers are independent of the atoms in the other end group. Hence the presence of this strong band at 1367 cm^{-1} indicates that the principal component in the sample, which is responsible for most of the intense bands, is H_2C:CFBr.

Two a' fundamentals are expected to be in the region between 1254 cm^{-1} and 900 cm^{-1}, one involving largely C-F stretching and the other C-H bending. The former should be weak and diffuse in the Raman spectrum, but strong in the infrared spectrum. Actually, there is a strong infrared band at 1164 cm^{-1}. The corresponding Raman band occurs near 1150 cm^{-1} and is very weak and diffuse. The apparent large frequency shift may be due in part to the fact that the wave number of the Raman band could not be determined very

accurately. These bands are assigned as an a' fundamental.

The weak Raman band at 944 cm^{-1} and the rather intense infrared band at 945 cm^{-1} are assigned as an a' fundamental involving mainly CH bending.

The strong infrared band at 839 cm^{-1} has definitely type C contour. The separation of P and R branches has approximately the predicted value. This band is undoubtedly the highest a" fundamental, the motion involved being essentially CH_2 wagging. It occurs at 845 cm^{-1} in the Raman spectrum and is very weak and diffuse. The two other a" fundamentals must evidently be identified with the infrared bands at 729 cm^{-1} and 416 cm^{-1}, both of which have type C contours. The separations between the PR branches seem to be somewhat higher than the calculated values. This is probably not significant, since it is hard to fix accurately the maxima of the P and R branches. These fundamentals occur in the Raman spectrum as very weak and diffuse bands at 717 cm^{-1} and 421 cm^{-1}. These fundamentals are probably associated with twisting and CFBr wagging. The fundamentals of wave numbers 839 and 729 occur in the general region where such vibrations are observed in similar molecules previously studied by other workers, as shown in Table X.

The intense infrared bands at 614, 476 and 363 cm^{-1} and the corresponding Raman bands at 614, 475 and 365 cm^{-1} undoubtedly represent the remaining a' fundamentals. The Raman band at 614 cm^{-1} is strong and the other two are weak.

They involve C-Br stretching, CFBr deformation and planar rocking, respectively. The deformation and rocking motions are probably greatly mixed. The fundamentals assigned to CH_2:CFBr are listed in Table IX.

Discussion

Although most of the bands are probably due to CH_2:CFBr the assignment cannot be taken as conclusive without further confirmation by a claculation of the fundamental vibrational frequencies and an observation of the spectrum with better resolution. Some of the uncertainties which occur from the shape of the contours have been mentioned earlier. It has also been indicated that the abundance of bands shows the presence of more than one isomeric form in the sample.

On the basis of the assigned fundamentals an attempt has been made to explain the observed bands in infrared and Raman spectra. Though it has been possible to interpret most of the observed bands there are a few that cannot be explained as binary combinations of the fundamentals. Their rather hign intensity leads one to suspect that they may be due to a second molecular species, probably of the type CHF:CHBr. These bands are indicated in Tables VII and VIII with superscript 'a.' Thus, the infrared bands at 325, 564 and 1036 cm^{-1} seem to be fundamentals of such a second molecular species. These bands have fairly high intensities and could possibly be ascribed to the major component. If this were done,

the infrared bands at 365, 614 and 946 cm^{-1} would have to be ascribed to the minor constituent. Here a calculation of the fundamental vibrational frequencies may be of great help.

For the sake of comparison the assigned fundamentals of CH_2:CFBr are listed in Table X along with the vibrational fundamentals of molecules of type CH_2:CXY (with X same as Y and different from Y) assigned by previous investigators.[44]

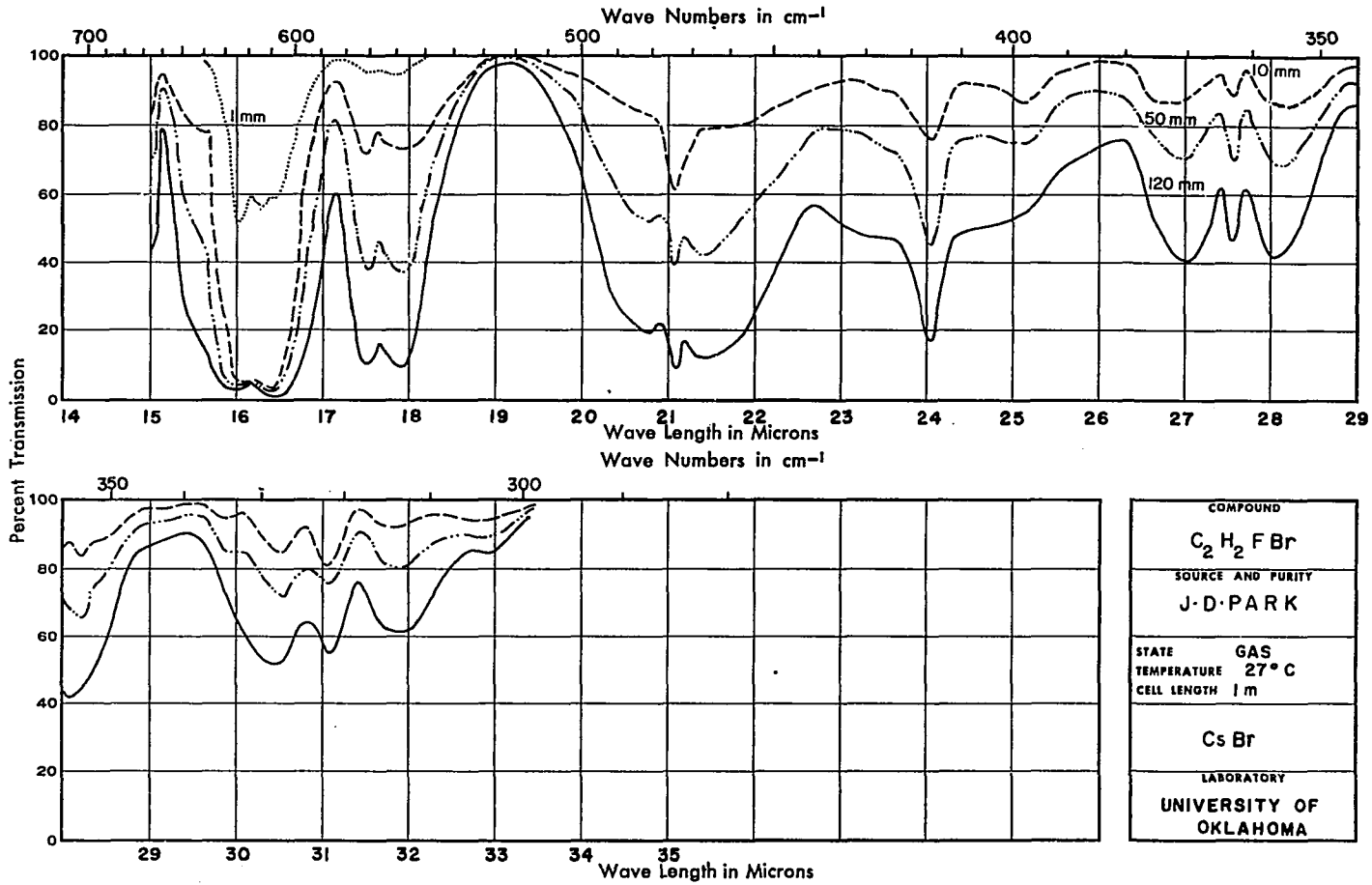


Fig. 13. Infrared Spectrum of Gaseous C_2H_2FBr (CsBr Region).

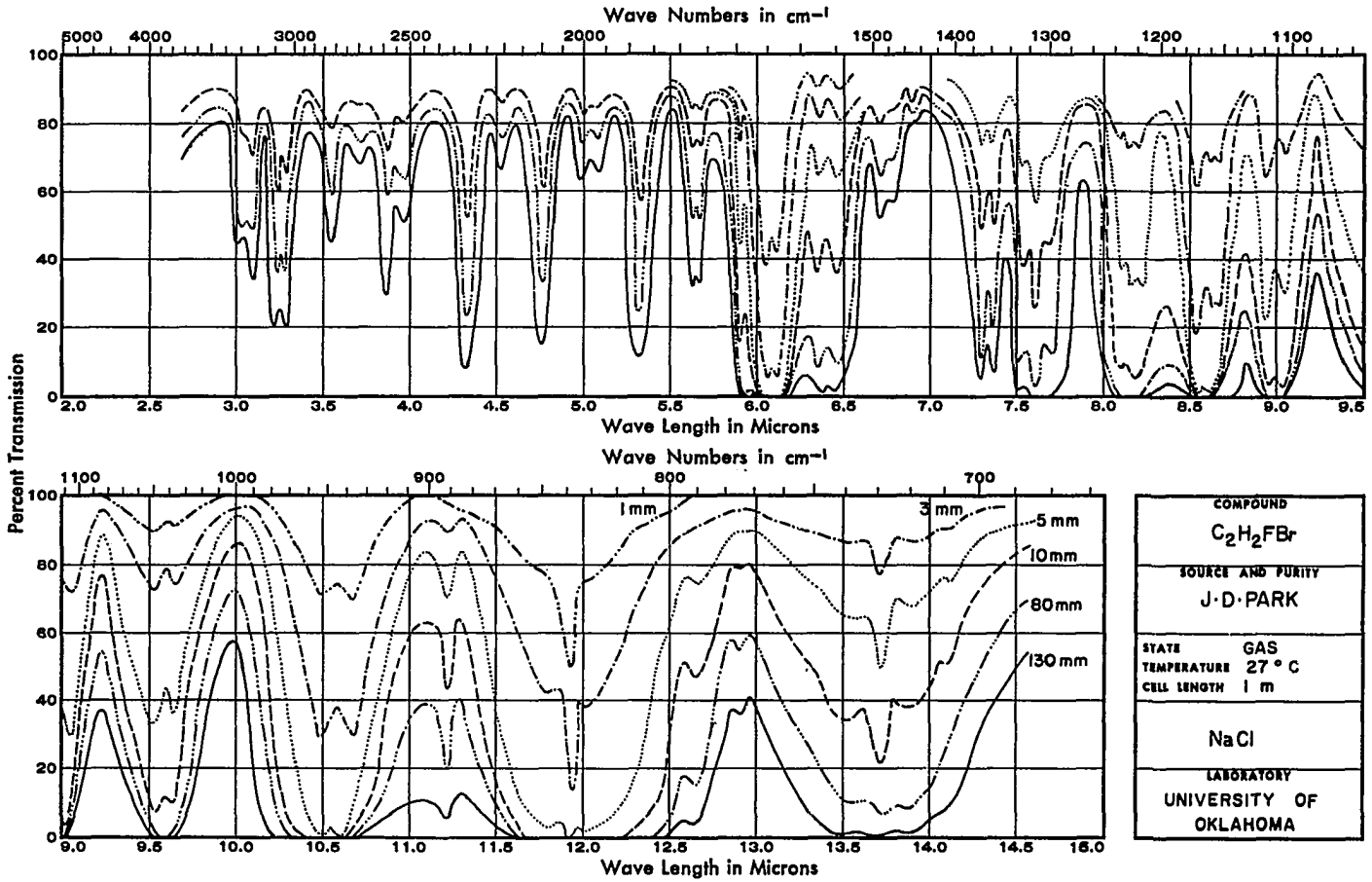


Fig. 14. Infrared Spectrum of Gaseous C_2H_2FBr (NaCl Region).

