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The Infra-Red Spectrum of C_2H_6

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The infra-red spectrum of C_2H_6 gas has been studied in the region between 1.6 and 13μ with a spectrometer of high resolving power. From measurements on four resolved $\|$ bands the value $I_{B0}=(42.234\pm0.011)\times10^{-40}$ g cm^2 has been obtained for the large moment of inertia in the ground state. From measurements on the three fundamental $\perp$ bands the best value at present available for the small moment of inertia is $I_A=10.81\times10^{-40}$ g cm^2. Because of uncertainties concerning the perturbations of degenerate state ν_8, of which a semi-quantitative explanation which is apparently basically correct has been obtained, this value is provisional but appears to be fairly reliable. With these values of I_{B0} and I_A, if one assumes $C-C=1.55$A, one obtains $C-H=1.098$A and $\sphericalangle HCC=109°\,3'$. From the considerations of the perturbations of state ν_8 and of the frequencies and line spacings of the combination $\perp$ bands, spectroscopic evidence indicating that the configuration of C_2H_6 is staggered (point group D_{3d}) has for the first time been obtained. Also from these considerations the reliable value $\nu_8=1472.2$ cm^{-1} and the values $\nu_4=290$ cm^{-1} for the torsion frequency and $\nu_{12}=1190$ cm^{-1} for the "uncertain" frequency have been obtained. The latter two values are perhaps somewhat more reliable and not inconsistent with values obtained previously by other methods. These and other results are summarized in Figs. 1 and 14 and in Tables XII–XV.

I. INTRODUCTION

THIS report deals with the results of experiments on the near infra-red spectrum between 1.6 and 13μ of C_2H_6 gas performed at Princeton University before the recent war with a spectrometer of high resolving power. A preliminary account of some of these results was given at the Princeton meeting of The American Physical Society in December 1941 by Smith and Woodward.[1] Also, some of the results were recalculated for inclusion in Professor Herzberg's latest book.[2] All values reported here have been re-examined and analyzed more thoroughly than previously and are slightly different from those reported in either reference 1 or reference 2.

Previous investigations of the Raman and infra-red spectra and of the heat capacity of C_2H_6 and C_2D_6 have yielded values of the twelve fundamental frequencies of each molecule, which are for the most part quite reliable, but have failed to determine whether the configuration of each is staggered (point group D_{3d}) or eclipsed (point group D_{3h}). These results are well summarized by Herzberg[3] who points out that some chemical evidence favors the staggered configuration.[4] The experiments described here add considerable detailed data to these results because of the greater resolution employed than by others, particularly in the case of weaker combination bands, because many spectra of C_2H_6 gas at temperatures between -80°C and -100°C were obtained for the first time and because atmospheric absorptions were for the most part effectively removed from the spectrometer.

A level diagram of the twelve fundamental vibration states of C_2H_6 based both on the results of previous investigations and on those to be described here is shown in Fig. 1 wherein the states are divided into five symmetry classes which are designated at the bottom of the diagram by the usual symbols for both point groups D_{3d} and D_{3h}. In Fig. 1 and throughout this paper the notation for the twelve vibrations given in reference 3 is employed. The frequency values in Fig. 1 are essentially the same as those given in reference 3 except in the cases of ν_4, ν_8 and ν_{12}.

II. EXPERIMENTAL

The ethane used in these experiments was very kindly prepared by Professor John Turkevich of the Princeton Chemistry Department by hydrogenation of ethylene. Unfortunately no record of the purity of the ethane was kept but

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[1] L. G. Smith and W. M. Woodward, Phys. Rev. 61, 386A (1942).

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

[3] Reference 2, p. 342.

[4] The staggered configuration is also favored by the recent theoretical considerations of E. N. Lassettre and Laurence B. Davis (J. Chem. Phys. 16, 151 (1948)).

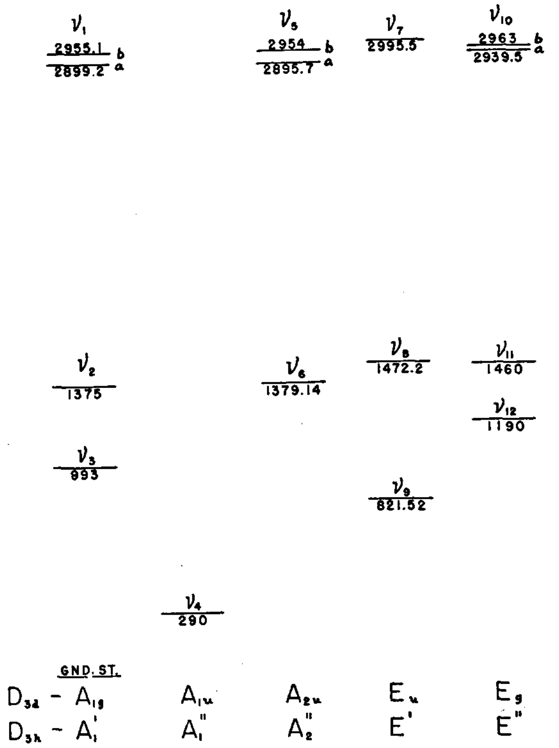

FIG. 1. Level diagram of the twelve fundamental vibrational states of C_2H_6. The wave number values (in cm^{-1}) are considered the best now available in the light of previous results and those reported here.

no evidences of the strong absorptions of any likely impurities were found.

The prism-grating spectrometer and associated carbon rod source and fixed absorption cell (133 mm long) together with the methods employed for removing water vapor and CO_2 from the optical path, for cooling the cell, for obtaining automatic photographic records of galvanometer deflection *vs.* angular position of the divided circle and hence *vs.* wave number and for periodically recording the zero position of the galvanometer on these records have been previously described.[5] Spectrograms of nearly all regions in which infra-red absorption by ethane gas has been reported by other investigators as well as of a region between 5700 and 6000 cm^{-1} not previously studied have been obtained with this equipment and these techniques with the gas at room temperature. In addition spectrograms of the regions below 1600 cm^{-1} and those between 2600 and 3500 cm^{-1} have been obtained with the gas at a temperature near −100°C. Spectrograms of each region studied are reproduced in Figs. 2–12 from tracings made from the original photographs.[6] The value of pressure recorded in each of Figs. 2–12 represents that of the gas in the cell at room temperature (not, in the cases of the low temperature runs, of this gas at the reduced temperature). The 7200 line/inch and 1800 line/inch, replica, echelette gratings used throughout this work were made by Professor R. W. Wood and each had a ruled surface 4 inches high by 6 inches wide. Each grating was calibrated with the third and fourth doublets in the *P* branch of the fundamental H Cl band at 3.46μ observed in the first order with the 7200 line/inch grating and in the third order with the 1800 line/inch grating. The wave numbers of the four lines were obtained from smooth curves for the entire H Cl band fitted to the data of Meyer and Levin[7] in the manner described by Herzberg.[8]

It is evident on comparison of Fig. 3a with Fig. 3b and of Fig. 9 with a spectrogram (not shown) of the same region with the gas at room temperature that reliable measurements of the wave numbers of the rotation lines of the fundamental $\|$ bands ν_6 at 1379 and ν_{5a} at 2896 cm^{-1} can only be obtained with the gas at low temperature. This is undoubtedly due to appreciable population at room temperature of the lowest excited states of the low lying torsional vibration ν_4. By undergoing transitions from states $n\nu_4$ to states $\nu_6+n\nu_4$ and $\nu_{5a}+n\nu_4$ molecules cause absorption at frequencies very nearly but not exactly the same as those undergoing transitions from the ground state to states ν_6 and ν_{5a}. Except in the case of $\perp$ band ν_8 where a few isolated peaks appear to be strongly temperature sensitive, the fine structures in other regions below 1600 cm^{-1} and between 2600 and 3500 cm^{-1} were not found to be markedly different at the two temperatures, though in general the absorption peaks were sharper at the lower temperatures.

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[5] L. G. Smith, Rev. Sci. Inst. **13**, 54, 63 and 65 (1942).

[6] In the case of Fig. 2b the curve was replotted from the original photograph which was marred by bad zero drift. Hence in this figure the dashed zero line is straight and horizontal.

[7] C. F. Meyer and A. Levin, Phys. Rev. **34**, 44 (1929).

[8] G. Herzberg, *Molecular Spectra and Molecular Structure I. Diatomic Molecules* (Prentice-Hall Inc., New York, 1939), p. 60.

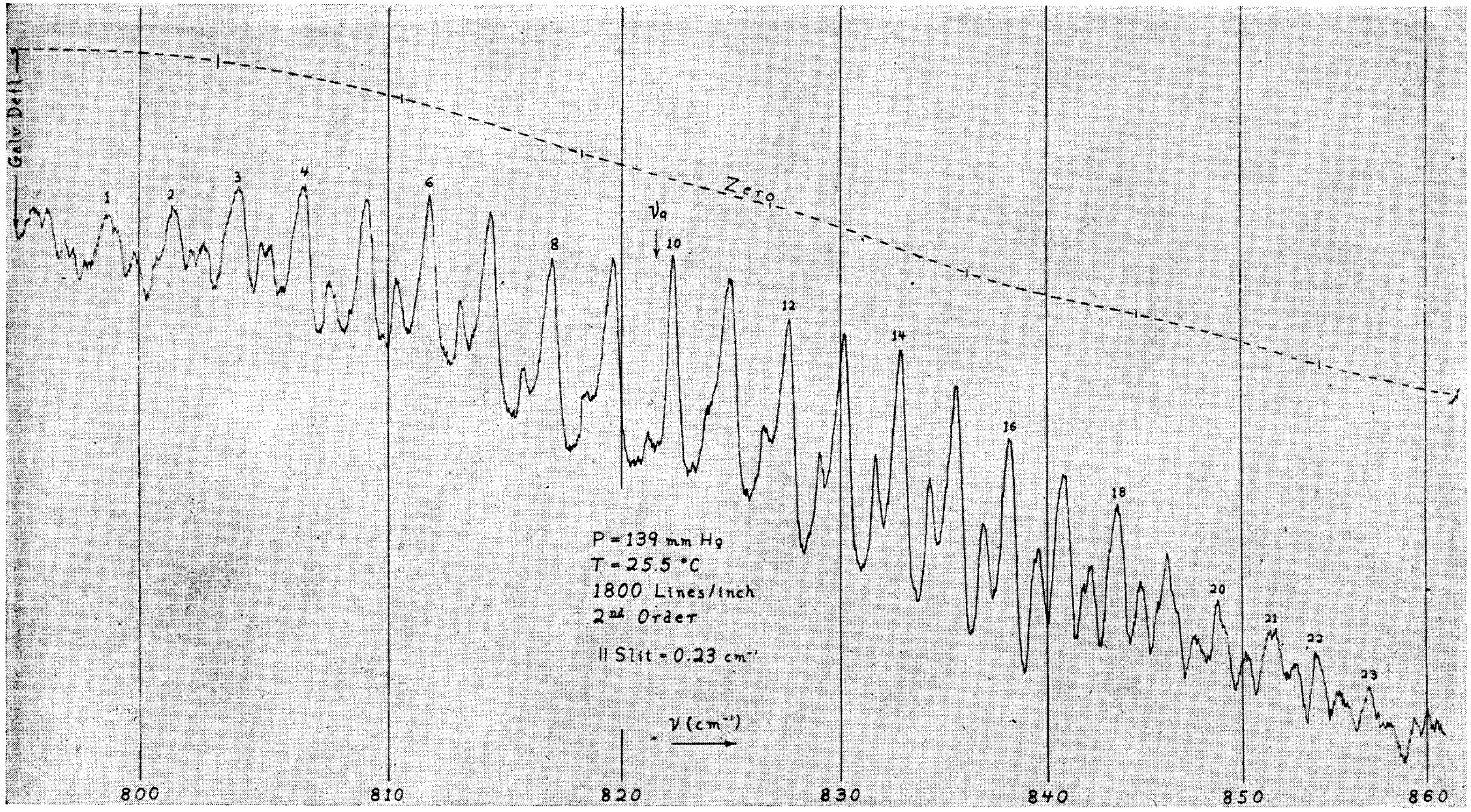

FIG. 2a. Record of fundamental ⊥ band ν_9 with gas at room temperature.

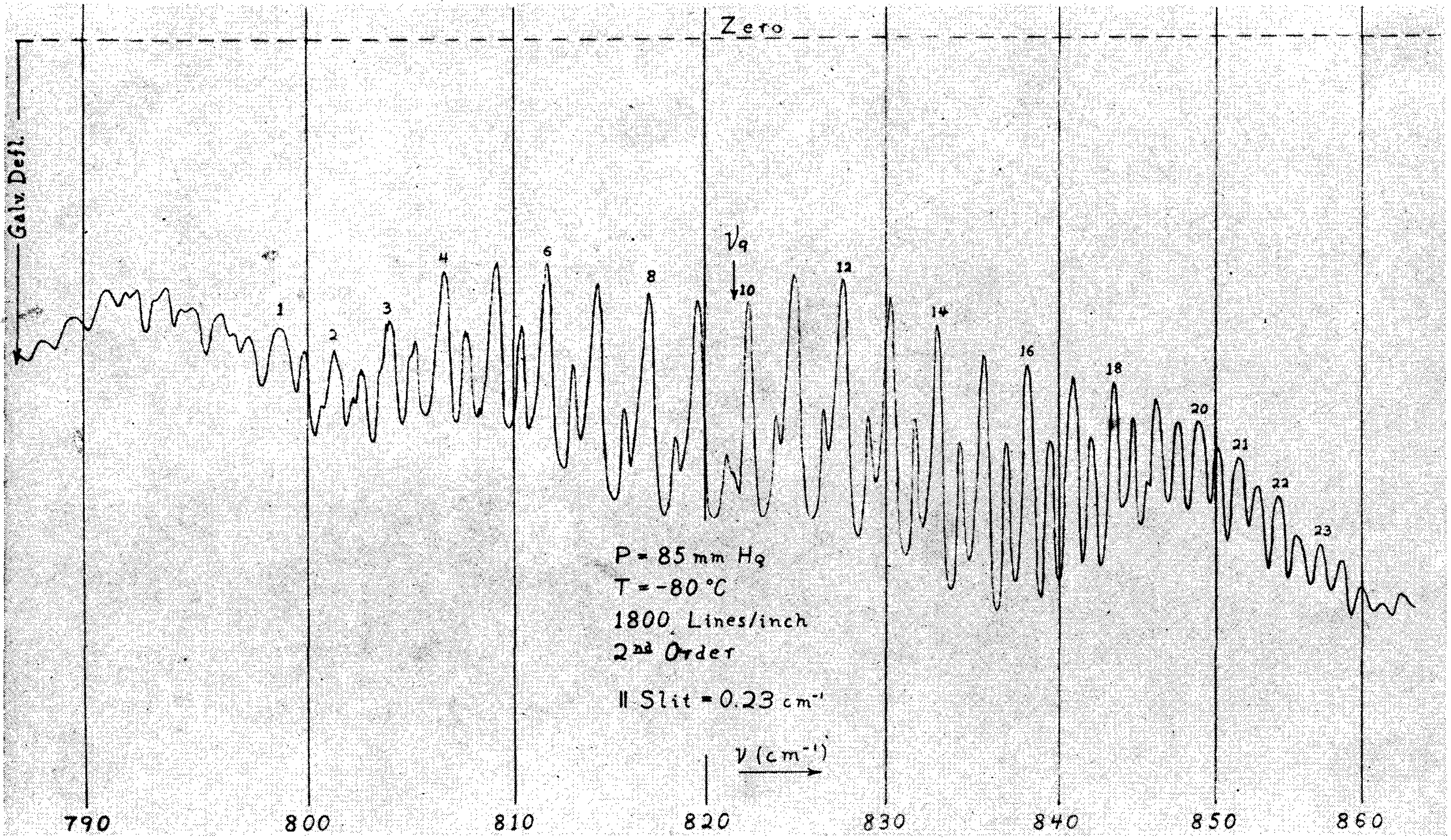

FIG. 2b. Record of fundamental ⊥ band ν_9 with gas at low temperature.

