

InfraRed Absorption Spectra of the C2 to C4 MonoOlefins and of 2Methyl-2 Butene

R. S. Rasmussen and R. Robert Brattain

Citation: [The Journal of Chemical Physics](#) **15**, 120 (1947); doi: 10.1063/1.1746440

View online: <http://dx.doi.org/10.1063/1.1746440>

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Infra-Red Absorption Spectra of the C₂ to C₄ Mono-Olefins and of 2-Methyl-2-Butene

R. S. RASMUSSEN AND R. ROBERT BRATTAIN
Shell Development Company, Emeryville, California

(Received October 28, 1946)

The infra-red absorption spectra from 2 to 15 μ of ethylene, propylene, 1-butene, *cis*-2-butene, *trans*-2-butene, isobutene, and 2-methyl-2-butene in the vapor state have been obtained. Features common to all the spectra are discussed and their aid in determining the structure of new compounds is pointed out. The fundamental frequencies and vibrational assignments of ethylene and propylene are discussed.

I. INTRODUCTION

DURING the last few years there have been several investigations of the infra-red absorption spectra of higher paraffin hydrocarbons (C₃ to C₈, principally).¹ This paper reports a complementary survey of the vapor spectra of the C₂ to C₄ olefins and of one C₅ olefin, 2-methyl-2-butene. These spectra were obtained both for their general spectroscopic and molecular-structural interest, and also for use in the infra-red spectrophotometric analysis of hydrocarbon mixtures.²

The spectrum of ethylene has been the subject of many investigations, principally under high resolution with gratings,³ and the wave-lengths of its absorption maxima have been accurately

determined. The purpose in redetermining this spectrum with a high-resolution prism instrument was to get a more accurate idea of the intensities of absorption than is obtainable with a grating, and to check the wave-length calibration of the spectrograph used in this work.

Other salt-prism work has appeared in the literature on the spectra of propylene,^{4,5} 1-butene,⁶ *cis*- and *trans*-2-butene,⁷ mixed 2-butenes,⁶ and isobutene.⁶

II. EXPERIMENTAL

The spectra were obtained with the research infra-red spectrograph of this laboratory.⁸ This instrument employs a rocksalt prism in a Wadsworth-Littrow mounting and automatically records a curve of wave-length against a first approximation of percent transmission. During a recording the energy is kept approximately constant throughout the 2 μ to 15 μ region by continuously and automatically opening the slits to compensate for the decrease of energy toward long wave-lengths. Transmission values were obtained from recordings of short sections of the spectrum with the same cell filled and empty, so that no corrections for cell absorption or reflection were necessary.

All spectra were obtained in a cell 15 cm long, at pressures indicated on the absorption curves. Each curve shown in the figures is the average

¹ B. L. Crawford, W. H. Avery, and J. W. Linnett, J. Chem. Phys. **6**, 682 (1938)—ethane.

F. Stitt, J. Chem. Phys. **7**, 297 (1939)—hexadeuteroethane.

V. L. Wu and E. F. Barker, J. Chem. Phys. **9**, 487 (1941)—propane.

S. E. Whitcomb, H. H. Nielsen, and L. H. Thomas, J. Chem. Phys. **8**, 143 (1940)—*n*-undecane.

W. H. Avery and C. F. Ellis, J. Chem. Phys. **10**, 10 (1942)—ethane, 2,2-dimethylbutane.

G. A. Stinchcomb, J. Chem. Phys. **7**, 853 (1939)—*n*-pentane.

J. J. Fox and A. E. Martin, Proc. Roy. Soc. (London) **A175**, 208 (1940)—some C₇ to C₃₄ hydrocarbons in 3 μ region.

C. F. Kettering and W. W. Sleator, Physics **4**, 39 (1933)—various C₅ to C₈ hydrocarbons.

D. Barca-Galateanu, Bull. Soc. Roumaine Phys. [70], **38**, 109 (1938)—*n*-hexane, *n*-heptane, *n*-dodecane.

P. Lambert and J. Lecomte, Ann. de physique **18**, 329 (1932), and earlier work by these authors—some C₆, C₇, and C₈ hydrocarbons.

R. A. Oetjen, H. M. Randall, and W. E. Anderson, Rev. Mod. Phys. **16**, 260, 265 (1944)—all C₈ paraffins.

H. W. Thompson, J. Chem. Soc. **183** (1944)—2,2- and 2,3-dimethylbutanes.

² R. R. Brattain and O. Beeck, J. App. Phys. **13**, 699 (1942). R. R. Brattain, R. S. Rasmussen, and A. M. Cravath, J. App. Phys. **14**, 418 (1943).

³ W. S. Gallaway and E. F. Barker, J. Chem. Phys. **10**, 88 (1942). This paper gives earlier references.

⁴ E. B. Wilson, Jr. and A. J. Wells, J. Chem. Phys. **9**, 319 (1941).

