and ω_3. The effect of this interaction would be to decrease B' for ν_1 and to increase B' for ν_2. Since these frequencies are of about the same magnitude and the motions correspond to displacements along the AS—H bonds in both cases, but to no change in the bond angle we shall assume that the convergence in both instances is the same except for the Coriolis contribution. Inspection of the quantities α_1 and α_2 in reference 7 will then show that the Coriolis contribution $2\omega_2{}^2\xi_{12}{}^2/(\omega_2{}^2-\omega_1{}^2) \approx 2\omega_1{}^2\xi_{12}{}^2/(\omega_2{}^2-\omega_1{}^2) \approx 2\nu_1{}^2\xi_{12}{}^2/(\nu_2{}^2-\nu_1{}^2) = 0.03$. In this relation ξ_{12} is the Coriolis coupling coefficient between ω_1 and ω_2. From this relation $|\xi_{12}|$ may be computed to be $\xi_{12}=0.01$. We shall make the approximation of setting ξ_{12} equal to zero. Shaffer's expression for ξ_{12} then makes it possible to derive the relation

$$\mu(\omega_1{}^2+\omega_3{}^2)-\mu'(\omega_1'{}^2+\omega_3'{}^2)$$
$$=\left[\frac{(C-1)}{2C}\omega_1{}^2+\frac{(C+1)}{2C}\omega_3{}^2\right](\mu-\mu'/2), \quad (8)$$

where the primes refer to the isotopic molecule, $\mu=3mM/(3m+M)$ and $C=[(k_1/\mu)-(k_3/m)]$. Equation (8) supplies the additional relation required to evaluate ω_1 and ω_3. We have obtained the following values for these: $\omega_1=2209.2$ cm^{-1}, $\omega_3=973.3$ cm^{-1}, $\omega_1'=1571.2$ cm^{-1}, and $\omega_3'=696.3$ cm^{-1}. These values of ω_1 and ω_3 are probably less reliable than those obtained for ω_2 and ω_4, because the double minimum effect of the poten-

tial energy makes it more difficult to take the anharmonicity satisfactorily into account for ω_3. The separation of the components of ω_3 is only about 2.5 cm^{-1} and, since one may expect the doubling in the normal state to be quite negligible, the doubling of the first excited state must be about 2.5 cm^{-1}. Since this splitting is rather small (especially when compared to the splitting in the case of NH$_3$), this method of approximating to the frequencies ω_1 and ω_3 is, nevertheless, probably quite good.

The constants of the harmonic portion of the potential energy function have also been evaluated. They are $\alpha=2.768\times10^5$, $\beta=1.665\times10^5$, $\gamma=1.204\times10^5$ dynes/cm, and $a=3.622\times10^5$, $b=2.2076\times10^5$, $c=0.6851\times10^5$ in Dennison's notation. The last three of these are, respectively, equivalent to the constants k_1, k_3, and k_2 in Shaffer's notation. In Tables III and IV are summarized the information obtained concerning the size, shape, and structure of the AsH$_3$ molecule from a study of the fundamental bands ν_1 and ν_2. In a later paper we hope then to give a discussion of the structure of the bands ν_3 and ν_4 in the spectra of AsH$_3$ and AsD$_3$.

Infra-Red Bands in the Spectrum of Difluoromethane

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Eight absorption bands have been observed in the infra-red spectrum of CH$_2$F$_2$. Seven of these are believed to be fundamental bands and have been identified as follows; the symmetry species of the band being given in parentheses: $\omega_1(A_1)=2949$ cm^{-1}, $\omega_2(A_1)=1116$ cm^{-1}, $\omega_4(A_1)=528.6$ cm^{-1}, $\omega_6(B_1)=3015.2$, $\omega_7(B_1)=1176.1$ cm^{-1}, $\omega_8(B_2)=1089.7$ cm^{-1} and $\omega_9(B_2)=1435.4$ cm^2. A band of species B_1 is observed at 2945 cm^{-1}. It is identified as $\omega_5+\omega_9$ and from this it is inferred that $\omega_5(A_2)=1510.6$ cm^{-1}. Rotational constants for the normal state are found to be $B''=0.354$ cm^{-1} and $C''-B''=1.303$ cm^{-1}. From these values the values $r_0(C-F)=1.32$A and $\angle(F-C-F)=107°$ are obtained assuming that $r_0(C-H)=1.094$A and $\angle(H-C-H)=110°$.

I. INTRODUCTION

THE infra-red spectra of a considerable number of pentatomic molecules, in particular molecules of the type XY$_4$ (i.e., CH$_4$,

SiH$_4$, GeH$_4$, etc.) and the XYZ$_3$ type (i.e., CH$_3$F, CH$_3$Cl, etc.), have been investigated under high dispersion. With the exception of the spectrum of CH$_2$D$_2$ which was resolved by

Ginsburg and Barker,[1] no spectra of molecules belonging to the XY_2Z_2 type have been studied under high dispersion. The difluoromethane molecule is a more general molecule of this type and is sufficiently light that one might expect to resolve most of the bands into rotational structure. This is particularly true since fluorine has no isotopes. Earlier work on this molecule confines itself to the Raman measurements by Glockler and Leader,[2] the electron diffraction measurements of Brockway[3] and the very recent work of Barker and Kao.[4] From the measurements of Brockway the $C-F$ distance is determined to be $(1.36\pm0.02)\times10^{-8}$ cm, the $F-F$ distance is found to be $(2.23\pm0.03)\times10^{-8}$ cm^{-1} and the $F-CF$ angle, $110°\pm1°$. In this paper we wish to report on the high dispersion measurements made by us on the spectrum of this molecule and the information which may be inferred from them.