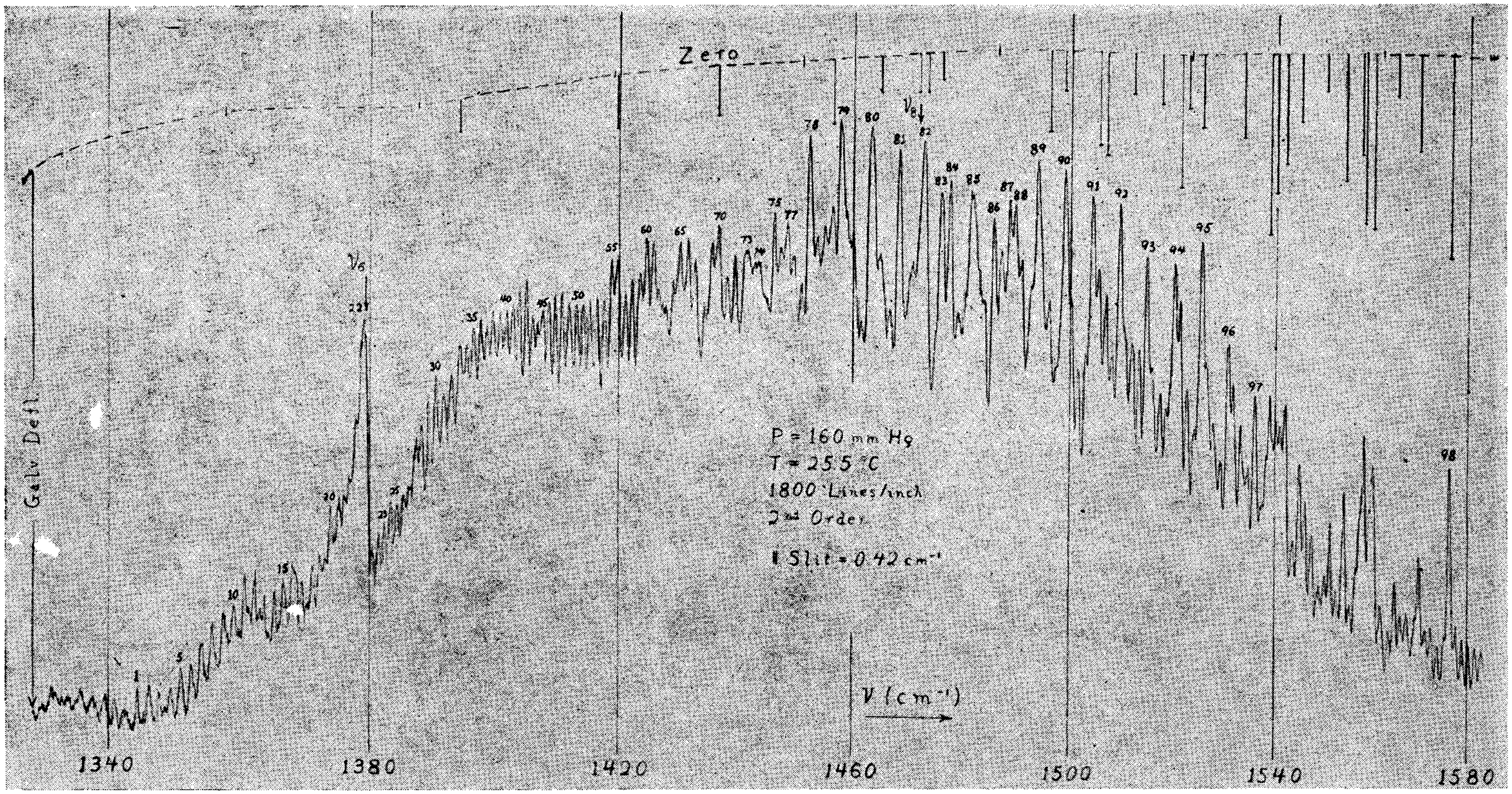

FIG. 3a. Record of fundamental || band ν_6 and fundamental ⊥ band ν_8 with gas at room temperature. Lines drawn down from the zero line show the positions and roughly the correct intensities of interfering water vapor lines which have not been subtracted from the record.

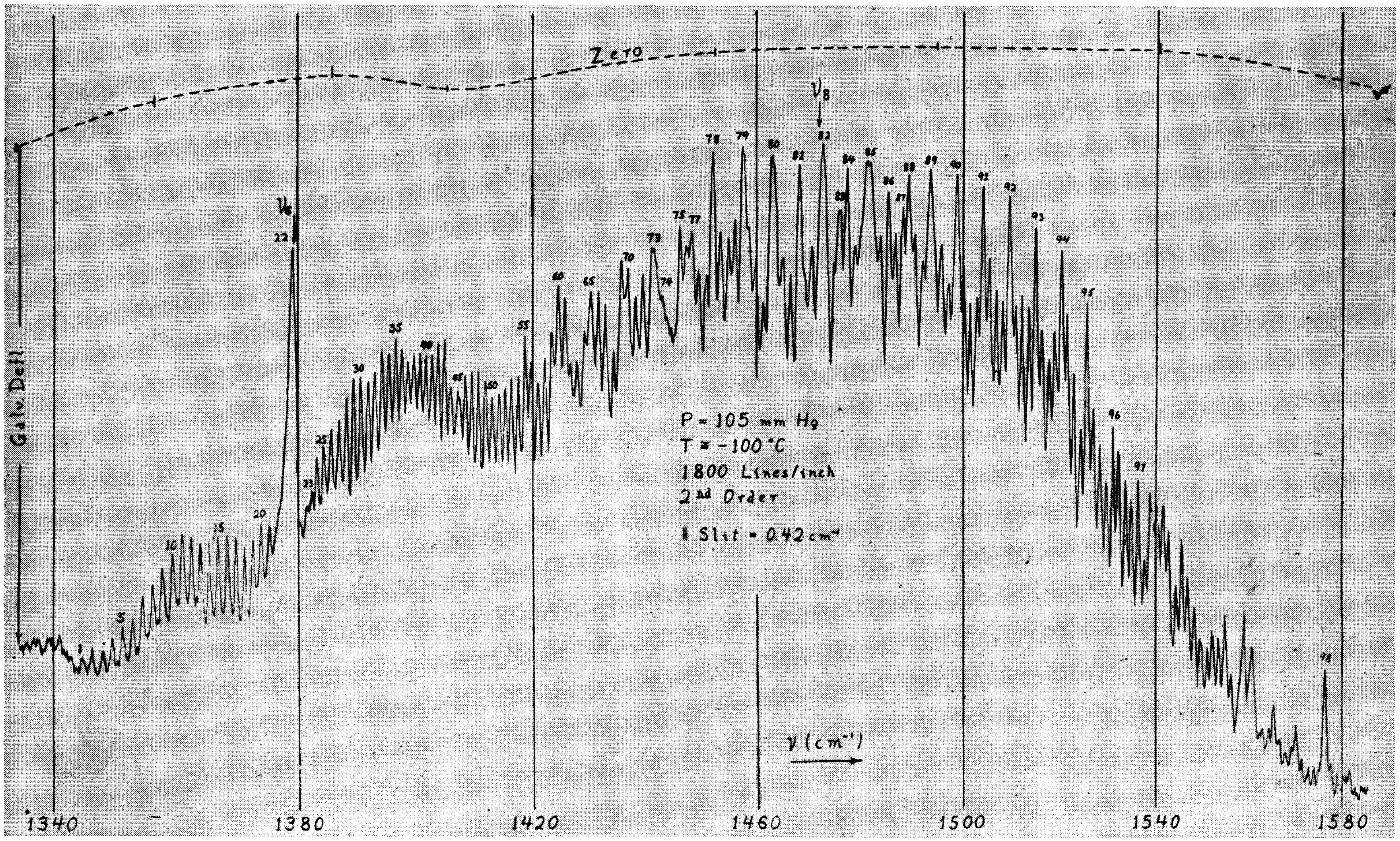

FIG. 3b. Record of fundamental ∥ band ν_6 and fundamental ⊥ band ν_8 with gas at low temperature. Water vapor absorption, as indicated by peak 98, is appreciably less than in Fig. 3a.

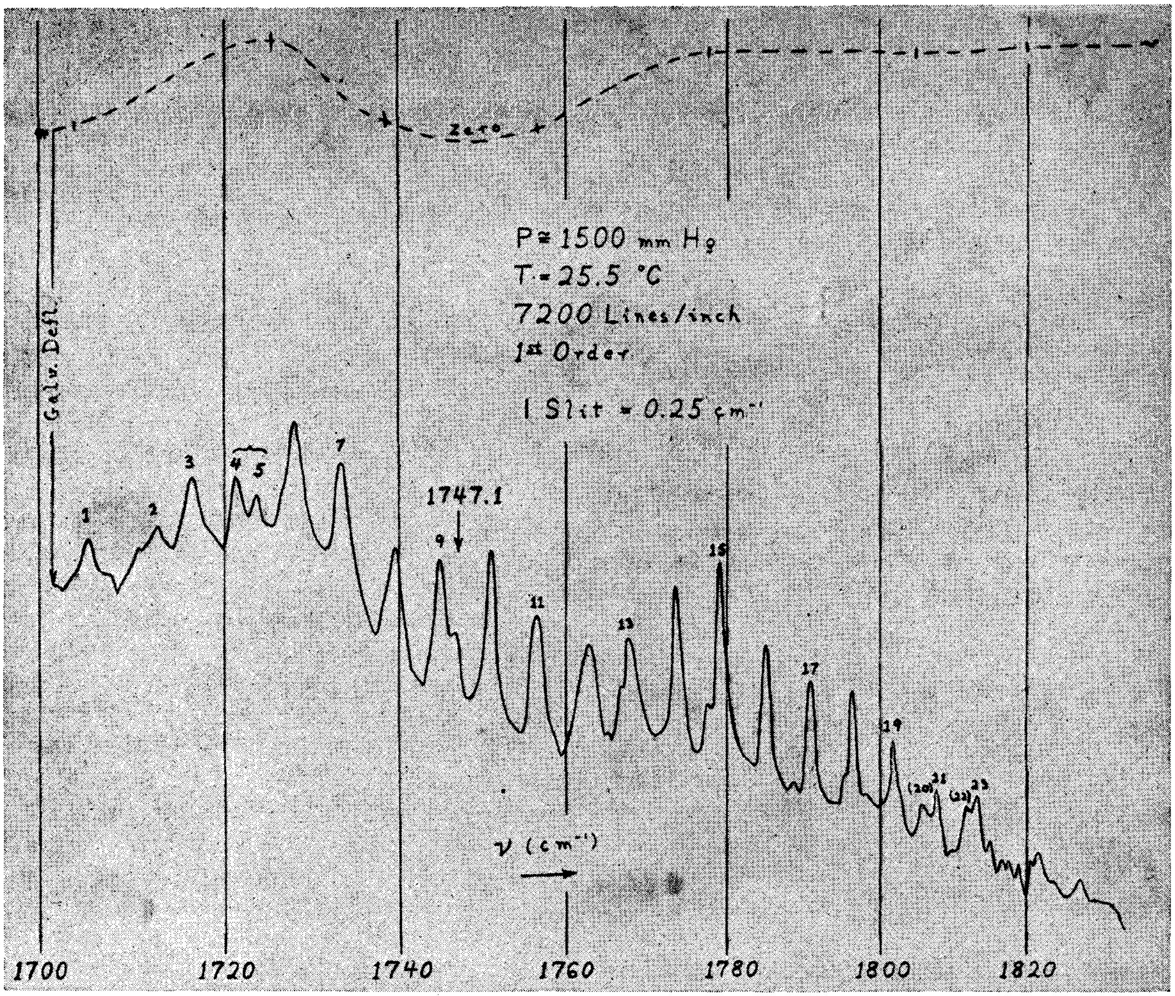

FIG. 4. Record of combination $\perp$ band at 1747.1 cm^{-1}. A few water vapor peaks, present because the spectrometer was not well dried when this record was taken, have been subtracted from the original record of absorption due to both C_2H_6 and water vapor.

It is further evident from Fig. 6, wherein is shown a background run with no gas in the cell, that measurement of the $\|$ band at 2369 cm^{-1} would be impossible without very complete removal from the spectrometer of atmospheric CO_2. Studies of the bands ν_6 and ν_8, both shown in Fig. 3, require not only low temperature (at least in the case of ν_6) but also thorough removal of water vapor, as a comparison of Fig. 4 of reference 5, which was obtained over the same spectral region, will show. Water vapor absorption is practically negligible in the case of Fig. 3b, though it is not completely negligible in Fig. 3a wherein lines drawn down from the zero line indicate the correct positions and roughly the correct intensities of interfering water lines. (No correction of the observed spectra for water vapor absorption has been made in Fig. 3a or Fig. 3b.) Absorption by water vapor caused some interference in the region shown in Fig. 4. In this case the water lines have been subtracted from the absorption resulting from both water vapor and ethane.