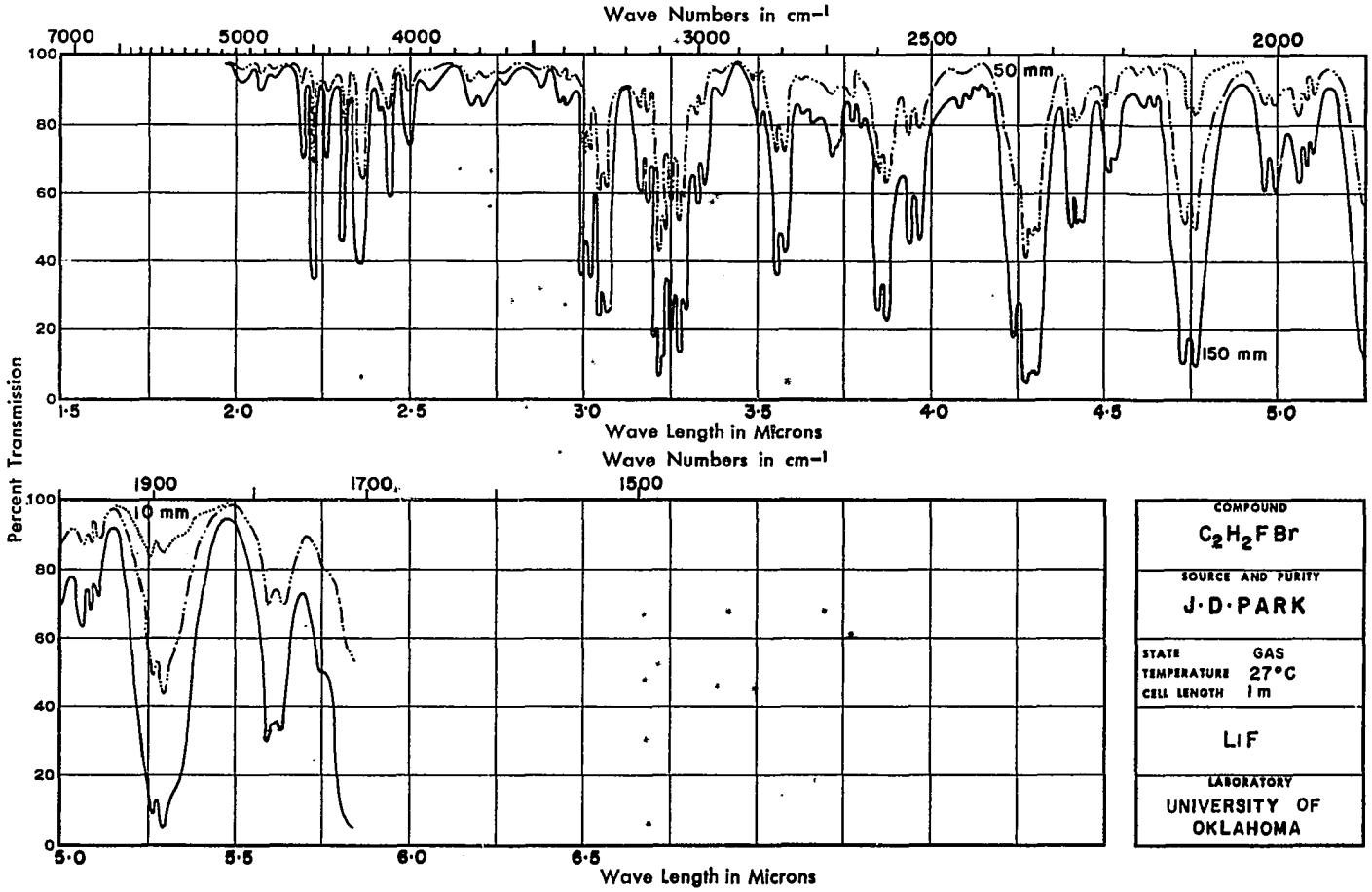


Fig. 15. Infrared Spectrum of Gaseous C_2H_2FBr (LiF Region).

TABLE VII

INFRARED SPECTRAL DATA FOR GASEOUS C_2H_2FBr

Wave number	Description	Interpretation
315	w	
323	w	a fundamental[a]
328	w	
355	m	
363	m	a' fundamental
374	m	
405	m	
416	m	a" fundamental
425	m	
467	s	
476	s	a' fundamental
480	s	
556	s	a fundamental[a]
572	s	
608	s	
614	s	a' fundamental
622	s	
649	w	
707	s	2 x 363 = 726 (F)
720	s	
729	vs	a" fundamental
739	s	

TABLE VII--Continued

Wave number	Description	Interpretation
775	m	363 + 416 = 779
790	s	
834	vs	a" fundamental
839	vs	
848	vs	
892	s	416 + 475 = 891
937	vs	a' fundamental (945)
955	vs	
1036	vs	fundamental[a] (1043)
1049	vs	
1104	vs	416 + 729 = 1145 (F)
1120	vs	
1159	vs	a' fundamental
1164	vs	
1172	vs	
1215	vs	2 x 614 = 1228
1228	vs	
1240	s	416 + 839 = 1255
1300	vs	475 + 841 = 1316
1314	vs	
1329	vs	
1358	s	a' fundamental (1367)
1371	s	

TABLE VII--Continued

Wave number	Description	Interpretation
1446	vvw	614 + 839 = 1453
1455	vvw	2 x 729 = 1458
1478	w	325 + 1164 = 1489
1494	w	
1554	vs	614 + 946 = 1560
1572	vs	729 + 839 = 1568
1632	vs	a' fundamental
1648	vs	
1676	m	2 x 839 = 1678 (F)
1699	m	
1712	w	
1734	w	363 + 1367 = 1730
1773	m	416 + 1367 = 1783
1788	m	841 + 946 = 1787
1872	s	2 x 946 = 1892
1889	s	729 + 1164 = 1893
1899	s	
1960	w	325 + 1640 = 1965
1968	w	
1975	w	614 + 1367 = 1981
1991	m	
2004	m	363 + 1640 = 2003
2015	m	841 + 1164 = 2005

TABLE VII--Continued

Wave number	Description	Interpretation
2093	s	729 + 1367 = 2096
2119	s	946 + 1164 = 2110 475 + 1640 = 2206
2210	w	839 + 1367 = 2206
2217	w	
2255	m	
2263	m	614 + 1640 = 2254
2270	m	
2322	s	946 + 1367 = 2313
2331	s	2 x 1164 = 2328
2339	s	
2357	s	729 + 1640 = 2369
2402	vw	1043 + 1367 = 2410
2437	w	
2484	vvw	839 + 1640 = 2479
2525	w	1164 + 1367 = 2531
2539	w	
2584	s	946 + 1640 = 2682
2597	s	
2681	w	1042 + 1640 = 2682
2695	w	
2735	vw	2 x 1367 = 2734
2756	vw	

TABLE VII--Continued

Wave number	Description	Interpretation
2805	s	1164 + 1640 = 2804
2815	s	
2851	w	
2869	w	
2945	vw	
2994	w	1367 + 1640 = 3007
3008	m	
3042	s	
3056	s	a' fundamental
3074	s	
3107	s	
3109	s	a' fundamental
3123	s	
3145	w	a' fundamental
3159	w	
3271	m	2 x 1640 = 3280
3283	m	
3316	m	
3331	m	
3377	w	
3398	w	
3407	vw	363 + 3060 = 3423
3476	vw	416 + 3060 = 3476

TABLE VII--Continued

Wave number	Description	Interpretation
3600	vvw	
3690	w	614 + 3110 = 3724
3710	w	
3900	vvw	841 + 3060 = 3901
4005	w	946 + 3060 = 4006
4100	w	
4223	m	1164 + 3060 = 4224
4441	w	1367 + 3060 = 4427
4513	m	
4562	w	
4693	vvw	1640 + 3060 = 4700
4755	vvw	1640 + 3110 = 4750

[a]Bands assigned to the less abundant molecular species.