⁵ W. H. Avery and C. F. Ellis, J. Chem. Phys. **10**, 10 (1942).

⁶ R. B. Barnes, U. Liddel, and V. Z. Williams, Ind. Eng. Chem., Anal. Ed. **15**, 83 (1943); W. W. McCarthy and J. Turkevich, J. Chem. Phys. **12**, 461 (1944).

⁷ H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 247 (1938).

⁸ R. R. Brattain, Phys. Rev. **60**, 164 (1941).

of at least two runs at the indicated pressure. Because of galvanometer drift and slow heating effects inside the spectrograph, the transmission values are usually accurate to only 2.5 percent. In a few especially bad cases, principally at $\lambda > 12.5\mu$, the accuracy may be only 5 or 10 percent.

The wave-length range covered was 2μ to 14.5μ or 15.0μ and the spectral slit widths \dagger at various points in this interval are indicated by the distances between the short vertical lines at 3μ , 6μ , 9μ , and 12μ . The wave-length calibration of the spectrograph is empirical and is based on wave-lengths in the spectra of ammonia and carbon dioxide taken from grating work in the literature. Wave-length errors due to non-reproducibility are believed to be not greater than $\pm 0.01\mu$ for $\lambda > 5\mu$. At shorter wave-lengths the error increases, becoming ± 0.02 at $\lambda = 3\mu$.

The sources and purities of the various hydrocarbons used are as follows:

Ethylene. The ethylene was Ohio Chemical Company product, containing, so far as all chemical information obtainable goes, no impurities other than small amounts of permanent gases. Gallaway and Barker,³ using ethylene from the same source, found evidence of an impurity in a very weak band at 5.66μ , whose fine structure indicated that it was not due to ethylene. No band at this wave-length of sufficient intensity to be noticeable was observed in the present work, although a weak one may have escaped notice. In any case, the impurity indicated is certainly too small to affect the main features of the spectrum.

Propylene. The propylene used was made from di-isopropyl ether, and was specially redistilled. A cylinder of product representing a 20 percent heart cut was taken, and the sample used for the present work was drawn from this cylinder. The purity is believed to be better than 99.0 percent. Mass spectrometric analysis indicated 0.1 percent acrolein, and essentially no propane.

1-Butene. The sample of 1-butene was obtained

from a pilot plant distillation of normal butylenes obtained from *sec*-butyl alcohol. Comparison with laboratory preparations of high purity indicated a probable purity of 99.3 percent.

***cis*-2-Butene.** A large sample of 2-butene (approximately 75 percent *cis*, 25 percent *trans*) was distilled in a pilot plant still under high reflux, and a cylinder of high-boiling end taken which analyzed *circa* 95 percent *cis*-2-butene by standard spectrophotometric methods. Calibration standards for this analysis were obtained from Dr. W. E. Vaughan of these laboratories, and were part of the *cis*- and *trans*-2-butenes prepared at Harvard University.⁹ The 95 percent material was redistilled in an 80-plate low-temperature laboratory column and several cuts were obtained which were spectrophotometrically indistinguishable in purity from the Harvard sample.

***trans*-2-Butene.** A sample of 2-butene analyzing 85 percent *trans* form was redistilled in the same laboratory column as was used for the *cis*-2-butene. The best cut, which analyzed 99.6 percent *trans*-2-butene spectrophotometrically, was used for the present work.

Isobutene. The sample of isobutene used was made from *tert*-butyl alcohol and was distilled in a plant column. Standard gas analysis procedures and comparison with highly purified laboratory products indicated a probable purity of 99.6 percent.

Mass spectrometric examination of all these butene samples indicated that saturates were negligibly low (< 0.1 percent).

2-Methyl-2-butene. The sample of 2-methyl-2-butene used was prepared from *tert*-amyl alcohol, and carefully distilled. Physical constants were: specific gravity (20/4), 0.6622; n_D^{20} , 1.3872.

III. RESULTS

The absorption curves are shown in Figs. 1 to 7. Table I gives the observed wave-lengths and frequencies of the absorption maxima of ethylene from 12.3 to 15μ , since these have not been reported previously in the grating work referred to, although Thompson and Harris have shown a salt-prism curve of the peaks.¹⁰ The observed

\dagger These are the actual wave-length limits included by the slits; the effective slit widths or theoretical intervals which can be resolved are one half of these values. The resolution actually achieved is slightly better than the spectral slit widths, but is considerably poorer than the effective slit widths.

⁹ G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, J. Am. Chem. Soc. **57**, 876 (1935).

¹⁰ H. W. Thompson and G. P. Harris, Trans. Faraday Soc. **40**, 295 (1944).