In Tables I–XI are given values of the wave numbers (all corrected to vacuum) of the absorption peaks shown in Figs. 2–12 measured from the original photographic records. Also given where possible are values of J'' and J' for the lower and upper states respectively of $\|$ bands and of K'' and K' for $\perp$ bands assigned

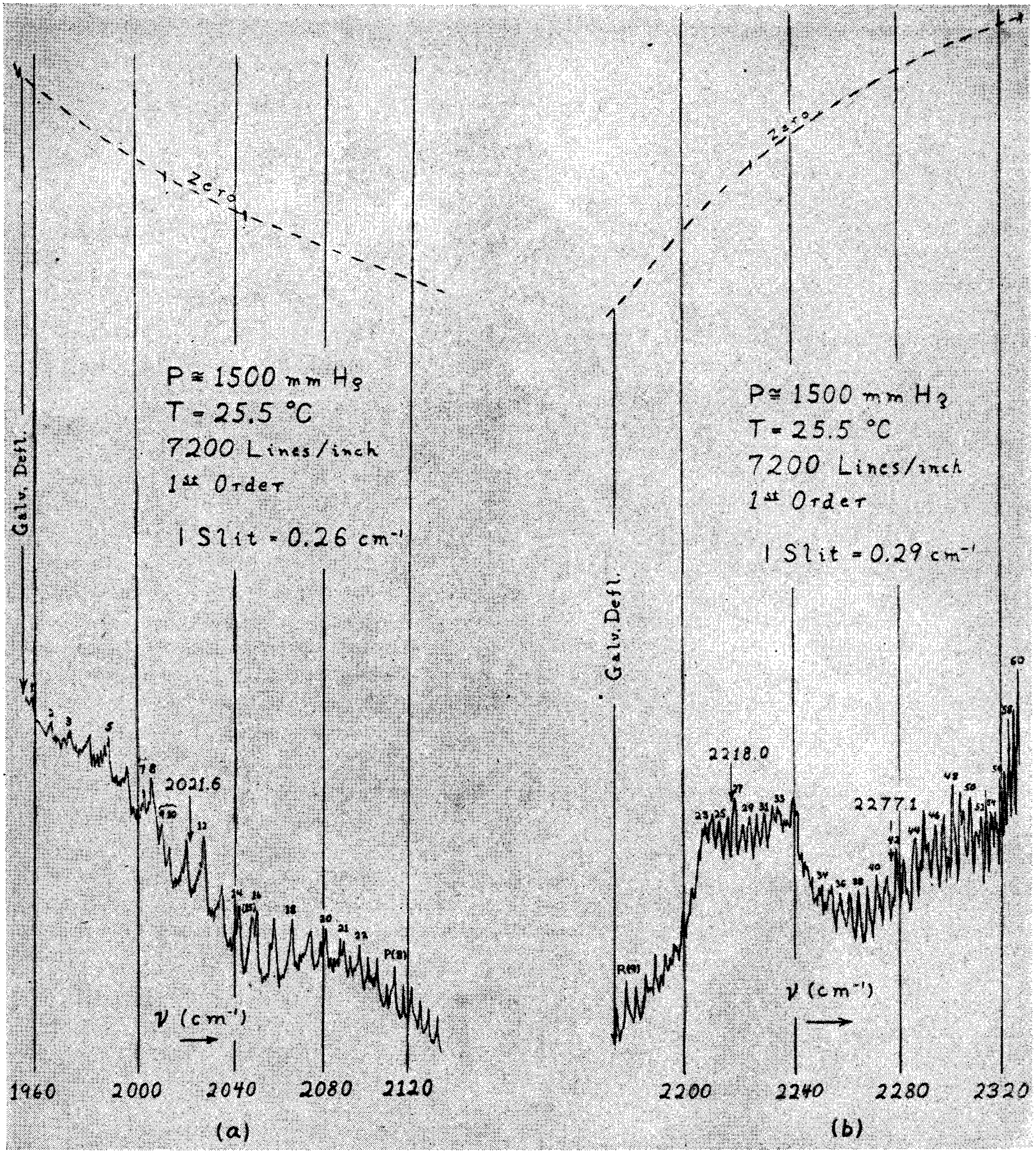

FIG. 5. Record of combination ⊥ bands at 2021.6, 2218.0 and 2277.1 cm^{-1}. Some lines of the fundamental band of CO are present because of a slight leak in the carbon rod source. Of these lines, $P(8)$ and $R(9)$ are marked.

in accordance with the reasonings discussed below. In the cases of the absorption regions shown in Figs. 4, 5 and 12, of which unfortunately only preliminary records were made, the calibration lines were placed on the photographic records by an automatic contactor and hence the wave numbers given in Tables III, IV and XI are somewhat less reliable than in other cases where calibration lines were put on manually, because of errors in the worm wheel that drove the divided circle. This plus the fact that in Fig. 5b the angular interval between calibration lines was quite large

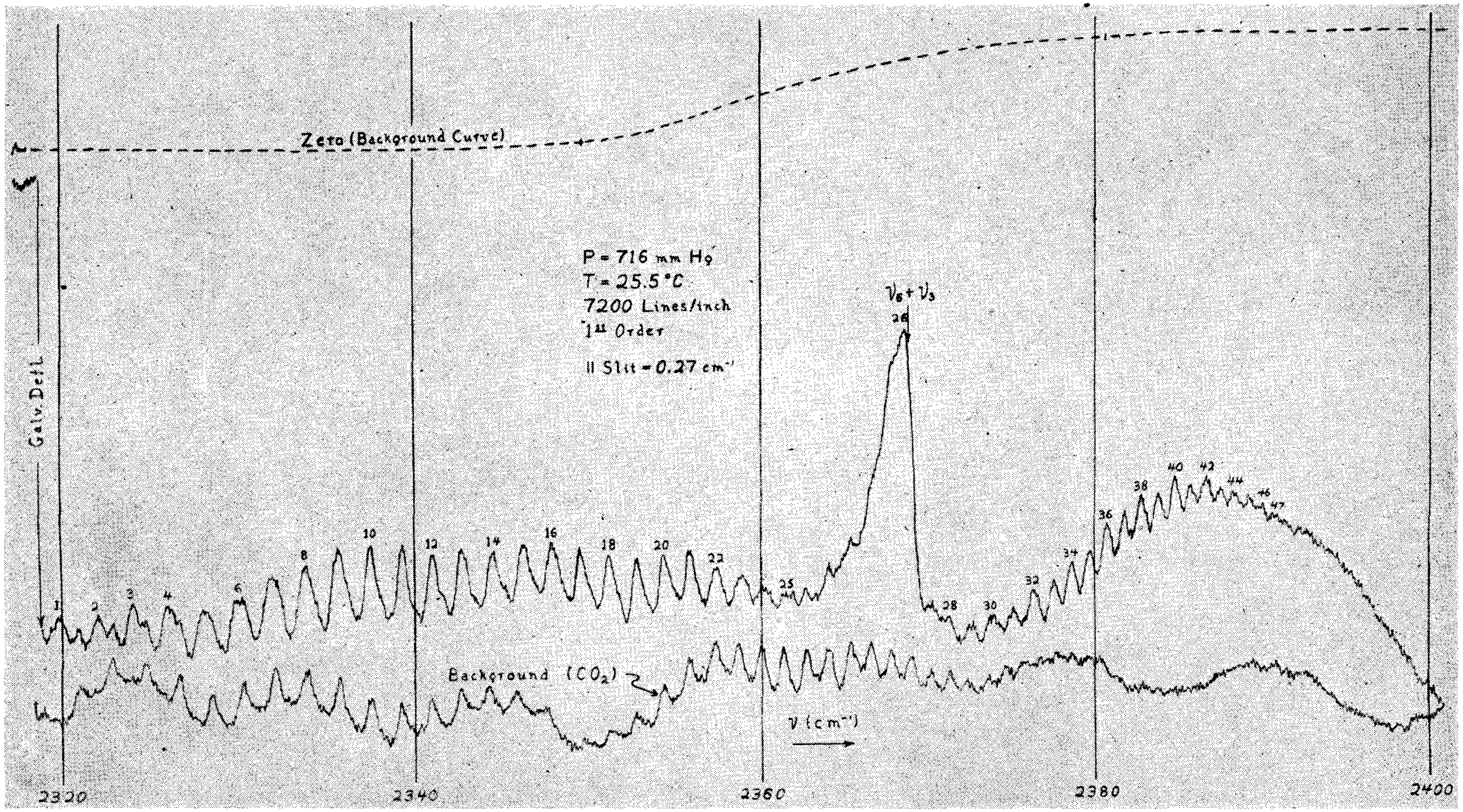

FIG. 6. Record of the combination || band $\nu_3+\nu_6$. CO_2 absorption is less intense in the upper record than in the background record because the former was taken first, immediately after the circulating fans (see reference 5) had been turned off.

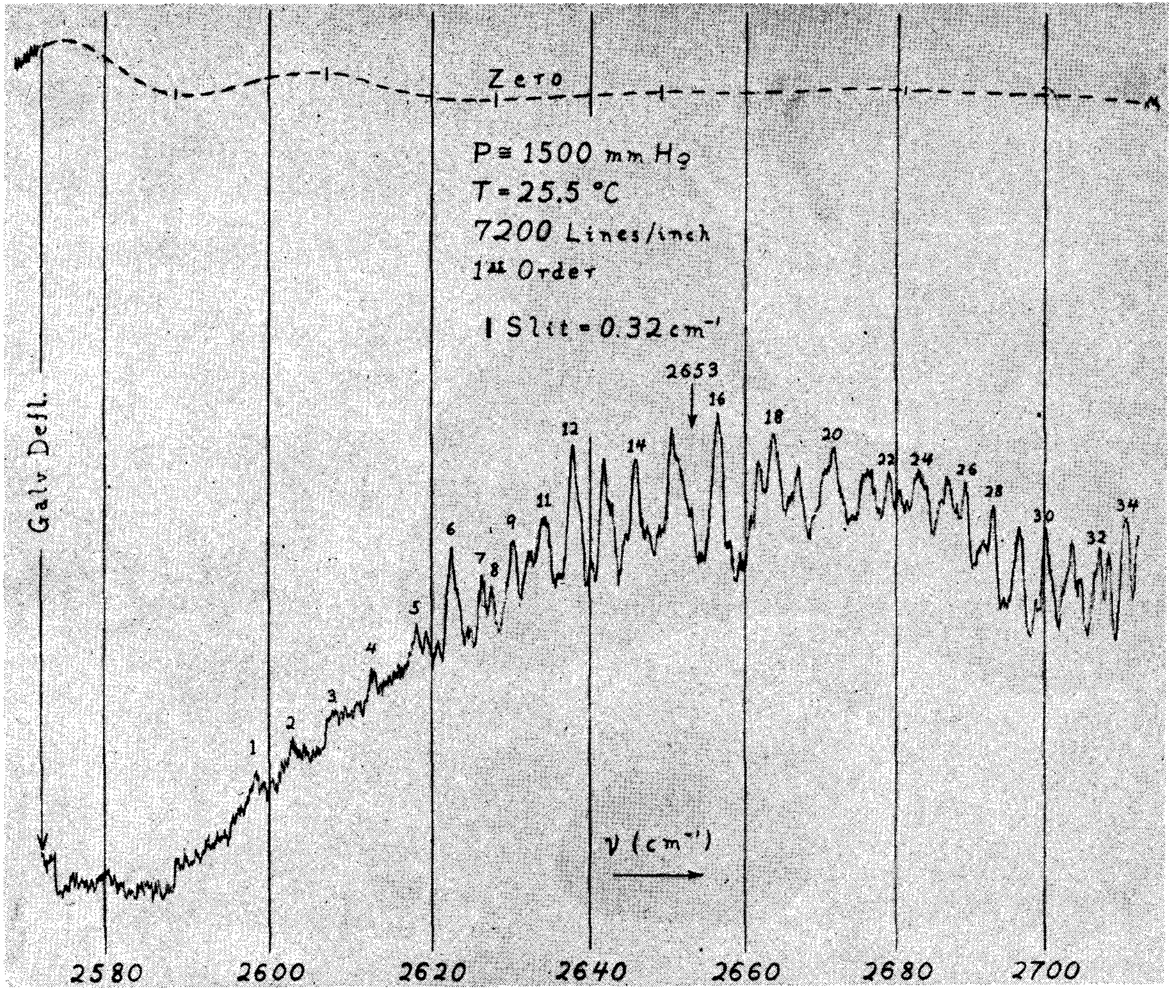

FIG. 7. Record of the combination ⊥ band (or bands) near 2653 cm⁻¹.

doubtless accounts for the discrepancies between values of the wave numbers of lines 57–60 in Table IV and those of the same lines (2–5) in Table V.

III. || BANDS AND THE LARGE MOMENT OF INERTIA I_B

The rotational fine structures of four || bands have been resolved. These are: the fundamental band ν_6 at 1379 cm⁻¹ (Fig. 3); the combination bands at 2369 cm⁻¹ (Fig. 6) and 2753 cm⁻¹ (Fig. 8) which doubtless correspond respectively to $\nu_3+\nu_6$ and $\nu_2+\nu_6$; and the low frequency component ν_{5a} of the doublet 2896–2955 cm⁻¹ (Fig. 9) generally attributed to Fermi resonance between the fundamental state ν_5 and the combination state $\nu_8+\nu_{11}$.

To determine "best" values of ν_0, the band origin, and of the differences in rotational constants $B'-B_0$ and $D'-D_0$ for each of the four || bands, values of $\frac{1}{2}[R(J-1)+P(J)]$ were fitted by least squares to the theoretical quadratic function[9] of J^2,

$$\tfrac{1}{2}[R(J-1)+P(J)]=\nu_0+[(B'-B_0)-(D'-D_0)]J^2-(D'-D_0)J^4. \quad (1)$$

In the cases of bands ν_6, $\nu_3+\nu_6$ and $\nu_2+\nu_6$, $(D'-D_0)$ was entirely negligible. However, this was not so in the case of band ν_{5a}.

In order to determine a "best" value of B_0,

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[9] Here, as elsewhere in this report, the notation is essentially that used throughout references 2 and 8, the subscript 0 instead of the superscript $''$ is used on rotational constants of the ground state and $J\equiv J''$.

a value of D_0 was first calculated with the aid of the potential function involving three force constants given by Howard.[10] This constant D_0, which measures the degree of centrifugal stretching of the rotating, non-vibrating molecule, is given in general for a linear or symmetric top molecule by the expression

$$D_0=\frac{16\pi^2c^2B_0{}^3}{I_{B0}}\left(\frac{\delta I_{B0}}{\omega^2}-\frac{2V}{\omega^4}\right), \quad (2)$$

where I_{B0} is the moment of inertia of the non-rotating (and non-vibrating) molecule about an axis perpendicular to the symmetry axis, c is the velocity of light, and ω is the angular rotation frequency, and where δI_{B0} is the change in I_{B0} and V the potential energy, both caused by the centrifugal stretching. For the particular case of ethane and Howard's potential function this becomes

$$\begin{aligned}D_0=\frac{4\pi^2c^2B_0{}^3}{I_{B0}}\Bigg\{&\frac{M^2a^2}{K_3}\\&+\frac{m^2\sin^2\alpha(1+3\cos^2\alpha)}{K_2(1+15\cos^2\alpha)}\\&\times[6(a+b\cos\alpha)^2\\&+b^2(1+3\cos^2\alpha)]\\&+\frac{3m^2}{K_1}[2a^2\cos^2\alpha\\&+b^2(3+2\cos^2\alpha+3\cos^4\alpha)\\&+4ab\cos\alpha(1+\cos^2\alpha)]\Bigg\}, \quad (3)\end{aligned}$$

where, M and m are respectively the masses of the carbon and hydrogen atoms, a, b and α are

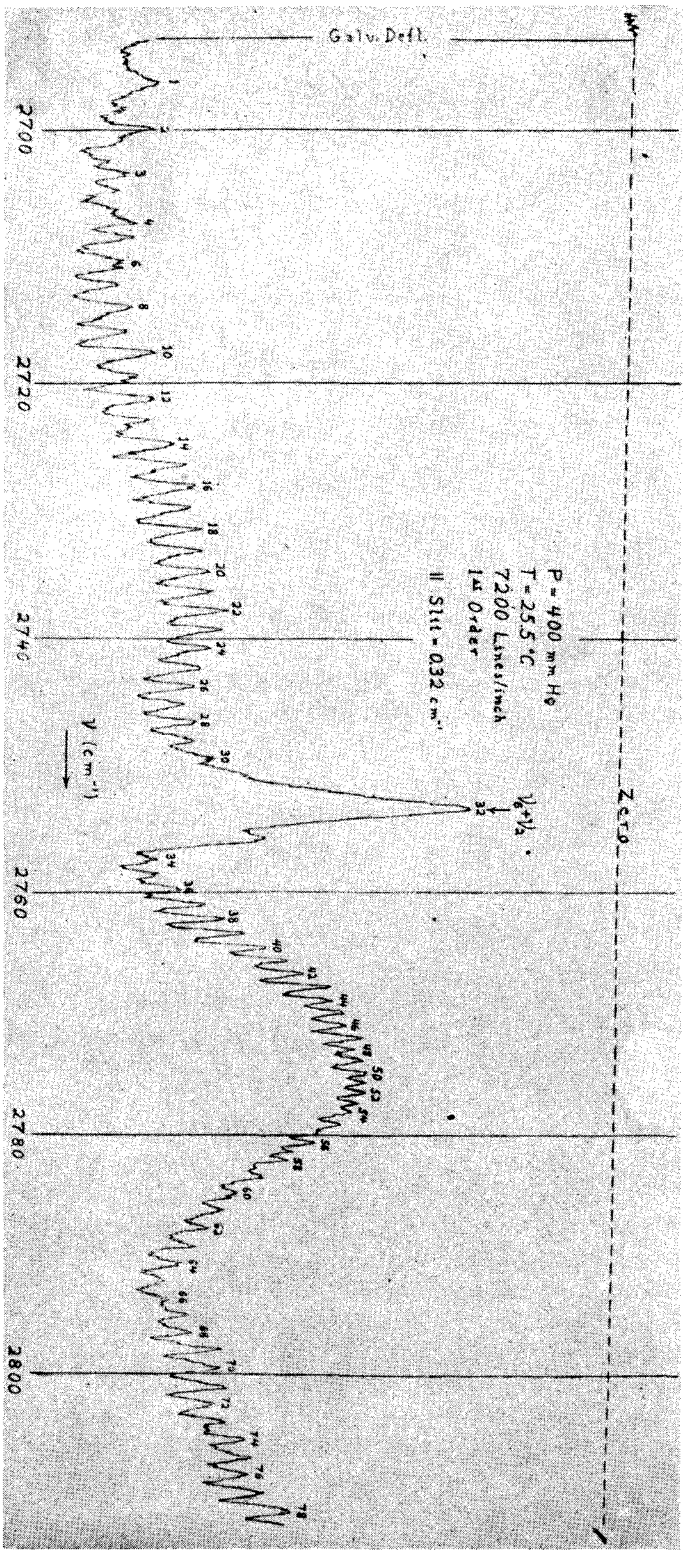

FIG. 8. Record of the combination || band $\nu_2+\nu_6$ and the combination ⊥ band near 2800 cm^{-1}.