II. GENERAL CONSIDERATIONS

The XY_2Z_2 molecular model has been studied theoretically by several authors, but most completely by Shaffer and Herman[5] who have derived complete energy expressions for the rotation-vibration levels. The CH_2F_2 molecule has a twofold axis of rotation (the z axis) and two vertical reflection planes (the xz and yz planes which contain, respectively, the CH_2 and CF_2 triangles) and belongs to the symmetry point group C_{2v}. It has nine modes of vibration of which none are degenerate. The vibration may be divided into four symmetry species; namely, A_1 and A_2 which are symmetric to a rotation of the molecule about the z axis, through an angle π, but, respectively, symmetric and antisymmetric to a reflection of it in the xz plane; B_1 and B_2 which are antisymmetric to a rotation of the molecule about the z axis through an angle π, but respectively symmetric and antisymmetric to a

reflection of it in the xz plane. The nature of the vibrations is illustrated in Fig. 1, where it may be seen that of species A_1 there are four, of the species A_2 there is only one, and of the species B_1 and B_2 there are, respectively, two. The dipole moment contains components A_1, B_1, and B_2. Consequently, eight of the fundamental frequencies and all overtone or combination frequencies belonging to these species might be
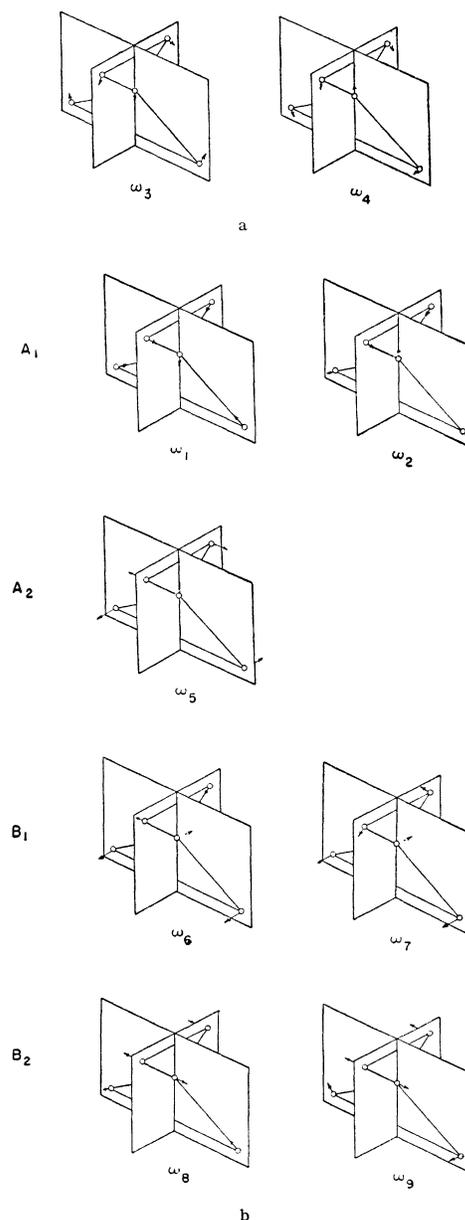
Fig. 1. Nature of vibrations.

[1] N. Ginsburg and E. F. Barker, J. Chem. Phys. 3, 668 (1935).

[2] G. Glockler and G. R. Leader, J. Chem. Phys. 7, 382 (1939).

[3] L. O. Brockway, J. Phys. Chem. 41, 185 (1937).

[4] E. F. Barker and C. L. Kao (private communication).

[5] J. E. Rosenthal, Phys. Rev. 45, 538 (1934); J. E. Rosenthal, Phys. Rev. 46, 730 (1934); Ta-You Wu, Vibrational Spectra and Structure of Molecules (Prentice-Hall, Inc., New York, 1939), p. 224; Ta-You Wu, J. Chem. Phys. 10, 116 (1942); W. H. Shaffer and R. C. Herman, J. Chem. Phys. 12, 494 (1944); W. H. Shaffer and R. C. Herman, J. Chem. Phys. 13, 83 (1945).

expected to be infra-red active. It may be shown, moreover, that all nine fundamental frequencies are Raman active.

As a guide to the subsequent attempt to identify the observed bands, it is convenient to make use of the formulation by Shaffer and Herman[5] of the vibration problem to estimate the positions in the spectrum of the fundamental bands. This may be accomplished in as much as the molecular shape and its dimensions are quite well-established and because the more important valence force constants involved in the CH_2F_2 vibration problem may be arrived at from the vibration frequencies of such molecules as CH_4, CH_3F, CHF_3, and CF_4. The predicted values of the positions of the vibration bands can be regarded as good estimates only, however, since these force constants were determined from bands in the spectra of the above molecules without having corrections made for anharmonicity and possible resonance. The force constants used in this calculation are those of Crawford and Brinkley[6] and those stated by Herzberg.[7] In the notation of Shaffer and Herman[5] the constants are

$$C_1(C-H \text{ bond constant}) = 4.79 \times 10^5 \text{ dynes/cm},$$
$$C_1'(C-F \text{ bond constant}) = 5.96 \times 10^5 \text{ dynes/cm},$$
$$C_2(H-C-H \text{ angle constant}) = 0.46 \times 10^5 \text{ dynes/cm},$$
$$C_2'(F-C-F \text{ angle constant}) = 1.24 \times 10^5 \text{ dynes/cm},$$
$$C_2''(H-C-F \text{ angle constant}) = 0.62 \times 10^5 \text{ dynes/cm}.$$

Using the valence symmetry coordinates adopted by Shaffer and Herman,[5] the kinetic and potential energy constants have been calculated and substituted into the secular determinant which yields the classical vibration frequencies. For the frequencies ω_1, ω_2, ω_3, and ω_4 which belong to the A_1 type, the following computed values were obtained, respectively, 2930, 1064, 1406, and 575 cm^{-1}. For ω_5 which is the single band belonging to the type A_2 the value 1335 cm^{-1} was obtained. The frequencies ω_6 and ω_7 belonging to the type B_1 are predicted at 2994 and 1034 cm^{-1}, respectively, while the frequencies ω_8 and ω_9 of type B_2 should lie near 1090 and 1607 cm^{-1}. This information will be found restated in Table V.

[6] B. L. Crawford and S. R. Brinkley, J. Chem. Phys. 9, 69 (1941).

[7] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 182 and 193.

