The Infra-Red Spectrum of Methyl Fluoride

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All of the important bands in the spectrum of methyl fluoride except the 8μ (1200 cm^{-1}) band, have been remeasured under considerably higher resolution than that available to Bennett and Meyer. In this work the parallel bands as well as the perpendicular bands have been resolved. The approximate average spacing between lines in the P and R branches of the parallel type bands was found to be about 1.7 cm^{-1}. New and more precise determinations of band centers and molecular constants have been achieved.

I. INTRODUCTION

THE spectrum of methyl fluoride was investigated by Bennett and Meyer[1] who were able to resolve the Q branches in the perpendicular type bands and to separate rather incompletely the lines in one of the parallel type bands. In the time that has elapsed since this investigation was made infra-red spectroscopy has been much improved. Moreover, the theory of the infra-red bands of polyatomic molecules has been carefully studied and suggests many new and interesting details to look for in the spectra of symmetric molecules. This has given impetus to the remeasurement of the bands in the infra-red spectrum of methyl fluoride, particularly since the measurements of Bennett and Meyer already gave evidence of anomalies in the rotational structure which could not be explained readily. In this investigation all the bands except the 8.0μ perpendicular type band observed by Bennett and Meyer have been re-examined and quite completely resolved. The improvement in the resolution is particularly noticeable in the parallel type bands.

II. EXPERIMENTAL WORK

The methyl fluoride gas was produced by heating dimethyl sulphate, $(CH_3)_2SO_4$, with potassium fluoride, KF, to about 160°C. The gas was purified by partial distillation and stored in glass flasks from which it could be drawn when desired.

The absorption cell was of a conventional type, made of 2″ glass tubing fitted at the ends with windows of polished rocksalt. The absorption cell was 10 cm long and had a stopcock for admitting the gas. For the more intense bands a gas pressure of about 5 cm Hg was sufficient, but for the less intense bands it was found necessary to fill the cell with gas to about 20 cm Hg.

The spectrometer is a prism-grating instrument used in previous measurements and is operated manually. In this investigation three gratings were employed; two replica gratings produced by R. W. Wood with 7200 lines per inch and 3600 lines per inch to scan the spectrum from 3 microns (μ) to 8μ, and a grating ruled by Wood with 800 lines per inch for the 9μ to 10μ region. In every case, it was possible to operate the spectrograph so that the slits subtended a wave-length interval of not more than 0.3 cm^{-1}. Observations were made on the spectrum at intervals on the spectrometer circle of 5 seconds of arc or about every 0.15 cm^{-1}. The grating was calibrated using a strong infra-red line in the emission spectrum of mercury near 1.0μ.

III. EXPERIMENTAL RESULTS

There are four principal regions of absorption in the spectrum of methyl fluoride. These regions lie, respectively, near 3.5μ, 7.0μ, 8μ, and 9.6μ and embrace the six fundamental bands in the spectrum and two weaker bands of the parallel type. In the following sections will be given a description of the characteristics of these absorption regions together with the frequency positions of the most important lines.

A. The 3.5μ Region

Figure 1 shows the data recorded on the less intense portion of the absorption region near 3.5μ.

[1] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).
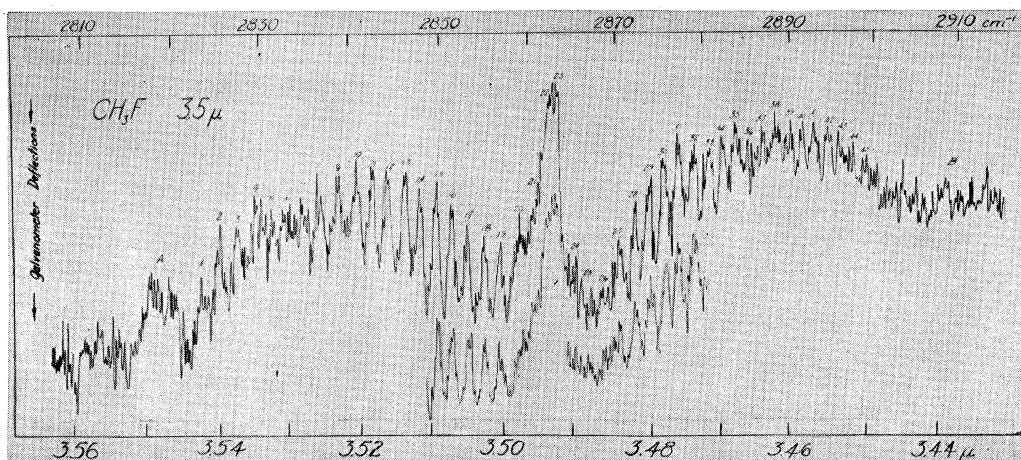
FIG. 1. The 3.5μ absorption region of CH₃F.

The curve given is a composite curve of several sets of data and is representative of the details which repeat from run to run. A scale of frequencies and wave-lengths has been substituted for the actual circle settings. The band is evidently of the parallel type. The high frequency end overlaps to a degree with the more intense bands which lie in this general neighborhood. This accounts for the fact that it is very complex in appearance and does not fall off in intensity in the usual manner. The low frequency end of the band is also complex. This is caused by the overlapping of this band with another weaker band of the parallel type, the Q branch of which lies at 2818 cm^{-1}.[2] The frequency positions of the most significant lines corrected to vacuum are given in Table I.

Figure 2 depicts the more intense portion of this absorption region. Measurements were here made with less gas in the cell than in the former case, and the curve is again a composite of all the data taken. In this region there is some absorption caused by water vapor and to eliminate this effect it was necessary to take readings at each setting of the circle, with the cell in the light beam and the cell out of the beam. Compensation for the diminution of the energy due to the windows has been made. The region is evidently made up of a band of the parallel type