TABLE VIII

RAMAN SPECTRAL DATA FOR LIQUID C_2H_2FBr

Wave number	Description	Interpretation
324	m sh	fundamental[a]
365	m sh	a' fundamental
421	vvw	a" fundamental
475	vw d	a' fundamental
ca522	vvw d	[illegible]
562	vvw d	fundamental[a]
614	s sh	a' fundamental
ca717	vvw	a" fundamental
744	vvw	
845	w d	a" fundamental
931	vw d	365 + 562 = 927
944	vw d	a' fundamental
1032	vw d	fundamental[a]
1150	vvw d	a' fundamental
1185	vvw d	
1208	vvw	365 + 841 = 1206
1296	vvw	
1316	vvw	475 + 845 = 1320
1367	s sh	a' fundamental
1640	s sh	a' fundamental
2995	w	a' fundamental
3140	m d	a' fundamental

TABLE IX

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF CH_2:CFBr
(in cm^{-1})

Species	Infrared gas	Description	Raman Liquid	Description	Approximate motion
a'	363	m	365	m sh	CFBr rocking
a"	416	m	421	vvw	CFBr deformation
a'	476	s	475	vw d	CFBr bending
a'	614	s	614	s sh	CBr stretching
a"	729	vs	717	vvw	twisting
a"	839	vs	845	w d	CH_2 deformation
a'	945	vs	944	vw d	CH_2 rocking
a'	1164	vs	1150	vvw d	CF stretching
a'	1367	s	1367	s sh	CH_2 bending
a'	1640	vs	1640	s sh	C=C stretching
a'	3056	s	2995	w	CH stretching
a'	3109	s	3140	m d	CH stretching

TABLE X

FUNDAMENTAL VIBRATIONAL FREQUENCIES FOR MOLECULES OF TYPE $CH_2=CXY$ (in cm^{-1})

Species & mode	$CH_2:CF_2$	$CH_2:CCl_2$	$CH_2:CBr_2$	$CH_2:CFCl$	Species & mode	$CH_2:CFBr$
$b_1(\omega CH)$	3100	3130	3108	3069	$a'(\nu CH)$	3109
$a_1(\omega CH)$	3058	3035	3023	3016	$a'(\nu CH)$	3056
$a_1(\nu CC)$	1728	1620	1593	1656	$a'(\nu CC)$	1640
$a_1(\delta CH_2)$	1414	1391	1379	1383	$a'(\delta CH_2)$	1367
$b_1(\nu)$	1302(C-F)	794(CCl)	696(CBr)	1186	$a'(\nu CF)$	1164
$b_1(\rho CH_2)$	955	1094	1065	947	$a'(\rho CH_2)$	945
$a_1(\nu)$	926(C-F)	605(CCl)	467(CBr)	699(CCl)	$a'(\nu)$	614(CBr)
$a_1(\delta)$	550(CF_2)	299(CCl_2)	184(CBr_2)	432(CFCl)	$a'(\delta)$	475(CFBr)
$b_1(\rho)$	438(CF_2)	375(CCl_2)	322(CBr_2)	371(CFCl)	$a'(\rho)$	365(CFBr)
$b_2(\beta CH_2)$	803	872(CH_2)	886	836	$a''(\beta CH_2)$	841
$a_2(\tau)$	714	686(τ)	668(τ)	607(τ)	$a''(\tau)$	729(τ)
$b_2(\beta)$	611(CF_2)	458(CCl_2)	405(CBr_2)	515(CFCl)	$a''(\beta)$	416(CFBr)

CHAPTER V

INFRARED AND RAMAN SPECTRA OF $CF_2Br-CHBr_2$

As mentioned in chapter I, the vibrational spectra of a number of substituted ethanes of the form $CX_2Y-CX'_2Y'$ have been studied in the past. The compound $CF_2Br-CHBr_2$ was first synthesized many years ago by Swarts.[45] However, its infrared and Raman spectra have not been investigated previously. Likewise, no study of the rotational spectrum of this compound by microwave spectroscopy has been reported and no structure determination has been made by electron diffraction.

A detailed account of the infrared and Raman spectra of $CF_2Br-CHBr_2$ is given in the present chapter.

Experimental

The sample (bp 143°-145°C at 750 mm pressure) was prepared in the laboratory of Prof. A. L. Henne at Ohio State University. The spectra indicate that it is of a high degree of purity.

The infrared absorption spectrum of the gas at room temperature in the region 2 to 35 μ was obtained with a

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[45]F. Swarts, Bull. Acad. Roy. Belg. 563.

Perkin-Elmer Model 112 double-pass spectrometer equipped with CsBr, NaCl, and LiF prisms and a 1-m cell. The observed spectrum is not very rich in bands because of the low vapor pressure of the sample. The infrared spectrum of the gas at different temperatures from room temperature up to 150°C was also obtained. However, when the sample was heated beyond 150°C decomposition occurred, and bands belonging to $CF_2:CBr_2$ and $CF_2:CHBr$ appeared.

The infrared spectrum of the liquid at room temperature, in the region 2 to 26 μ was obtained with the cells described in Chapter II. The frequencies of the bands coincide very well with those obtained from the Raman spectrum. In order to study the variation of the intensities of the bands with temperature, which might be due to rotational isomerism, the infrared spectrum of the liquid in the LiF region was recorded at different temperatures. Particular attention was given to the C-H stretching frequencies.

The infrared spectrum of the solid at -180°C was obtained with the aid of the low temperature cell described in Chapter II.

The infrared spectra are shown in Figs. 17-21 and the wave numbers of the bands are listed in Tables XI-XIII.

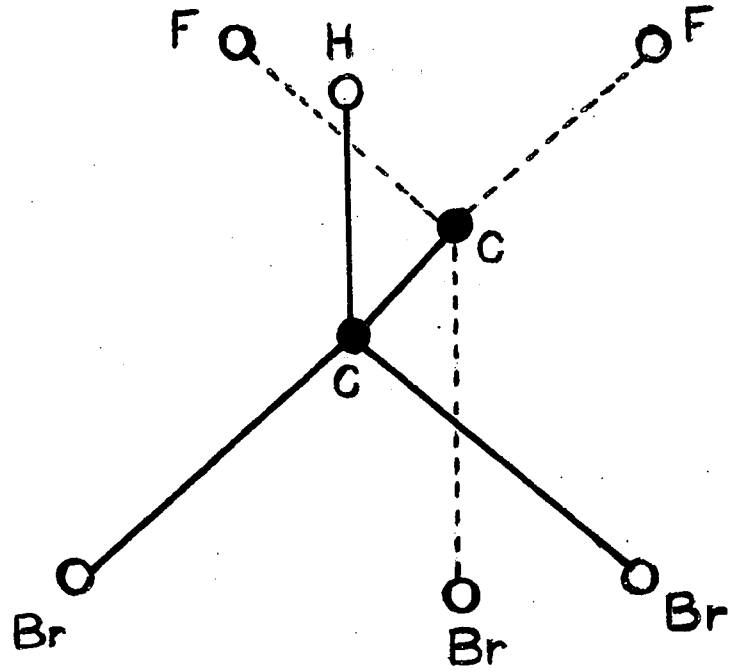
The infrared spectra of the compound in the liquid state and in solution in different solvents were obtained in the region 2 to 15 μ with a Perkin-Elmer Model 21 double beam spectrophotometer. The solvents used were carbon

disulphide, carbon tetrachloride, benzene, chloroform, acetonitrile and nitromethane. Since there are some uncertainties in the region 1300-2500 cm^{-1} in the observations made with the Model 112 spectrometer due to the presence of water vapor, the wave numbers of some of the bands listed in Table XII are taken from the record obtained with the double-beam spectrophotometer. These wave numbers agree with those obtained on the Model 112 spectrometer to within 3 cm^{-1}.

The Raman spectrum of the sample contained in a sealed Pyrex tube at room temperature was obtained in the manner described in Chapter II. Polarization measurements were made by the Crawford-Horwitz method.[23] The Raman spectral data are listed in Table XIV.

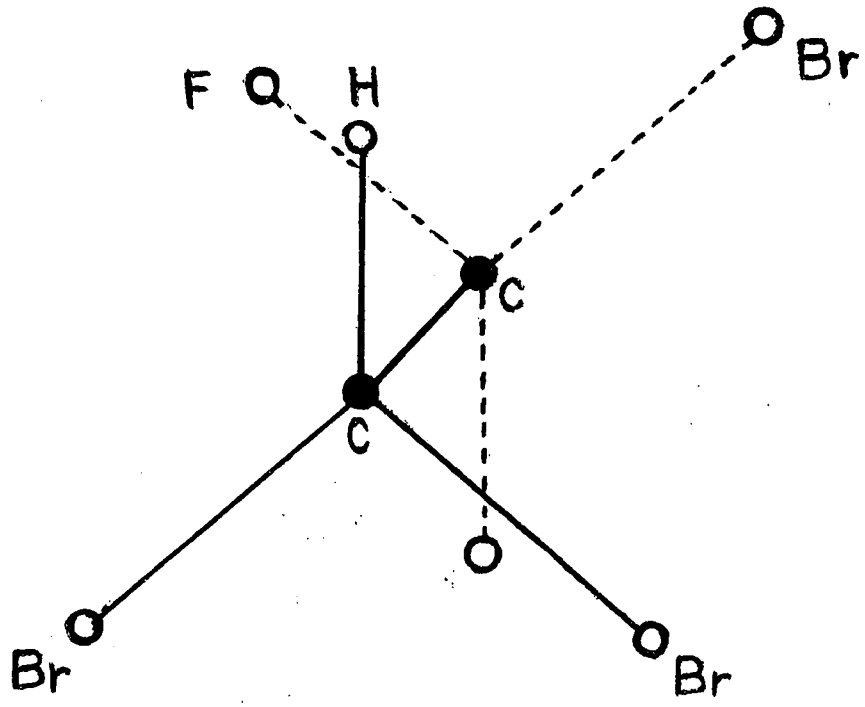
Interpretation

It will be assumed that the equilibrium configurations of the molecule CF_2Br-$CHBr_2$ have the staggered forms. When the bromine and hydrogen atoms are in trans position as shown in Fig. 16a, the CF_2Br-$CHBr_2$ molecule has the symmetry C_s, and its eighteen normal vibrations can be classified as eleven of species a' and seven of species a". In the other staggered configuration, which we shall refer to as the gauche form shown in Fig. 16b, the molecule has no symmetry at all, and the eighteen fundamentals are all of the same species. The large number of strong bands in both the Raman and the infrared spectrum indicates the presence of two rotational isomers.