With the aid of the molecular dimensions obtained by Brockway[3] and assuming the C$-$H distances and the H$-$C$-$H angle to be the same as in the methane molecule, the three principal moments of inertia for CH_2F_2 may be estimated to be about $I_{xx} = 92.3 \times 10^{-40}$, $I_{zz} = 81.0 \times 10^{-40}$, and $I_{yy} = 16.7 \times 10^{-40}$ g cm^2. The molecule is therefore an asymmetric rotator where two of the moments of inertia are nearly alike. One should therefore expect the bands belonging to the three species types to be sufficiently different so that they may be readily identified. Vibrations of species A_1 induce electric moments along the axis z, vibrations belonging to species B_1 induce electric moments along the axis x, and the vibrations of species B_2 give rise to electric moments along the axis y. The first two types represent vibrations normal to the axis y which is the unique axis of the molecule considered as a rotator. To the extent that this molecule may be approximated as a symmetric rotator, these are, therefore, "perpendicular" bands, and the lines which will be prominent in these bands will be ^RQ and ^PQ branches arising from quantum transitions $\Delta J = 0$, $\Delta K = \pm 1$. Bands of species B_2 correspond to the "parallel" bands which occur in symmetric rotator molecules. They are characterized by a strong Q branch with P and R branches on the low and the high frequency sides.

The principal effect of the asymmetry in a molecule of the dimensions of CH_2F_2 is to split the rotation levels where $K \neq 0$ into two components. This effect increases with J and is most prominent for small values of K. There will, therefore, be essential differences in the appearances of species A_1 and B_1 near the center of the bands. The selection rules for the asymmetric rotator show that for bands of species A_1 the components of the Q branches near the center spread away from the center for increasing values of J. This gives to these bands the appearance of having a region of small absorption near the center of the band. For bands of species B_1, however, the selection rules for the asymmetric rotator show that the components of the Q branches near the center crowd toward the center as the J value increases. This gives to these bands the appearance of a strong absorption peak at the center of the band which is sometimes referred to as a "gathered Q branch."

At some distance from the center the two types of bands will resemble each other, the frequency interval between two neighboring Q branches being about $\Delta\nu = 2(C-B)$ where B is taken to mean

$$B = (h/8\pi^2 c)\tfrac{1}{2}(1/I_{xx}+1/I_{zz}) \text{ and } C = (h/8\pi^2 c I_{yy}).$$

The spacing between lines in a band type B_2 will be about $2B$.

In order to analyze the bands in the spectrum it is convenient to make use of certain combination relations analagous to those which have been so helpful in the analysis of the spectra of symmetric molecules. As we have seen, there is reason to believe that the CH_2F_2 molecule is rather nearly a symmetric rotator. Witmer[8] and Wang[9] have demonstrated that it is possible in such cases to calculate the energy levels by a perturbation method. The unperturbed energy levels are given by the energies of a symmetric rotator where the quantity $(1/I_{xx})$ is replaced by $\tfrac{1}{2}[(1/I_{xx})+(1/I_{zz})]$, and the perturbation corrections are functions of the asymmetry of the molecule, i.e., $(1/I_{xx})-(1/I_{zz})$. From the resulting energy relations and observing the fact that for our purpose the selection rules may be taken to be those for a symmetric rotator (i.e., $\Delta J = \pm 1, 0$; $\Delta K = 0$ for parallel (type B_2) bands and $\Delta J = \pm 1, 0$; $\Delta K = \pm 1$ for perpendicular (type A_1 and B_1) bands, we may arrive at com-

bination relations which are applicable to our case.

In the case of the B_2 type bands (i.e., parallel) it will be seen that only the low frequency side of the band is resolved. It is, therefore, necessary to use a combination relation which involves only the $P(J)$ lines. Two useful relations are the following:

$$\nu_0 - P(J) = (B'+B'')+(B''-B')J, \qquad (1)$$

$$P(J)+P(J-1)-2J^2(B'-B'')$$
$$= 2\nu_0-(2J-1)B', \qquad (2)$$

where the B's have already been defined. The primes and double primes refer, respectively, to the excited and normal states of the molecule. If the correct value of ν_0 is used, the left side of (1) plotted against J yields a straight line, where $(B''-B')$ is the slope and $(B''+B')$ is the intercept. If too small a value for ν_0 is used, the curve deviates from a straight line for small values of J, and if too large a value for ν_0 is used, the curve deviates from a straight line in the opposite direction. When the correct value for ν_0 has been determined, the values of $(B''-B')$ may be read from the graph and inserted in (2). The value $2\nu_0$ will then be the intercept, and $2B'$ will be the slope of the resulting straight line if the left side of (2) is plotted against $(2J-1)$.

Combination relations which are useful in dealing with the bands of type A_1 and type B_1
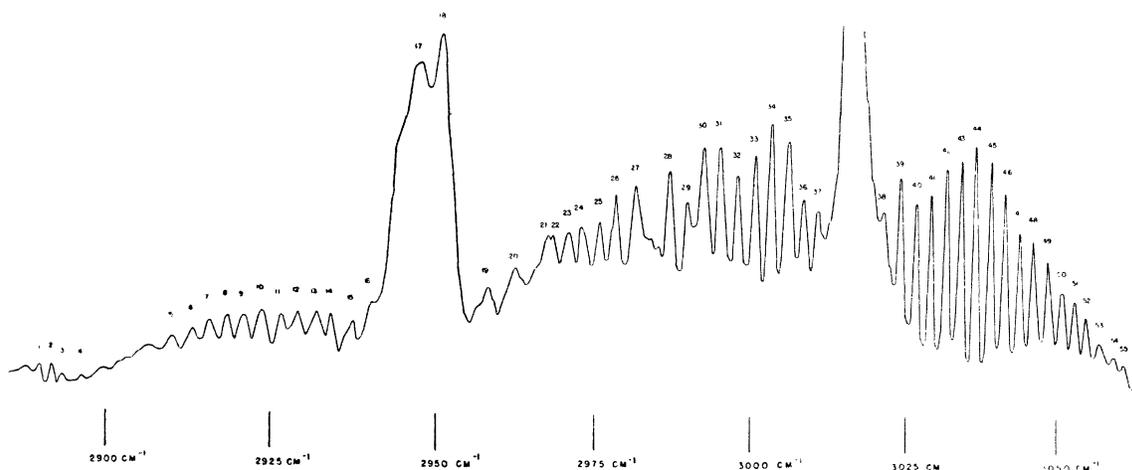
Fig. 2. Spectrum of CH_2F_2 in the 3.3-μ region.

