

The Infra-Red Absorption Spectra of Ethylene and Tetra-Deutero-Ethylene under High Resolution

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The fine structure of several infra-red absorption bands of C_2H_4 and C_2D_4 have been resolved. From the rotational constants so found, the C—C and C—H distances in this molecule were calculated to be 1.353 and 1.071A, and the H—C—H angle to be $119^\circ 55'$. An assignment of fundamental frequencies has been made which is consistent with the observed data.

INTRODUCTION

THE infra-red and Raman spectra of ethylene have been the subject of several investigations aiming to determine the molecular dimensions and fundamental frequencies of this molecule. Neither of these goals has been completely attained. From measurements in the photographic infra-red it has been possible to find the rotational constants of C_2H_4 . However these do not provide sufficient information to permit the calculation of intermolecular distances without recourse to an estimation of at least one of the dimensions. Similarly, a unique assignment of fundamental frequencies is not possible with the available data.

By investigating the infra-red spectrum of C_2D_4 and re-examining parts of the spectrum of C_2H_4 , new data have now been obtained which yield values for all the molecular dimensions, and also give a definite assignment of fundamental frequencies.

EXPERIMENTAL

The light ethylene (C_2H_4) used in these experiments was obtained from the Ohio Chemical Company. No information concerning the purity of the gas was available but only one region of absorption was found to indicate the presence of an impurity.

From a sample of $C_2D_4Br_2$, supplied by J. M. Delfosse from the University of Louvain, the heavy ethylene (C_2D_4) was prepared by a reaction of the ethylene dibromide with zinc in a solution of methyl alcohol. The gaseous yield was swept slowly through the purifying and collecting system by a stream of helium. A water condenser, a bulb containing $CaCl_2$ and one of

dehydrite, and a dry ice trap effectively removed all traces of water and alcohol. Two liquid-air traps collected the desired product. No evidence of impurities was observed except for two regions of absorption which may be assigned to a hybrid molecule involving a mixture of deuterium and hydrogen.

Throughout the experiments, a grating spectrometer with a rocksalt foreprism was used. This instrument has been described by Barker and Meyer.¹ The addition of a divided circle on the tangent screw makes it possible to turn the grating by steps of 10 seconds of arc. A recent recalibration of the gratings (reported by Gillette and Eyster²) has reduced the absolute errors to the same order of magnitude as the relative errors in locating the line positions, which are about 5 seconds of arc or less. The individual points used for plotting were obtained as the result of several deflections of the galvanometer with and without the gas cell in the beam. The absorption of the NaCl windows has been subtracted. Table I lists the experimental conditions under which the various regions of absorption were studied.

The perpendicular type bands belonging to C_2H_4 at 3.22 and 10.55 μ , which were resolved by Levin and Meyer,³ have been reexamined to obtain the positions of the lines with greater precision so that the spacing, and thus the moment of inertia, could be calculated more certainly. Considerable improvement was gained by using finer gratings, narrower slits, smaller

¹ E. F. Barker and C. F. Meyer, *Trans. Faraday Soc.* **25**, 912 (1929).

² R. H. Gillette and E. H. Eyster, *Phys. Rev.* **56**, 1113 (1939).

³ A. Levin and C. F. Meyer, *J. Opt. Soc. Am.* **16**, 137 (1928).

TABLE I. Experimental conditions used in examining the various regions of absorption.

Gas	Band (μ)	Center (cm^{-1})	Uncertainty (cm^{-1})	Grating (lines per inch)	Interval of reading* (cm^{-1})	Effective slit width (cm^{-1})	Pressure (cm Hg)	Cell length (cm)
C ₂ H ₄	3.22	3105.5	0.2	4800	0.43	1.5	15	6
	3.35	2989.5	0.2	4800	0.22	1.0	15	6
	5.29	1889.6	0.1	4800	0.16	0.63	72	6
	5.66	1766	1.0	2400	0.46	1.5	75	80
	10.05	995	2	2400	0.28, 0.09	0.56	15	6
	10.55	949.20	0.05	2400	0.24, 0.08	0.49	5	6
C ₂ D ₄	2.16	4628.0	0.3	7200	2.10, 0.7	3.2	70	11
	2.23	4478.6	0.9	7200	1.80	2.7	70	11
	2.26	4429.5	0.3	7200	1.80, 0.6	2.7	70	11
	2.59	3862.8	2.2	4800	2.20	2.6	70	11
	2.95	3387.8	0.6	4800	1.70	2.0	70	11
	2.98	3345.3	0.3	4800	1.70, 0.6	2.0	70	11
	3.12	3204.3	1.5	4800	1.5	1.7	70	11
	3.28	3049.0	0.2	4800	1.30, 0.4	1.5	70	11
	4.25	2345	1	4800	0.35	1.2	15	11
	4.54	2200.2	0.1	4800	0.31	0.90	15	11
	6.27	1595.1	0.1	2400	0.75, 0.25	1.05	70	11
	6.68	1495.7	0.1	2400	0.66, 0.22	1.10	35	11
	7.76	1289.1	0.1	2400	0.50, 0.16	0.70	70	11
	9.26	1077.9	0.1	2400	0.10	0.45	12	11
	10.88	919.0	0.1	1200	0.50	1.10	70	11
	13.88	720.00	0.03	2400	0.12	0.48, 0.68	5	11

* Where two values for the interval of readings are reported for the same region, it should be understood that the smaller steps were used only near sharp absorption maxima.

intervals of reading, and a better amplifier. The new results do not disagree seriously with the previous values but are much more consistent. However, due to the increased resolving power, much new detail was found at the longer wave-lengths, where several weak lines were observed between each strong one. In addition, an important band was found for the first time at 10.05μ . It has long been known that an infrared active fundamental should appear near 1000 cm^{-1} . Therefore, for the double purpose of finding this frequency and obtaining more lines belonging to the observed band at 10.55μ , the region was examined with a higher gas pressure in the cell. Figure 1(e) shows definitely the presence of this new band.