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[10] J. B. Howard, J. Chem. Phys. 5, 442 (1937).

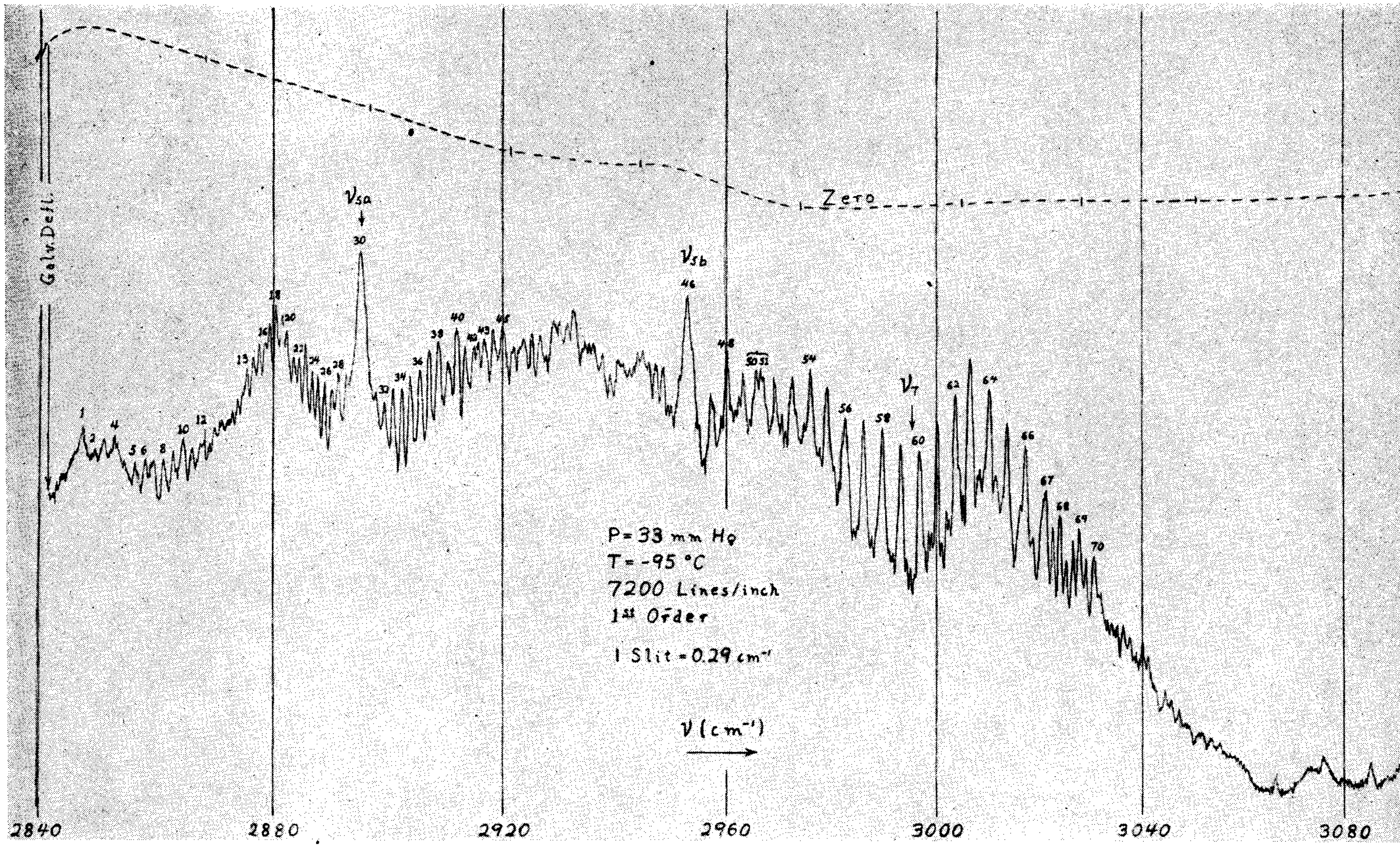

FIG. 9. Record of the combination ⊥ band near 2860 cm^{-1}, the fundamental double ∥ band ν_{5a} and ν_{5b} and the fundamental ⊥ band ν_7.

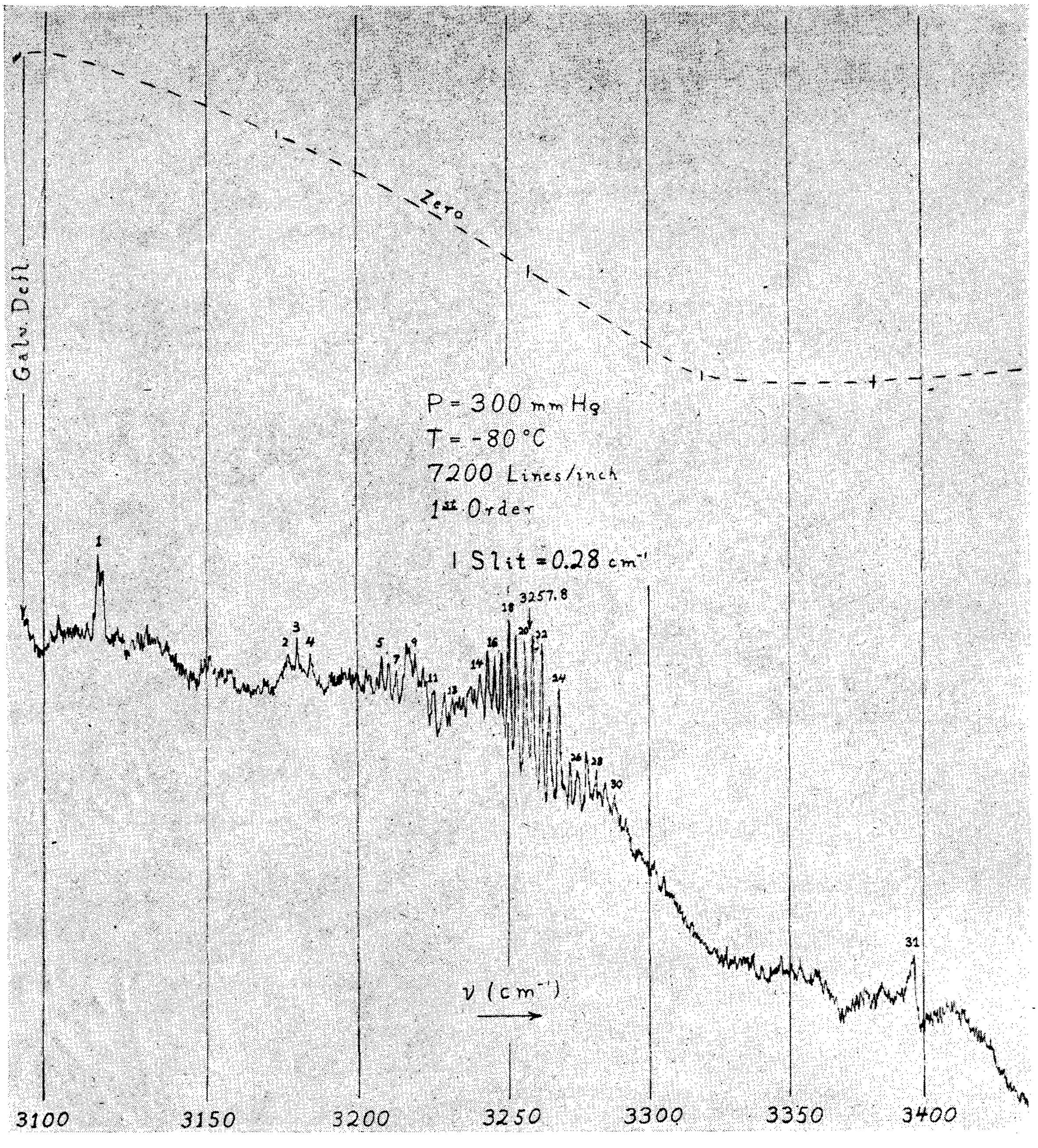

FIG. 10. Record of the combination ⊥ band at 3257.8 cm^{-1} showing in addition what may be combination ‖ bands (peaks 1 and 31) as well as other peaks which may be due to combination ⊥ bands.

respectively the equilibrium values of the C—C distance, the C—H distance and the supplement of the HCC angle, and K_1, K_2, K_3 are the force constants given by Howard. Since $D_0 \ll B_0$, only approximate values of the parameters need be used to determine D_0. Hence it was assumed that the HCC and HCH angles are tetrahedral ($\cos\alpha = \frac{1}{3}$), that $a = 1.55A$, $b = 1.10A$, K_1, K_2 and K_3 have the values given by Howard, $B_0 = 0.6626$ cm^{-1} and $I_{B0} = 42.23 \times 10^{-40}$ g cm^2. These values are consistent with the final results of the measurements.

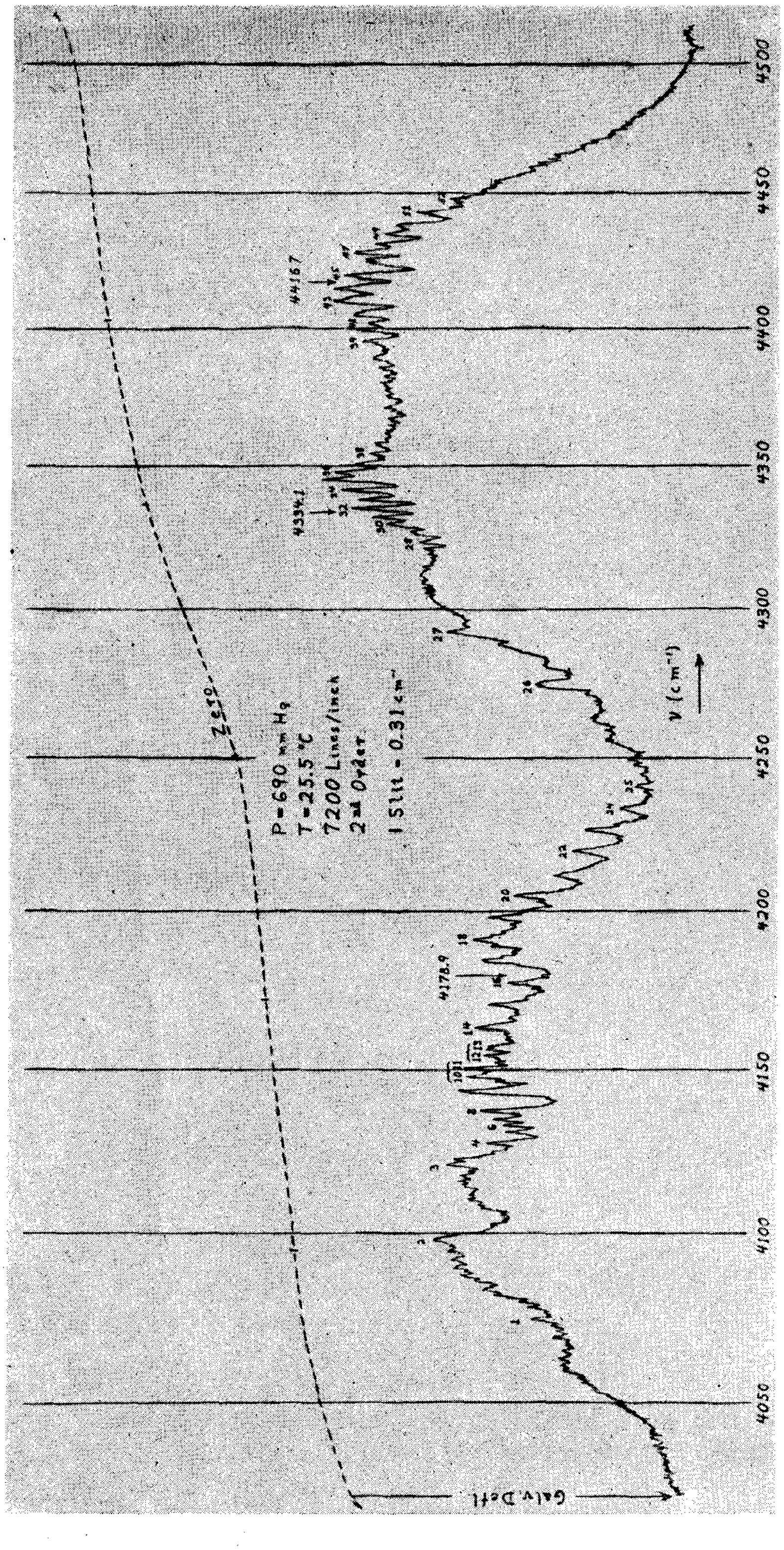

FIG. 11. Record of absorption between 4000 and 4500 cm^{-1}.