[8] E. E. Witmer, Proc. Nat. Acad. Sci. 13, 60 (1927).
[9] S. C. Wang, Phys. Rev. 34, 243 (1929).

(i.e., the perpendicular bands) are

$$\tfrac{1}{2}(^{R}Q_{K}+{}^{P}Q_{K})=\nu_{0}+(C'-B')$$
$$+K^{2}[(C'-B')-(C''-B'')],\quad(3)$$

$$(^{R}Q_{K}-{}^{P}Q_{K})=4K(C'-B'),\quad(4)$$

$$(^{R}Q_{K-1}-{}^{P}Q_{K+1})=4K(C''-B'').\quad(5)$$

When the left side of (3) is plotted against K^{2}, the intercept will be $\nu_{0}+(C'-B')$. By plotting relations (4) and (5) against $4K$, the values $(C'-B')$ and $(C''-B'')$ may be determined, respectively. In this manner the band center ν_{0} is determined. Relations (3), (4), and (5) will, as we have seen, be valid only for K values corresponding to lines at some distance from the band center.

III. EXPERIMENTAL DETAILS

The difluoromethane used in this investigation was obtained from the Jackson Laboratory of the E. I. duPont de Nemours Company, Wilmington, Delaware. The sample had been fractionated within $0.5°C$ of the actual boiling point of CH_2F_2 which is at $-51.6°C$. The only impurities present in the gas were probably air and traces of CH_2FCl which boils at $-9°C$.

A description of the spectrograph used in this investigation can be found elsewhere.[10] The instrument is an automatic recording prism grating spectrometer which is mounted in a tank that can be evacuated, thereby making it possible to remove the water vapor and carbon dioxide from the optical path. Three gratings were used, namely, a replica grating made by R. W. Wood with 7500 lines per inch and having its blaze near 3μ, a replica grating made by Wood with 3600 lines per inch and having its blaze near 6μ, and a grating ruled at the University of Michigan with its blaze near 16μ. The spectrometer was calibrated by determining the grating constants for the first two of the above gratings by measuring several infra-red lines of mercury in several orders. The grating constant of the third grating was obtained by measuring in several orders several lines in a band of the CH_2F_2 spectrum, used as substandards, which had been previously measured with the replica grating with 3600 lines per inch.

The absorption cell was a cylindrical glass tube, 2 inches in diameter and $5\tfrac{1}{2}$ inches long, with a tube extending from the cell wall to the exterior of the spectrometer tank. This permitted chang-
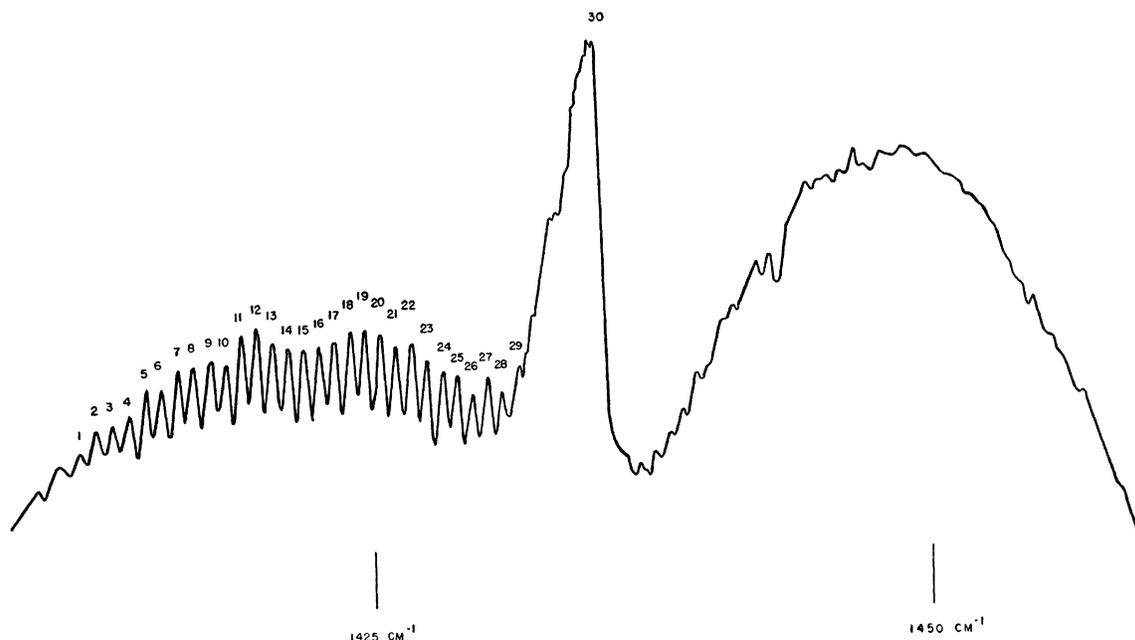
Fig. 3. Spectrum of CH_2F_2 in the $7.0\text{-}\mu$ region.

[10] E. E. Bell, R. H. Noble, and H. H. Nielsen, Rev. Sci. Inst. **18**, 48 (1947).

ing the gas pressure in the cell without opening up the spectrometer. The cell was closed at the ends by windows of potassium bromide to permit measurements to be made to 20μ.

It was found practicable to operate the spectrograph throughout the spectrum with slits subtending an angle equivalent to as little as 0.25 cm^{-1}.

IV. EXPERIMENTAL RESULTS

The spectrum has been scanned with the self-recording spectrometer from near 2.5μ to 20μ, and the four principal regions of absorption recorded. These regions were found to lie near the positions 3.3μ, 7.0μ, 9.0μ, and 19.0μ in the spectrum, respectively.

The 3.3-μ Region

Figure 2 is a reproduction of the recorded spectrum in the 3.3-μ region. The figure is simply a tracing of the record obtained automatically and is therefore not quite a linear representation of the frequency scale. This region appears to consist of three rather badly overlapping vibration bands of which the main lines are given in Table I.

The 7.0-μ Region

The spectrum obtained in the 7.0-μ region is shown in Fig. 3. The band structure and line spacing leaves no doubt that this is a parallel band. The line spacing in the P branch is practically the limit of the resolving power of the instrument, and as may be seen, the R branch is not resolved. As before, the frequency scale is not quite linear. The frequency positions of the main lines in this band are given in Table II.