(a)

trans



(b)

gauche

Fig. 16. Staggered Configurations of CF_2Br-$CHBr_2$

Assuming the interatomic distances, C-C=1.54, C-F=1.37, C-H=1.09, C-Br=1.98 A,[46] and tetrahedral angles, the principal moments of inertia were obtained as follows: 895.8, 973.9, and 1477.7 x 10^{-40}gcm^2 for the trans form and 723.1, 1716.1, and 2210.2 x 10^{-40}gcm^2 for the gauche form. From these values of the moments of inertia, the Badger-Zumwalt[29] parameters were calculated, and approximate values of the PR or QQ separations of the bands were determined. For the trans form the separations are approximately 5 cm^{-1} for types A and C and 1 cm^{-1} for type B bands. Since a large extrapolation from the Badger-Zumwalt curves was required for the gauche form little information could be obtained. However, since the molecule is approximately a symmetric top, the band contours and doublet separations were estimated from the paper of Gerhard and Dennison.[30] The bands are classified roughly as parallel and perpendicular. The estimated PR separations for the former was 6 cm^{-1}. The perpendicular bands should be broad. All the calculated separations are too small to be definitely resolved. Hence the band contours could not be used for differentiating between the bands belonging to the two isomers.

The intense Raman bands at 2979 cm^{-1} and 3010 cm^{-1} must surely be fundamentals ascribed to C-H stretching. The corresponding bands appear in the infrared spectrum of the

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[46]Landolt-Bornstein: Zahlenwerte und Functionen, Spriger Verlag, Berlin, Germany (1951), Vol. I, Part II.

gas at 3001 and 3028 cm^{-1}. The fact that there are two distinct bands in this region shows that two rotational isomers are present in the sample. Since the band of higher wave number, both in the Raman and the infrared spectrum, is much stronger than the other band, it is assumed that one isomeric form is more abundant than the other. Use will be made of this in the assignment of fundamentals. The more abundant rotational isomer will be referred to as I and the other as II. Since it is not clear which of the two isomers, I or II, has the symmetry C_S and which no symmetry (C_1) the question of the symmetry species of the assigned fundamentals will be deferred until all the fundamentals have been assigned.

In the spectral region between 900 and 1250 cm^{-1} there should be five fundamentals belonging to each isomeric form. The Raman bands at 1253 and 1002 cm^{-1}, the counterparts of which are found at 1253 and 1009 cm^{-1} in the infrared spectrum of the gas, are probably fundamentals of I and may be associated largely with CH bending. The intense infrared bands at 1112 cm^{-1} and 1193 cm^{-1} in the gas and the weak and diffuse Raman bands at 1107 cm^{-1} and 1192 cm^{-1} are undoubtedly fundamentals of I. The spectral characteristics indicate that they probably involve C-F stretching.

In this region there is a weak Raman band at 1145 cm^{-1} and a medium intensity band at 1140 cm^{-1} in the infrared spectrum of the gas. These are assigned as a fundamental of

II, although they could also be interpreted as a binary combination of fundamentals ascribed to I. Other evidence for this choice is discussed later.

The strong infrared band at 947 cm^{-1} and the very strong Raman band at 944 cm^{-1} undoubtedly represent a fundamental of I largely due, probably, to C-C stretching.

In the region from 500 cm^{-1} to 800 cm^{-1} there should again be five fundamentals of each rotational isomer. The three intense Raman bands at 643, 703 and 775 cm^{-1} almost certainly represent three fundamentals of I. They appear as strong bands at 648, 708 and 780 cm^{-1} in the infrared spectrum of the gas and at 644, 706, and 778 cm^{-1} in the infrared spectrum of the solid. The motions are probably largely C-Br stretching. There is a weak Raman band at 757 cm^{-1}; the corresponding band occurring at 744 cm^{-1} in the infrared spectrum of the gas is strong. In the infrared spectrum of liquid and solid it appears as a strong band near 755 cm^{-1}. These bands may be a fundamental belonging to the less abundant isomer II or a combination band of I whose intensity is enhanced by Fermi resonance with the fundamental at 775 cm^{-1}. Four bands are observed at 526, 564, 574 and 593 cm^{-1} in the Raman spectrum, of which the first and last are very sharp, though not very intense. These are assigned as fundamentals of I. The infrared bands corresponding to these are at 524 and 594 cm^{-1} in the gas and near 523 and 595 cm^{-1} in the liquid and solid. In all the three infrared spectra there is a strong band at 564 cm^{-1} and a band of medium

intensity near 594 cm^{-1} of which the band near 564 cm^{-1} is more intense. It is possible that the latter is an overtone of the fundamental at 284 cm^{-1} and the other a combination band; or the band at 564 cm^{-1} is a fundamental belonging to II and the one at 574 cm^{-1} is the overtone of the fundamental at 284 cm^{-1}.

The bands in the region below 400 cm^{-1} do not present any serious problem. However the presence of more than seven strong bands in this region indicates again the presence of two rotational isomers in the sample. Two intense bands are observed at 365 and 333 cm^{-1} in the Raman spectrum. In the infrared spectrum of the solid there is a weak band at 365 cm^{-1}. This band and the Raman band at 333 cm^{-1} are without doubt fundamentals of I, and are probably associated largely with CF_2Br deformation. All the other bands of wave number below 340 are observed only in the Raman spectrum. The very strong Raman bands at 284 and 204 cm^{-1} are undoubtedly fundamentals of I, the motions may be characterized as rocking. The strong band at 156 cm^{-1} in the Raman spectrum and the rather weak band at 113 cm^{-1} are assigned as the other fundamentals largely involving rocking. There is no doubt that the Raman band at 65 cm^{-1} is a fundamental associated largely with torsional motion. The other two Raman bands at 194 and 169 cm^{-1} are far too intense to be interpreted as combination bands. They are probably fundamentals of II. The assigned fundamentals of isomer I are

listed in Table XV.

In Table XVI are listed the fundamentals of the two rotational isomers. Only those fundamentals which are different for the two isomers are given in the third and fourth columns. All the observed bands in the Raman and infrared spectra not interpreted as fundamentals can be explained as binary combinations of the assigned fundamentals of the more abundant rotational isomer. Two or three weak infrared bands observed may be ternary combinations or binary combinations of the less abundant isomer II.

Discussion

The total number of strong bands observed is six more than the fundamentals of a single rotational isomer. It is reasonable to assume that several of the fundamentals will be common to the two isomers. Hence it is difficult to determine the species of the fundamentals. Since some of the bands appear polarized and some do not the species can in certain cases be specified. From the Raman spectral data the fundamentals of wave number 113 and 333 seem to be a" and probably the fundamental (i.e. the part contributed by the trans form) of lowest frequency 65 cm^{-1} is also a". Of the two fundamentals of wave number 204 and 284 one should be a". It is probably the band at 284 cm^{-1}. The band at 708 cm^{-1} appears to be an a" fundamental; though it is difficult to determine the depolarization ratios of the weak bands at 1002 and 1107 cm^{-1}, it is likely that these bands are the other two a"

fundamentals. Since most of the bands coincide it is difficult to say which of the two forms trans or gauche is more abundant. From the intensity of the a" bands it appears the trans form is more abundant.

In order to find the effects of steric repulsions if any in the trans form, which might rule out the possibility of this form being more stable, the distance ~~(d)~~ between the bromine atom in one end group and one of the bromine atoms in the other end group is calculated, assuming the structural parameters ~~as~~ mentioned earlier in the chapter. It is found to be slightly less that the sum of the Van der Waals radii for two bromine atoms. The same distance is calculated with the bromine atom replaced by one of the fluorine atoms of the same end group, as in the gauche form (assuming that the end group is rotated through exactly 120°). This distance also is found to be slightly less than the corresponding Van der Waals radii for bromine and fluorine. Hence the two forms are equally probable. However from electrostatic considerations it appears the trans form is less energetic. Nevertheless, further confirmation, by other measurements such as electron diffraction and an accurate determination of the dipole moments, is needed to establish this fact definitely.

An attempt has been made to differentiate between the fundamentals of the two isomers on the basis of temperature variation of the band intensities and from the infrared spectrum in the solid state. In the latter all the bands

present in liquid and gas appeared. This may either be due to the substance not being in the crystalline state or to the presence of both rotational isomers in the solid crystalline state. The fact that the frequencies in the solid state differ very little from those in the liquid (except for the C-H stretching vibrations) indicates that the solid formed may be a glass rather than a crystalline aggregate.

For the study of temperature variations of the intensities, very few bands occur in advantageous positions in the infrared spectrum. The intensities of the bands near 1140 cm^{-1} were observed at different temperatures. Though there is no great change in the ratio of the intensities of the bands near 1140 and 1107 cm^{-1} there seems to be a slight change indicating the two are due to different isomers. The bands occurring at 3028 and 3001 cm^{-1} in the infrared spectrum of the gas are better for this study because they are well separated. The ratio between their intensities at different temperatures is determined and a curve, Fig. 23, is drawn showing the relation between $\ln(I_B/I_A)$ and $1/T$; where T is the absolute temperature, I_A and I_B are the integrated intensities of the bands belonging to the two isomers I and II (or trans and gauche isomers as defined previously). The slope of the curve gives $\Delta H_o^o/R$ where R is the gas constant and ΔH_o^o is the difference between the total heat functions for one mole of the two isomers, at 0^oK, for the ideal gaseous state. If the bands are almost of the same width, the integrated intensities can be taken as

proportional to the peak intensities. Since that is approximately the case, the ratios of the peak intensities were used. A value of 500 ± 150 cal/mole was obtained.

For the liquid the observed intensity difference was very small for small changes of temperature; so a similar curve could not be drawn. However, an estimate of ΔH is made from the value of the intensities at room temperature and 120°C. It gave the value of about 200 cal/mole.

The above results show that the difference in total heat functions for the two forms of the molecule is very small. This can probably be accounted for by the fact that the difference between the dipole moments of the two isomers, calculated by taking the vector components of the bond dipole moments[47] is very small. The calculated values are 0.8 and 1.2 debyes for the trans and gauche forms respectively. It can also be seen from the positions of the atoms in the end groups. The end group with two fluorine atoms and a bromine atom is almost cylindrically symmetrical with the symmetry axis coinciding with the C-C bond, for there is very little difference in the bond dipole moments of C-F and C-Br. Hence it is probable that the trans form is the more stable of the two.