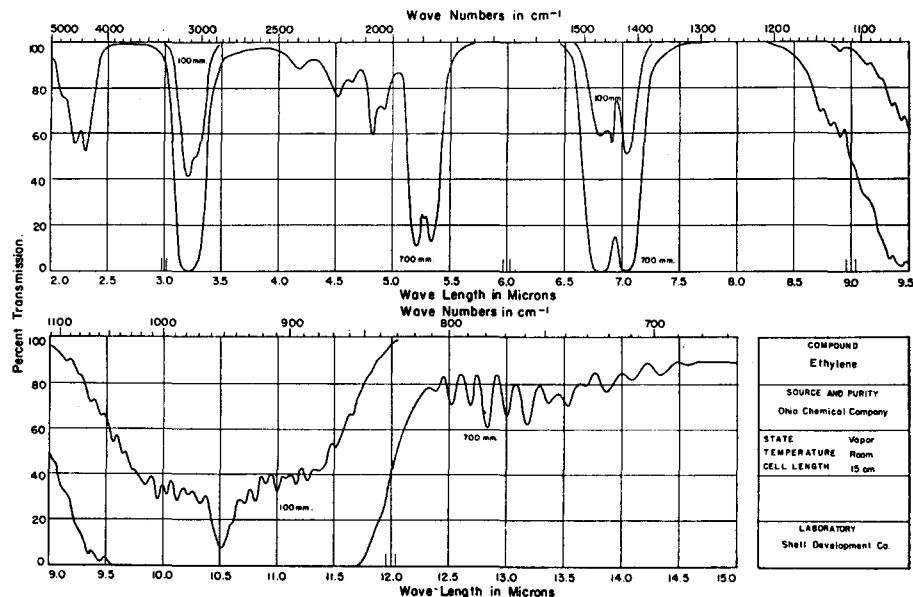


FIG. 1. Infra-red absorption spectrum of ethylene.

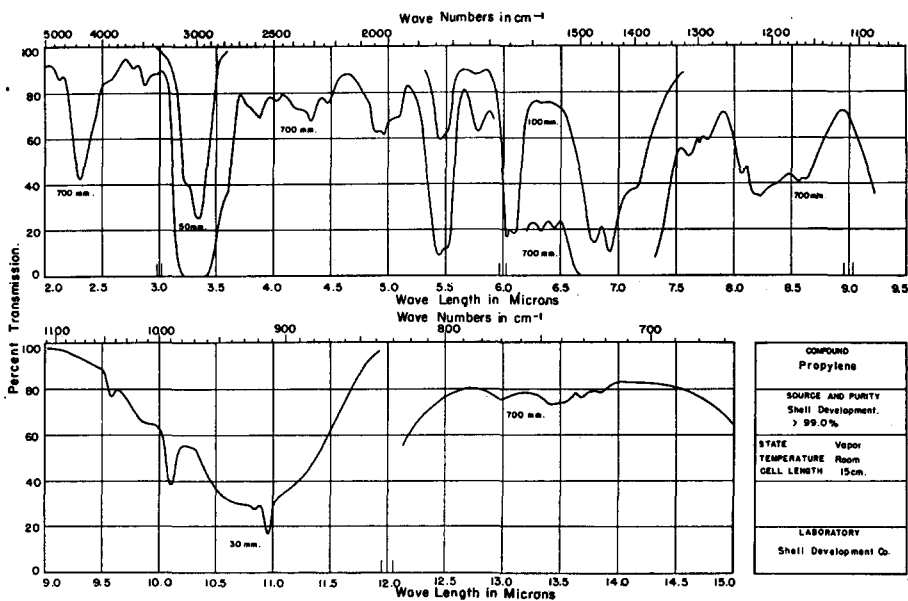


FIG. 2. Infra-red absorption spectrum of propylene.

wave-lengths, frequencies, and intensities of the absorption maxima of the other compounds are shown in Table II. The intensities given in these tables are taken from the spectra at 100 mm Hg pressure and are in units of 10 percent absorption; thus 0 indicates less than 5 percent absorption, 1 indicates between 5 and 15 percent absorption, etc. Estimated absorption due to tails of other bands has been subtracted in obtaining these values. Brackets indicate the

intensity of a whole band, individual features of which are given by the wave-lengths enclosed. Bands of wave-length less than 5μ have their frequencies rounded off to the nearest 5 cm^{-1} .

The spectra presented here show in general greater resolution than previously published curves (except, of course, in the case of ethylene). However, the earlier work is generally in good agreement with the present, with one exception: a moderately strong band at 1233 cm^{-1} shown by

FIG. 3. Infra-red absorption spectrum of 1-butene.