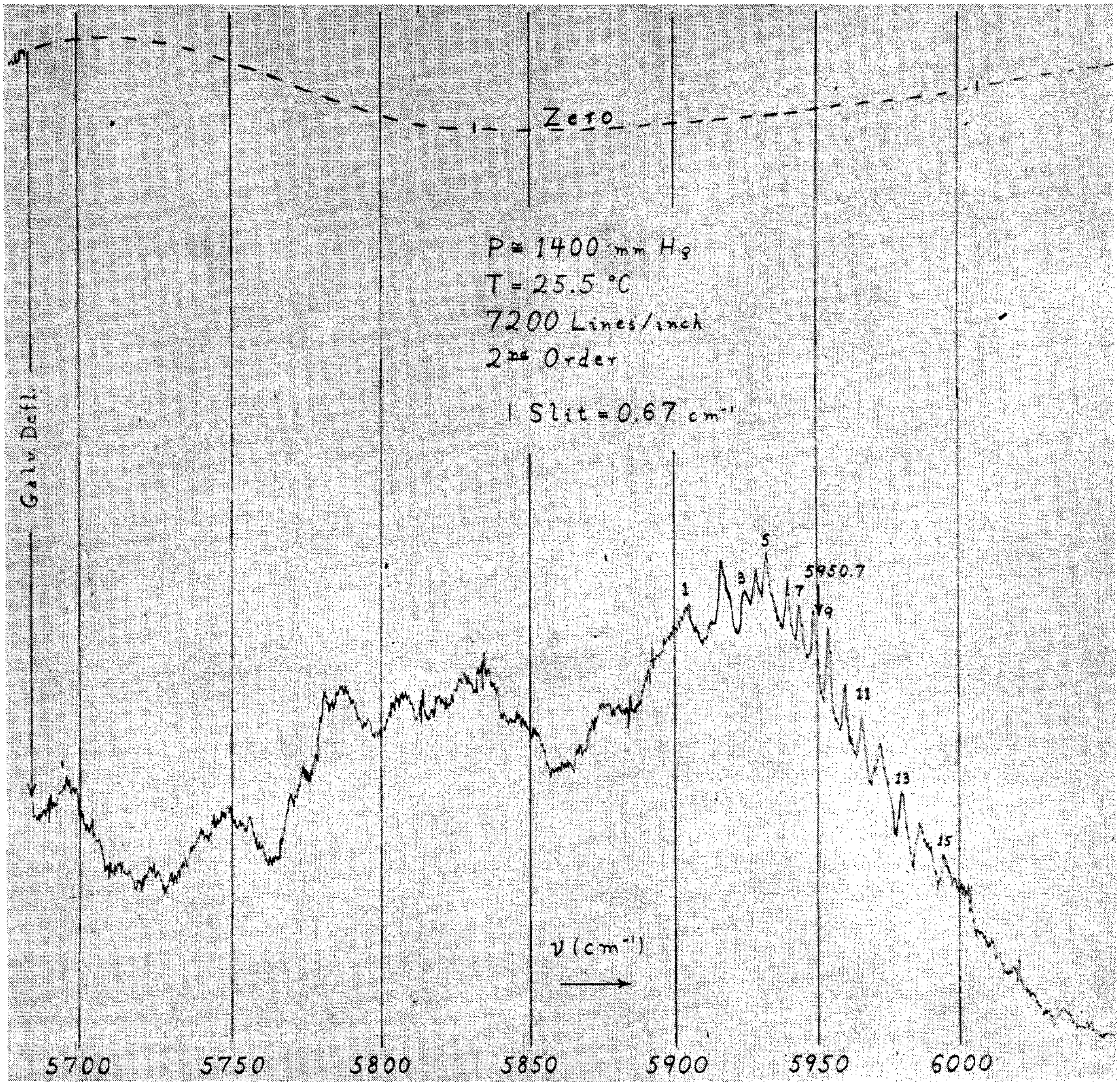

FIG. 12. Record of absorption between 5700 and 6000 cm⁻¹.

With the value of D_0 obtained thus a "best" value of B_0 was determined by fitting by least squares values of $\Delta_2F_0(J)/2(2J+1)$, determined from measurements on all four || bands, to the theoretical linear function of $(2J+1)^2$,

$$\frac{\Delta_2F_0(J)}{2(2J+1)}=\frac{R(J-1)-P(J+1)}{2(2J+1)}=(B_0-\tfrac{3}{2}D_0)-\frac{D_0}{2}(2J+1)^2. \quad (4)$$

The measured values of these quantities together with the least squares regression line are shown plotted as a function of $(2J+1)^2$ in Fig. 13. The intercept of the regression line was determined from the relation

$$(B_0-\tfrac{3}{2}D_0)=\frac{\sum_{i=1}^{4}g_i\{\sum(2J+1)\Delta_2F_0+D_0\sum(2J+1)^4\}_i}{2\sum_{i=1}^{4}g_i\{\sum(2J+1)^2\}_i}, \quad (5)$$

TABLE I. Wave numbers of lines shown in Fig. 2.

Line No.	Band	K''	K'	ν (cm^{-1})
1	ν_8	9	8	798.77
2		8	7	801.31
3		7	6	803.88
4		6	5	806.53
5		5	4	809.09
6		4	3	811.71
7		3	2	814.29
8		2	1	816.94
9		1	0	819.58
10		0	1	822.27
11		1	2	824.82
12		2	3	827.49
13		3	4	830.12
14		4	5	832.81
15		5	6	835.51
16		6	7	838.14
17		7	8	840.78
18		8	9	843.46
19		9	10	846.06
20		10	11	848.79
21		11	12	851.50
22		12	13	854.05
23		13	14	856.79

which differs from that given in reference 8 (p. 200) in that the term $\frac{3}{2}D_0$ and the four weight factors g_i $(i=1, \cdots 4)$ have been included. The factors g_i, which take account of the fact that wave number measurements are not equally reliable in the cases of the four bands (being least reliable in the case of ν_{5a}), were taken to be inversely proportional to the mean squared deviations of measured values of the combination sums $\frac{1}{2}[R(J-1)+P(J)]$ from their regression line values. (Omission of the term $\frac{3}{2}D_0$ and the factors g_i makes an insignificant change in the final value of B_0.)

In Table XII are listed the "best" values of ν_0, $B-B_0$, B and I_B for the ground state and the upper states of each of the four resolved || bands as well as D for the ground state and the state ν_{5a}. The values of I_B were obtained from the B values by use of the latest value of Planck's constant recommended by DuMond and Cohen,[11] namely $h=(6.6234\pm0.0011)\times10^{-27}$ erg sec. The errors given for the values of $B-B_0$, B and D are probable errors estimated by standard statistical methods from the scatter of the measured combination sums and differences about their regression line values while those for the values of I_B include in addition allowance for the uncertainty in h. Though no additional allowance has been made for possible systematic errors in the angle measurements, some account of this is included in the errors as given for B_0 and I_{B0} since the final values of B_0 and I_{B0} were obtained from measurements on four different bands over four different angular ranges. The error given for each value of ν_0 includes allowance for "internal" error, including that involved in location of the central image, and for an assumed systematic or "external" error of 5 seconds in the angle measurements as well as for errors in determination of the grating constant due both to errors in angle measurements and an assumed probable error of 0.05 cm^{-1} in the wave numbers of the H Cl lines used for calibration.

It will be noted that the value obtained for ν_0 in each case is very close to the measured wave number for the maximum of the Q branch. At first sight it may appear that, because each Q branch does not fall farther to one side of ν_0, errors in the assignment of J-values in Tables II, V, VII and VIII have been made. However, the considerations on page 416 ff. of reference 2 show that it is quite possible for the maximum of the Q branch of a || band of a symmetric top molecule to coincide with the band origin. That the numbering scheme adopted for each || band is correct is placed beyond question by the consideration that if the assigned numbering for any band is shifted by 1 unit the resulting values of $\Delta_2F_0(J)/2(2J+1)$ for that band will be changed on the average by an amount $B'-B_0$. Thus, for no set of numbering schemes other than that adopted is it possible to obtain agreement within experimental uncertainty between values of this quantity for all four bands such as is shown in Fig. 13.

The fact that B for state ν_{5a} is greater than B_0 so that I_B for this state is less than I_{B0} leads to the conclusion that ν_{5a} is a perturbed state, because the symmetry of any || vibration of C_2H_6 involving a change of dipole moment is such that the instantaneous value of I_B is a minimum when all atoms are in their equilibrium positions so that I_B for the unperturbed upper state of any || band must be greater than I_{B0}. Furthermore, this fact cannot be explained on the basis of a perturbation of the Fermi type, which almost certainly occurs between states ν_{5a}

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[11] J. W. M. DuMond and E. R. Cohen, Rev. Mod. Phys. 20, 82 (1948).

TABLE II. Wave numbers of lines shown in Fig. 3.

Line No.	Band	J''	J'	ν (cm^{-1})
1	ν_6	23	22	1345.03
2		22	21	1346.70
3		21	20	1348.26
4		20	19	1349.88
5		19	18	1351.49
6		18	17	1353.06
7		17	16	1354.65
8		16	15	1356.17
9		15	14	1357.73
10		14	13	1359.23
11		13	12	1360.81
12		12	11	1362.28
13		11	10	1363.75
14		10	9	1365.20
15		9	8	1366.77
16		8	7	1368.05
17		7	6	1369.61
18		6	5	1370.96
19		5	4	1372.31
20		4	3	1373.74
21		3	2	1375.07
22		0	0	1379.01
23		1	2	1382.21
24		2	3	1383.06
25		3	4	1384.25
26		4	5	1385.47
27		5	6	1386.89
28		6	7	1387.99
29		7	8	1389.17
30		8	9	1390.47
31		9	10	1391.60
32		10	11	1392.75
33		11	12	1393.99
34		12	13	1395.07
35		13	14	1396.24
36		14	15	1397.38
37		15	16	1398.32
38		16	17	1399.35
39		17	18	1400.58
40		18	19	1401.46
41		19	20	1402.48
42		20	21	1403.63
43		21	22	1404.70
44		22	23	1405.77

TABLE II.—*Continued.*

Line No.	Band	K''	K'	ν (cm^{-1})
45	ν_8			1407.07
46				1408.27
47				1409.32
48				1410.53
49				1411.71
50				1412.89
51				1414.13
52				1415.18
53				1416.30
54				1417.50
55				1418.71
56				1419.75
57				1421.00
58				1422.20
59				1423.37
60				1424.56
61				1425.83
62				1426.73
63				1427.92
64				1429.38
65				1430.34
66				1431.62
67				1433.17
68				1434.25
69				1435.65
70				1436.85
71				1438.21
72				1439.63
73				1441.36
74				1443.40
75				1446.38
76				1447.45
77				1448.52
78		4	3	1452.41
79		3	2	1457.91
80		2	1	1463.48
81		1	0	1468.45
82		0	1	1472.95
83		0	1	1475.87
84		1	2	1477.48
85		2	3	1481.49
86		1	2	1485.64
87		2	3	1488.28
88		2	3	1489.29
89		3	4	1493.68
90		4	5	1498.90
91		5	6	1504.13
92		6	7	1509.47
93		7	8	1514.65
94		8	9	1519.85
95		9	10	1525.14
96		10	11	1530.51
97		11	12	1535.80
98	H_2O			1576.04

and ν_{5b}, because in such a perturbation the B values of both perturbed states lie between those of the perturbing states, which, by the symmetry argument, are both less than B_0. For these reasons and also because of the abnormally large value of D of state ν_{5a}, we conclude that a Coriolis perturbation of this state by a nearby vibrational state exists in addition to the Fermi perturbation. If, as appears virtually certain, the matrix elements of this Coriolis perturbation depend primarily on J, the other state involved must be of the same species as the upper states of active $\perp$ bands, since the product of this species with that of ν_{5a} must be the species of a rotation (R_x, R_y) about an axis perpendicular to the symmetry axis of the molecule.[12] Furthermore, because the rotational levels for which $J>0$ of ν_{5a} lie higher relative to the level $J=0$ than they would in the absence of a Coriolis perturbation, the perturbing state evidently lies below ν_{5a}. Though there is evidence in Figs. 8

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[12] Jahn's rule, cf. reference 2, p. 276 and Tables 20, 22 and 31.

TABLE III. Wave numbers of lines shown in Fig. 4.

Line No.	Band	K''	K'	ν (cm^{-1})
1	1747.1	8	7	1705.25
2		7	6	1712.25
3		6	5	1716.57
4		5	4	1721.38
5				1723.67
6		4	3	1727.97
7		3	2	1733.21
8		2	1	1739.38
9		1	0	1744.87
10		0	1	1750.87
11		1	2	1756.36
12		2	3	1762.71
13		3	4	1767.81
14		4	5	1773.66
15		5	6	1779.29
16		6	7	1785.11
17		7	8	1790.89
18		8	9	1796.44
19		9	10	1801.80
20				1805.79
21		10	11	1807.54
22				1811.67
23		11	12	1813.18

and 9 of states of the proper species just below ν_{5a}, no attempt to identify the state in question or to investigate the perturbations of ν_{5a} in further detail has been made to date.

IV. FUNDAMENTAL ⊥ BANDS AND THE SMALL MOMENT OF INERTIA I_A

Spectrograms of the three fundamental ⊥ bands of C_2H_6 (ν_9, ν_8 and ν_7) are shown in Figs. 2, 3 and 9. These spectrograms show the same principal absorption peaks as did those of Levin and Meyer,[13] which peaks Howard[14] has demonstrated are to be identified with the strong, regularly spaced ^PQ and ^RQ "lines" (actually groups of superposed lines) that theory predicts should be the most prominent features of the ⊥ bands of a symmetric top molecule with out free rotation whose two equal moments of inertia (I_B) are greater than its third (I_A). Figs. 2, 3 and 9 also reveal much more clearly than the spectrograms of Levin and Meyer the presence and nature of absorption peaks other than those corresponding to the ^PQ and ^RQ lines. These other absorptions may at first sight appear to arise in part from coincidence of other bands with ν_7, ν_8, and ν_9. In fact, in each case the existence of one or more such other bands has been suggested by other workers. The present results together with the following interpretations indicate that most of these suggestions are invalid.

In band ν_9 (Fig. 2) there is, between each pair of adjacent major peaks, a minor peak, whose existence was first reported by Smith and Woodward.[1] Owens and Barker,[15] who also reported their existence, suggested that the minor peaks might be due to absorptions by molecules initially in a low lying excited vibrational state. However, the low temperature spectrogram reported on by Smith and Woodward and reproduced here in Fig. 2b shows that at −100°C the intensities of the minor relative to the major peaks are not less than at room temperature but, in fact, appear to be slightly greater. This result indicates strongly that the minor as well as the major peaks arise from absorptions by molecules initially in the ground state. The apparent small increase in intensity of the minor peaks as the temperature is lowered is doubtless because of sharpening of all peaks and consequent improvement of resolution.

An entirely reasonable explanation of these minor peaks appears when one notes the fact that the spacing of the major peaks is almost exactly twice the mean spacing ($2B_0$) of the lines of the fundamental || band ν_6. In such a case the ^PP, ^PR, ^RP and ^RR sub-band lines would be expected to be grouped in lines, one of which should occur approximately half way between each adjacent pair of ^PQ and ^RQ lines, instead of forming an unresolved background to the latter as they usually do in such ⊥ bands. This explanation allows us to state with a high degree of confidence that the origin of ν_9 lies between line 9 and line 10 (Fig. 2 and Table I) since it should lie between the same two major peaks as the weakest minor peak. Thus there is little question concerning the correctness of the assignment of values of K given in Table I for ν_9. This assignment of K values agrees with that of Owens and Barker[15] which these authors based on the slight enhancement of every third line near the middle of the band.

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[13] A. Levin and C. F. Meyer, J. Opt. Soc. Amer. **16**, 137 (1928).

[14] J. B. Howard, J. Chem. Phys. **5**, 451 (1937).

[15] R. G. Owens and E. F. Barker, J. Chem. Phys. **10**, 146 (1942). The wave number values reported by these authors are systematically lower than those in Table I by about 0.1 cm^{-1}.

TABLE IV. Wave numbers of lines shown in Fig. 5.