In Fig. 1(a) and (b) the data taken at 3.35 and 5.29μ are plotted, each with well-resolved fine structure. Only the envelopes of these parallel bands were obtained by Levin and Meyer, but Smith⁴ has resolved the band at 3.35μ . No atmospheric absorption was encountered except near 5μ , where a few lines due to water vapor were observed. The reported positions of the ethylene lines are quite reliable,

though the intensities are not determined so certainly.

The curves for C₂H₄ reported by Coblenz⁵ showed a small irregularity near 1725 cm^{-1} . Since a combination band involving the inactive torsional frequency of this molecule might appear here, the region was examined with a cell 80 cm long containing gas at a pressure of one atmosphere. The band shown in Fig. 1(f) was observed at 5.66μ (1766 cm^{-1}) but it must have been due to an impurity, since the line spacing is different from that appropriate to C₂H₄.

The spectrum of C₂D₄ was recorded from 2μ to 16μ with an evacuated prism spectrometer, using a cell 11 cm long containing gas at 70 cm pressure. The many regions of absorption so found were then examined under the conditions given in Table I. The detailed study showed sixteen distinct bands. Those lying above 3000 cm^{-1} were not resolved, due to insufficient dispersion. In this group atmospheric absorption was troublesome only in the neighborhood of the perpendicular type band at 2.59μ , of which even the envelope given in Fig. 2 is somewhat uncertain. The minimum at the center is very

⁴ L. G. Smith, J. Chem. Phys. 8, 798 (1940).

⁵ W. W. Coblenz, *Investigations of Infra-Red Spectra*, (Carnegie Institution, 1905), p. 35.

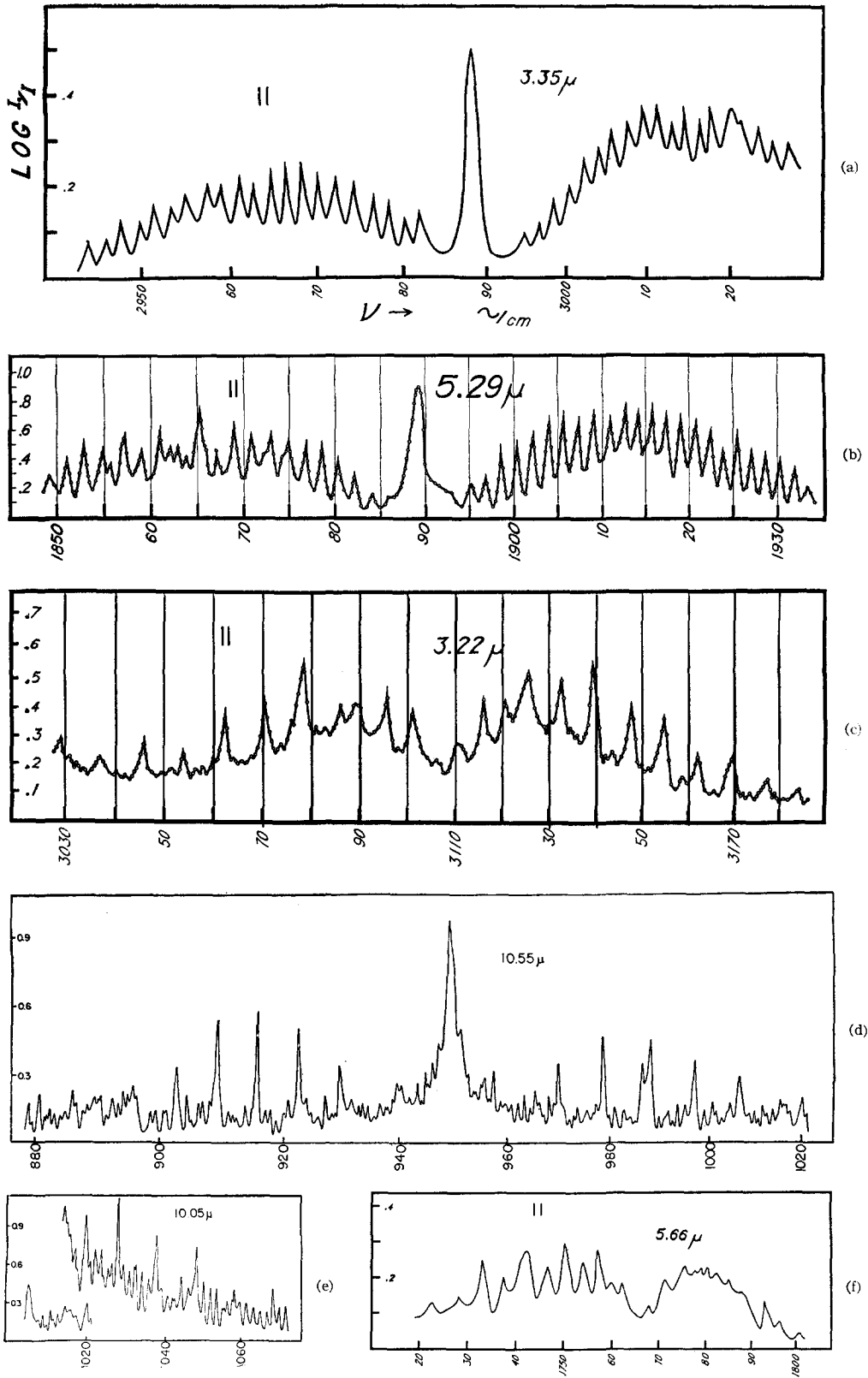
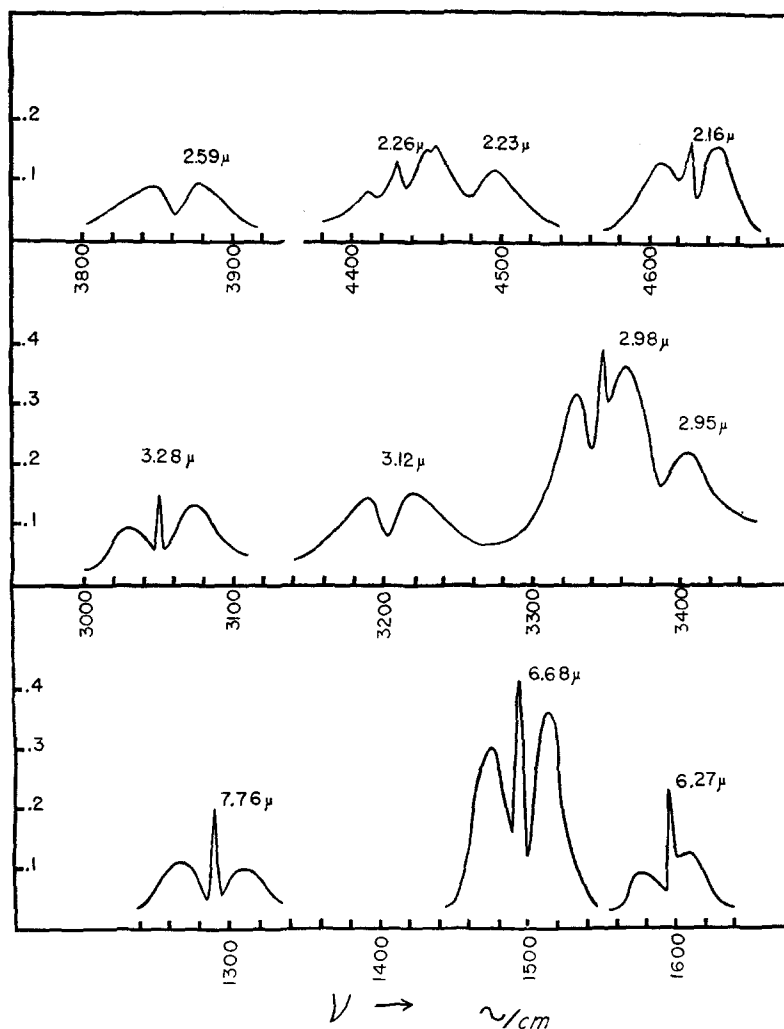