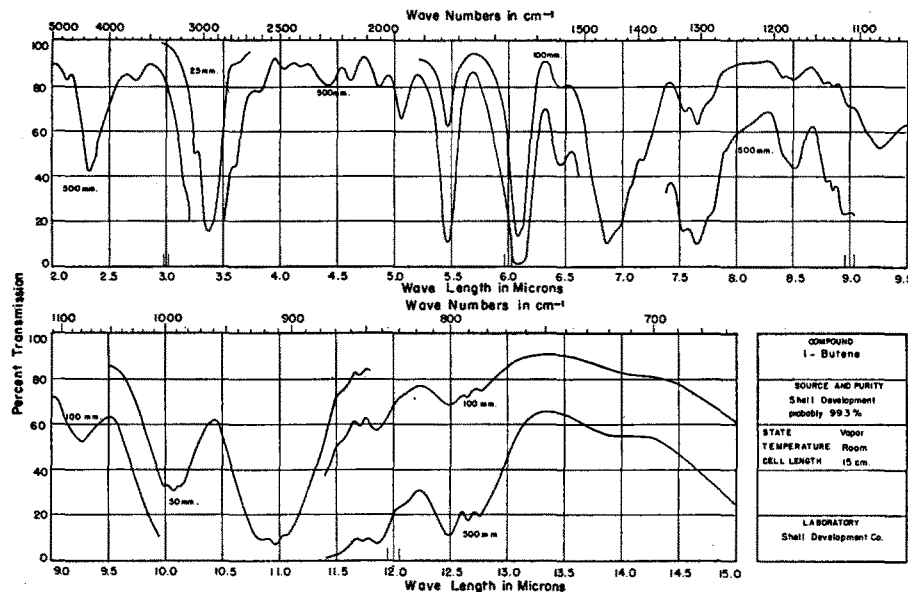
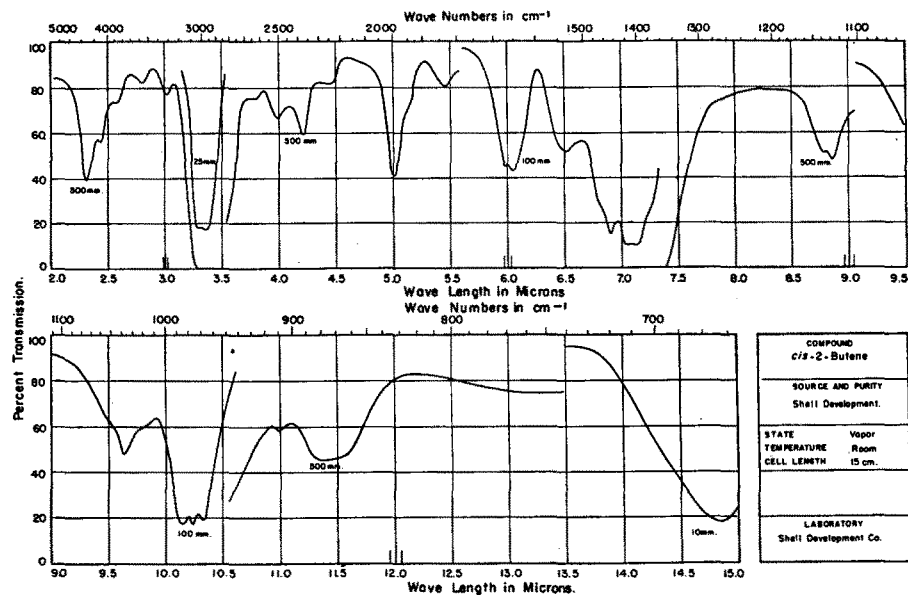


FIG. 4. Infra-red absorption spectrum of *cis*-2-butene.



Gershinowitz and Wilson⁷ in the spectrum of *cis*-2-butene was not found in the present work.

IV. GENERAL DISCUSSION

Aside from specific frequency assignments for individual molecules, several points of interest are to be noticed in the spectra of the olefins taken as a group. Many of these points have

been noted also in recent articles by Thompson and Torkington.¹¹

In the 3μ region, the four molecules having the olefinic CH_2 group (ethylene, propylene, 1-butene and isobutene) show a band at *circa* 3.2μ (3100 cm^{-1}), which in the case of all but ethylene appears as a shoulder on the strong band at *circa*

¹¹ H. W. Thompson and P. Torkington, Trans. Faraday Soc. 51, 247 (1945); Proc. Roy. Soc. (London) A184, 3 (1945).