at the low frequency end, and a band of the perpendicular type at the high frequency end. The frequency positions, corrected to vacuum, of the most important lines are given in Table II.
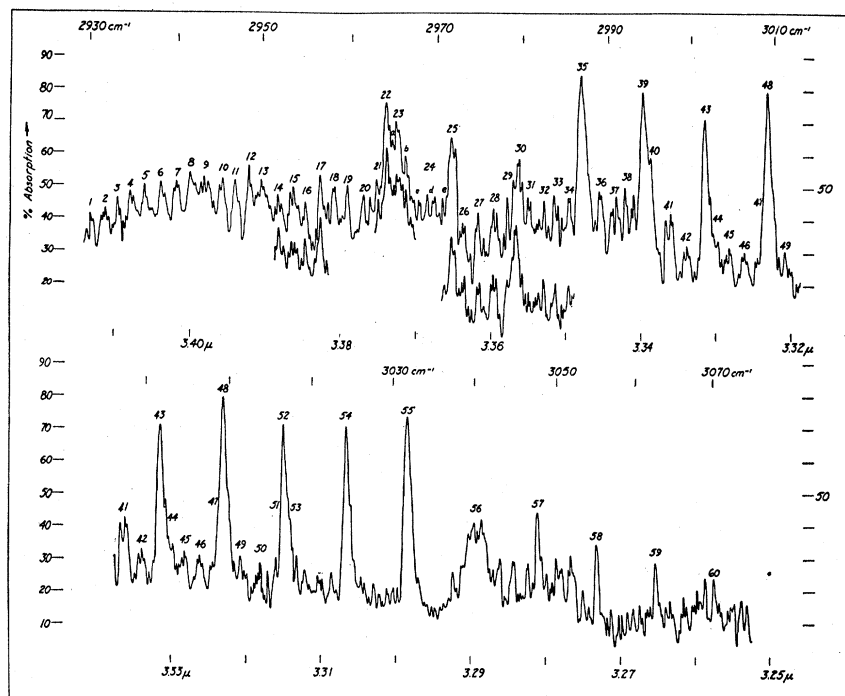
B. The 7.0μ Region

There are strong atmospheric water vapor lines throughout this region. For this reason the spectrometer was sealed and carefully dried with

TABLE I. Frequency positions and identification of lines in the 3.5μ parallel band.

Line No.	Identification	Frequency	Line No.	Identification	Frequency
1	$P(22)$	2821.5	25	$R(1)$	2864.7
2	$P(21)$	2823.5	26	$R(2)$	2866.8
3	$P(20)$	2825.5	27	$R(3)$	2868.7
4	$P(19)$	2827.3	28	$R(4)$	2870.5
5	$P(18)$	2829.2	29	$R(5)$	2872.3
6	$P(17)$	2830.8	30	$R(6)$	2874.0
7	$P(16)$	2832.8	31	$R(7)$	2875.7
8	$P(15)$	2834.8	32	$R(8)$	2877.3
9	$P(14)$	2836.9	33	$R(9)$	2879.1
10	$P(13)$	2838.9	34	$R(10)$	2880.7
11	$P(12)$	2840.7	35	$R(11)$	2882.3
12	$P(11)$	2842.5	36	$R(12)$	2883.9
13	$P(10)$	2844.4	37	$R(13)$	2885.5
14	$P(9)$	2846.1	38	$R(14)$	2887.1
15	$P(8)$	2848.0	39	$R(15)$	2888.6
16	$P(7)$	2849.7	40	$R(16)$	2890.2
17	$P(6)$	2851.5	41	$R(17)$	2891.6
18	$P(5)$	2853.4	42	$R(18)$	2893.1
19	$P(4)$	2855.3	43	$R(19)$	2894.6
20	$P(3)$	2857.2	44	$R(20)$	2895.9
21	$P(2)$	2859.1	45	$R(21)$	2897.3
22	$P(1)$	2860.9	46	$R(22)$	2898.7
23	Q	2861.9	47	$R(23)$	2900.1
24	$R(0)$	2863.0	48	$R(24)$	2901.7
			49	$R(25)$	2903.3

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[2] This band has just been observed by Robert Noble in scanning the 3.5μ region with the Ohio State University self-recording grating spectrometer.

FIG. 2. The 3.35μ and 3.37μ bands of CH$_3$F.

P$_2$O$_5$. In spite of this, some falsification of the absorption pattern due to methyl fluoride is

TABLE II. Frequency positions and identifications of lines in the 3.4μ bands.

Line No.	Identification	Frequency	Line No.	Identification	Frequency
1	P(22)	2929.8	26		2972.8
2	P(21)	2931.6	27		2974.5
3	P(20)	2933.1	28		2976.5
4	P(19)	2934.7	29		2978.4
5	P(18)	2936.3	30	$^{P}Q(4)$	2979.3
6	P(17)	2938.0	31		2980.3
7	P(16)	2939.7	32		2982.0
8	P(15)	2941.6	33		2983.7
9	P(14)	2943.2	34		2985.5
10	P(13)	2945.0	35-a	$^{P}Q(3)$	2986.7
11	P(12)	2946.5	35-b		2987.2
12	P(11)	2948.2	36		2989.0
13	P(10)	2949.6	37		2990.8
14	P(9)	2951.3	38		2992.5
15	P(8)	2953.0	39-a	$^{P}Q(2)$	2994.0
16	P(7)	2954.5	39-b		2994.3
17	P(6)$^{P}Q(7)$	2956.1	40		2995.8
18	P(5)	2957.8	41		2997.5
19	P(4)	2959.3	42		2999.4
20	P(3)	2961.1	43	$^{P}Q(1)$	3001.6
21	P(2)	2962.7	48	$^{R}Q(0)$	3009.1
22	$^{P}Q(6)$	2963.9	52	$^{R}Q(1)$	3016.5
a	P(1)	2964.4	54	$^{R}Q(2)$	3024.1
b	Q	2965.2	55	$^{R}Q(3)$	3031.6
c		2967.7	56	$^{R}Q(4)$	3039.4
d		2969.3	57	$^{R}Q(5)$	3044.6
e		2971.0	58	$^{R}Q(6)$	3055.0
25	$^{P}Q(5)$	2971.5	59	$^{R}Q(7)$	3062.4
			60	$^{R}Q(8)$	3069.8

apparent in Fig. 3 where a composite picture of the data is given. The reason for the falsification is discussed in a footnote by Cameron, Sears. and Nielsen[3] and need not be repeated here, This region consists of two almost coincident bands, one of the parallel type and another of the perpendicular type and in Table III the frequencies of many of the most intense maxima are given.

C. The 8.0μ Region

This band was quite well resolved in the earlier work of Bennett and Meyer and it was not deemed necessary to remeasure this band in the present investigation.