FIG. 1. The resolved bands of C_2H_4 .

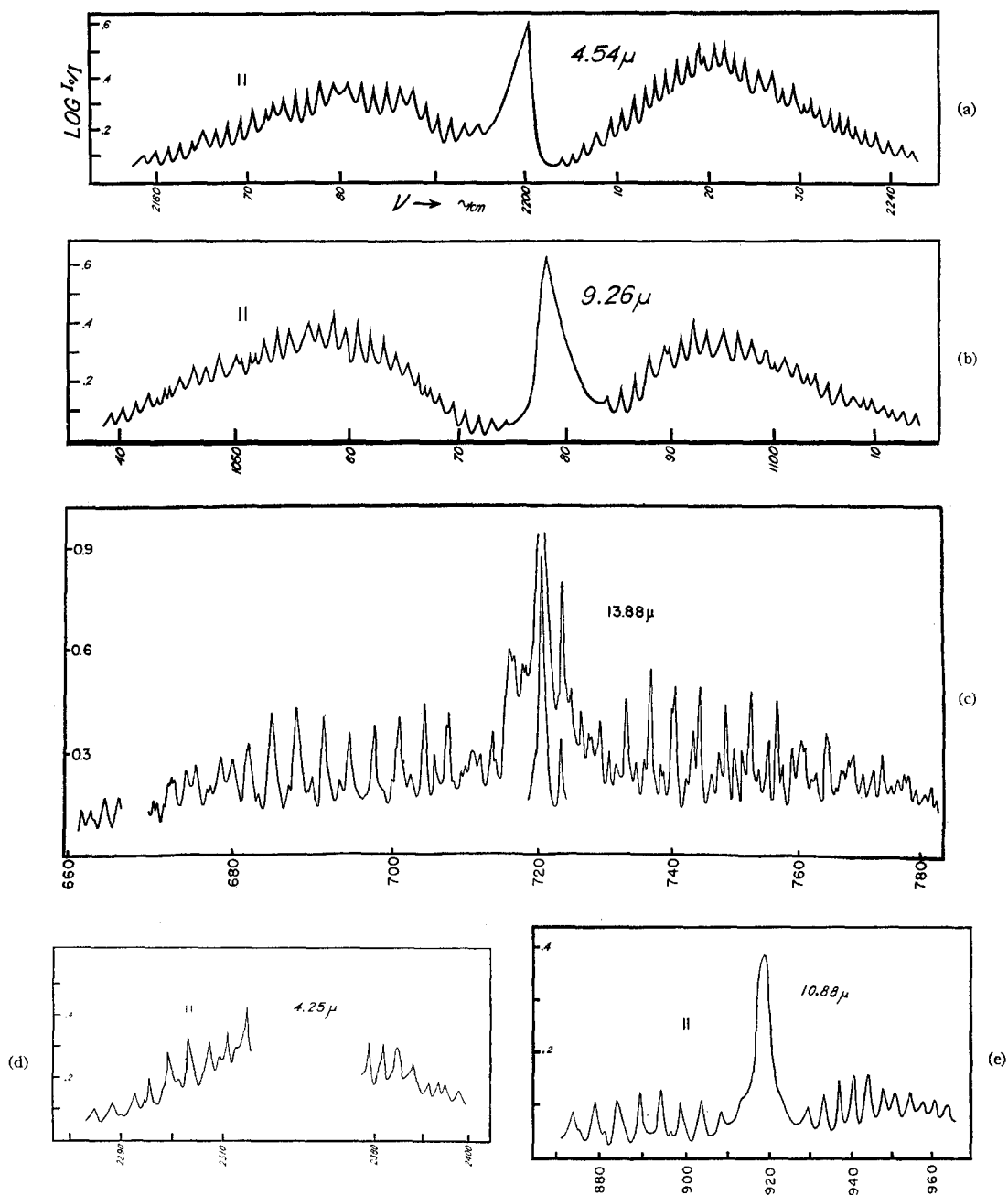
FIG. 2. The unresolved bands of C_2D_4 .