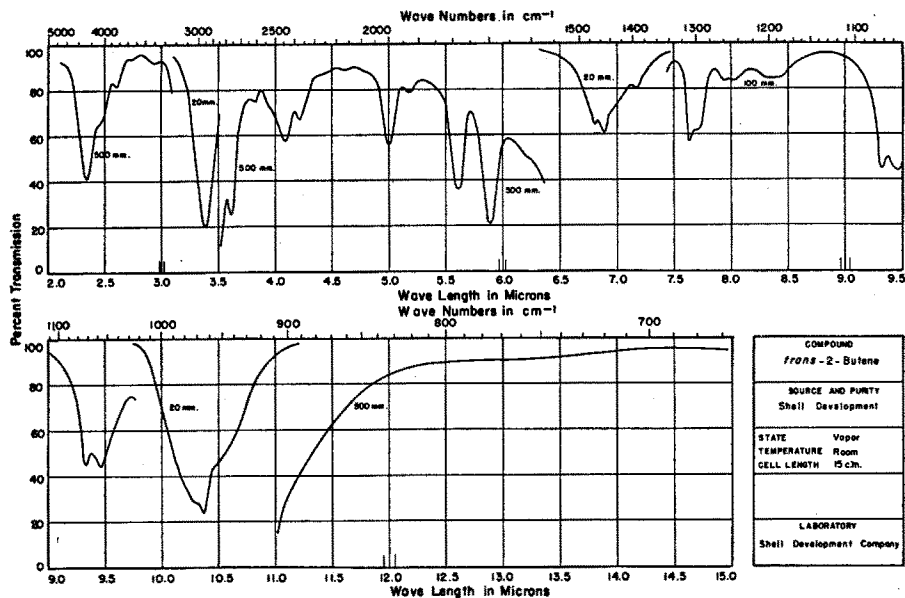


FIG. 5. Infra-red absorption spectrum of *trans*-2-butene.

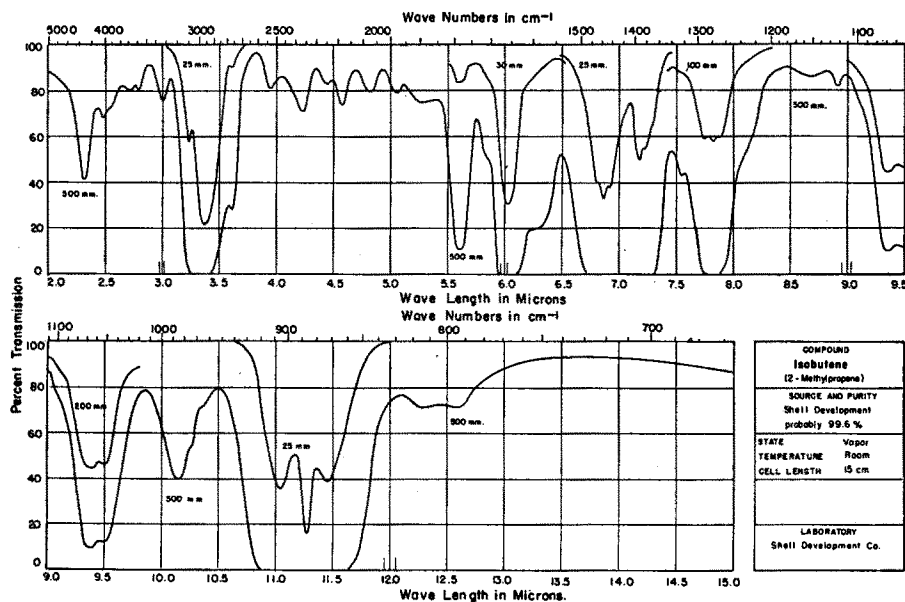


FIG. 6. Infra-red absorption spectrum of isobutene.

3.37μ (2970 cm^{-1}). This 3.2μ band is not found in the spectra of molecules lacking this group. It undoubtedly represents the antisymmetric CH stretching vibration of the CH_2 group, the symmetric one (of lower frequency) being found with all the aliphatic CH stretching frequencies in the strong 2970 cm^{-1} band (or in the case of ethylene as a weak shoulder on the side of the 3120 cm^{-1} band³). Frequencies corresponding to

the 3.2μ band are found in the Raman effect at *circa* 3080 cm^{-1} .¹²

The region 10 to 12.5μ shows a feature that is apparently characteristic of olefins in general. All of the compounds discussed here and in the two following articles show either two (in the case of molecules having the $\text{CHR}=\text{CH}_2$ con-

¹² J. H. Hibben, *The Raman Effect and its Chemical Applications*, A. C. S. Monograph (Reinhold Publishing Corporation, New York, 1939), Chap. 11.

figuration) or one (in the case of other olefins) very strong bands in this region. These bands (or at least the stronger one if there are two) all show 90 percent or more absorption at their maxima for a pressure of 100 mm Hg of olefin in a 15-cm cell. This is stronger absorption by a factor of two or more than the most intense bands of paraffin hydrocarbons. In ethylene this band occurs at 10.5μ , and is known to be caused by the infra-red active out-of-plane bending of the hydrogen atoms. Hence, by analogy, these strong bands in higher olefins may be ascribed to out-of-plane motions of hydrogens attached to the double-bonded carbons. The exact wave-lengths at which these strong bands are found are highly characteristic of the type of substitution around the double bond, as shown in Table III.¹³ In the region 5 to 6μ each of the substances has a fairly strong band which may reasonably be assigned as the first overtone of the strong band at 10 to 12μ , or as a combination with some nearby frequency in the cases where the first overtone is forbidden by symmetry (ethylene, *trans*-2-butene).¹⁴ In the compounds containing