It has been observed by earlier workers[11] that in solution the intensities of the infrared bands belonging to

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[47]C. P. Smyth, Dielectric Behavior and Structure (International Chemical Series, McGraw Hill Book Co. Inc., 1955).

the isomer with larger dipole moment increased considerably more than the intensities of the bands belonging to the isomer with smaller dipole moment. Therefore the ratio of the intensities of the bands belonging to the two isomers increases as the dielectric constant of the solvent is increased. In order to study the intensities of the infrared bands in solution in the present case the pairs of bands in the regions 1100 and 750 cm^{-1} were chosen. Although there is no striking difference in the intensities of the bands in the different solutions there appears to be some change indicating the bands are due to different isomers. The ratio of the intensities of the bands due to the different isomers changed by about 25 per cent from CCl_4 (dielectric constant 2.24) to acetonitrile (dielectric constant 38.8) for the bands in the 1100 cm^{-1} region, which is the most favorable for this study.

The potential barrier opposing internal rotation can be estimated very roughly from the formula[48]

$\nu = (\sigma_i/2)(V_o/I_r)^{\frac{1}{2}}$ where σ_i is the internal symmetry number, V_o the maximum height of potential barrier, I_r reduced moment of inertia and ν the frequency of torsional oscillation. A value of 14400 cal/mol was obtained.

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[48] S. Glasstone, Theoretical Chemistry (D. Van Nostrand Co. Inc., New York, N. Y., 1944).

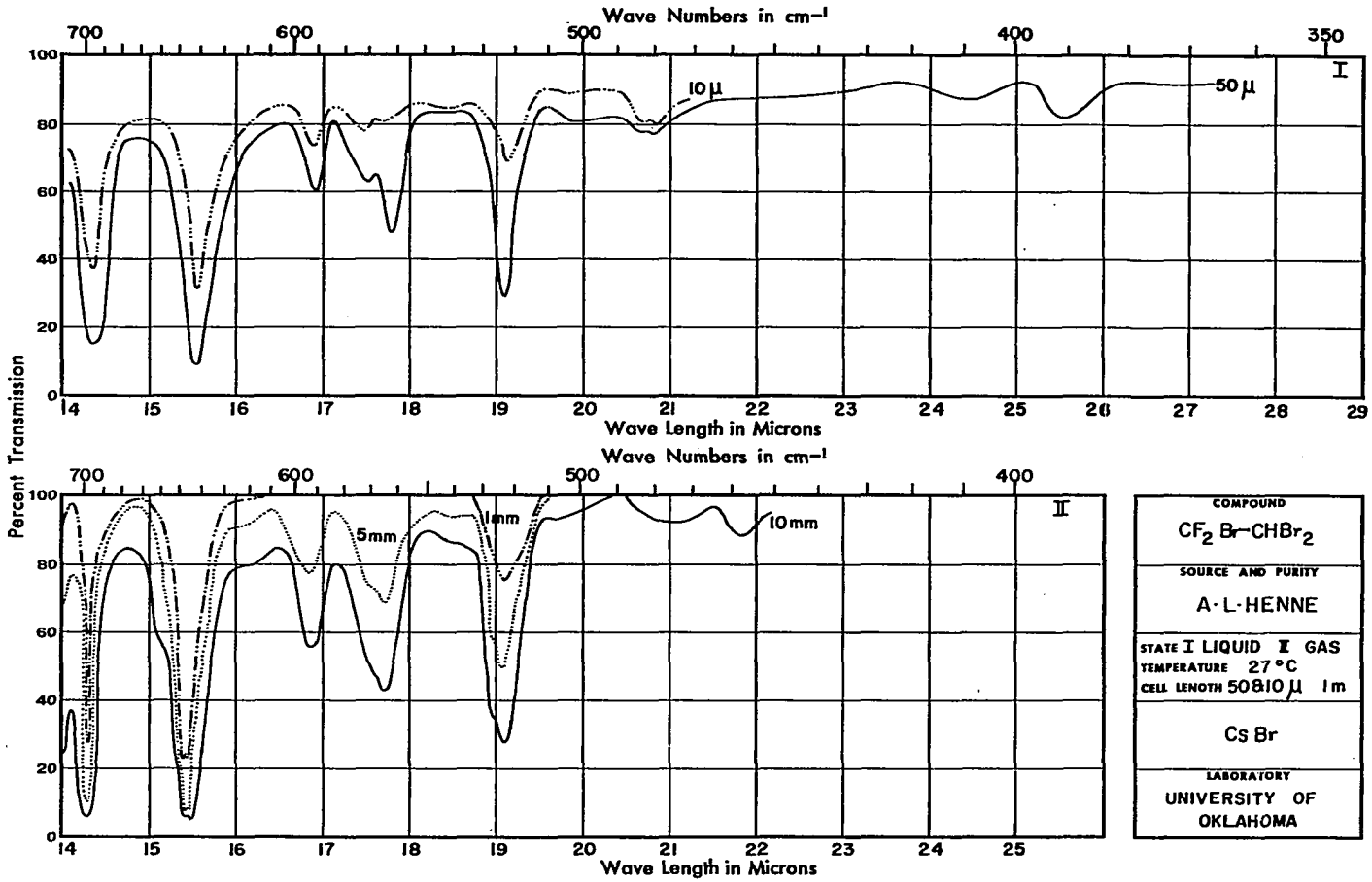


Fig. 17. Infrared Spectra of Gaseous and Liquid $CF_2Br-CHBr_2$ (CsBr Region)

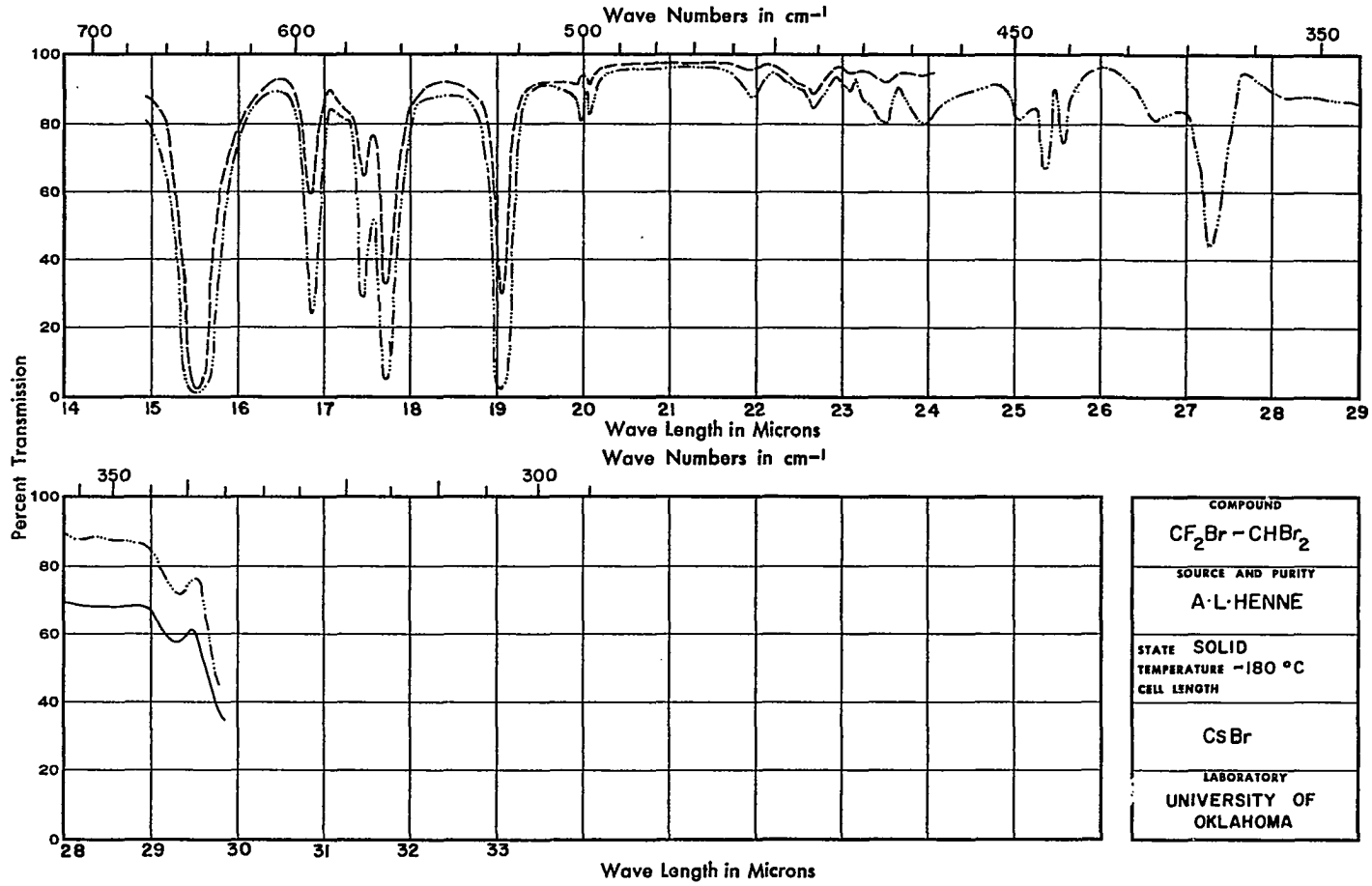


Fig. 18. Infrared Spectrum of Solid $CF_2Br-CHBr_2$ (CsBr Region).