The 9.0-μ Region

This region is shown in Figs. 4 and 5 which were recorded under different gas pressure conditions. The two records overlap slightly. The CH_2F_2 gas absorbs very strongly in this region from 1060 cm^{-1} to 1115 cm^{-1} (Fig. 4). With a gas pressure of 0.1 cm of Hg an absorption of over 50 percent was observed. The pressure maintained to obtain the record shown in Fig. 5 was about 1.0-cm Hg. The 9.0-μ region appears to consist of three bands, one near 1090 cm^{-1}, a

TABLE I. Frequencies and identifications of CH_2F_2 absorption lines in the 3.3-μ region.

Line number	Identification	Frequency
1		2889.8
2		2891.5
3		2892.9
4		2895.9
5		2909.8
6		2912.6
7		2915.1
8		2918.0
9		2920.5
10		2923.4
11		2926.2
12		2928.8
13		2931.7
14		2934.0
15		2937.3
16		2940.3
17		2947.1
18		2951.4
19		2957.8
20		2962.3
21		2967.4
22		2968.2
23	$^rQ(17)$	2970.7
24	$^rQ(16)$	2972.8
25	$^rQ(15)$	2975.9
26	$^rQ(14)$	2978.2
27	$^rQ(13)$	2981.3
28	$^PQ(11)$	2986.8
29	$^PQ(10)$	2989.6
30	$^PQ(9)$	2992.3
31	$^PQ(8)$	2994.8
32	$^PQ(7)$	2997.6
33	$^PQ(6)$	3000.4
34	$^PQ(5)$	3003.0
35	$^PQ(4)$	3005.7
36	$^PQ(3)$	3008.1
37	$^PQ(2)$	3010.3
38	$^RQ(2)$	3020.9
39	$^RQ(3)$	3023.8
40	$^RQ(4)$	3026.6
41	$^RQ(5)$	3028.9
42	$^RQ(6)$	3031.5
43	$^RQ(7)$	3034.0
44	$^RQ(8)$	3036.3
45	$^RQ(9)$	3038.8
46	$^RQ(10)$	3041.3
47	$^RQ(11)$	3043.6
48	$^RQ(12)$	3045.9
49	$^RQ(13)$	3048.4
50	$^RQ(14)$	3051.0
51	$^RQ(15)$	3052.9
52	$^RQ(16)$	3054.8
53	$^RQ(17)$	3056.5
54	$^RQ(18)$	3059.6
55	$^RQ(19)$	3061.4
56	$^RQ(20)$	3063.7

second near 1115 cm^{-1}, and a third near 1175 cm^{-1}. The frequency positions of the principal lines in this region are given in Table III.

The 19.0-μ Region

This region consists of a single band which shows the structure characteristic of a band of

TABLE II. Frequencies and identifications of CH_2F_2 absorption lines in the 7.0-μ region.

Line number	Identification	Frequency
1	$P(33)$	1411.2
2	$P(32)$	1412.0
3	$P(31)$	1412.8
4	$P(30)$	1413.5
5	$P(29)$	1414.2
6	$P(28)$	1415.0
7	$P(27)$	1415.8
8	$P(26)$	1416.5
9	$P(25)$	1417.3
10	$P(24)$	1418.0
11	$P(23)$	1418.8
12	$P(22)$	1419.5
13	$P(21)$	1420.3
14	$P(20)$	1421.0
15	$P(19)$	1421.7
16	$P(18)$	1422.4
17	$P(17)$	1423.1
18	$P(16)$	1423.8
19	$P(15)$	1424.5
20	$P(14)$	1425.3
21	$P(13)$	1426.0
22	$P(12)$	1426.6
23	$P(11)$	1427.4
24	$P(10)$	1428.1
25	$P(9)$	1428.8
26	$P(8)$	1429.5
27	$P(7)$	1430.1
28	$P(6)$	1430.9
29	$P(5)$	1431.7
30	(Q)	1435.4

the type A_1. The energy is small in this region, and the record shows the principal lines (Q branches) plotted on a percentage absorption basis. The center is near 530 cm^{-1}. The frequency positions of the lines are given in Table IV.

V. DISCUSSION OF THE RESULTS

Only three of the four A_1 type fundamental bands which can occur have been observed, the two B_1 type fundamental bands and the two B_2 type fundamental bands have all been observed. The observed bands will be discussed in the following sections according to symmetry types.

Bands of Symmetry Type A_1

In general, the bands belonging to the symmetry type A_1 appear to be of low intensity. Of the four fundamental bands belonging to this type it was possible to determine the center of only one with great assurance.

The band ω_1 is predicted to fall near 2930 cm^{-1}. It is observed not only to be of low intensity, but to be badly overlapped by two bands of the symmetry type B_1. For this reason

it is impossible to apply the combination relations to it to determine its center or the values of the rotational constants. The Raman value of 2963 cm^{-1} does, however, not seem inconsistent with the measurements reported here. A value which we might have chosen as the value of ω_1 is 2950 cm^{-1}. The correct value may, perhaps, best be obtained from Raman measurements on CH_2F_2 in the gas phase.

A band of the type A_1 is found in the region near 1120 cm^{-1}. It lies between two other intense bands, one on the low frequency side of type B_2 and one on the high frequency side of type B_1. The band of type B_2 has its center near 1090 cm^{-1} and is a region of intense absorption which obscures much of the type A_1 band. This band appears too intense to be regarded as an overtone ($2\omega_4$, for example) or a difference band, and since it lies in the region predicted for ω_2 and is of the right type, we have assigned it as the fundamental ω_2. Here again it is impossible to apply the combination relations to any advantage, but the center has been estimated to be 1116 cm^{-1}. The spacing between ^RQ branches appears to diverge rather rapidly from a value of about 2.5 cm^{-1} near the band center to 3.6 cm^{-1} at the edge of the band. For this effect we have no immediate explanations.

No absorption band was found in the region predicted for ω_3, i.e., near 1400 cm^{-1}, although the region was explored in an attempt to locate it. It is proposed that either the Raman frequency 1262 cm^{-1} or the Raman frequency 1508 cm^{-1} is the frequency ω_3. For reasons to be discussed at a later point we chose it to be the frequency 1262 cm^{-1}.