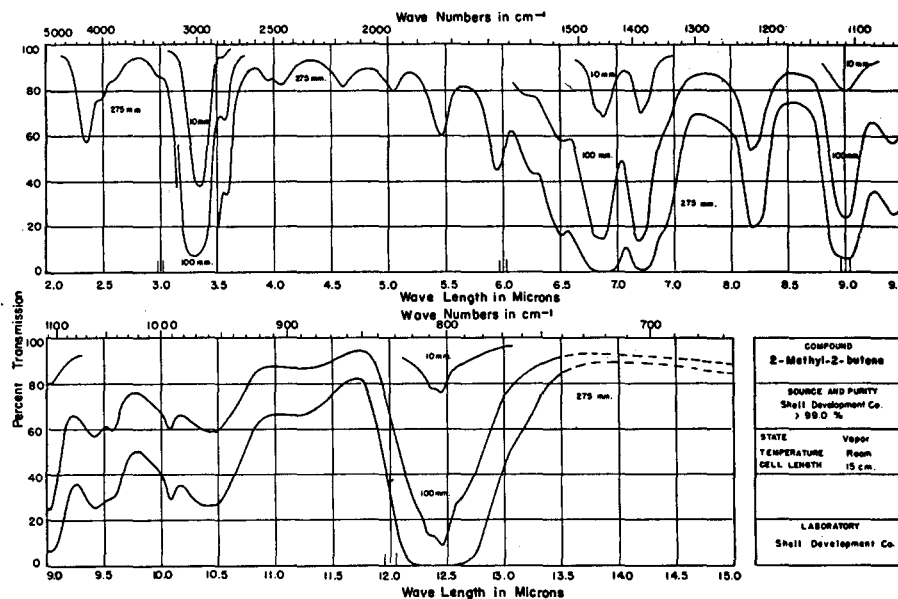
TABLE I. Wave-lengths and frequencies of absorption maxima of ethylene, 12.5–15 μ .

$\lambda(\mu)$	$\omega(\text{cm}^{-1})$
12.39	807.1
12.535	797.7
12.69	788.0
12.845	778.5
13.01	768.6
13.19	758.2
13.375	747.7
13.54	738.6
13.705	729.6
13.88	720.5
14.10	709.2
14.345	697.1
14.575	686.0

the olefinic CH_2 group these bands are remarkably intense, whereas in the other molecules they are only slightly stronger than other overtones.

These three regions, 3μ , 5 to 6μ and 10 to 12μ , have an important application in the identification of the type of olefin when the complete structure is unknown or uncertain, and have been used in conjunction with other physical and chemical data with considerable success for this purpose.^{11, 15}

FIG. 7. Infra-red absorption spectrum of 2-methyl-2-butene.



¹³ P. Lambert and J. Lecomte, *Comptes rendus* 206, 1007 (1938) have enunciated a similar rule regarding strong absorption bands in this region, which was deduced from unpublished spectra of branched and unbranched higher olefins. However, the exact method of application of the rule is not very clear, nor does it seem to apply to the spectra shown here and in the next two articles. This rule has been correctly stated in the recent paper of Thompson and Torkington (reference 11).

¹⁴ This overtone band in 1-butene at 5.43μ was erroneously interpreted by Barnes *et al.* (reference 6) as being caused by an impurity of 1,3-butadiene.

¹⁵ R. S. Rasmussen, *Phys. Rev.* 64, 188 (1943).

TABLE II. Wave-lengths, frequencies, and intensities of absorption maxima (vapor spectra).