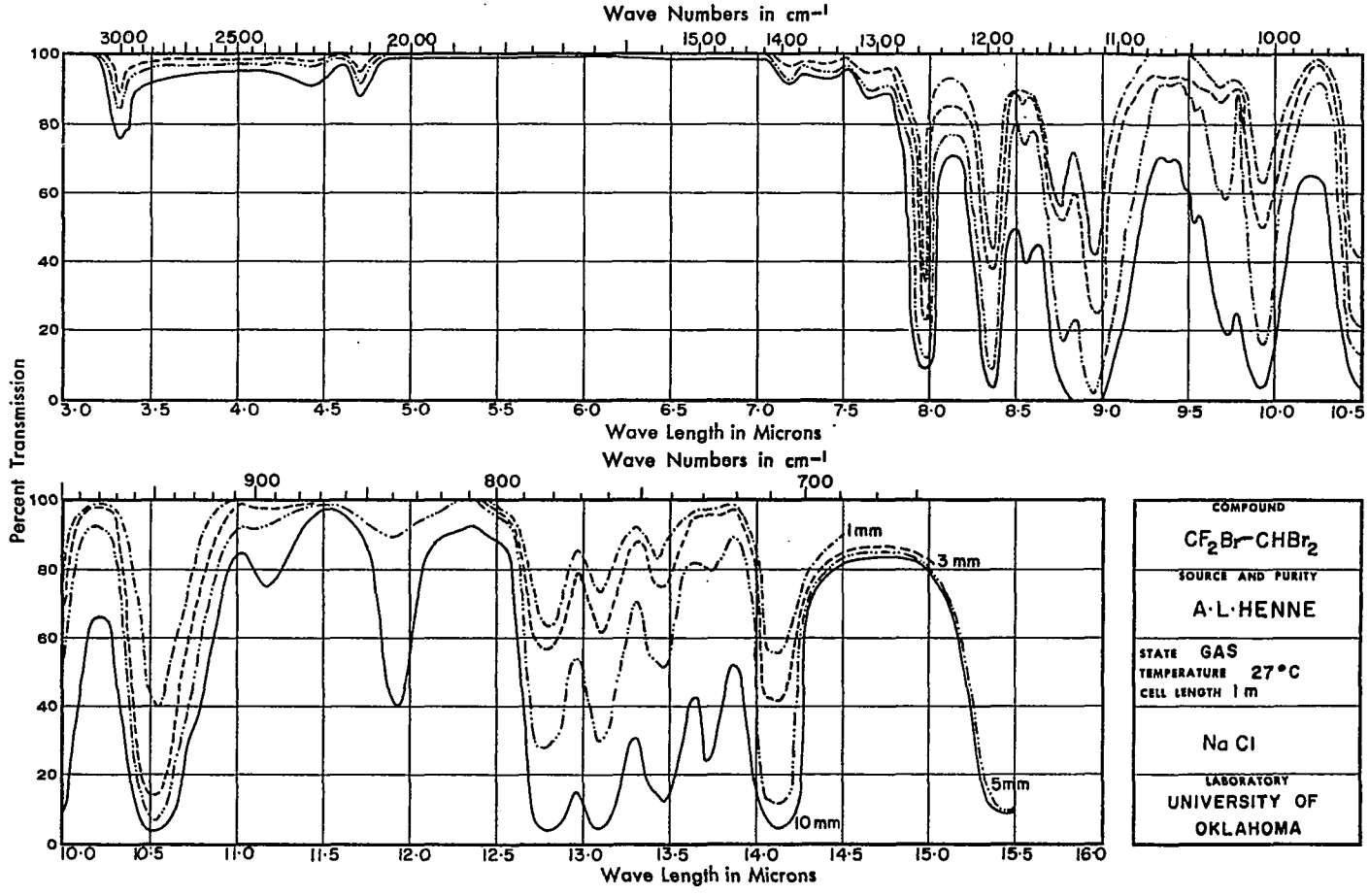


Fig. 19. Infrared Spectrum of Gaseous $CF_2Br-CHBr_2$ (NaCl Region).

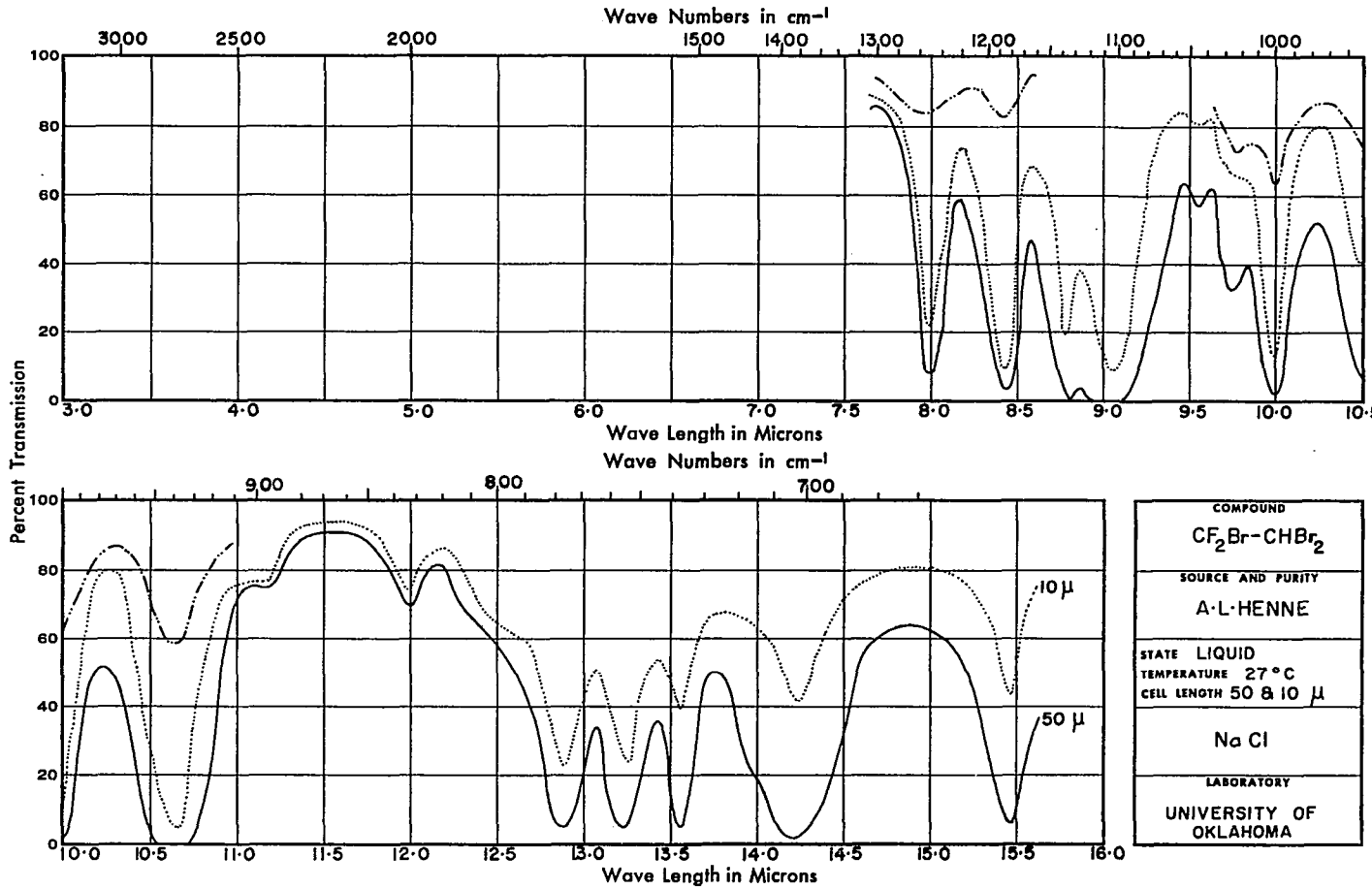


Fig. 20. Infrared Spectrum of Liquid $CF_2Br-CHBr_2$ (NaCl Region).

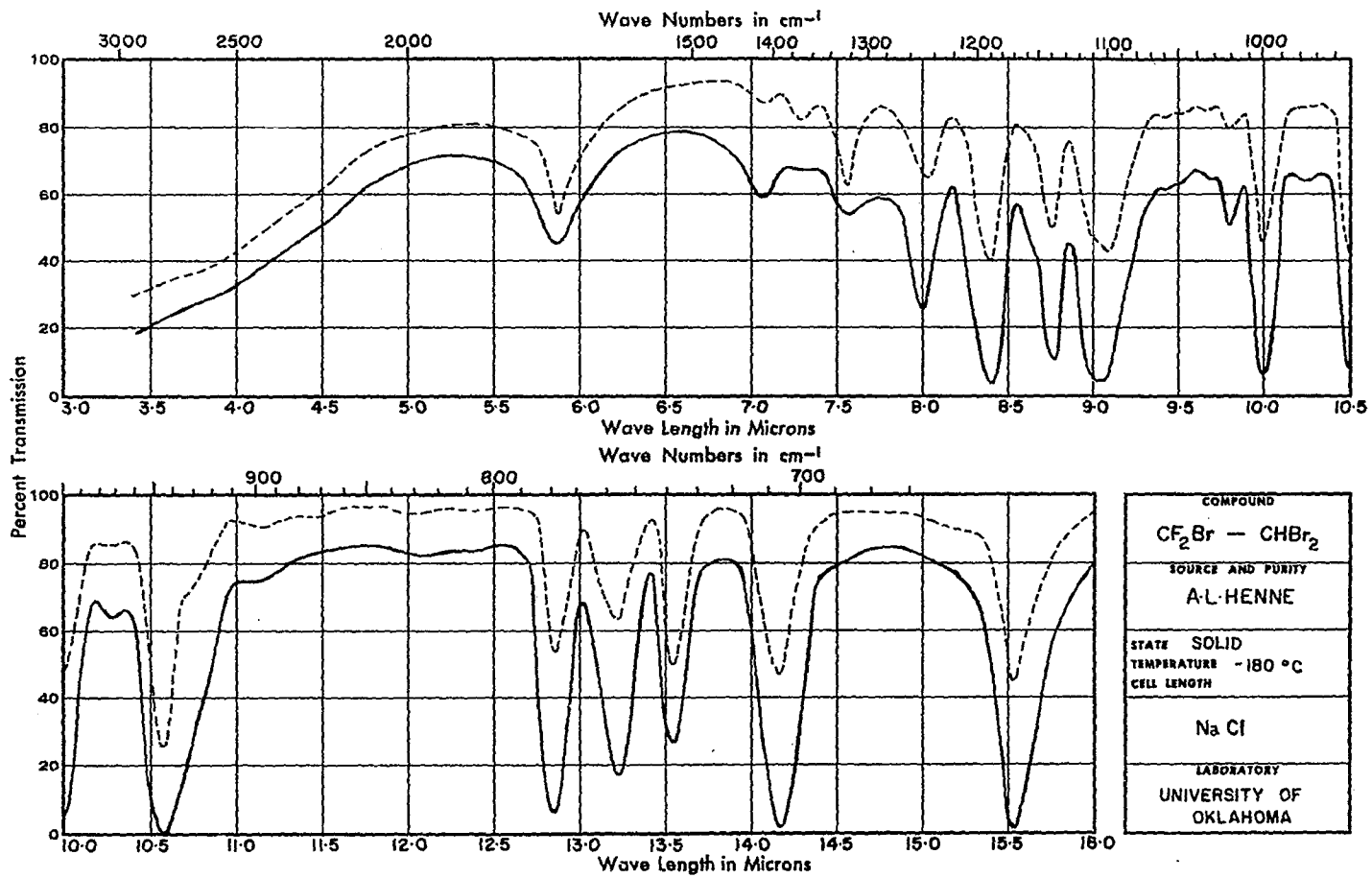


Fig. 21. Infrared Spectrum of Solid CF_2Br-$CHBr_2$ (NaCl Region).