D. The 9.5μ Region

The 9.5μ band is a parallel type band and was partially resolved by Bennett and Meyer.[1] Their data on this band gave indications that the structure of the band was not simple as indicated by the simple theory. On re-examination this effect is confirmed, although much greater detail than that observed by Bennett and Meyer was

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[3] D. C. Cameron, W. C. Sears, and H. H. Nielsen, J. Chem, Phys. 7, 994 (1939).
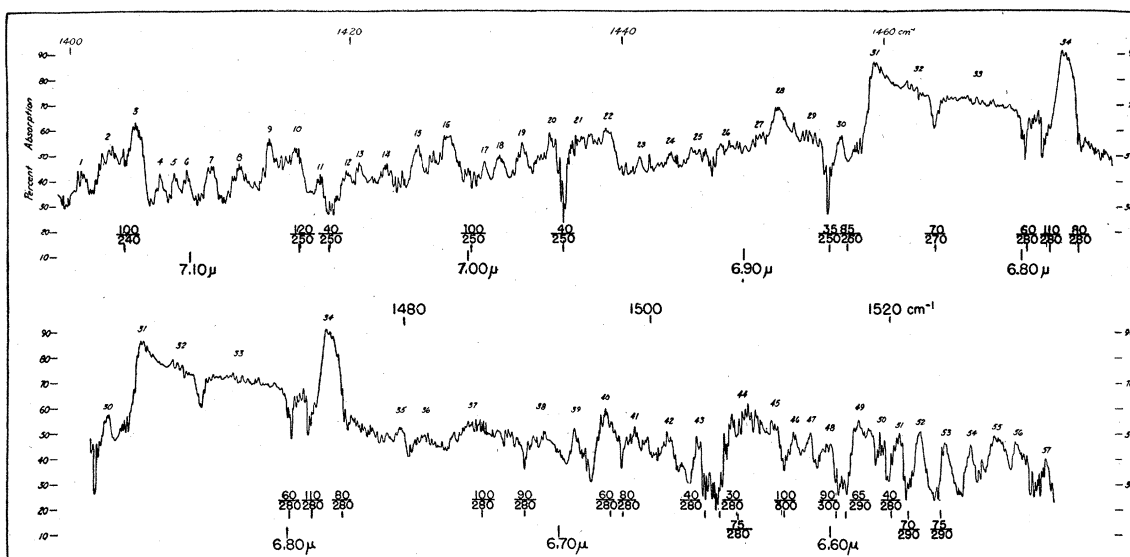
FIG. 3. The 7.0μ absorption region of CH_3F.

recorded. In Fig. 4 is shown a composite curve of the data taken in several runs across this band where circle settings have been replaced by a scale of frequencies. In Table IV are given the frequency positions of the lines in the band, where by a line is meant the most intense of a group of closely lying line components. Certain of the details in the structure lie just on the threshold of the practical resolving power of the instrument and are difficult to distinguish from the background. Much of the detail, however, can be repeated from time to time.

IV. DISCUSSION OF THE RESULTS

The lines in a vibration-rotation band arise from quantum transitions between two vibration-rotation levels. The energy of a vibration-rotation level for a symmetric polyatomic molecule is given to a good approximation by the relation:

$$(E/hc) = (E_v/hc) + J(J+1)B_v - K^2(B_v - C_v)$$
$$\mp 2\sum_t \zeta_t d_t K c_v - J^2(J+1)^2 D_J$$
$$- J(J+1)K^2 D_{JK} - K^4 D_K. \quad (1)$$

In Eq. (1), (E_v/hc) is the vibration energy; ζ_t is the Coriolis coupling factor which is different from zero only for the twofold degenerate frequencies and depends in an involved manner

upon the normal coordinates; and

$$B_v = B_e - \sum_s \alpha_s(v_s + g_s/2)$$

where

$$B_e = (h/8\pi^2 c I_{xx}{}^{(e)}); \quad C_v = C_e - \sum_s \gamma_s(v_s + g_s/2)$$

TABLE III. Frequency positions of the principal absorption lines at 6.8μ.

Line No.	Frequency	Line No.	Frequency
1	1402.3 cm⁻¹	30	1458.2 cm⁻¹
2	1404.4	31	1461.0
3	1406.2	32	1464.0
4	1407.9	33	1468.8
5	1408.9	34	1477.1
6	1409.8	35	1481.4
7	1411.5	36	1483.4
8	1413.5	37	1487.5
9	1415.7	38	1493.0
10	1417.6	39	1495.5
11	1419.4	40	1498.2
12	1421.3	41	1500.5
13	1422.3	42	1503.2
14	1424.2	43	1505.7
15	1426.4	44	1509.6
16	1428.7	45	1512.0
17	1431.5	46	1513.8
18	1432.5	47	1515.1
19	1434.2	48	1516.5
20	1436.3	49	1519.6
21	1438.5	50	1521.0
22	1440.5	51	1521.6
23	1443.1	52	1524.4
24	1445.4	53	1526.6
25	1447.0	54	1528.7
26	1449.6	55	1531.0
27	1452.1	56	1532.6
28	1453.4	57	1535.1
29	1456.0		
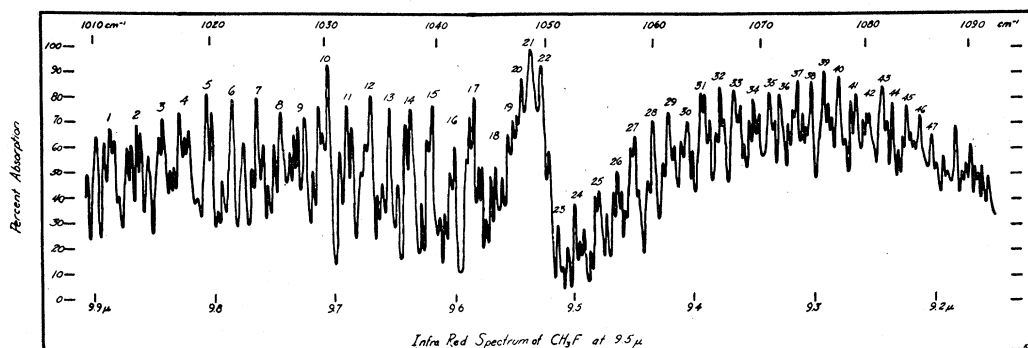
FIG. 4. Infra-red spectrum of CH_3F at 9.5μ.

and

$$c_v = C_e - \sum_t \Gamma_t(v_t + 1)$$

where[4]

$$C_e = (h/8\pi^2 c I_{zz}^{(e)});$$

D_J, D_{JK}, and D_K are centrifugal distortion constants. α_s, γ_s, and Γ_t in the above are correction terms to the reciprocals of inertia arising out of the non-rigidity of the rotator, and g_s is a constant which is equal to 1 or 2 depending upon whether the oscillation is non-degenerate or twofold degenerate. l_t is a quantum number which has values only for the twofold degenerate

TABLE IV. Frequency positions and identification of lines in the 9.5μ parallel band.