reproducible however. It should also be noted that at 2.95 and 3.12μ there was some evidence of lines spaced about 4 cm^{-1} apart, but the variations in absorption were too small to be reliable.

The atmospheric absorption near 6μ prevented resolution of the two bands in this region, though the sharp central maxima were well determined. Figure 3 shows the five bands of C_2D_4 which were resolved. Only those at 9.26 and 10.88μ are in regions where the atmosphere is completely transparent. At 4.25μ the CO_2 absorption is so intense that the few lines shown in Fig. 3(d) are the only ones observable with certainty. It was impossible to locate the band center with

the grating instrument, but the record from the evacuated prism spectrometer indicates that it lies 5 cm^{-1} below the center of the CO_2 band. Hence the value 2345 cm^{-1} is obtained. Fortunately the effect of the carbon dioxide is very small at 4.54μ . The parallel band in this position is more clearly resolved and has a more regular spacing than the one at 9.26μ , in spite of the use of relatively wider slits.

The rather complex band at 720.0 cm^{-1} was studied with extreme care, since two fundamentals should occur in this region corresponding to the frequencies 949.2 and 995 cm^{-1} of C_2H_4 . Only the stronger one is definitely established, however, though the presence of a weaker band

FIG. 3. The resolved bands of C_2D_4 .

may account for some of the many observed lines. Here again carbon dioxide in the air caused some difficulty, though the CO_2 band structure is quite coarse. Fortunately none of the strong C_2D_4 lines was superimposed upon those of CO_2 except in a small interval near 668 cm^{-1} .

ASSIGNMENT OF FREQUENCIES

A reasonable assignment of seven of the twelve fundamental frequencies for C_2H_4 has been made by several authors.⁶ The remaining five are

⁶ A comprehensive bibliography is given by G. B. B. M. Sutherland and G. K. T. Conn, Proc. Roy. Soc. A172, 172 (1939).

ν_7 , ν_9 , ν_{10} , ν_{11} , and ν_{12} in Dennison's⁷ notation. These vibrations are the torsional oscillations of the CH₂ groups. The frequency associated with the motions of these two groups about a common axis containing the carbon nuclei is designated by ν_7 . When the axes are perpendicular to the plane of the molecule, the resulting oscillation is called ν_9 or ν_{10} depending on whether the motions of the two groups are in phase or out of phase. The frequencies ν_{11} and ν_{12} correspond to oscillations in and out of phase about axes in the plane of the molecule, and perpendicular to the axis of the carbon atoms. Of these, ν_7 is inactive, while ν_9 and ν_{11} are infra-red active, and ν_{10} and ν_{12} appear in Raman scattering. From data on similar molecules, the last four are known to be in the neighborhood of 1000 cm⁻¹ while ν_7 should be somewhat lower. Table II shows the various assignments which have been made.

The frequency ν_{11} is the sole representative of the only group of fundamental vibrations which should yield infra-red bands having a coarse spacing and a central maximum. Since the very strong band at 10.55 μ is the only one corresponding to this symmetry, the assignment of the value 949.2 cm⁻¹ is very definite. The identification of the Raman line found at 950 cm⁻¹ is not so immediate for the reason that it may be due to ν_{10} or ν_{12} . The latter choice is clearly indicated by the existence of a parallel band at 1889.6 cm⁻¹, due to the combination $\nu_{11} + \nu_{12}$. No other interpretation of this band is consistent with the selection rules and Boltzmann factors. The numerical agreement is satisfactory considering the fact that Bonner⁸ estimates an uncertainty of 10 cm⁻¹ in ν_{12} .

One of the contributions of this investigation was the discovery of a region of absorption at

TABLE II. Various assignments of four of the fundamentals for C₂H₄

Author	Frequency of the fundamental in cm ⁻¹			
	ν_9	ν_{10}	ν_{11}	ν_{12}
Mecke (1932)	1100	970	950	940
Teller and Topley (1935)	730	1160	950	1097
Bonner (1936)	950	950	940	1100
Thompson and Linnett (1937)	950	1160	—	—
Mannebach and Verleysen (1937)	950	950	—	—
Sutherland and Conn (1939)	1020	1030	950	943
Galloway and Barker (1941)	995	1055	949	950

⁷ D. M. Dennison and G. B. B. M. Sutherland, Proc. Roy. Soc. **A148**, 250 (1935).