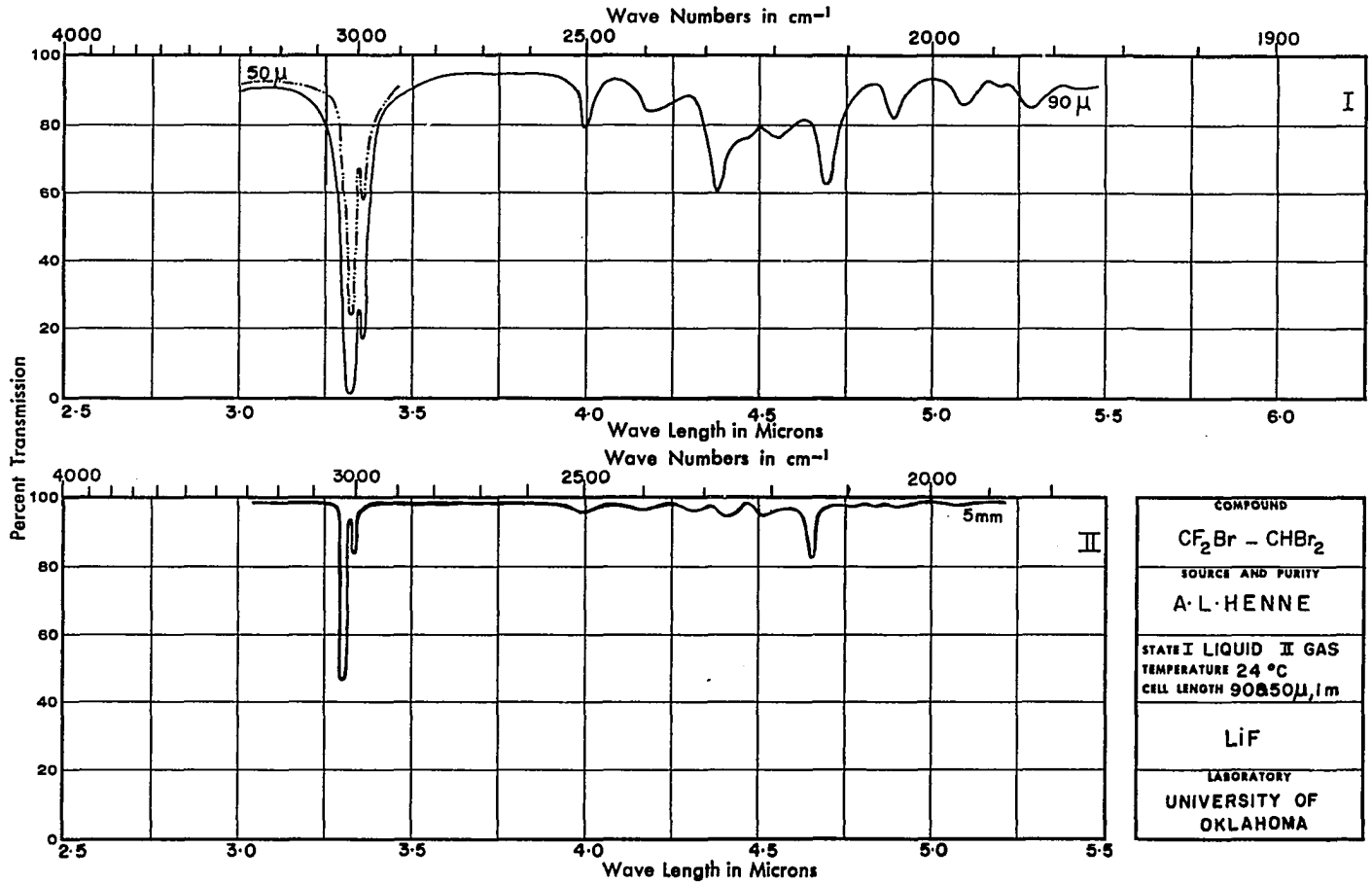


Fig. 22. Infrared Spectrum of Gaseous and Liquid CF_2Br-$CHBr_2$ (LiF Region).

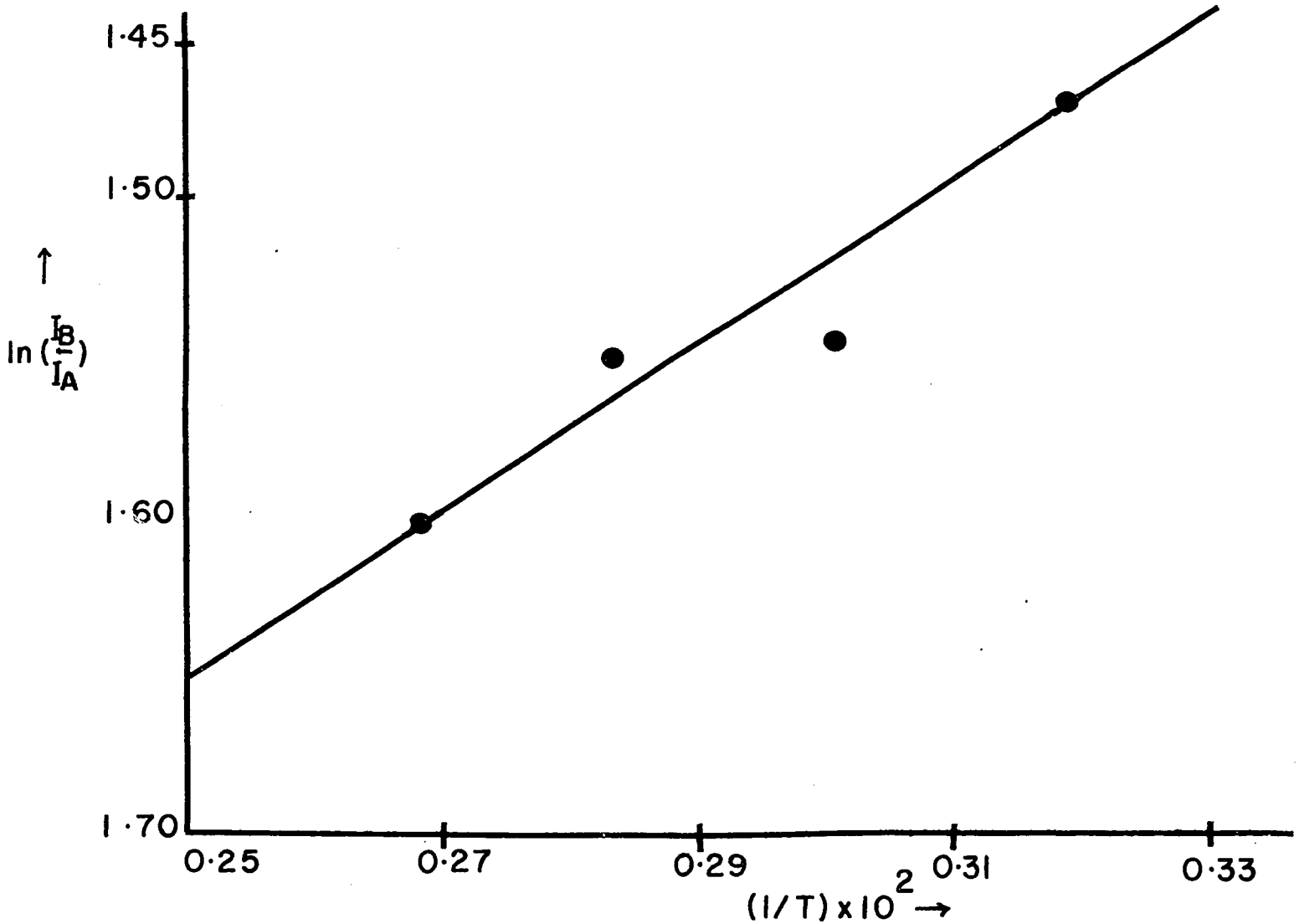


Fig. 23. Curve Showing the Relation Between $\ln(I_B/I_A)$ and 1/T.