Line No.	Identification	Frequency	Line No.	Identification	Frequency
1	$P(20)$	1010.4	25	$R(2)$	1054.2
2	$P(19)$	1012.7	26	$R(3)$	1056.1
3	$P(18)$	1014.9	27	$R(4)$	1057.7
4	$P(17)$	1017.0	28	$R(5)$	1059.3
5	$P(16)$	1019.1	29	$R(6)$	1060.7
6	$P(15)$	1021.1	30	$R(7)$	1062.5
7	$P(14)$	1023.1	31	$R(8)$	1064.0
8	$P(13)$	1025.3	32	$R(9)$	1065.6
9	$P(12)$	1027.5	33	$R(10)$	1067.2
10	$P(11)$	1029.3	34	$R(11)$	1068.8
11	$P(10)$	1031.1	35	$R(12)$	1070.3
12	$P(9)$	1033.1	36	$R(13)$	1071.5
13	$P(8)$	1034.9	37	$R(14)$	1072.8
14	$P(7)$	1036.8	38	$R(15)$	1074.3
15	$P(6)$	1038.6	39	$R(16)$	1075.6
16	$P(5)$	1040.5	40	$R(17)$	1077.1
17	$P(4)$	1042.3	41	$R(18)$	1078.4
18	$P(3)$	1044.2	42	$R(19)$	1079.7
19	$P(2)$	1046.1	43	$R(20)$	1081.3
20			44	$R(21)$	1082.1
21	$P(1)$	1047.6	45	$R(22)$	1083.4
22	Q	1048.9	46	$R(23)$	1084.8
23	$R(0)$	1050.5	47	$R(24)$	1086.1
24	$R(1)$	1052.4			

[4] H. H. Nielsen, Phys. Rev. **70**, 184 (1946).

frequencies ω_t. For a quantum number v_t where ω_s is twofold degenerate, l_t may take the values v_t, $v_t - 2$, $\cdots 1$ or 0.

There occur two types of bands in the spectra of molecules like CH_3F, namely the parallel type and the perpendicular type. The first of these arises from an electric moment induced parallel to the axis of symmetry and occurs when the selection rules $\Delta J = \pm 1, 0$; $\Delta K = 0$ prevails. The second type arises from an electric moment induced normal to the axis of symmetry, and occurs when the selection rule $\Delta J = \pm 1, 0$; $\Delta K = \pm 1$ prevails. The perpendicular bands are twofold degenerate.

A. The Parallel Type Band

When the selection rules $\Delta J = \pm 1, 0$; $\Delta K = 0$; $\Delta l = 0$ are applied to two sets of energy states of the form (1) a series of overlapping bands, one component band for each value of K, is obtained.[5] The band center of these component bands is in each case the same. The $P(J)$ and $R(J-1)$ lines for a component band, the number in the parenthesis being the value of J in the normal state, will be found to be the following:

$$\left.\begin{array}{c} P(J) \\ R(J-1) \end{array}\right\} = \nu_0 \mp J(B' + B'') + J^2(B' - B'') + K^2[C' - C'' + B'' - B'], \quad (2)$$

B'', B' and C'', C' being, respectively, the B_v and C_v values in the normal and final states. In the case of the diatomic molecule where K takes some single value, say $K = 0$, it has been

[5] See for example G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 418.

fruitful to employ certain combination relations between the lines of Eq. (2) to arrive at the band centers and the rotational constants. For any component band of the parallel type for a polyatomic molecule the combination relations are, of course, still valid. For these we may write

$$R(J-1, K) - P(J+1, K) = 4(J+\tfrac{1}{2})B'', \quad (3a)$$

$$R(J, K) - P(J, K) = 4(J+\tfrac{1}{2})B', \quad (3b)$$

$$R(J-1, K) + P(J, K)$$
$$= 2[\nu_0 + J^2(B' - B'')]. \quad (3c)$$

The resolution is in general not sufficient to separate completely a parallel band into its component bands and hence the above relations cannot be applied directly. Some progress may be made, nevertheless, if one takes as the Jth line in the P and R branches the most intense of the Jth lines in the P and R branches of the K component bands. Neglecting symmetry considerations this will be associated with the value $K=0$. One may now again use the combination principles.

The entire parallel band at 9.6μ and at least the central portion of the parallel band at 3.5μ do not overlap with other bands. In these two instances it has been possible to identify the $P(J)$ and $R(J)$ lines on both sides of the center to a considerable distance. The parallel band at 3.4μ overlaps badly on the high frequency side, but it is possible to identify a considerable number of the $P(J)$ lines. The identifications of the lines are set down in the second columns of the tables.

When the combination principle (3a) is applied to the lines in Tables I and IV, i.e., when the differences $R(J-1) - P(J+1)$ are plotted against $4(J+\tfrac{1}{2})$ for the two bands, it is seen that the points in both cases lie along the same straight line. This indicates that the initial state from which the molecule makes its transition is in each case the same. Since the 9.6μ band is unquestionably a fundamental band B'' is the B_γ value for the normal state. The value of B'' as read from the graph shown in Fig. 5 is $B'' = 0.8688$ cm^{-1}.

If now the combination principle (3c) is applied and the sum $R(J-1) + P(J)$ is plotted against J^2

for each of the above two bands, the slope of the resulting straight lines will give twice the values of the differences $B' - B''$, and the intercept will be twice the value of the frequency of the band center, ν_0, B' being the Bv values in the excited states. The values of ν_0 obtained for the 9.6μ and the 3.5μ bands are 1049.5 cm^{-1} and 2862.9 cm^{-1}, respectively. The corresponding B' values are, respectively, 0.8606 cm^{-1} and 0.8635 cm^{-1}. The B' values derived in this manner may be verified by the application to the above data of the combination rule (3b).