Line No.	Band	K''	K'	ν (cm^{-1})
1	2021.6	9	8	1959.40
2		8	7	1966.41
3		7	6	1973.75
4		6	5	1981.05
5		5	4	1988.83
6		4	3	1996.03
7		3	2	2002.83
8				2006.47
9		2	1	2009.86
10				2013.16
11		1	0	2020.17
12		0	1	2027.37
13		1	2	2034.75
14		2	3	2042.46
15				2047.85
16		3	4	2050.26
17		4	5	2057.41
18		5	6	2065.55
19		6	7	2073.49
20		7	8	2080.43
21		8	9	2088.43
22		9	10	2095.96
23	2218.0	4	3	2207.69
24		3	2	2210.67
25		2	1	2213.18
26		1	0	2216.25
27		0	1	2218.95
28		1	2	2221.92
29		2	3	2224.20
30		3	4	2226.73
31		4	5	2229.56
32		5	6	2232.42
33		6	7	2234.76
34	2277.1	8	7	2249.63
35		7	6	2253.67
36		6	5	2257.38
37		5	4	2260.95
38		4	3	2264.13
39		3	2	2267.71
40		2	1	2271.21
41		1	0	2274.98
42		0	1	2278.60
43		1	2	2281.70
44		2	3	2286.23
45		3	4	2289.48
46		4	5	2293.91
47		5	6	2297.41
48		6	7	2300.91
49		7	8	2304.43
50		8	9	2307.75
51		9	10	2310.12
52		10	11	2311.94
53		11	12	2313.93
54		12	13	2316.18
55		13	14	2318.18
		J''	J'	
56	$\nu_3+\nu_6$	29	28	2319.86
57		28	27	2321.42
58		27	26	2323.17
59		26	25	2325.36
60		25	24	2327.34

TABLE V. Wave numbers of lines shown in Fig. 6.

Line No.	Band	J''	J'	ν (cm^{-1})
1	$\nu_3+\nu_6$	29	28	2319.87
2		28	27	2322.16
3		27	26	2324.08
4		26	25	2326.13
5		25	24	2328.08
6		24	23	2330.12
7		23	22	2331.98
8		22	21	2333.92
9		21	20	2335.77
10		20	19	2337.48
11		19	18	2339.28
12		18	17	2341.04
13		17	16	2342.76
14		16	15	2344.55
15		15	14	2346.21
16		14	13	2348.02
17		13	12	2349.55
18		12	11	2351.29
19		11	10	2353.00
20		10	9	2354.38
21		9	8	2355.92
22		8	7	2357.50
23		7	6	2358.92
24		6	5	2360.26
25		5	4	2362.05
26		0	0	2368.59
27		0	1	2370.25
28		1	2	2371.33
29		2	3	2372.42
30		3	4	2373.77
31		4	5	2375.11
32		5	6	2376.32
33		6	7	2377.39
34		7	8	2378.57
35		8	9	2379.72
36		9	10	2380.76
37		10	11	2381.76
38		11	12	2382.70
39		12	13	2383.69
40		13	14	2384.72
41		14	15	2385.56
42		15	16	2386.43
43		16	17	2387.33
44		17	18	2388.10
45		18	19	2389.00
46		19	20	2389.88
47		20	21	2390.60

In band ν_7 (Fig. 9) the ^PQ and ^RQ absorption maxima are superposed on an unresolved background which has maxima of intensity at about 2970 and 3005 cm^{-1} and a minimum at about 2995 cm^{-1}. The maximum of background absorption at about 2970 cm^{-1} is evidently due at least in part to overlapping of the unresolved R branch of the $||$ band ν_{5b} centered at 2955 cm^{-1}. That at about 3005 cm^{-1} doubtless corresponds to the absorption maximum observed under considerably lower dispersion by Bartholomé and Karweil[16] and attributed by them to the Q branch of a $||$ band, a suggestion maintained by subse-

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[16] E. Bartholomé and J. Karweil, Zeits. f. physik. Chemie **B39**, 1 (1938).

TABLE VI. Wave numbers of lines shown in Fig. 7.

Line No.	Band	K''	K'	ν (cm^{-1})
1	2653			2598.28
2				2603.26
3				2608.25
4				2612.84
5				2618.12
6				2622.75
7				2626.52
8				2627.78
9				2630.45
10				2632.55
11				2634.40
12				2637.89
13				2641.72
14				2645.70
15				2650.77
16				2656.62
17				2662.05
18				2663.99
19				2667.10
20				2671.79
21				2676.31
22				2679.04
23				2680.30
24				2682.79
25				2686.87
26				2689.15
27				2691.51
28				2692.81
29				2696.44
30				2700.21
31				2703.49
32				2707.26
		J''	J'	
33	$\nu_2+\nu_6$	28	27	2708.43
34		27	26	2710.55

quent authors.[3] Figure 9 shows no trace of such a Q branch, the width of the intensity maximum being considerably too large to be explained thus. This figure suggests rather that the background absorption, while caused in part by the R branch of ν_{5b} is otherwise due entirely to the sub-band lines of ν_7 itself. Because the spacing of the Q lines of ν_7 is about 2.5 times $2B_0$, these sub-band lines should form an unresolved background and not give rise to minor peaks as in ν_9.

The intensity distribution of background absorption due to unresolved sub-bands in ⊥ bands of symmetric top molecules has been treated by Gerhard and Dennison.[17] Though their computations are not strictly applicable since they did not take account of the then unknown phenomenon of rotation-vibration interaction in degenerate vibrational states, it happens, as will be shown below, that in level ν_7 the vibrational angular momentum is quite small so that one can compare qualitatively the background intensity distribution of band ν_7 with that computed according to these authors for a value of $\beta=(\Delta\nu_\perp/\Delta\nu_{||})$ of about 2.5. The computed intensity distribution of background absorption for such a value of β shows a minimum at the band center flanked by two maxima. Though the calculations do not show a larger maximum of background under the ^RQ branch than under the ^PQ branch this is to be expected from the intensity distribution of the minor peaks of band ν_9. These considerations indicate that the origin of ν_7 lies near the minimum of background absorption. The assignment of K values given in Table VIII is based on the assumption that the origin lies between lines 59 and 60. This assignment is considerably less certain than that of band ν_9 and the K values may well be in error by ±1.

Figures 3a and 3b show that band ν_8 (at least in part) consists of 20 major peaks (lines 78 to 97) extending from 1452 to 1536 cm^{-1} superposed on a background of which much fine structure is resolved. The spacings of major peaks throughout the region above 1493 cm^{-1} (line 89) are evidently highly regular and have an average value almost exactly four times $2B_0$. Hence the existence of three minor peaks between each adjacent pair of major peaks in this region is readily explained in the same manner as the existence of the minor peaks in band ν_9. However, the fine structure of absorption below 1493 cm^{-1} is highly anomalous, particularly between lines 82 and 89 and on the low frequency side of line 78. In the former region there appear to be some "extra" Q lines as a plot of the measured wave numbers of the 20 major peaks *vs.* their ordinal number indicates. In the latter region several major peaks appear to be missing, for the background absorption just below line 78 is nearly maximum and ν_8 in Fig. 3b should show a few more recognizable Q lines than ν_9 in Fig. 2b since the maximum overall absorption in Fig. 3b is greater than in Fig. 2b. Furthermore, below peak 73 and extending down at least to peak 45 there is a long series of minor peaks with a regular spacing of 1.17 cm^{-1} which certainly do not belong to || band ν_6.

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

TABLE VII. Wave numbers of lines shown in Fig. 8.

Line No.	Band	K''	K'	ν (cm^{-1})
1	2653			2696.40
2				2699.91
3				2703.38
4				2707.22
		J''	J'	
5	$\nu_2+\nu_6$	28	27	2708.45
6		27	26	2710.40
7		26	25	2712.07
8		25	24	2714.01
9		24	23	2715.82
10		23	22	2717.52
11		22	21	2719.40
12		21	20	2721.35
13		20	19	2722.95
14		19	18	2724.76
15		18	17	2726.48
16		17	16	2728.12
17		16	15	2729.70
18		15	14	2731.33
19		14	13	2733.04
20		13	12	2734.63
21		12	11	2736.11
22		11	10	2737.69
23		10	9	2739.20
24		9	8	2740.80
25		8	7	2742.13
26		7	6	2743.64
27		6	5	2745.08
28		5	4	2746.65
29		4	3	2747.95
30		3	2	2749.37
31		2	1	2750.52
32		0	0	2753.35
33		1	2	2755.71
34		2	3	2757.17
35		3	4	2758.46
36		4	5	2759.66
37		5	6	2760.90
38		6	7	2762.01
39		7	8	2763.20
40		8	9	2764.47
41		9	10	2765.49
42		10	11	2766.72
43		11	12	2767.69
44		12	13	2768.74
45		13	14	2769.68
46		14	15	2770.71
47		15	16	2771.74
48		16	17	2772.80
49		17	18	2773.76
50		18	19	2774.73
51		19	20	2775.54
52		20	21	2776.35
53		21	22	2777.19
54		22	23	2777.88
55		23	24	2779.03
56	2800			2780.55
57				2781.30
58				2782.02
59				2783.38
60				2784.81
61				2786.29
62				2787.83
63				2789.24
64				2790.71
65				2792.16
66				2793.83
67				2795.05
68				2796.46
69				2797.81
70				2799.40
71				2801.08
72				2802.23
73				2803.61
74				2805.07
75				2806.66
76				2808.12
77				2809.56
78				2810.95

The fine structure in the neighborhood of line 85 strongly suggests that some rotational levels of vibrational state ν_8 with low K values are perturbed by levels of another nearly coincident vibrational state of C_2H_6. This perturbation, because of its limited extent and the fact that major peaks are recognizable though their intensities and positions are anomalous, appears to be a "rotational" perturbation of the Fermi type in which interacting levels have the same K value ($\Delta K=0$) and the elements of the energy matrix are independent of K or J. Furthermore, it would appear that the difference in energy of unperturbed levels of the two states with the same J and K values, which difference, for any given value of J, is a linear function of K with slope proportional to the difference in ζ values of the two states, passes through zero at a low value of K, the levels of state ν_8 being lower for smaller values of K.[18]

The fine structure on the low frequency side of line 78 indicates that those $-l$ levels of ν_8 with K values greater than that corresponding to line 78 are also strongly perturbed by levels of another vibrational state of C_2H_6. This perturbation appears to be of the Coriolis type for which $\Delta K=\pm 1$, and for which a dependence of the energy matrix on J as well as K is to be expected, since, in this region, major peaks are not recognizable, though broad intensity maxima, the intervals between which are about equal to

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[18] It is assumed here that the energies of each set of levels are represented by a single-valued function of K in which K is taken positive for $+l$ levels (transitions to which give rise to ^RQ lines) and negative for $-l$ levels (cf. reference 2, p. 403).

TABLE VIII. Wave numbers of lines shown in Fig. 9.

Line No.	Band	K''	K'	ν (cm^{-1})
1	2860			2847.69
2				2849.75
3				2851.19
4				2853.06
5				2856.57
6				2858.16
7				2859.58
8				2861.33
9				2863.04
10				2864.60
11				2866.12
12				2867.93
		J''	J'	
13	ν_{5a}	18	17	2875.63
14		17	16	2876.80
15		16	15	2877.78
16		15	14	2878.88
17		14	13	2879.60
18		13	12	2880.68
19		12	11	2881.83
20		11	10	2882.69
21		10	9	2884.02
22		9	8	2885.01
23		8	7	2886.00
24		7	6	2886.95
25		6	5	2888.09
26		5	4	2889.23
27		4	3	2890.62
28		3	2	2891.78
29		2	1	2893.27
30		0	0	2895.60
31		1	2	2898.34
32		2	3	2899.84
33		3	4	2901.31
34		4	5	2902.69
35		5	6	2904.16
36		6	7	2905.89
37		7	8	2907.52
38		8	9	2909.13
39		9	10	2910.71
40		10	11	2912.33
41		11	12	2913.91
42		12	13	2915.48
43		13	14	2917.20
44		14	15	2918.76
45		15	16	2920.49
46	ν_{5b}	0	0	2954.05

TABLE VIII.—*Continued.*

Line No.	Band	K''	K'	ν (cm^{-1})
47	ν_7	12	11	2958.35
48		11	10	2961.36
49		10	9	2964.22
50		9	8	2966.87
51				2967.77
52		8	7	2970.19
53		7	6	2973.49
54		6	5	2976.98
55		5	4	2980.00
56		4	3	2983.44
57		3	2	2986.79
58		2	1	2990.09
59		1	0	2993.57
60		0	1	2996.88
61		1	2	3000.49
62		2	3	3003.79
63		3	4	3006.84
64		4	5	3010.38
65		5	6	3013.81
66		6	7	3017.28
67		7	8	3020.83
68		8	9	3023.93
69		9	10	3027.60
70		10	11	3030.52

those between the regularly spaced major peaks, are visible.

The fact that serious structural irregularities are exhibited by only part of band ν_8 leads to the conclusion that the perturbations are of the "rotational" type and that the perturbing state or states must lie very close to state ν_8. A review of our present knowledge of the locations of the 12 fundamental vibrational states of C_2H_6 shows beyond reasonable doubt that the only states sufficiently close to ν_8 to cause such perturbations are ν_{11} and $\nu_{12}+\nu_4$. Of these only $\nu_{12}+\nu_4$ is of the same species as ν_8 and is thus the only one which could interact with ν_8 by means of a Fermi perturbation. According to Jahn's rule,[14] if C_2H_6 belongs to point group D_{3h}, a Coriolis perturbation in which $\Delta K = \pm 1$ is possible between ν_8 and ν_{11} but none is possible between ν_8 and $\nu_{12}+\nu_4$, while, if C_2H_6 belongs to D_{3d}, a Coriolis perturbation in which $\Delta K = 0$ as well as one in which $\Delta K = \pm 1$ is possible between ν_8 and $\nu_{12}+\nu_4$ but none is possible between ν_8 and ν_{11}.

Now Nielsen[19] has shown that to second order of approximation, wherein vibrational functions are assumed to be of the harmonic oscillator variety, Coriolis perturbations can occur between two vibrational states only if the difference between the quantum numbers of each vibration in the two states is unity for two vibrations and zero for all others. Thus, to this approximation, state ν_8 can be perturbed as a result of Coriolis forces only by ν_{11} and hence only if C_2H_6 belongs to D_{3h}. However, as Howard[14] has pointed out, a Coriolis perturbation between ν_8 and ν_{11} should be vanishingly small because in executing these two vibrations each atom moves in very nearly the same straight line. Moreover, as will be shown in the Section V below, the ζ values of states ν_8 and ν_{11} are very probably so nearly

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[19] H. H. Nielsen, Phys. Rev. 60, 794 (1941).

equal that if a Coriolis perturbation occurred between them effecting strongly the $-l$ levels of ν_8 it should also effect strongly the $+l$ levels of ν_8. Further evidence that a perturbation of ν_8 by ν_{11} does not exist is provided by the regular structure of a band at 1747.1 cm^{-1} for which, as we shall see in Section V, the only reasonable assignment is $\nu_{11}+\nu_4$. The assumption that a perturbation between ν_8 and ν_{11} exists would almost certainly require a nearly equally strong perturbation between states $\nu_{11}+\nu_4$ and $\nu_8+\nu_4$.

An attempt to obtain a quantitative explanation of the irregular structure of band ν_8 on the assumption that state ν_8 is perturbed in both a Fermi and a Coriolis perturbation by state $\nu_{12}+\nu_4$ (and hence on the assumption that C_2H_6 belongs to D_{3d}) has been recently undertaken by Mr. Gordon Hansen of the University of Michigan under Professor Dennison's direction. These considerations have shown that a small Coriolis coupling between rotational levels of ν_8 and $\nu_{12}+\nu_4$ whose K values differ by unity may occur in third order of approximation but that none can occur between levels of the same K value in any approximation. A good account of the relative intensities of both the major and minor peaks above line 89 in Fig. 3b has been given which has led to the adoption of the K values given in Table II for these lines and shows beyond any reasonable doubt that not only these K values but also the explanation of the minor peaks above line 89 given above are correct. Furthermore, a good account of the relative intensities and positions of all the numbered peaks above line 78 has been obtained on the assumptions: (1) of resonable values of ζ for states ν_8 and $\nu_{12}+\nu_4$; (2) that state $\nu_{12}+\nu_4$ lies about 8 cm^{-1} above state ν_8; and (3) that in the absence of the perturbations considered the wave numbers of the lines of band ν_8 would be given (in cm^{-1}) by the formula

$$\nu_8(m)=1475.84+5.550m-0.0125m^2, \quad (6)$$

where $m \equiv K''$ for ^RQ lines and $-K''$ for ^PQ lines.