TABLE XI

INFRARED SPECTRAL DATA FOR GASEOUS $CF_2Br-CHBr_2$

Wave number	Description	Interpretation
524	s	a' fundamental
533	vw	204 + 333 = 537
565	m	2 x 284 = 568
580	w	204 + 365 = 569
594	w	65 + 524 = 589
620	vvw	284 + 333 = 617
646	vs	a' fundamental (648)
649	vs	
662	vw	2 x 333 = 666
706	vs	a" fundamental (708)
711	vs	
729	m	204 + 525 = 729 2 x 365 = 730
742	s	a' fundamental (744) II
746	s	
762	s	113 + 648 = 761 or fundamental II
778	s	a' fundamental (780)
781	s	
796	vvvw	204 + 594 = 798
839	m	65 + 780 = 845
895	vw	113 + 780 = 893
947	s	a' fundamental

TABLE XI--Continued

Wave number	Description	Interpretation
1009	s	a" fundamental
1028	w	a" fundamental II
1034	vvw	333 + 708 = 1041
1049	vvvw	2 x 524 = 1048
1053	vvvw	113 + 947 = 1060
1065	vvvw	65 + 1009 = 1074 284 + 780 = 1064
1112	vs	a' fundamental
1140	s	a' fundamental II
1170	vw	524 + 648 = 1172 65 + 1112 = 1177
1193	s	a' fundamental
1253	s	a' fundamental
1305	vvvw	524 + 780 = 1304 113 + 1193 = 1306
2146	vw	947 + 1193 = 2140
2219	vw	2 x 1112 = 2224
2279	vvvw	2 x 1140 = 2280
2312	vvvw	1112 + 1193 = 2305
2511	vvw	2 x 1253 = 2506
3001	w	fundamental II
3028	m	a' fundamental

TABLE XII

INFRARED SPECTRAL DATA FOR LIQUID $CF_2Br-CHBr_2$

Wave number	Description	Interpretation
394	vvw	65 + 333 = 398
408	vvw	2 x 204 = 408
483	vw	204 + 284 = 488 157 + 333 = 490
523	m	a' fundamental
539	vvw	204 + 333 = 537
562	w	2 x 284 = 568
572	vw	204 + 365 = 569
595	vw	fundamental II
614	vvw	284 + 333 = 617
643	s	a' fundamental
703	s	a" fundamental
720	w	204 + 523 = 723
738	s	2 x 365 = 730
756	s	113 + 643 = 756 or fundamental II
776	s	a' fundamental
834	vw	65 + 776 = 841
894	vvw	113 + 776 = 889
946	s	a' fundamental
1000	s	a" fundamental
1025	w	fundamental II
1033	vw	333 + 703 = 1036

TABLE XII--Continued

Wave number	Description	Interpretation
1047	vw	2 x 523 = 1046
1106	vs	a" fundamental
1137	s	365 + 776 = 1141
1186	vs	a' fundamental
1242	s	595 + 643 = 1238
1253	s	a' fundamental
1330[a]	w	333 + 1000 = 1333
1351[a]	w	113 + 1253 = 1366 365 + 1000 = 1365
1377[a]	w	284 + 1106 = 1390
1404[a]	w	157 + 1253 = 1410
1439[a]	vvw	333 + 1106 = 1439
1463[a]	vw	523 + 946 = 1469
1500[a]	vw	333 + 1186 = 1519
1540[a]	vvw	595 + 946 = 1541 365 + 1186 = 1551
1580[a]	vw	333 + 1253 = 1586 643 + 946 = 1589
1629[a]	vw	523 + 1106 = 1629
1642[a]	vw	643 + 1000 = 1643 703 + 946 = 1649
1692[a]	w	595 + 1106 = 1701
1710[a]	vw	523 + 1186 = 1709
1810[a]	vw	703 + 1106 = 1809
1860[a]	vw	595 + 1253 = 1848
1890	vvw	2 x 946 = 1892

TABLE XII--Continued

Wave number	Description	Interpretation
1938[a]	vw	946 + 1000 = 1946
2016[a]	vw	776 + 1253 = 2029
2046	vvw	946 + 1106 = 2052
2092[a]	w	1000 + 1106 = 2106
2160	w	
2196	w	946 + 1253 = 2199
2232[a]	vw	1000 + 1253 = 2253
2279	w	
2309[a]	vw	1186 + 1253 = 2439
2450[a]	vw	1186 + 1253 = 2439
2506	vw	2 x 1253 = 2506
2980	s	fundamental II
3008	vs	a' fundamental

[a]Data taken by the Perkin-Elmer 21 spectrophotometer.

TABLE XIII

INFRARED SPECTRAL DATA FOR SOLID CF_2Br-$CHBr_2$

Wave number	Description	Interpretation
342	vvw	2 x 169 = 338
346	vvw	65 + 284 = 349
351	vvw	157 + 204 = 361
365	w	a' fundamental
387	vw	
391	vw	113 + 284 = 397
398	vw	65 + 333 = 398
418	vvw	2 x 204 = 408
425	vvw	
429	vvw	65 + 365 = 430
440	vw	157 + 284 = 441
455	vvw	113 + 365 = 478
500	vvw	157 + 365 = 522
525	s	a' fundamental
565	s	2 x 284 = 568 or fundamental II
572	m	204 + 365 = 569
592	m	65 + 525 = 590
626	vvw	113 + 524 = 637
644	vs	a' fundamental
706	vs	a" fundamental
738	s	2 x 365 = 730

TABLE XIII--Continued

Wave number	Description	Interpretation
755	s	113 + 644 = 757 or fundamental II
778	s	a' fundamental
897	vvw	113 + 778 = 891 204 + 706 = 910
931	w	284 + 644 = 928 157 + 778 = 935
946	vs	a' fundamental
974	vvw	333 + 644 = 977
1001	s	a" fundamental
1021	m	fundamental II
1033	w	333 + 706 = 1039
1051	vw	113 + 946 = 1059 2 x 525 = 1050
1061	vw	65 + 1001 = 1066
1101	s	157 + 946 = 1103
1106	s	a" fundamental
1141	s	365 + 778 = 1143 or fundamental II
1189	s	a' fundamental
1243	m	65 + 1189 = 1250
1252	m	a' fundamental
1279	vvw	2 x 646 = 1292
1316	vw	65 + 1252 = 1317
1330	vw	157 + 1189 = 1346

TABLE XIII--Continued

Wave number	Description	Interpretation
1382	vw	284 + 1106 = 1390 204 + 1189 = 1393
2044	vvvw	946 + 1106 = 2052
2130	vvvw	946 + 1189 = 2135
2191	vvvw	946 + 1252 = 2198
2277	vvw	1112 + 1189 = 2301
2485	vvw	2 x 1252 = 2504
2966	w	fundamental II
2996	w	a' fundamental I
3221	vw	204 + 2996 = 3200
3355	vvw	365 + 2996 = 3361
4112	vw	1112 + 2996 = 4108
4225	vw	1252 + 2996 = 4228

TABLE XIV

RAMAN SPECTRAL DATA FOR LIQUID $CF_2Br-CHBr_2$

Wave number	Description	Depolarization ratio	Exciting[a] Hg lines	Interpretation
ca 65	s d	dep	d, ± eh	a" fundamental
113	md	0.9	d, ± e	a" fundamental
156	s sh	0.6	± e d	a' fundamental
169	s sh	0.6	± e	fundamental II
194	s sh	0.6	± e	fundamental II
204	vvs sh	0.6	d, + e, i	a' fundamental
284	s d	0.9	d, + e, i, k	a" fundamental
310	vw sh		+ e	2 x 156 = 312
333	vs	0.9	d, + e, i, k	a" fundamental
365	s sh		+ e	a' fundamental
395	vw	0.4	+ e	2 x 204 = 408
526	m sh	0.4	+ e	a' fundamental
564	vw	0.8	+ e	2 x 284 = 568 or fundamental II
574	vvw		+ e	204 + 365 = 569
593	m sh	0.8	+ e, i	a' fundamental
643	s d	0.6	+ e, k, i	a' fundamental
655	vvw		+ e	2 x 333 = 666
703	md	1.0	+ e, k, i	a" fundamental
739	vw		+ e, k	2 x 365 = 730
757	vw		+ e, k	113 + 643 = 756
775	vs	0.7	+ e, k, i	a' fundamental

TABLE XIV--Continued

Wave number	Description	Depolarization ratio	Exciting[a] Hg lines	Interpretation
846	vvw d	0.7	e	204 + 643 = 847
894	vvw d		e	204 + 703 = 907
944	vsd	0.7	e,f	a' fundamental
1002	vw	1.0	e	a" fundamental
1107	vvw	1.0	e	a" fundamental
1145	w d	1.0	e	fundamental II or 204 + 944 = 1148
1192	vw		e	fundamental II
1253	m d		e	a' fundamental
1345	vvw		e	204 + 1145 = 1349 157 + 1192 = 1349
1476	vvw		e	284 + 1192 = 1476 703 + 775 = 1478
1508	vvw		e	365 + 1145 = 1510
1557	vvw		e	2 x 775 = 1550
1584	vvw		e	333 + 1253 = 1586
1719	vvw		e	775 + 944 = 1719
1873	vvw		e	775 + 1107 = 1882 2 x 944 = 1888
2449	vvw		e	1193 + 1253 = 2446
2979	m	0.7	e,k,i	fundamental II
3010	s	0.6	e,k,i	a' fundamental

[a]Refer to Table III.

TABLE XV

VIBRATIONAL FUNDAMENTALS FOR $CF_2Cr-CHBr_2$ (in cm^{-1})

Species	Infrared Gas		Infrared Liquid		Infrared Solid		Raman (Liquid)		Approx. motion
a"							ca 65	s	Torsion
a"							113	m	Rocking
a'							157	s	Rocking
a'							204	vvs	Rocking
a"							284	s	Rocking
a"							333	vs	CF_2Br def.
a'					365	w	365	s	CF_2Br def.
a'	524	s	523	m	525	s	525	m	CF_2Br def.
a'	594	w	595	vw	592	m	593	m	$CHBr_2$ def.
a'	648	vs	643	s	644	vs	641	s	CBr stret.
a"	708	vs	703	s	706	vs	703	m	CBr stret.
a'	780	s	776	s	778	s	775	vs	CBr stret.
a'	947	s	946	s	946	vs	944	vs	C-C stret.
a"	1009	s	1000	s	1001	s	1002	vw	CH bending
a"	1112	vs	1106	vs	1106	s	1107	vvw	CF stret.
a'	1193	s	1186	vs	1189	s	1192	vw	CF stret.
a'	1253	s	1253	s	1252	m	1253	m	CH bending
a'	3028	m	3008	vs	2996	w	3010	s	CH stret.

TABLE XVI

VIBRATIONAL FUNDAMENTALS FOR THE TWO FORMS OF $CF_2Br-CHBr_2$

I				II			
Raman (liquid)		Infrared (gas)		Raman (liquid)		Infrared (gas)	
65	s						
113	m						
157	s			169	s sh		
204	vvs			194	s sh		
284	s						
333	vs						
365	s						
525	m	524	s	564	vw	565	m
593	m	594	w	574	vvw	580	w
641	s	648	vs				
703	m	708	vs				
775	vs	780	s				
944	vs	947	s				
1002	vw	1009	s			1028	w
1107	vvw	1112	vs	1145	w d	1140	m
1192	vw	1193	s				
1253	m	1253	s				
3010	s	3028	m	2979	m	3001	w

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