Propylene			1-Butene			<i>cis</i> -2-Butene		
$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>	$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>	$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>
2.11	4740	0	2.12	4715	0	2.30	4350	1
2.30	4350	1	2.32	4310	1	2.45	4080	0 _a
2.44	4100	0 _a	2.37	4220	0 _a	2.59	3860	0 _a
2.58	3875	0 _a	ca. 2.49	ca. 4015	0 _a	2.80	3570	0
2.77	3710	0	2.73	3665	0	3.01	3320	0 _a
2.87	3485	0	3.14	3185	0 _a	3.28	3050	10
2.97	3365	0 _a	3.25	3075	1 _a	3.37	2965	
3.22	3105	2 _a	3.365	2970	10	3.61	2740	0 _a
3.34	2995	9	3.42	2925		3.81	2625	0
3.61	2770	0 _a	3.61	2770	0 _a	3.98	2515	0
3.75	2665	0 _a	3.82	2620	0 _a	4.22	2370	1
3.87	2585	0	4.03	2480	0	4.47	2235	0 _a
4.02	2485	0	4.17	2400	0	5.005	1998	2
4.18	2390	0 _a	4.42	2260	0	5.16	1938	0 _a
4.325	2310	0	4.62	2165	0	5.46	1832	0
4.47	2235	0	4.86	2060	0	5.99	1669	5
ca. 4.76	ca. 2100	0 _a	5.06	1976	0	6.06	1650	
4.89	2045	1	5.46	1832	4	6.17	1621	3 _a
4.96	2016	1	6.08	1645	9	6.51	1536	
5.08	1969	0 _a	6.12	1634	9	6.78	1475	1 _a
5.44	1838	3	6.45	1550	1 _a	6.905	1448	8
5.51	1815		6.74	1485	9	7.04	1420	
5.78	1730	1 _a	6.865	1457		7.16	1397	1 _a
6.03	1658	8	6.98	1433	0 _a	7.27	1376	
6.10	1639		7.08	1412		8.79	1138	1
6.33	1580	0 _a	7.19	1391	1 _a	8.865	1128	
6.45	1550	0 _a	7.54	1326	3	9.44	1059	4
6.79	1473	7	7.65	1307		9.635	1038	
6.92	1445		7.78	1285	0 _a	9.84	1016	7
7.16	1397	0	7.91	1264		10.14	986	
7.60	1316		ca. 8.11	ca. 1235	0 _a	10.245	976	0
7.70	1299	0 _a	8.40	1190	1	10.335	968	
7.78	1285		8.52	1174		11.00	909	1
8.07	1239	1	8.78	1139	1 _a	ca. 11.30	ca. 880	
8.17	1224		8.85	1130		ca. 11.58	ca. 864	0
8.23	1215	0	8.97	1115	4	ca. 13.30	ca. 750	
ca. 8.39	ca. 1190		ca. 9.15	ca. 1090		14.86	673	10
8.55	1170	9	9.265	1079	9			
8.64	1157		9.98	1002	10			
ca. 9.35	ca. 1070	1	10.07	993				
9.58	1044		10.14	986	1			
ca. 9.85	ca. 1015	3	10.82	924				
10.10	990		10.965	912	0 _a			
ca. 10.55	ca. 950	10	11.07	903				
10.84	923		ca. 11.57	ca. 864	2			
10.95	913	0	11.72	853				
11.25	889		11.85	844	1 _a			
12.98	770	0	12.12	825				
13.41	746		12.48	801	1 _a			
13.54	739	0	12.65	791				
13.68	731		12.76	784	1 _a			
13.85	722	0	ca. 13.90	ca. 719				

In the 6μ region, the C=C stretching frequency is found as expected in all the spectra except those of ethylene and *trans*-2-butene, where it is forbidden by symmetry. The regularities found in this frequency in the Raman effect for various types of substituted ethylenes¹² are followed to some extent in the infra-red, but the shifts are in general so small that the difficulty of fixing the origin of the infra-red bands makes this property of less use in the infra-red spectra of vapors.

Not much regularity can be found in the 7μ (1400 cm^{-1}) region. From the Raman¹⁶ and infra-red¹ spectra of paraffins, it appears that the non-symmetrical HCH bending frequencies of the CH_3 group, and the HCH bending frequencies of the CH_2 group, are found from 1440

to 1475 cm^{-1} (6.78 to 6.95μ), and are strong in both the Raman and infra-red. The symmetrical HCH bending frequencies of the CH_3 group are found at 1375 to 1395 cm^{-1} (7.18 to 7.28μ), and are somewhat weaker in the infra-red and either very weak or missing in the Raman effect. As used here, "non-symmetrical" and "symmetrical" refer to the symmetry within the methyl group; that is, to vibrations which in an isolated methyl group (point group C_{3v}) would have representations E and A_1 respectively. The Raman spectra of olefins containing the $=\text{CH}_2$ group show in addition to the above frequencies a fairly strong line at 1415 cm^{-1} , evidently the olefinic HCH bending frequency. The spectra of propylene, 1-butene, isobutene, and 2-methyl-2-butene fit the above picture fairly well, showing the 6.8μ and 7.2μ bands for CH_3 and aliphatic

¹⁶ Hibben, reference 9, Chap. 7.

TABLE II.—Continued.