⁸ L. G. Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

TABLE III. The fundamental frequencies of ethylene.

	C ₂ H ₄	C ₂ D ₄
ν_8	1623.3	1515
ν_2	3019.3	2251
ν_4	1342.4	981
ν_1	2989.5	2200.2
ν_3	1443.9	1077.9
ν_5	3105.5	2345
ν_9	995	740*
ν_6	3069	2304
ν_{10}	1055†	860*
ν_{11}	949.2	720.0
ν_{12}	950	780
ν_7	825‡	585‡

* Calculated from $\nu_9 + \nu_{10} = 1595$ for C₂D₄.

† Calculated from $\nu_9 + \nu_{10} = 2047$ for C₂H₄.

‡ Calculated from $2\nu_7 = 1654$ for C₂H₄ and from Eq. (1g) for C₂D₄.

10.05 μ . Unfortunately, as seen by Fig. 1(e), it does not lie completely free of the strong 10.55 μ band. The overlapping is just sufficient to prevent a direct observation of the minimum at the center. However, a reasonable assignment of ordinal numbers of the lines may be made by comparison with the band of similar type at 3.22 μ . Then, by extrapolation, the center is found to lie at 995 cm⁻¹. Since ν_9 has the proper symmetry and should lie in this region, the correlation is quite convincing.

The parallel band at 2047 cm⁻¹ reported by Levin and Meyer can be explained only by a combination of ν_9 and ν_{10} . This bit of data permits us to assign the value of 1055 cm⁻¹ to ν_{10} . This frequency has not yet been found in the Raman spectrum.

Various values for the torsional fundamental have previously been given which range from 700 to 850 cm⁻¹. If the small absorption found by Coblenz at 1725 cm⁻¹ is taken as real, then ν_7 may be placed at either 670 or 775 depending on whether the band is a combination of ν_7 with ν_{10} or ν_{12} . Eucken and Parts⁹ have estimated from specific heat data that this frequency should lie in the region 750–800 cm⁻¹. These authors used slightly different values than are given here for the other frequencies. Burcik, Eyster, and Yost¹⁰ have recently recalculated the specific heat curve using both 700 and 825 cm⁻¹ for ν_7 and the remaining fundamentals as here reported. Considerably better agreement is ob-

⁹ A. Eucken and F. Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).

¹⁰ E. J. Burcik, E. H. Eyster, and D. M. Yost, J. Chem. Phys. **9**, 118 (1941).

TABLE IV. Calculated results for Eqs. (1).

Equation	Left Side	Right Side	% Difference
(1a)	1.922	1.988	3.3
(1b)	1.632	1.654	1.3
(1c)	1.820	1.869	2.6
(1d)	1.777	1.869	4.9
(1e)	1.318	1.322	0.3
(1f)	1.218	1.217	0.1

tained with the upper value though it seems slightly high. A convincing argument for a value near 825 cm^{-1} is provided by the observed Raman line at 1654 cm^{-1} which must represent the overtone of the torsional oscillation. No other combination could explain this line, since no other fundamentals have frequencies below 825 cm^{-1} . Combination tones are usually observable in Raman scattering only when accentuated by resonance with a Raman-active fundamental of the same symmetry; hence there must be interaction in this case with ν_8 at 1623 cm^{-1} . Therefore, the motion to which the line at 1654 cm^{-1} is due must be totally symmetric, and if it involves ν_7 at all it must be the harmonic $2\nu_7$, for ν_7 is the only representative of its symmetry class, and could combine in a totally symmetric way with no other fundamental.

In a very similar manner, the fundamentals of C_2D_4 may be determined. It is also possible to estimate the values for the frequencies of the heavier molecule from those of the lighter one by use of an approximate value for the reduced mass. A reasonably accurate check on the data listed in Table III may be obtained from the product rule, which gives the ratio of the products of the normal frequencies in the same symmetry class for the light molecule to the corresponding products for the heavy molecule. According to Sutherland,⁶ these relations are

$$\frac{(\omega_2\omega_4\omega_8)_H}{(\omega_2\omega_4\omega_8)_D} = \frac{m_D}{m_H} \quad (1a)$$

$$\frac{(\omega_6\omega_{10})_H}{(\omega_6\omega_{10})_D} = \left(\frac{m_D\mu'_D}{m_H\mu'_H}\right)^{\frac{1}{2}} \quad (1b)$$

$$\frac{(\omega_1\omega_3)_H}{(\omega_1\omega_3)_D} = \left(\frac{m_D\mu_D}{m_H\mu_H}\right)^{\frac{1}{2}} \quad (1c)$$

$$\frac{(\omega_5\omega_9)_H}{(\omega_5\omega_9)_D} = \left(\frac{m_D\mu_D}{m_H\mu_H}\right)^{\frac{1}{2}} \quad (1d)$$

$$\frac{(\omega_{11})_H}{(\omega_{11})_D} = \left(\frac{\mu_D}{\mu_H}\right)^{\frac{1}{2}} \quad (1e)$$

$$\frac{(\omega_{12})_H}{(\omega_{12})_D} = \left(\frac{\mu''_D}{\mu''_H}\right)^{\frac{1}{2}} \quad (1f)$$

$$\frac{(\omega_7)_H}{(\omega_7)_D} = \left(\frac{m_D}{m_H}\right)^{\frac{1}{2}} \quad (1g)$$

where the subscripts H and D refer to hydrogen and deuterium and

$$1/\mu = 1/m + 2/M$$

$$\frac{1}{\mu'} = \frac{1}{m} + \frac{2}{M} \left(1 + \frac{4l^2}{L^2} + \frac{4l}{L} \cos \frac{\theta}{2}\right)$$

$$\frac{1}{\mu''} = \frac{1}{m} + \frac{2}{M} \left(1 + \frac{2l}{L} \cos \frac{\theta}{2}\right)^2$$

M = mass of the carbon nucleus

m = mass of the H or D nucleus

l = C-H distance

L = C-C distance

θ = H-C-H angle.