A band is found near 530 cm^{-1} which is the only band of the species A_1 which is entirely free from overlapping. It is the only one where the combination relations may be used with advantage, and the center determined with confidence. Applying the combination rule (3), the band center is found to be 528.5 cm^{-1}. Although the Q branches are not as sharp in this band as in others, a fairly accurate value of $C-B$ can be found. Using the combination relations (4) and (5) the following values are obtained

$$(C'-B') = 1.315 \pm 0.007 \text{ cm}^{-1}$$

and

$$(C''-B'') = 1.307 \pm 0.007 \text{ cm}^{-1},$$
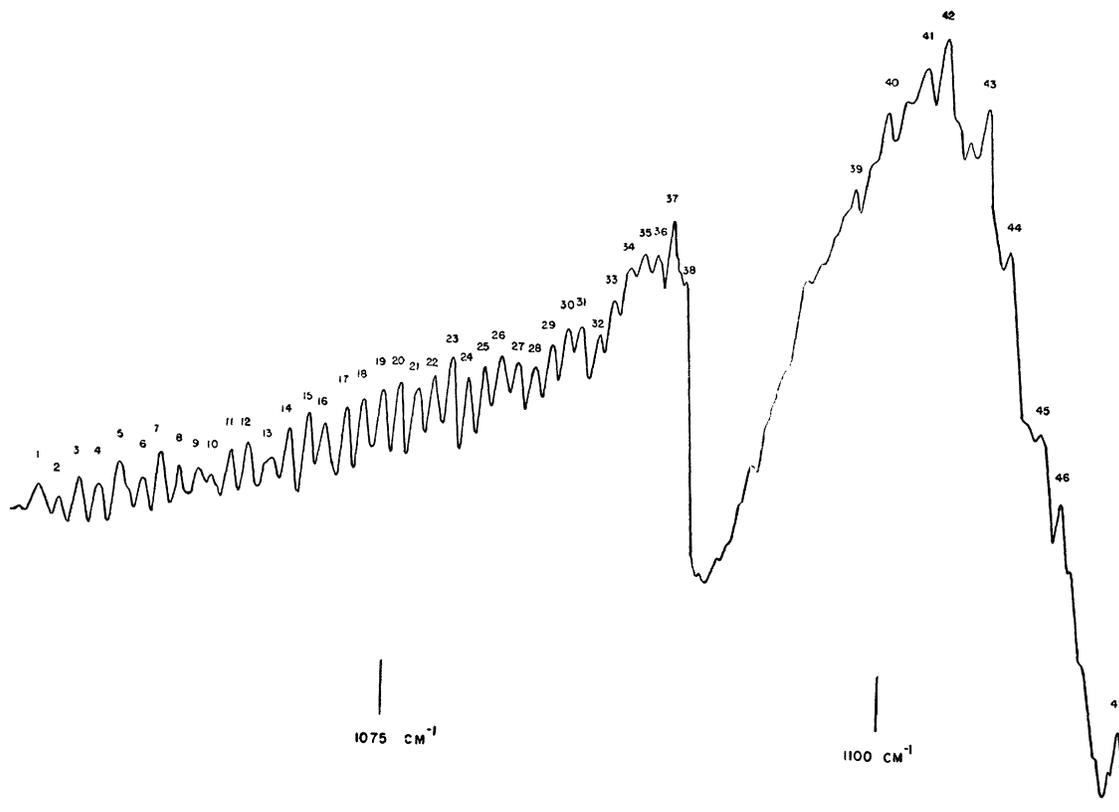
Fig. 4. Spectrum of CH_2F_2 in the 9.0-μ region.
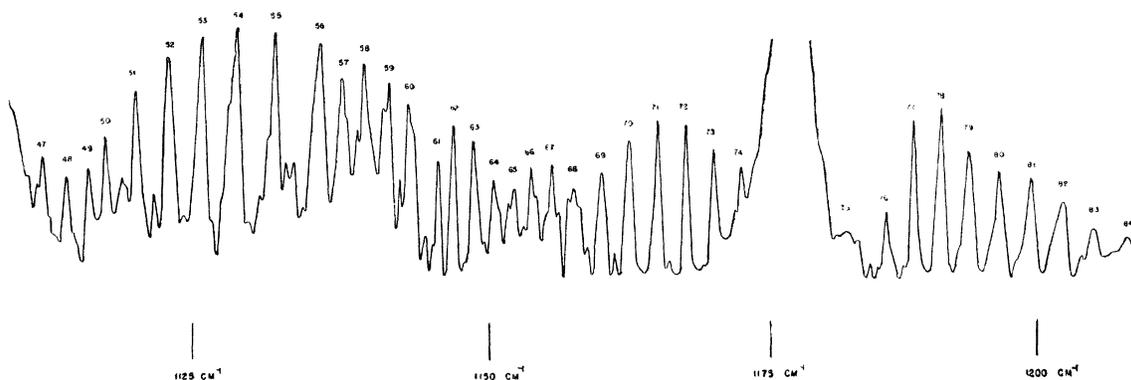
Fig. 5. Spectrum of CH_2F_2 in the 9.0-μ region.

Bands of Symmetry Type B_1

As was suggested earlier there are only two fundamental bands of the type B_1. Both of these have been observed experimentally and in addition a third band of this type has been observed.

The frequency ω_6 has been predicted to fall near 2994 cm^{-1}. It is observed actually to be near 3015 cm^{-1}. The central region of this band is quite free from overlapping by other bands so that use of the combination relations may here be made with profit. When the combination relation (3) is applied, the band center is found to be 3015.2 cm^{-1}. The individual ^PQ and ^RQ

TABLE III. Frequencies and identifications of CH_2F_2 absorption lines in the 9.0-μ region.