In the 3.4μ band the $R(J)$ lines cannot be identified with any certainty although the $P(J)$ lines are quite clearly discernible. The combination rules (3), therefore, cannot be used. If, however, one takes the differences between the two P lines $P(J) - P(J-1)$ one obtains

$$P(J) - P(J-1)$$
$$= -(B' + B'') + (2J-1)(B' - B''). \quad (4)$$

When the differences $P(J) - P(J-1)$ for the above band are plotted against $2J$ as ordinates the slope of the resulting straight line gives the difference $(B' - B'')$ and the intercept will be $-(B' + B'')$. The value obtained for B'' in this manner agrees well with the value B'' obtained for the two other parallel bands referred to before. This indicates that this band is caused by a vibrational transition originating in the normal vibration state. The value of B' determined in this manner is found to be $B' = 0.872$ cm^{-1}.

To arrive at a value for the frequency of the band center the sum $P(J) + P(J-1)$ is taken. It gives

$$P(J) + P(J-1) - 2J^2(B' - B'')$$
$$= 2[\nu_0 - (2J-1)B']. \quad (5)$$

If the left-hand side of Eq. (5) is plotted against $2(2J-1)$ the slope will give an independent value for B', and $2\nu_0$ may be arrived at by reading the intercept from the graph. The value of ν_0 is found to be 2966.5 cm^{-1}.

The information derived from these three bands is summarized in Table V.

In the 7.0μ region there is found still another parallel type band. The Q branch of this band coincides almost exactly with the center of the perpendicular band which is found here. The
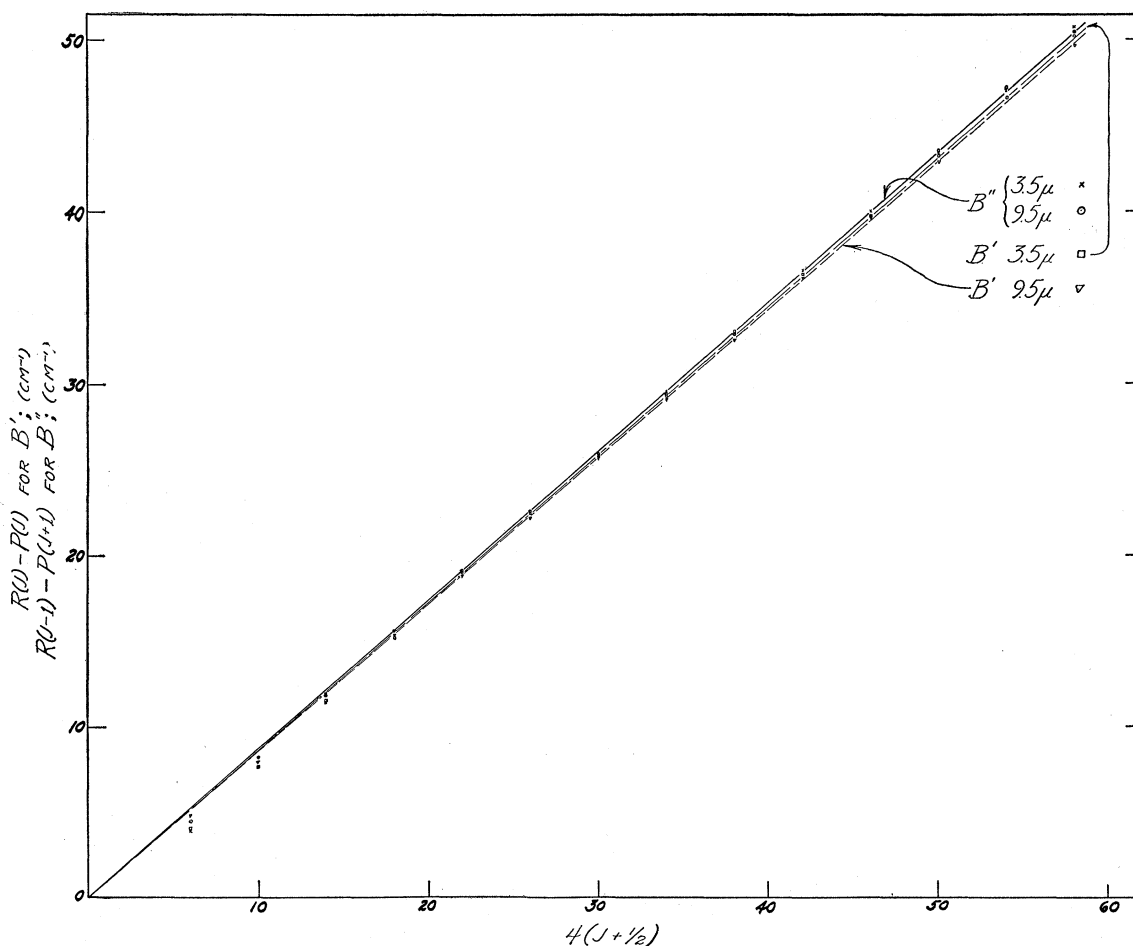
FIG. 5. Infra-red absorption of CH_3F. Determination of B'' and the B''s from the 3.5μ and 9.5μ bands.

discussion of the 7.0μ parallel band is deferred for Section V which concerns itself with this region quite in general.

B. The Perpendicular Bands

When the selection rules $\Delta J = \pm1, 0$; $\Delta K = \pm1$, $\Delta l = \pm1$ are applied to two sets of energy levels like those described in (1), one of which is the normal state, a series of overlapping component bands, each of which has the general appearance of a parallel type band, is obtained.[6] If it were possible to resolve such a band completely, a set of combination relations of the form (3) could be applied to the lines in each of the component bands. This is not

[6] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

possible, at least in the case of molecules like CH_3F. The prominent lines present in perpendicular bands like those observed here are Q lines. Those on the high frequency side are known as ^RQ branches and those on the low frequency side as ^PQ branches. With the aid of the selection rule $\Delta K = \Delta l = \pm1$ one obtains as the frequency positions of these

$$\left.\begin{array}{c} ^RQ_K \\ ^PQ_K \end{array}\right\} = \nu_0 + [C' - 2c'\zeta_t - B'] \\ \pm 2[C' - c'\zeta_t - B']K + [(C' - C'') \\ - (B' - B'')]K^2 + J(J+1)(B' - B''). \quad (6)$$

The effect of the last term in Eq. (6) is to cause the Q branches to spread out and it may be neglected at this point. If, as suggested by Herzberg,[5] the sum of $^RQ_K + {}^PQ_K$ is plotted

against K^2 a straight line results, the slope of which is $2[(C'-C'')-(B'-B'')]$ and which has the intercept $2[\nu_0+C'-2c'\zeta_t-B']$. Moreover, if the quantities $^RQ_K-[(C'-C'')-(B'-B'')]K^2$ and $^PQ_K-[(C'-C'')-(B'-B'')]K^2$ are plotted against K, straight lines are obtained, the slopes of which are $2[C'-c'\zeta_t-B']$. Figure 6 shows these graphs for the 3.36μ perpendicular band. Values of the constants obtained from the above are given in Table VI. In Table VI are also stated the constants arrived at when the above procedure is applied to the data of Bennett and Meyer for the 8μ perpendicular band.