From the theoretical formula for the Q lines of a $\perp$ band of a symmetric top molecule, namely[20]

$$\nu(m)=\nu_0+[(A'-B')-2A'\zeta] +2[(A'-B')-A'\zeta]m +[(A'-B')-(A_0-B_0)]m^2, \quad (7)$$

where again $m \equiv K''$ for ^RQ lines and $-K''$ for ^PQ lines, it is evident that the band origin (ν_0) is given by

$$\nu_0=\nu(m=-1)+(A_0-B_0), \quad (8)$$

that the mean line spacing ($\Delta\nu$), which we shall define as $(d\nu/dm)_{m=-1}$, is given by

$$\Delta\nu \equiv (d\nu/dm)_{m=-1}=2[(A_0-B_0)-A'\zeta], \quad (9)$$

and therefore that

$$A_0-B_0=\tfrac{1}{6}(\Delta\nu_7+\Delta\nu_8+\Delta\nu_9) +\tfrac{1}{3}(A_7\zeta_7+A_8\zeta_8+A_9\zeta_9). \quad (10)$$

The latter relation allows us to determine values of the A's and hence of the ν_0's and ζ's in the fairly good approximation that the dependences

TABLE IX. Wave numbers of lines shown in Fig. 10.

Line No.	Band	J''	J'	ν (cm^{-1})
1	‖?	0	0	3116.71
		K''	K'	
2	⊥?			3177.00
3				3179.68
4				3183.71
5	⊥?			3207.00
6				3209.26
7				3211.80
8				3215.87
9				3218.34
10				3220.59
11				3224.59
12				3228.14
13				3230.82
14	3257.8	7	6	3240.30
15		6	5	3242.58
16		5	4	3245.26
17		4	3	3247.45
18		3	2	3250.13
19		2	1	3252.88
20		1	0	3255.90
21		0	1	3258.85
22		1	2	3261.82
23		2	3	3264.69
24		3	4	3267.86
25		4	5	3271.60
26		5	6	3274.26
27		6	7	3277.28
28		7	8	3280.58
29		8	9	3283.92
30		9	10	3287.40
		J''	J'	
31	‖?	0	0	3396.15

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[20] Cf. reference 2, p. 429 and footnote 9.

TABLE X. Wave numbers of lines shown in Fig. 11.

Line No.	Band	K''	K'	ν (cm^{-1})
1	⊥?			4073.85
2				4098.07
3				4120.57
4				4127.05
5				4130.67
6				4132.75
7				4134.42
8				4137.04
		J''	J'	
9	‖?	0	0	4143.27
		K''	K'	
10	4178.9	5	4	4147.74
11				4150.30
12		4	3	4155.10
13				4156.51
14		3	2	4163.27
15		2	1	4170.38
16		1	0	4176.48
17		0	1	4183.88
18		1	2	4190.86
19		2	3	4197.79
20		3	4	4204.71
21		4	5	4211.14
22		5	6	4219.49
23		6	7	4226.50
24		7	8	4233.74
25		8	9	4240.89
		J''	J'	
26	‖?	0	0	4274.35
27	‖?	0	0	4292.53
		K''	K'	
28	4334.1	4	3	4323.26
29		3	2	4326.37
30		2	1	4329.45
31		1	0	4331.95
32		0	1	4334.84
33		1	2	4337.68
34		2	3	4341.24
35		3	4	4344.95
36		4	5	4347.62
37		5	6	4350.28
38		6	7	4353.94
39	4416.7	6	5	4394.87
40		5	4	4498.86
41		4	3	4401.85
42		3	2	4404.54
43		2	1	4409.84
44		1	0	4413.95
45		0	1	4419.05
46		1	2	4424.44
47		2	3	4427.41
48		3	4	4430.69
49		4	5	4434.45
50		5	6	4437.68
51		6	7	4442.59
52		7	8	4447.86

of (1) the ζ's and (2) the A's on vibrational quantum numbers are neglected: i.e., in the approximation (1) that the ζ-sum rule, shown by Howard[14] to be

$$\zeta_7+\zeta_8+\zeta_9=0 \tag{11}$$

is valid and (2) that $A_7=A_8=A_9=A_0\equiv A$. Thus in this approximation we may write in place of (8), (9) and (10) the relations:

$$\nu_0=\nu(m=-1)+(A-B_0), \tag{8a}$$

$$\Delta\nu\equiv(d\nu/dm)_{m=-1}=2[(A-B_0)-A\zeta], \tag{9a}$$

$$A-B_0=\tfrac{1}{6}(\Delta\nu_7+\Delta\nu_8+\Delta\nu_9). \tag{10a}$$

Values of $[(A'-B')-(A_0-B_0)]$ and $\Delta\nu$ obtained from relation (6) for band ν_8 and similar empirical relations (wherein the coefficients were determined by least squares) for bands ν_7 and ν_9 as well as values of $A-B_0$, A, I_A, ν_0 and ζ obtained from the empirical coefficients with the aid of (8a), (9a) and (10a) are given in Table XIII. Errors given for $\Delta\nu$ and $[(A'-B')-(A_0-B_0)]$ for ν_7 and ν_9 are probable errors computed from the data. Those given for ν_0 include an assumed probable error of 0.06 cm^{-1} for $A-B_0$ in addition to the same allowances made in estimating the errors of values of the origins of the ‖ bands (Table XII). The value of $\Delta\nu_8$ obtained by Hansen is appreciably larger than the mean spacing of lines 89–97 of band ν_8 on which the value of I_A given in reference 2 was based. Hence the value of I_A given here is appreciably less than that given in reference 2 and yields, together with the value of I_{B0} in Table XII what are perhaps more reasonable relationships between the three structural parameters of the C_2H_6 molecule than did the previously determined value. Thus with the present values of I_{B0} and I_A, if we take C−C=1.55A as determined by Pauling and Brockway,[21] we obtain C−H=1.098A and ∢HCC=109° 3′. The rather large negative values of $[(A'-B')-(A_0-B_0)]$ for ν_8 also obtained by Hansen may possibly be due to a second Coriolis perturbation of state ν_8 of the type for which $\Delta K=0$ by a state lying above ν_8.

V. COMBINATION ⊥ BANDS

It appears from Figs. 4–12 that nearly all the fine structures in the regions of weaker absorption not so far discussed correspond to combina-

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[21] L. Pauling and L. O. Brockway, Jr., J. Am. Chem. Soc. 59, 1223 (1937).

tion bands of the ⊥ type, there being in addition a few scattered peaks, some of which are doubtless Q branches of combination || bands. For each group of lines which apparently comprises a ⊥ band values of mean line spacing ($\Delta\nu$), band origin (ν_0) and ζ are given in Table XIV. These were determined in the same fashion as for the fundamental ⊥ bands ν_7 and ν_9 except that the "regression" line on a graph of wave number *vs.* ordinal number of the lines of each group was determined "by eye" instead of by least squares. The points on each such graph were found to fit on a straight line within experimental uncertainty except those for the group of lines near 2653 cm^{-1} where the structure is so irregular (even at low temperature) that no single value of $\Delta\nu$ can be determined and those for the groups at 3257.8 and 5950.7 cm^{-1}. In the latter two cases the points fit on curved lines indicating large positive values of $[(A'-B')-(A_0-B_0)]$ for these bands. The assignment of K values for each combination ⊥ band was guided by the assumption that, as in the case of band ν_9, about 3/5 of the observed lines are ^RQ lines and about 2/5 are ^PQ lines and by evidence in the spectrograms of alternating intensities, which evidence, however, is fairly definite only in the case of the band at 3257.8 cm^{-1}. Thus some values of ν_0 may be in error by one or two line intervals.

A survey of information concerning the twelve fundamental vibrational states of C_2H_6 as given in reference 3 leads to the conclusion that the only reasonable assignment for the band at 1747.1 cm^{-1} is $\nu_{11}+\nu_4$. This assignment is supported by the fact that $\Delta\nu$ for this band is nearly the same as for band ν_8, as $\Delta\nu$ of band $\nu_{11}+\nu_4$ should be, since the ζ values of states ν_8 and ν_{11} as well as their frequencies should be approximately equal.[22] Also, the most reasonable assignment for the band at 3257.8 cm^{-1} is ν_4+a component of the multiple level ν_{10} (probably ν_{10b})[23] since there is no other binary combination in the neighborhood and such a combination should have roughly the same spacing as band ν_7.

TABLE XI. Wave numbers of lines shown in Fig. 12.

Line No.	Band	J''	J'	ν (cm^{-1})
1	||?			5904.35
2		0	0	5916.28
		K''	K'	
3	5950.7	6	5	5924.50
4		5	4	5928.65
5		4	3	5932.12
6		3	2	5939.49
7		2	1	5943.76
8		1	0	5948.73
9		0	1	5954.13
10		1	2	5959.75
11		2	3	5965.82
12		3	4	5972.60
13		4	5	5980.23
14		5	6	5986.50
15		6	7	5994.73

Subject to the validities of these two assignments and of the values of the two band origins, we may combine the latter with values of ν_{11} and ν_{10} obtained from Raman data to determine a value of ν_4. From Raman investigations of C_2H_6 gas it is fairly well established[24] that $\nu_{11}=1460$ cm^{-1}, whence we obtain $\nu_4=287.1$ cm^{-1}, while from Raman spectra of liquid C_2H_6[25] it appears that $\nu_{10b}=2963$ cm^{-1} from which we obtain $\nu_4=294.8$ cm^{-1}. In Fig. 1 the value $\nu_4=290$ cm^{-1} has been adopted as being not inconsistent with and perhaps somewhat more reliable than the value $\nu_4=275$ cm^{-1} determined from heat capacity data.[26] From the former value

TABLE XII. Results obtained from || bands.

State	ν_0 (cm^{-1})	$B-B_0$ (cm^{-1})	B (cm^{-1})	D (10^{-7} cm^{-1})	I_B* (10^{-40} g cm^2)
ν_{5a}	2895.66 ±0.16	0.0176 ±0.0006	0.6801 ±0.0006	165 ±28	41.14 ±0.04
$\nu_2+\nu_6$	2753.39 ±0.13	−0.01031 ±0.00006	0.65227 ±0.00014	—	42.901 ±0.011
$\nu_3+\nu_6$	2368.88 ±0.10	−0.01321 ±0.00010	0.64937 ±0.00016	—	43.093 ±0.012
ν_6	1379.14 ±0.07	−0.00722 ±0.00005	0.65536 ±0.00014	—	42.699 ±0.011
Ground	0	0	0.66258 ±0.00013	6.00†	42.234 ±0.011

* $h=(6.6234\pm0.0011)\times10^{-27}$ erg sec.
† Calculated.

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[22] The ζ value of a combination state and hence $\Delta\nu$ of the corresponding band are independent of what nondegenerate vibrations are excited in the state. (Cf. reference 30 below.)

[23] It is possible that the group of lines 5 to 13 of Fig. 10 near 3217 cm^{-1} whose spacings are rather irregular, but roughly the same as for the band at 3257.8 cm^{-1}, corresponds to a combination of ν_4 and another component of ν_{10}.

[24] S. Bhagavantam, Ind. J. Phys. 6, 596 (1931) and B. L. Crawford, Jr., W. H. Avery and J. W. Linnett, J. Chem. Phys. 6, 682 (1938).

[25] G. Glockler and M. M. Renfrew, J. Chem. Phys. 6, 295 (1938).

[26] G. B. Kistiakowsky, J. R. Lacher and F. Stitt, J. Chem. Phys. 7, 289 (1939).

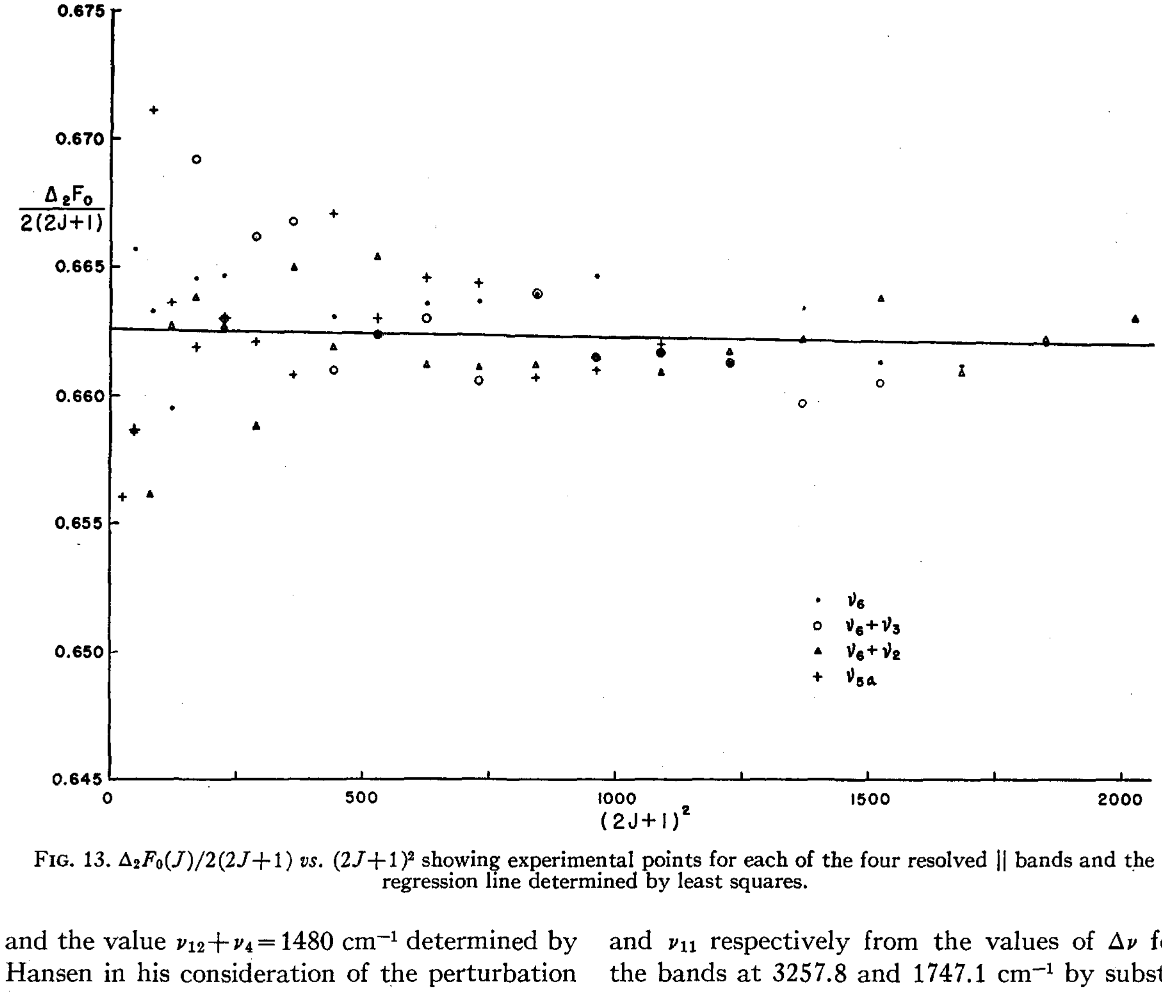

FIG. 13. $\Delta_2F_0(J)/2(2J+1)$ vs. $(2J+1)^2$ showing experimental points for each of the four resolved || bands and the regression line determined by least squares.

and the value $\nu_{12}+\nu_4=1480$ cm^{-1} determined by Hansen in his consideration of the perturbation of state ν_8 the value $\nu_{12}=1190$ cm^{-1} has also been adopted here. This is in fairly good agreement with the value $\nu_{12}=1170$ cm^{-1} determined by Stitt.[27]

Subject also to the validities of these assignments, we may determine ζ values for states ν_{10} and ν_{11} respectively from the values of $\Delta\nu$ for the bands at 3257.8 and 1747.1 cm^{-1} by substituting these in Eq. (9a). ζ_{12} may then be obtained from ζ_{10} and ζ_{11} by use of the ζ-sum rule for states ν_{10}, ν_{11} and ν_{12}, which may readily be shown to be[28]

$$\zeta_{10}+\zeta_{11}+\zeta_{12}=I_A/2I_{B0}=B_0/2A=0.128. \quad (12)$$

TABLE XIII. Results obtained from fundamental ⊥ bands.