Line number	Identification	Frequency
1	$P(37)$	1058.6
2	$P(36)$	1059.5
3	$P(35)$	1060.4
4	$P(34)$	1061.4
5	$P(33)$	1062.3
6	$P(32)$	1063.4
7	$P(31)$	1064.3
8	$P(30)$	1065.2
9	$P(29)$	1066.1
10	$P(28)$	1066.7
11	$P(27)$	1067.6
12	$P(26)$	1068.3
13	$P(25)$	1069.5
14	$P(24)$	1070.3
15	$P(23)$	1071.2
16	$P(22)$	1072.0
17	$P(21)$	1073.0
18	$P(20)$	1073.9
19	$P(19)$	1074.8
20	$P(18)$	1075.6
21	$P(17)$	1076.5
22	$P(16)$	1077.3
23	$P(15)$	1078.2
24	$P(14)$	1079.0
25	$P(13)$	1079.8
26	$P(12)$	1080.6
27	$P(11)$	1081.4
28	$P(10)$	1082.3
29	$P(9)$	1083.0
30	$P(8)$	1083.8
31	$P(7)$	1084.4
32	$P(6)$	1085.3
33	$P(5)$	1086.0
34	$P(4)$	1086.8
35	$P(3)$	1087.5
36	$P(2)$	1088.2
37	$P(1)$	1089.0
38		1089.7
39		1098.2
40		1099.7
41		1101.8
42		1102.8
43		1105.8
44		1106.3
45		1108.3
46		1109.5
47		1113.2
48		1115.1
49		1116.8
50		1118.1
51		1120.5
52		1123.3
53		1126.1
54		1129.0
55		1132.1
56		1135.8
57		1137.5
58		1139.4
59		1141.5
60		1143.1
61		1145.6
62		1147.0
63		1148.6
64	$^PQ(12)$	1150.4
65	$^PQ(11)$	1152.2
66	$^PQ(10)$	1153.6
67	$^PQ(9)$	1155.3
68	$^PQ(8)$	1157.2

TABLE III.—*Continued.*

Line number	Identification	Frequency
69	$^PQ(7)$	1159.9
70	$^PQ(6)$	1162.2
71	$^PQ(5)$	1164.7
72	$^PQ(4)$	1167.2
73	$^PQ(3)$	1169.8
74	$^PQ(2)$	1172.4
75	$^RQ(2)$	1182.2
76	$^RQ(3)$	1185.7
77	$^RQ(4)$	1188.2
78	$^RQ(5)$	1190.9
79	$^RQ(6)$	1193.8
80	$^RQ(7)$	1196.7
81	$^RQ(8)$	1199.7
82	$^RQ(9)$	1202.8
83	$^RQ(10)$	1205.8
84	$^RQ(11)$	1208.9

lines in the band are strong and well-resolved, thereby making it possible to measure the value $C-B$ very accurately. Applying the combination relations (4) and (5) to the lines in Table I the following values are found : $C'-B' = 1.294 \pm 0.005$ cm^{-1} and $C''-B'' = 1.303 \pm 0.005$ cm^{-1}.

The frequency ω_7 is predicted to lie near 1034 cm^{-1}. A band of this type is found at 1176 cm^{-1} which seems too intense to be due to anything but a fundamental transition. We therefore take this band to be ω_7. Here again the combination rules may be used with advantage. With the aid of combination relation (3) the band center is located at 1176.1 cm^{-1}, and using combination relations (4) and (5), the following values are obtained for $C'-B'$ and $C''-B''$: $C'-B' = 1.315 \pm 0.007$ cm^{-1} and $C''-B'' = 1.299 \pm 0.007$ cm^{-1}, using lines of K less than 8. The lines of larger K values are overlapped by lines of the band which we have identified as ω_2 and cannot be identified with certainty. These lines have therefore not been used in this analysis.

A third band of the type B_1 is found near 2945 cm^{-1}. The lines in the band, except for the central region, are too weak to make satisfactory use of the combination relations. This band has been observed by Barker and Kao[4] who have attributed it to the combination frequency $\omega_5 + \omega_9$, where ω_5 is the torsional frequency of symmetry species A_2, and ω_9 is a frequency of symmetry species B_2. As Barker and Kao have pointed out, the combination frequency $\omega_5 + \omega_9$ would be of the symmetry type B_1. It will be seen that if the value ω_9, which is later identified to lie at 1435
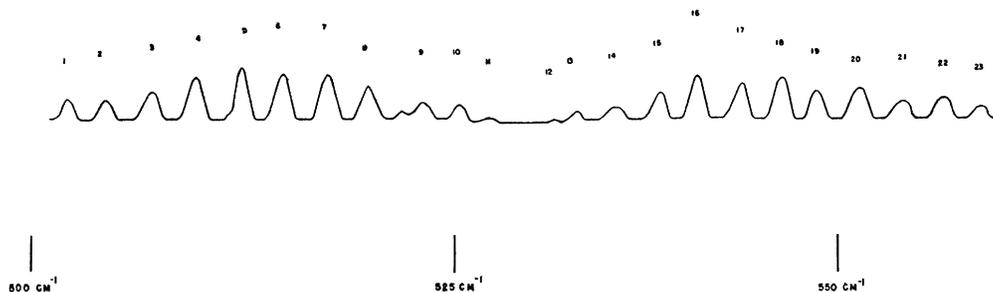
FIG. 6. Spectrum of CH_2F_2 in the 19.0-μ region.

cm^{-1}, is subtracted from 2945 cm^{-1}, the center of the band described here, a value $\omega_5 = 1510$ cm^{-1} is obtained. This is in good agreement with the Raman frequency observed at 1508 cm^{-1}. It is for this reason that ω_3 is identified with the Raman frequency at 1262 cm^{-1}. Barker and Kao[4] have explained the doubling of the central region as caused by the existence of the double minimum in the potential energy function associated with the torsional oscillation, ω_5.

Bands of Symmetry Type B_2

The two bands observed in the spectrum near 1090 cm^{-1} and 1435 cm^{-1} have a structure and line spacing which leaves no doubt that they are "parallel" bands and therefore must be identified as of the symmetry type B_2. Our earlier calculations indicated the fundamental frequencies of this symmetry species might be expected near 1090 cm^{-1} and 1600 cm^{-1}. We, therefore, identify these as ω_8 and ω_9, respectively.