The agreement shown in Table IV is sufficient to insure that the correct assignment of frequencies has been made. The discrepancies lie in the difference between the normal frequencies with infinitesimal amplitudes, designated by ω_i ,

TABLE V. The infra-red combination frequencies for ethylene.

Gas	Frequency (cm ⁻¹)	Assignment	Calculated frequency (cm ⁻¹)	Observed in both Molecules
C ₂ H ₄	4729.0	$\nu_5 + \nu_8$	4729	Yes
	4515.5	$\nu_3 + \nu_6$	4513	Yes
	4324.3	$\nu_4 + 3\nu_9$	4327	Yes
	4207.9	$2\nu_{11} + \nu_9 + \nu_4$	4236	No
	2047.0	$\nu_9 + \nu_{10}$	2050*	Yes
	1889.6	$\nu_{11} + \nu_{12}$	1899	Yes
C ₂ D ₄	4628.0	$\nu_5 + \nu_6$	4654	No
	4478.6	$\nu_1 + \nu_6$	4504	No
	4429.5	$\nu_2 + 3\nu_{11}$	4411	No
	3862.8	$\nu_5 + \nu_8$	3860	Yes
	3387.8	$\nu_3 + \nu_6$	3382	Yes
	3345.3	$\nu_2 + \nu_3$	3329	?
	3204.3	$\nu_4 + 3\nu_9$	3201	Yes
	3049.0	$\nu_9 + \nu_6$	3044	No
	1595.1	$\nu_9 + \nu_{10}$	1600†	Yes
	1495.7	$\nu_{11} + \nu_{12}$	1500	Yes

* Used to determine ν_{10} for C₂H₄.

† Used to determine ν_9 and ν_{10} for C₂D₄.

for which the equations were derived, and the fundamentals which were used to calculate the left members. Only a small percent anharmonicity need be assumed to obtain exact agreement in Table IV. The frequency 585 cm⁻¹ calculated for ν_7 of C₂D₄ cannot be checked by any available observations. In this case its harmonic does not appear in Raman scattering, since there is no totally symmetric fundamental near 1170 cm⁻¹ with which it might interact.

The high resolving power obtainable beyond 10 μ made it possible to observe many weak lines between the strong ones shown in Fig. 1(d). The latter group is identified with transitions in which $K = \pm 1$ and $J = 0$ and the former with $K = \pm 1$ and $J = \pm 1$. By a trial and error method, one can associate nearly all the observed lines with some transition. However, since the convergence of these weak P and R branches is not known and there is a lack of uniqueness, a definite assignment is not given. The presence of the fundamental at 10.05 μ also complicates the short wave-length side of the 10.55 μ band. A similar effect in C₂D₄ is observed at 13.88 μ where it appears that the less intense band lies even closer to the more intense one. In addition, the strong peak at 723.4 cm⁻¹ may be identified with the transition ν_{11} to $2\nu_{11}$.

The assignments for the combination bands given in Table V are probable ones chosen to fit

TABLE VI. The line positions in the parallel type bands of C₂H₄

The 5.29 μ band				The 3.35 μ band†			
J	P branch (cm ⁻¹)	J	R branch (cm ⁻¹)	J	P branch (cm ⁻¹)	J	R branch (cm ⁻¹)
4	1882.10	3	1896.77	4	2982.15	2	2994.81
5	1880.32	4	1898.50	5	2980.38	3	2996.68
6	1878.52	5	1900.28	6	2978.58	4	2998.51
7	1876.71	6	1902.08	7	2976.77	5	3000.61
8	1874.85	7	1903.87	8	2974.41	6	3002.10
9	1872.98	8	1905.55	9	2972.39	7	3003.85
10	1870.79	9	1907.22	10	2970.25	8	3005.60
11	1868.97	10	1908.95	11	2968.37	9	3007.54
12	1867.02	11	1910.87	12	2966.49	10	3009.34
13	1865.18	12	1912.54	13	2964.78	11	3011.19
14	1863.80	13	1914.02	14	2962.70	12	3012.77
15	1862.88	14	1915.68	15	2961.16	13	3014.27
16	1862.07	15	1917.28	16	2959.25	14	3016.13
17	1860.96	16	1918.92	17	2957.64	15	3017.54
18	1859.00	17	1920.73	18	2955.14	16	3020.07*
19	1857.09	18	1922.43	19	2953.40	17	3021.18
20	1855.57	19	1923.84	20	2951.50	18	3023.31
21	1854.85	20	1925.54	21	2949.73	19	3024.95
22	1852.87	21	1927.12	22	2947.50	20	3026.86
23	1851.05	22	1928.72	23	2945.94		
24	1849.29	23	1930.35	24	2943.72		
		24	1932.13				

Maxima of Q Branches at 1889.23 and 2988.51 cm⁻¹

* $PQ(11)$ of the 3.22 μ perpendicular band of C₂H₄.