It is possible to obtain an estimate of the value of $B'-B''$ from the breadth of the Q lines in a perpendicular band when it is well resolved. It was suggested earlier that the effect of the term $J(J+1)(B-B'')$ in Eq. (6) is to split the Q branches into component lines. These components cannot be resolved spectroscopically, but produce the effect of broadening the Q branches. By measuring the breadth of these lines, and observing that the components have begun to fall off rapidly in intensity by the time J has assumed the value $J=20$, a value for $B'-B''$ may be obtained by setting the average line equal to 20×21 $(B'-B'')$. This value, which must be regarded as not very accurate, takes the value $(B'-B'')=0.003$ cm^{-1} for the 3.33μ band. The algebraic sign to be attached to $(B'-B'')$ is determined by observing whether the Q branches taper off toward lower frequencies or toward higher frequencies. If the Q branches taper off toward lower frequencies $B'<B''$; if they taper off in the opposite direction $B'>B''$. It appears that $B'-B''$ is positive for the 3.33μ perpendicular band. No estimate of the value $B'-B''$ for the 8μ perpendicular band was attempted.

C. The 6.8μ Parallel-Perpendicular Band

Two bands, almost exactly coincident, occupy the 6.8μ region of the spectrum. Both bands are extremely intense and they have accordingly been identified by several authors as the parallel vibration ν_3, and the perpendicular vibration ν_4. It has been shown by Shaffer[7] that a Coriolis interaction exists between the two frequencies ν_3 and ν_4, the effect manifesting itself as a correction term to the moment of inertia effective for these frequencies. This correction term contains the resonance denominator $\omega_3-\omega_4$. In the case which here is considered $\omega_3\approx\omega_4$ so that the correction term becomes indefinitely large. When this condition prevails the usual methods of the perturbation theory fail, and it is necessary to compute the interaction in the manner discussed by Nielsen[8] where the frequencies ν_3 and ν_4 are regarded as degenerate. As may be seen from that discussion the computation of the energies is no simple matter. Certain generalities may, nevertheless, be stated. Because of the perturbation there results a mixing of the wave functions which characterize these states. For this reason, it is better to designate the two states by $(\nu_3:\nu_4)$ and $(\nu_4:\nu_3)$, respectively, where the frequency which occurs first within the parentheses is the frequency to which the state would degenerate if the resonance were removed.

Normally the selection rules for a perpendicular vibration are $\Delta J=\pm1, 0$ and $\Delta K=\pm1$, and for a parallel band they are $\Delta J=\pm1, 0$ and $\Delta K=0$. Because of the resonance both types of transitions may take place in each band, i.e., the band which normally would be perpendicular will have some parallel type transitions and *vice versa*. It may be seen in Fig. 3 that many of the Q lines of the band appear double; for example lines 2 and 3; 9 and 10, etc. It is suggested that the high frequency component in each case is caused by the transitions $\Delta K=\pm1$, $\Delta J=0$ in the band $(\nu_4:\nu_3)$, while the low frequency components are caused by the transition $\Delta K=\pm1$; $\Delta J=0$ in the

TABLE V. Rotational constants and frequencies obtained from parallel bands.

Band center in μ	Band center in cm^{-1}	Value of B''	Value of B'
3.4	2966.5 cm^{-1}	0.869	0.872
3.5	2862.9	0.8688	0.8635
9.6	1049.5	0.8688	0.8606

TABLE VI. Rotational constants and frequencies obtained from perpendicular bands.

Band center in μ	$[\nu_0+C' -2c'\zeta_t-B']$ cm^{-1}	$[C'-c'\zeta_t-B']$ cm^{-1}	$[(C'-C'') -(B'-B'')]$ cm^{-1}	$(B'-B'')$ cm^{-1}
3.36μ	3009.08	3.81	0.023	0.003
8.0μ	1200.03	2.85	0.011	—

[7] W. H. Shaffer, J. Chem. Phys. **10**, 1 (1942).
[8] H. H. Nielsen, Phys. Rev. **68**, 181 (1945).

FIG. 6. Infra-red absorption of CH$_3$F. Determination of $(C' - \zeta c - B')$ 3.35μ ($\perp$) band.
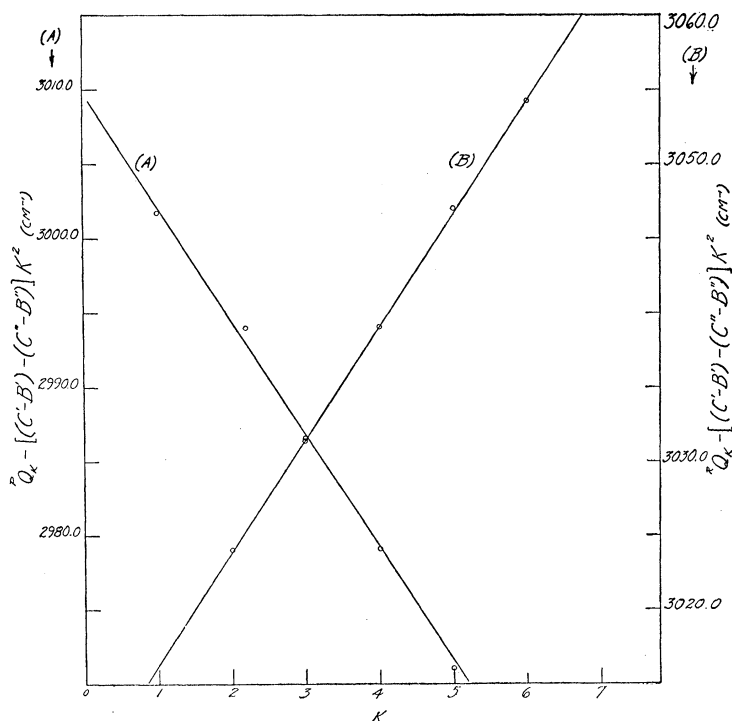
band ($\nu_3 : \nu_4$). The separations between the components will be seen to be roughly $\Delta\nu = 2.0$ cm^{-1}. It does not seem practicable to attempt to analyze the lines in this absorption region further than this owing to the extreme complexity of the pattern. An estimate may nevertheless be made of the band centers. We take the following as the values for ($\nu_3 : \nu_4$) and ($\nu_4 : \nu_3$), respectively, 1467.9 cm^{-1} and 1469.7 cm^{-1}. The separation between ($\nu_3 : \nu_4$) and ($\nu_4 : \nu_3$) is not inconsistent with the value $\Delta\nu = 2.0$ cm^{-1} between the components of the Q lines.