It will be seen that in both of these bands only the P branches have been resolved. For this reason we are compelled to use the combination relations (1) and (2) which involve only the lines in the P branches. Applying the combination principle (1) to both bands, the band centers are determined to be $\omega_8 = 1089.7$ cm^{-1} and $\omega_9 = 1435.4$ cm^{-1}. For the band ω_8 the values $B'' + B' = 0.712 \pm 0.010$ cm^{-1} and $B'' - B' = 0.0039$ cm^{-1} and for ω_9 the values $B'' + B' = 0.708 \pm 0.010$ cm^{-1} and $B'' - B' = 0.0005$ cm^{-1} are obtained. The B values will then be for ω_8, $B'' = 0.358 \pm 0.005$ cm^{-1}, $B' = 0.354 \pm 0.005$ cm^{-1}, and for ω_9, $B'' = B' = 0.354 \pm 0.005$ cm^{-1}.

It was indicated by our calculations in Section II that the frequency ω_2 should be lower than the frequency ω_8. This is equivalent to saying that

the symmetric stretching frequency of the CF_2 group should be lower than the antisymmetric stretching frequency of the CF_2 group. Indeed, it is reported that the analagous frequencies in the CCl_2 group of the CH_2Cl_2 molecule fall in this order. It is, moreover, true here that the symmetric stretching frequency for the CH_2 group is lower than the antisymmetrical stretching frequency of the CH_2 group. Nevertheless, the frequency ω_2 is here found to be 1116 cm^{-1} while ω_8 falls near 1090 cm^{-1}. This effect is explained by supposing a strong Fermi-type resonance to occur between ω_2 and $2\omega_4$, which is permitted by the symmetry properties of the molecule. Since the CF bond constant is known quite accurately, and since the computed frequency for the CF_2 antisymmetric stretching frequency agreed so well with experiment, it

TABLE IV. Frequencies and identifications of CH_2F_2 absorption lines in the 19-μ region.

Line number	Identification	Frequency
1	$^P Q(11)$	502.0
2	$^P Q(10)$	504.3
3	$^P Q(9)$	506.9
4	$^P Q(8)$	509.4
5	$^P Q(7)$	512.1
6	$^P Q(6)$	514.6
7	$^P Q(5)$	517.2
8	$^P Q(4)$	519.6
9	$^P Q(3)$	522.9
10	$^P Q(2)$	525.4
11	$^P Q(1)$	527.5
12	$^R Q(0)$	530.9
13	$^R Q(1)$	532.5
14	$^R Q(2)$	535.1
15	$^R Q(3)$	538.1
16	$^R Q(4)$	540.5
17	$^R Q(5)$	543.3
18	$^R Q(6)$	546.2
19	$^R Q(7)$	548.4
20	$^R Q(8)$	551.6
21	$^R Q(9)$	554.6
22	$^R Q(10)$	557.5
23	$^R Q(11)$	560.3

TABLE V. The identification of observed bands in the spectrum of CH_2F_2.

Observed frequency position in cm⁻¹	Calculated frequency position in cm⁻¹	Symmetry species	Identification
2949	2930	A_1	ω_1
1116	1064	A_1	ω_2
	1406	A_1	ω_3
528.5	575	A_1	ω_4
1510.6*	1335	A_2	ω_5
3015.2	2994	B_1	ω_6
2945		B_1	$\omega_5+\omega_9$
1176.1	1034	B_1	ω_7
1089.7	1090	B_2	ω_8
1435.4	1607	B_2	ω_9

* Arrived at from the combination band $\omega_5+\omega_9=2945$ cm⁻¹.

seems reasonable to expect the computed frequency $\omega_2 = 1064$ cm⁻¹ to be fairly accurate. The overtone, $2\omega_4$, should be very close to $2\omega_4 = 1057$ cm⁻¹. A Fermi resonance would cause ω_2 to appear at a higher frequency in the spectrum and $2\omega_4$ at a lower frequency. The region below 1057 cm⁻¹ was investigated to try to locate the band $2\omega_4$, but it was not found probably because ω_8 was too intense to allow a good inspection.

CONCLUSION

As a conclusion we shall summarize briefly the results we have obtained. In all, eight bands have been observed. Of these seven are believed to be fundamental bands, three of which are of symmetry type A_1, two are of symmetry type B_1 and two of species B_2. The eighth band observed is believed to be a combination band. Our identifications of the observed bands are stated in Table V.

It has been practicable to evaluate the rotational constant B for the upper and lower states for the frequencies ω_8 and ω_9 and the rotational constant $(B-C)$ for the upper and lower states for the frequencies ω_4, ω_6, and ω_7. Their values are stated in Table VI.

These values are, of course, not the equilibrium values of B and $C-B$. In fact, enough data are not available to evaluate the equilibrium values. The values of these constants must, however, be

TABLE VI. Rotational constants of the CH_2F_2 molecule.

Frequency	B'' cm⁻¹	B' cm⁻¹	$\dfrac{(C''-B'')}{cm⁻¹}$	$\dfrac{(C'-B')}{cm⁻¹}$
ω_4			1.307±0.007	1.315±0.007
ω_6			1.303±0.005	1.294±0.005
ω_7			1.299±0.007	1.315±0.007
ω_8	0.358±0.005	0.354±0.005		
ω_9	0.354±0.005	0.354±0.005		

rather close to the equilibrium values since it will be seen that the values change only very slightly from one vibration state to another. Even if the values B'' and C'' be taken to represent the equilibrium values of B and C quite accurately, these two rotational constants are not sufficient to evaluate all of the dimensions of the molecule. Nevertheless, an estimate of these may be made by assuming that the $C-H$ distance is the same here as in other hydrocarbon molecules and that the $H-C-H$ angle remains here also a tetrahedral angle. If we take then $r_0(C-H) = 1.094\times10^{-8}$ cm and $\angle(H-C-H) = 110°$ we may determine the value of $r_0(C-F)$ and $\angle(F-C-F)$. The values obtained here are the following:

$$r_0(C-F) = 1.32\pm0.01\text{A}$$

and

$$\angle(F-C-F) = 107°0'\pm30'.$$

It will be seen that the dimensions obtained from the infra-red data for the $C-F$ distance and the $F-C-F$ angle are somewhat smaller than those obtained by Brockway from electron diffraction measurements. It is also interesting to note that the $C-F$ distance in CH_2F_2 is considerably smaller than the $C-F$ distance in CH_3F, the latter being 1.398×10^{-8} cm. We feel, nevertheless, that the accuracies for the quantities from which our values of $r_0(C-F)$ and $\angle(F-C-F)$ have been determined are conservatively estimated.