† These values are in essential agreement with those recently reported by L. G. Smith, J. Chem. Phys. 8, 798 (1940).

TABLE VII. The line positions in the perpendicular type bands of C₂H₄.

The 3.22 μ band			The 10.55 μ band			
K	P branch (cm ⁻¹)	R branch (cm ⁻¹)	K	P branch (cm ⁻¹)	R branch (cm ⁻¹)	
0		3110.38	3	929.74	2	970.13
1	3100.74	3116.00	4	922.63	3	978.83
2	3095.35	3125.66	5	915.63		986.44
3	3085.78	3132.73	6	909.03	4	988.08
4	3078.22	3139.54	7	902.57	5	997.31
5	3069.79	3147.74	8	896.61	6	1006.55
6	3061.32	3155.24		890.81		1014.98
7	3053.27	3162.69	9	890.04	7	1015.92
8	3045.60	3170.36		886.47		1020.22
9	3036.87	3177.52		880.80		
10	3028.78	3184.66		878.89		
11	3020.07*					
	Central minimum at 3170.39 cm ⁻¹			Central maximum at 949.85 cm ⁻¹		

* Lies in 3.35 μ parallel band.

the data from both light and heavy molecules as well as possible. In a few cases other allowed combinations would not be excluded. It is noted immediately that the lower frequencies characteristic of the heavy molecule permit the observation of additional combinations below 5000 cm⁻¹. These are assigned so that the fewest number of frequencies are involved. The combinations $\nu_2 + \nu_3$ and $\nu_9 + \nu_6$ have not been definitely observed for C₂H₄, although the former may explain a weak peak at 4461 cm⁻¹, observed by Levin and Meyer. The analogue of the doublet combination band at 4207.9 cm⁻¹ has not been found in the spectrum of C₂D₄. It may be present but masked by other absorptions.

The two frequencies observed at 919.0 and 1289.1 cm⁻¹ which were not included in the above classification are assigned to a hybrid molecule involving a mixture of hydrogen and deuterium. The intensities and positions are such that the bands may be identified as ν_{11} and ν_3 of C₂HD₃. The spacing of the lines in the band at the longer wave-length supports this assignment.

THE MOMENTS OF INERTIA AND MOLECULAR DIMENSIONS

It is well known that the ethylene molecule is very nearly a symmetric top. Hence the rotational energy F may be expressed in the form

$$F = DJ(J+1) + \alpha J^2(J+1)^2$$

$$+ (C-D)K^2 + \beta K^4 + \dots$$

and used to calculate the following relations

TABLE VIII. The line positions in the parallel type bands of C₂D₄.

The 4.54 μ band		The 9.26 μ band				
J	P branch (cm ⁻¹)	R branch (cm ⁻¹)	J	P branch (cm ⁻¹)	R branch (cm ⁻¹)	
2		2203.97	3	1074.59	4	1084.31
3		2205.10	4	1073.37	5	1085.57
4	2195.04	2206.49	5	1072.17	6	1086.85
5	2193.37	2207.91	6	1070.91	7	1088.13
6	2191.86	2209.37	7	1069.75	8	1089.76
7	2190.51	2210.62	8	1068.49	9	1090.26
8	2189.25	2211.97		1067.60	9	1091.38
9	2187.79	2213.17	9	1067.15	10	1092.56
10	2186.36	2214.28		1066.50	11	1093.78
11	2185.01	2215.42	10	1065.56	12	1095.34
12	2183.60	2216.62	11	1064.41	13	1096.82
13	2182.31	2217.83	12	1063.34	14	1098.24
14	2180.80	2219.01	13	1062.09	15	1099.53
15	2179.24	2219.65	14	1060.90		1100.34
16	2177.84	2220.79	15	1059.85	16	1101.33
17	2176.53	2221.87	16	1058.74	17	1102.50
18	2175.18	2223.05	17	1057.48	18	1103.55
19	2173.89	2224.27	18	1056.31	19	1104.23
20	2172.78	2225.53	19	1054.60	20	1104.51
21	2171.96	2227.09	20	1053.60	21	1105.72
22	2170.59	2228.17	21	1052.43	22	1106.91
23	2169.38	2229.39		1051.67	22	1108.23
24	2167.99	2230.47	22	1051.16		1109.22
25	2166.76	2231.32		1050.40	23	1110.00
26	2165.46	2232.27	23	1049.90	24	1111.23
27	2164.28	2233.43	24	1048.51	25	1112.11
28	2163.03	2234.40	25	1047.42	26	1113.18
29	2161.84	2235.42	26	1046.30	27	1114.53
30	2160.45	2236.20	27	1045.13		
31	2159.12	2237.34		1044.27		
32		2238.52	28	1043.82		
33		2239.97		1043.22		
34		2241.48	29	1042.68		
35		2242.53	30	1041.61		
			31	1040.51		
			32	1039.51		

Maxima of Q branches at 2200.39 and 1078.10 cm⁻¹.

involving the line positions of the fine structure in the bands.