It appears, moreover, that the effect of the perturbations upon the energy levels, and consequently on the spectrum as well, decreases with increasing values of K. An estimate of the value $[C' - c'\zeta_t - B']$ may be made by noting the spacing between K lines near the extremity of the band. Our estimate for $[C' - c'\zeta_t - B']$ is 5.6 cm^{-1}. We restate these results in Table VII.

V. IDENTIFICATION OF THE OBSERVED BANDS

The information gained from the preceding paragraphs indicates that a review of the identification of the bands in the spectrum of CH$_3$F

might be desirable. We follow other authors and identify the bands at 9.6μ and 8μ (i.e., 1049.5 cm^{-1} and 1200 cm^{-1}) as ν_5 and ν_6, respectively. The two bands in the 7.0μ region we identify as ($\nu_3 : \nu_4$) and ($\nu_4 : \nu_3$) as has been suggested in the preceding section.

In the 3.5μ region there are found three bands of the parallel type with centers near 2818 cm^{-1}, 2862.9 cm^{-1}, and 2966.5 cm^{-1}. These we identify in the following manner ($\nu_1 : 2\nu_3 : 2\nu_4$) = 2862.9 cm^{-1}, $(2\nu_3 : 2\nu_4 : \nu_1)$ = 2966.5, and $(2\nu_4 : 2\nu_3 : \nu_1)$ = 2818 cm^{-1}, where ($\nu_1 : 2\nu_3 : 2\nu_4$) etc. indicates that the levels ν_1, $2\nu_3$, and $2\nu_4$ are three mutually resonating levels. The level ($\nu_1 : 2\nu_3 : 2\nu_4$) is the one which would degenerate to ν_1, the level $(2\nu_3 : 2\nu_4 : \nu_1)$ would reduce to $2\nu_3$, etc., if the perturbation between the levels were reduced to zero. The identification of the last three frequencies must be regarded as somewhat uncertain, but seems plausible and consistent with the conclusions arrived at by others.

The resonance which occurs here is of a rather complicated nature. The energy matrix for the CH$_3$F molecule contains elements along the principal diagonal which are of the form of the

TABLE VII. Vibration rotation constants estimated from the 7.0μ band.

Band	Band center	$[C'-C'\zeta_i-B']$
$(\nu_3:\nu_4)$	1467.9 cm^{-1}	5.6 cm^{-1}
$(\nu_4:\nu_3)$	1469.7 cm^{-1}	—

vibration-rotation energies of the XY$_3$Z type of molecule discussed by Shaffer.[9] All elements off the principal diagonal are of second or higher order of magnitude and may be neglected. When the frequencies $2\nu_3$ and $2\nu_4$ become very nearly equal to ν_1, as is the case here, a complication arises since the energies contain the denominators $(\omega_1-2\omega_3)$ and $(\omega_1-2\omega_4)$.[9] These terms originate with the cubic contributions to the potential energy $hck_{133}q_1q_3{}^2$ and $hck_{144}q_1q_4{}^2$. It has been pointed out by Fermi and Dennison[10] that it becomes necessary to regard the frequency ω_1 as degenerate with the frequencies $2\omega_3$ and $2\omega_4$. The result obtained has been discussed by Dennison[11] and more recently by Nielsen[8] who have shown that the diagonal terms are still the same as before except that the terms containing the denominators $2\omega_3-\omega_1$, etc., are absent. In addition, the terms $hck_{133}q_1q_3{}^2$, etc., now give rise to elements lying off the principal diagonal which are of first-order importance. These elements are the following:

$$(v_1-1, v_3+2, v_4, l_4\cdots|v_1, v_3, v_4, l_4\cdots)$$
$$=(v_1, v_3, v_4, l_4\cdots|v_1-1, v_3+2, v_4, l_4\cdots)$$
$$=(hck_{133}/2)[v_1/2]^{\frac{1}{2}}[(v_3+1)(v_3+2)]^{\frac{1}{2}},$$
$$(v_1-1, v_3, v_4+2, l_4\cdots|v_1, v_3, v_4, l_4\cdots)$$
$$=(v_1, v_3, v_4, l_4\cdots|v_1-1, v_3, v_4+2, l_4\cdots)$$
$$=(-hck_{144}/2)[v_1/2]^{\frac{1}{2}}[(v_4+2)^2-l_4{}^2]^{\frac{1}{2}}. \quad (7)$$

Moreover, when the frequencies $2\omega_3$ and $2\omega_4$ become very nearly equal to each other, as they do in the CH$_3$F molecule, a type of resonance described by Darling and Dennison[12] in connection with the water vapor spectrum may occur because of the terms $hck_{3344}q_3{}^2q_4{}^2$ in the quadratic part of the potential energy function and certain other terms in the cubic portion of the potential energy. In such cases it is necessary to treat $2\omega_3$

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[9] In this discussion ω_i is taken to be the value of the normal frequency and ν_i is the value of the band center.
[10] E. Fermi, Zeits. f. Physik. 71, 250 (1931).
[11] D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).
[12] B. T. Darling and D. M. Dennison, Phys. Rev. 57, 129 (1940).