Band	ν_0 (cm^{-1})	$\Delta\nu$ (cm^{-1})	ζ	$[(A'-B')-(A_0-B_0)]$ (cm^{-1})
ν_7	2995.5 ±0.2	3.362 ±0.006	0.095	0.0021 ±0.0009
ν_8	1472.2 ±0.1	5.563	-0.331	-0.0125
ν_9	821.52 ±0.07	2.6285 ±0.0012	0.236	0.00213 ±0.00015
$A-B_0=1.926$ cm^{-1}; $A=2.588$ cm^{-1}; $I_A=10.81\times10^{-40}$ g cm^2				

The ζ values thus obtained together with the present best estimates of the wave numbers of states ν_{10}, ν_{11} and ν_{12} are given in Table XV. Also given are values of $\Delta\nu$ for bands[29] ν_{10}, ν_{11} and ν_{12}. As is evident from Eqs. (9a), (10a) and (12), $\Delta\nu_{12}$ is given in terms of the experimentally measured quantities $\Delta\nu_7-\Delta\nu_{11}$ and B_0 by the equation:

$$\Delta\nu_{12}=\Delta\nu_7+\Delta\nu_8+\Delta\nu_9-B_0-\Delta\nu_{10}-\Delta\nu_{11}. \quad (13)$$

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[27] F. Stitt, J. Chem. Phys. 7, 297 (1939).

[28] Herzberg (reference 2, p. 405) citing Howard (see reference 14), who does not consider this sum, erroneously states that this sum is zero.

[29] We speak in this section of the $\Delta\nu$ of a band even though such a band is inactive.

The value of ζ_{12} in Table XV and that of ζ_8 in Table XIII are approximately equal to the values employed by Hansen in his considerations of the perturbations of ν_8 by $\nu_{12}+\nu_4$.

In an attempt to determine reasonable assignments for as many as possible of the observed combination $\perp$ bands and hence possibly to obtain more evidence as to the point group to which C_2H_6 belongs, two charts, Fig. 14a for D_{3d} and Fig. 14b for D_{3h}, have been prepared in which a $\perp$ band is represented by a point whose abscissa gives the origin (ν_0) and whose ordinate gives the mean line spacing ($\Delta\nu$) of the band. The observed bands are represented by crosses in each chart while the circles represent possible combination bands. In the region below 3500 cm^{-1} all possible active binary and ternary combinations exclusive of difference bands with lower states higher than ν_4 are represented, while between 3500 and 6000 cm^{-1} all possible active binary combinations are represented. The wave numbers of the possible combinations were determined as simple sums or differences of those for the fundamental states given in Fig. 1. Their mean spacings were determined from the values of $\Delta\nu$ for the fundamental bands given in Tables XIII and XV with the aid of the rules given by Johnston and Dennison.[30] These authors showed that, for molecules with three-fold axes such as the methyl halides and ethane, the appropriate ζ value for any state in which one and only one degenerate vibration ν_i is either singly or triply excited is ζ_i. Hence the line spacing of the corresponding band is $\Delta\nu_i$. They also showed that, for such molecules, the appropriate ζ values, for a state in which one and only one degenerate vibration ν_i is doubly excited and for a state in which two and only two degenerate vibrations ν_i and ν_j are each singly excited, are respectively $-2\zeta_i$ and $-(\zeta_i+\zeta_j)$. Hence the line spacings of the corresponding bands are, according to Eqs. (9a) and (10a),

$$\Delta\nu(2\nu_i)=\Delta\nu_7+\Delta\nu_8+\Delta\nu_9-2\Delta\nu_i, \tag{14}$$

and

$$\Delta\nu(\nu_i+\nu_j)=\Delta\nu_7+\Delta\nu_8+\Delta\nu_9-\Delta\nu_i-\Delta\nu_j. \tag{15}$$

TABLE XIV. Results obtained from combination $\perp$ bands.

ν_0 (cm^{-1})	$\Delta\nu$ (cm^{-1})	ζ
1747.1	5.69	−0.354
2021.6	7.64	−0.732
2218.0	2.70	+0.222
2277.1	3.65	+0.039
2653	?	?
2800	1.46	+0.463
2860	1.63	+0.429
3257.8	3.00	+0.164
4178.9	7.02	−0.612
4334.1	3.09	+0.147
4416.7	4.05	−0.039
5950.7	5.03	−0.228

It is evident from Fig. 14 that it is not possible on the basis of either point group to account well for any of the observed combination $\perp$ bands, except perhaps that at 2218.0 cm^{-1} and, of course, those at 1747.1 and 3257.8 cm^{-1}, without revising or adding to the assumptions that have gone into the determinations of the values of ν_0 or $\Delta\nu$ or both of some of the possible combination bands. This is not very surprising in view of all the possibilities for perturbations of either fundamental or combination states and for appreciable dependence of some ζ values on vibrational quantum numbers which have been neglected. Moreover, it appears that no less reasonable additions to or revisions of the assumptions on the basis of D_{3h} than on the basis of D_{3d} are required to account well for any of the observed bands with the outstanding exception of that at 2021.6 cm^{-1}.

To account for the band at 2021.6 cm^{-1} on the basis of D_{3h}, one must assume either: (1) that this band is due to an impurity, which seems most unlikely since it is evidently a $\perp$ band of a symmetric top molecule and does not correspond to a strong band of any likely impurity and since absorption in this region by C_2H_6 gas has also been observed by Avery and Ellis;[31] or

TABLE XV. Values of ν_0, $\Delta\nu$ and ζ for inactive fundamental $\perp$ bands (see reference 29).

Band	ν_0 (cm^{-1})	$\Delta\nu$ (cm^{-1})	ζ
ν_{10}	2963 2939.5	3.00	0.164
ν_{11}	1460	5.69	−0.354
ν_{12}	1190	2.20	0.318

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[30] M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

[31] W. H. Avery and C. F. Ellis, J. Chem. Phys. **10**, 10 (1942).

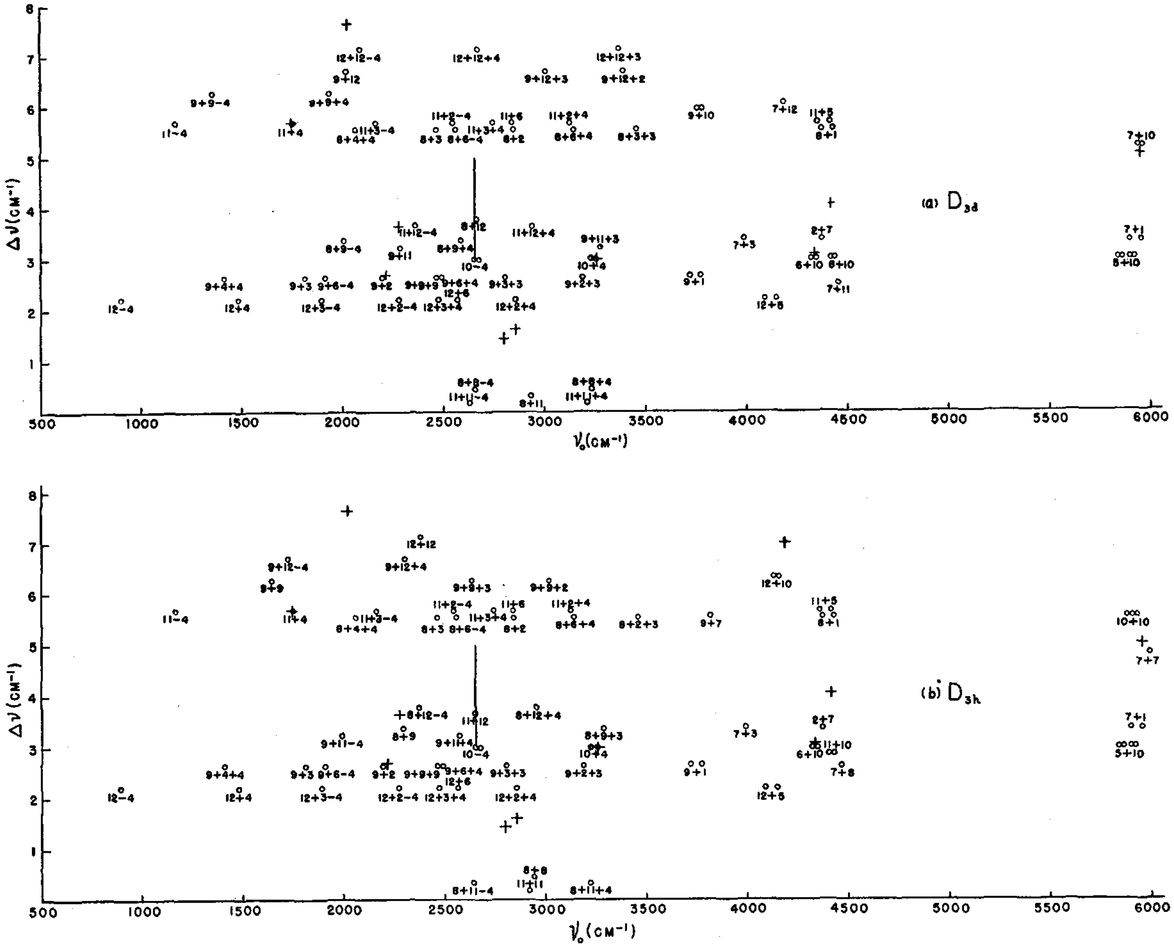

FIG. 14. Mean line spacing ($\Delta\nu$) *vs.* band origin (ν_0) for combination ⊥ bands. Crosses represent observed bands, except in the case of the band near 2653 cm^{-1} where a vertical line is used because $\Delta\nu$ for this band is uncertain, while circles represent possible active combination bands according as C_2H_6 belongs (a) to D_{3d} or (b) to D_{3h}. All possible binary and ternary combinations below 3500 cm^{-1} whose lower states are not higher than ν_4 are represented, while between 3500 and 6000 cm^{-1} all possible binary combinations are shown. Combinations involving ν_1, ν_5 and ν_{10} are represented by multiple points. Combination $\nu_{12}+\nu_3+\nu_4$ is represented by 12+3+4, etc.

(2) that this band is to be assigned to $2\nu_{12}$, which would lead to the very improbable conclusion that $\nu_{12}=1010$ cm^{-1}; or (3) that it is to be assigned either to $\nu_9+\nu_{12}+\nu_4$ or $\nu_9+\nu_{12}-\nu_4$, either of which assumptions would require an even less acceptable value of ν_{12}; or (4) that it is to be assigned to some combination such as $\nu_8+2\nu_4$ or $\nu_9+\nu_{11}-\nu_4$, for none of which could the spacing conceivably be as great as 7.64 cm^{-1}. On the other hand this band can be accounted for on the basis of D_{3d} if one makes a far less drastic assumption. Thus, as is perhaps most reasonable, one may assign this band as $\nu_9+\nu_{12}$ and assume that the discrepancy in $\Delta\nu$ is due to the fact that state ν_{10b} is perturbed or that the band at 3257.8 cm^{-1} has been wrongly assigned so that the true value of $\Delta\nu_{10}$ is greater by about 1 cm^{-1} than the value in Table XV. Alternatively we might assign this band as $2\nu_{12}-\nu_4$ and assume the value of $\Delta\nu_{10}$ in Table XV to be low by about 0.25 cm^{-1}, though this assignment is less likely because $2\nu_{12}-\nu_4$ is a ternary difference band.

It is perhaps significant that, if we do assume the staggered configuration for C_2H_6 and also postulate that the value of $\Delta\nu_{10}$ in Table XV is low by about 1 cm^{-1}, then not only may we assign the band at 2021.6 as $\nu_9+\nu_{12}$ but we may also assign that at 4178.9 cm^{-1} as $\nu_7+\nu_{12}$. Furthermore, on the basis of D_{3d} the group of lines near 2653 cm^{-1} may be assigned as a band $\nu_8+\nu_{12}$ whose structure would be expected to be about as irregular as that of band ν_8 because of a perturbation between states $\nu_8+\nu_{12}$ and $2\nu_{12}+\nu_4$. Thus we could account for three of the bands as combinations of the vibration ν_{12} with each of the three infra-red active vibrations. It should be noted that changing $\Delta\nu_{10}$ affects only the spacings of combination bands involving the vibrations ν_{10} or ν_{12}.

Concerning possible assignments for the remainder of the observed combination $\perp$ bands very little can be said that is not highly speculative. Possibly it is worth while to point out that better agreement between the spacing of the band at 2277.1 cm^{-1} and that of $\nu_9+\nu_{11}$ would result if a value of $\Delta\nu_8$ larger than 5.563 cm^{-1} were adopted.

VI. CONCLUSION

The measurements on the fine structures of the infra-red bands of C_2H_6 described here have yielded an accurate value of the moment of inertia I_{B0} and a fairly reliable value of I_A. They have also yielded some very puzzling results from considerations of which new estimates of the values of the fundamental vibration frequencies ν_4 and ν_{12} and a reliable value of ν_8 have been obtained. Finally, from considerations of the apparent perturbations of state ν_8 and an analysis of combination $\perp$ bands, definite spectroscopic evidence that C_2H_6 belongs to point group D_{3d} has for the first time been obtained. Though not conclusive, this evidence carries considerable weight. Further high resolution work including obtaining of better records of some of the combination bands and a search for bands $\nu_{12}-\nu_4$, near 900 cm^{-1} and $\nu_{11}-\nu_4$ near 1170 cm^{-1} with a cell including a long absorbing path would be very desirable.[32] Also, the results of high resolution measurements on the spectrum of C_2D_6 now being undertaken by Mr. Gordon Hansen at the University of Michigan should prove highly enlightening.

The author wishes to express sincere thanks to Professor John Turkevich for providing the ethane used, to Drs. Van Zandt Williams and William Woodward for much assistance in gathering the data and to Mr. Gordon Hansen and Professor D. M. Dennison for many valuable suggestions concerning the interpretation of the results, particularly those on the band ν_8, on which many of the values obtained depend.

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[32] Very weak absorption near 1216 cm^{-1} has been observed under low dispersion by Avery and Ellis (see reference 31) and attributed by them to band $\nu_{11}-\nu_4$.