$$\frac{R(J) - P(J)}{2(2J+1)} = (D' + \frac{3}{2}\alpha')$$

$$+ 2\alpha'(J + \frac{1}{2})^2 + \dots, \quad (2a)$$

$$\frac{R(J-1) - P(J+1)}{2(2J+1)} = (D'' + \frac{3}{2}\alpha'')$$

$$+ 2\alpha''(J + \frac{1}{2})^2 + \dots, \quad (2b)$$

$$\frac{{}^RQ(K) - {}^PQ(K)}{4K} = (C' - D' + 2\beta')$$

$$+ 2\beta'K^2 + \dots, \quad (2c)$$

$$\frac{{}^RQ(K-1) - {}^PQ(K+1)}{4K} = (C'' - D'' + 2\beta'')$$

$$+ 2\beta''K^2 + \dots, \quad (2d)$$

$$\frac{R(J-1) + P(J)}{2} = \nu_0 + (D' - D''$$

$$+ \alpha' - \alpha'')J^2 + \dots, \quad (2e)$$

$$\frac{{}^RQ(K) + {}^PQ(K)}{2} = \nu_0 + (C' - D' + \beta')$$

$$+ (C' - D' - C'' + D'' + 6\beta')K^2 + \dots \quad (2f)$$

The values of the constants A , B , C and D are

$$A = \frac{h}{8\pi^2cI_a}, \quad B = \frac{h}{8\pi^2cI_b}, \quad C = \frac{h}{8\pi^2cI_c}$$

and

$$D = \frac{A+B}{2}$$

if the frequencies are measured in cm⁻¹, a , b , and c designating the axes of greatest, middle and least moments of inertia. The values of J and K refer to the lower (double primed) state.

It is interesting to note that the positions of the lines in the bands of C₂H₄ fit quite well with the symmetric rotator formulae yet the intensities are definitely those of an asymmetric molecule. Solutions of the Wang equation for the energy levels of an asymmetric top show that, for C₂H₄, Eqs. (2) are correct up to $J=K=20$ within the experimental error. The deviations are greatest for low K and high J . In general, the results indicate that the lines are broadened but not shifted appreciably. Similar calculations for C₂D₄ were not made. However, the greater asymmetry of the heavy molecule would predict a more pronounced broadening of the lines and an observable shift. These conclusions are verified in the parallel bands. The broadening is shown by the fact that the troughs between the lines are filled in thus making resolution difficult. The shift in position is noted when a Fortrat plot is made. A smooth curve could not be drawn except for low J . However, the perpendicular band for C₂D₄ follows the symmetric rotator formula. This is understandable in view of the fact that, while more lines are observed than for the light molecule, the deviations due to asymmetry are smaller for the high K levels.

Since Eqs. (2) may be put into linear form, the data given in Tables VI to IX were fitted by least squares to a straight line. This procedure yielded, for the ground state,

$$D_H = 0.9116 \text{ cm}^{-1},$$

$$C_H - D_H = 3.955,$$

$$D_D = 0.6522,$$

$$C_D - D_D = 1.785.$$

In order to estimate the reliability of these values, the coefficients found for the right sides

of Eqs. (2) were used to calculate the left sides. The deviations from the observed results were taken as a measure of the reliability of the above constants. The average deviations were 0.5 percent or less except for D_D . In this case, not only were the deviations larger, but the values found from the two parallel type bands differed by a few percent. A simple average yields 0.6522 cm^{-1} . The remaining results given are averages weighted according to the average deviations, which were of the same order of magnitude as the differences of the values found from different bands.

A check may be made between these constants. From the first two, C_H can be found. Then, since the relation

$$C_H/C_D = m_D/m_H$$

TABLE IX. The line positions in the perpendicular type bands of C₂D₄.

K	The 13.88 μ band		The 4.54 μ band	
	P branch (cm ⁻¹)	K	R branch (cm ⁻¹)	R branch (cm ⁻¹)
	715.58		723.38	2285.30
2?	713.48	1?	726.26	2289.02
3?	710.85	2	728.90	2292.72
4	707.58	3	732.92	2295.94
5	704.39	4	736.63	2299.67
6	701.03	5	740.52	2303.41
7	697.81	6	744.43	2307.67
8	694.58	7	748.43	2311.35
9	691.46	8	752.34	2315.16
10	688.19	9	756.28	
11	685.27	10	760.18	
12	682.22	11	764.27	
	680.09	12	768.68	
13	678.85		769.62	
14	676.28	13	772.05	
	675.38		773.51	
15	673.81	14	776.71	
16	671.02		777.67	
	667.18		781.89	
18	665.58			
19	664.20			
	663.00			

Central maximum at 720.30 cm^{-1}

should hold, one may calculate C_D . The value thus obtained for $C_D - D_D$ may then be used to find $D_D = 0.652$ which agrees remarkably well.

The positions of the lines in the resolved bands were also used to determine the band centers. These results are given in Table I. The uncertainties indicated are estimated from the upper limit of the absolute errors in calibration.

Since the ethylene molecule is planar, it follows that

$$I_a = I_b + I_c$$

or

$$1/A = 1/B + 1/C$$

also

$$A = D \left(1 - \frac{D}{2C} + \frac{1 \cdot 3 \cdot D^3}{2!2^2 C^3} - \frac{1 \cdot 3 \cdot 5 D^5}{3!2^3 C^5} + \dots \right)$$

and

$$B = D \left(1 + \frac{D}{2C} - \frac{1 \cdot 3 \cdot D^3}{2!2^2 C^3} + \frac{1 \cdot 3 \cdot 5 D^5}{3!2^3 C^5} - \dots \right).$$

The moments of inertia may now be calculated. For C₂H₄ they are

$$I_a = 33.84 \times 10^{-40} \text{ g cm}^2,$$

$$I_b = 28.09,$$

$$I_c = 5.750,$$

and for C₂D₄

$$I_a = 49.41,$$

$$I_b = 37.92,$$

$$I_c = 11.49.$$

From these values, it is found that the C-H and C-C distances are 1.071 and $1.353 \text{ \AA} \pm 0.01$, respectively, while the H-C-H angle is $119^\circ 55' \pm 30'$.

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