and $2\omega_4$ as degenerate frequencies with the result that certain new elements which do not lie on the principal diagonal will arise. In this case these may be shown to be:

$$(v_3, v_4\cdots|v_3-2, v_4+2, \cdots)$$
$$=(v_3-2, v_4+2, \cdots|v_3, v_4\cdots)$$
$$=hc\{(k_{3344}/4)-(k_{344}{}^2/2\omega_4)$$
$$+(k_{333}k_{344}/4\omega_3)$$
$$-(k_{441}k_{133}/8\omega_1)[\omega_1/(2\omega_4+\omega_1)]$$
$$+(k_{445}k_{533}/4\omega_5)[\omega_5{}^2/(4\omega_4{}^2-\omega_5{}^2)]\}$$
$$\times\{[v_3(v_3-1)]^{\frac{1}{2}}[(v_4+2)^2-l_4{}^2]^{\frac{1}{2}}\}. \quad (8)$$

The matrix elements described above will be grouped together about the principal diagonal in a little box. This sub-matrix can then be diagonalized by itself. For the case where $(v_1=1, v_3=v_4=0)$, $(v_1=0, v_3=2, v_4=0)$ and $(v_1=0, v_3=0, v_4=2, l_4=0)$ the sub-matrix takes the form

	$v_1=1$ $v_3=v_4=0$	$v_1=v_4=0$ $v_3=2$	$v_1=v_3=0$ $v_4=2, l_4=0$	
$v_1=1$ $v_3=v_4=0$	$W-\epsilon$	$(hck_{133}/2)$	$(-hck_{144}/\sqrt{2})$	
$v_1=v_4=0$ $v_3=2$	$(hck_{133}/2)$	$W'-\epsilon$	$(hc\gamma/\sqrt{2})$	, (9)
$v_1=v_2=0$ $v_4=2, l_4=0$	$(-hck_{144}/\sqrt{2})$	$(hc\gamma/\sqrt{2})$	$W''-\epsilon$	

where W, W', and W'' are the diagonal elements of the matrix corresponding, respectively, to $(v_1=1, v_3=v_4=0)$, etc., and γ is the value of the term inside the first set of braces in Eq. (8). The energy values determined from (9) will be seen to be given by the roots of the cubic equation:

$$\epsilon^3-(W+W'+W'')\epsilon^2$$
$$+(WW'+W'W''+W''W$$
$$-(h^2c^2/2)(k_{144}+k_{133}/2)$$
$$-[WW'W''-h^3c^3k_{133}k_{144}\gamma-2h^2c^2\gamma^2]=0. \quad (10)$$

The effect of the latter perturbation, if the first kind were absent, would be to separate the levels $(2\nu_3:2\nu_4)$ and $(2\nu_4:2\nu_3)$ abnormally away from each other, while the level ν_1 would remain unaltered. The presence of the elements in the energy sub-matrix corresponding to the former type of interaction would further alter the positions of the levels, but it does nevertheless seem reasonable to assume that the bands at 2818 cm^{-1} and 2966.5 cm^{-1} are caused by transi-

TABLE VIII. Identification of the observed bands in the CH$_3$F spectrum.

Band center in cm^{-1}	Identification	Character
1049.5	ν_5	parallel
1200.0	ν_6	perpendicular
1467.9	$(\nu_3:\nu_4)$	parallel-perpendicular
1469.7	$(\nu_4:\nu_3)$	perpendicular-parallel
2818.0	$(2\nu_4:2\nu_3:\nu_1)$	parallel
2862.9	$(\nu_1:2\nu_3:2\nu_4)$	parallel
2966.5	$(2\nu_3:2\nu_4:\nu_1)$	parallel
3009.1	ν_2	perpendicular

tions to the levels $(2\nu_4:2\nu_3:\nu_1)$ and $(2\nu_3:2\nu_4:\nu_1)$, respectively, hence fixing the band at 2862.9 cm^{-1} as $(\nu_1:2\nu_4:2\nu_3)$. The band at 2818 cm^{-1} is assigned as $(2\nu_4:2\nu_3:\nu_1)$ because it has the lesser intensity of the two. A further argument for identifying the band at 2862.9 cm^{-1} as $(\nu_1:2\nu_3:2\nu_4)$ is the following. There exists a Coriolis interaction between the frequency ν_1 and ν_2 as has been shown by Shaffer.[7] The effect is to cause the Q branches in the higher frequency perpendicular band ν_2 to converge toward higher frequencies (i.e., the low frequency side is sharp), while the Q branch of the lower frequency band ν_1 will converge toward lower frequencies. The band 2862.9 cm^{-1} has this characteristic while the band at 2966.5 converges in the opposite sense. It should be pointed out that this last argument is not entirely rigorous since each of these three bands is a mixture of the frequencies ν_1, $2\nu_3$, and $2\nu_4$ but it seems reasonable to suppose the band $(\nu_1:2\nu_3:2\nu_4)$ to resemble ν_1 more than the other two, $(2\nu_3:2\nu_4:\nu_1)$ to resemble $2\nu_3$ most, etc. The identifications of the observed bands as we have proposed them are given in Table VIII.
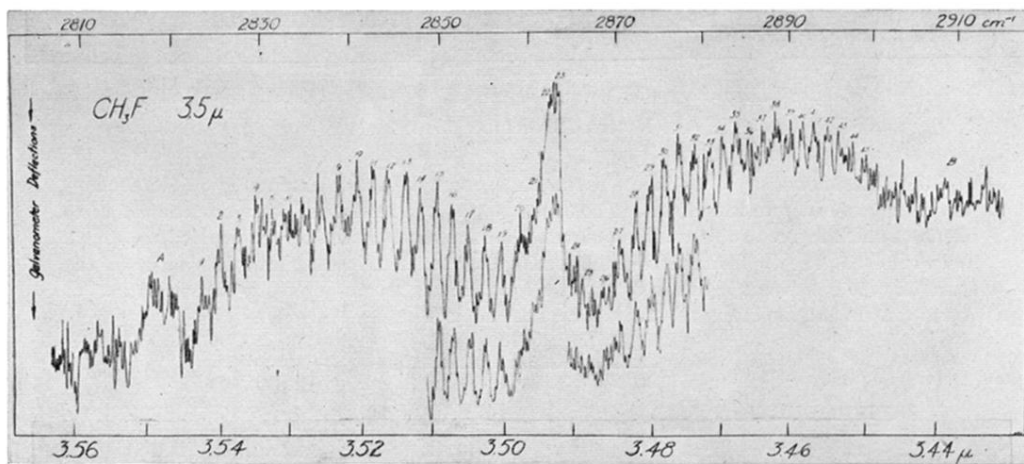
Fig. 1. The 3.5μ absorption region of CH₃F.