<i>trans</i> -2-Butene			Isobutene			2-Methyl-2-butene		
$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>	$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>	$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	<i>I</i>
2.34	4275	2	2.32	4310	1	2.33	4290	1
2.47	4050	0 _s	2.49	4015	0 _s	2.47	4050	0 _s
2.60	3845	0	2.56	3905	0 _s	2.60	3845	0 _s
2.75	3635	0	2.73	3665	0	3.025	3305	0 _s
2.94	3400	0	2.80	3570	0	3.38	2960	9
3.38	2960	9	3.01	3320	0	3.61	2770	2 _s
3.62	2760	2 _s	3.24	3085	2 _s	3.98	2515	0
3.83	2610	0	3.37	2965	1	4.10	2440	0
3.94	2540	0 _s	3.62	2760	1 _s	4.64	2170	0
4.09	2445	1	3.95	2530	0	5.07	1972	0
4.22	2370	0 _s	4.23	2365	1	5.475	1830	1
4.44	2250	0	4.43	2255	0	5.955	1679	1
4.61	2170	0	4.59	2180	0	6.27	1595	0 _s
4.79	2090	0	4.83	2070	0	6.50	1538	1 _s
5.00	2000	1	5.06	1976	0	6.81	1471	7
5.18	1931	0	ca. 5.28	ca. 1890	0	6.88	1453	7
5.61	1783	1	5.59	1789	3	7.19	1391	7
5.89	1698	2	5.65	1770	0 _s	7.26	1377	0 _s
6.19	1616	0 _s	5.83	1715	9	7.40	1351	5
6.80	1471	8	6.04	1656	1	8.17	1224	7
6.90	1449		ca. 6.34	ca. 1575	10	8.21	1218	3
7.02	1425		6.81	1468	9	8.25	1212	1
7.18	1393		6.865	1457	10	8.95	1117	7
7.63	1311	4	6.925	1444	9	9.00	1111	3
7.73	1294	1	7.185	1392	0	9.04	1106	3
7.95	1258	1	7.235	1382	4	9.45	1058	1
8.04	1244	5	7.30	1370	0	9.61	1041	3
8.32	1202	1	7.55	1325	2	10.12	988	1
8.43	1186	5	7.75	1290	0	10.47	955	1
9.325	1072	0	7.83	1277	0	ca. 11.25	ca. 890	9
9.46	1057		7.89	1271	0	12.28	814	9
ca. 10.20	ca. 980	10	ca. 8.19	ca. 1220	0	12.37	808	1 _s
10.37	964		8.68	1152	0	12.47	802	0 _s
ca. 10.62	ca. 940		8.92	1121	0	ca. 12.7	ca. 790	
ca. 13.0	ca. 770	0	9.37	1067	2	ca. 13.2	ca. 760	
			9.52	1050	1			
			10.15	985	0 _s			
			10.28	973	0 _s			
			10.37	964	0 _s			
			11.04	906	10			
			11.275	887	0			
			11.46	873	0			
			12.26	816	0			
			12.63	792	0			

"s" indicates shoulder on an adjacent stronger band.

Some of the weak bands found in the higher pressure runs may be attributable to impurities. In particular the 5.78μ band in propylene (Fig. 2) is explicable as caused by the trace of acrolein present in the sample (see Section II), and weak bands of other compounds in this region may also be due to traces of carbonylic materials.

CH_2 groups, but showing little or no indication of the 1415 cm^{-1} frequency of olefinic CH_2 . Propylene shows none in the present work, but Wilson and Wells,⁴ with somewhat better resolution in this region, found a slight bump at 1415 cm^{-1} . 1-Butene shows some filling in at this wave-length indicative of a weak band; isobutene shows no indication of a band. The 2-butenes appear to be anomalous in that they show strong absorption around 7.0μ (1430 cm^{-1}), where methyl groups in other molecules do not exhibit bands. The inability to resolve the complex of bands in this whole region, and the strong dependence of their relative intensities on structure, make it difficult to deduce any useful or instructive generalizations.

V. FREQUENCIES AND VIBRATIONAL ASSIGNMENT OF ETHYLENE

The only new feature of the ethylene spectrum is the series of fine structure maxima in the

region 12.3 to 14.5μ .¹⁷ The band is weak, as indicated in Fig. 1. Only the series of P_Q maxima were observed, since the long wave-length side of the strong 950 cm^{-1} band overlies the R_Q side. Since this band had never been reported at the time this work was done, the possibility of its being due to an impurity was checked by carrying out a rough distillation in which the first and last quarter fractions were rejected. The middle fraction showed the band with the same intensity. Furthermore, the average spacing between thirteen maxima is 10.1 cm^{-1} (average deviation 0.8 cm^{-1}). This spacing is of the correct magnitude for the perpendicular type of band in ethylene.

The lack of a central Q_Q branch shows the band to be of the B_{2u} type (symmetry designation

¹⁷ A preliminary report of this work appears in Phys. Rev. 62, 301 (1942); Thompson and Harris (reference 10) have given a short discussion of the band.

TABLE III. Strong bands of olefins, 10.0–12.5 μ .

Type	Compounds	Wave-lengths of strong bands (μ)
CH ₂ =CH ₂	Ethylene	10.52
CHR=CH ₂	Propylene	10.10, 10.95
	1-butene	10.07, 10.965
	1-pentene	10.02, 10.94
	3-methyl-1-butene	10.01, 10.96
	1-octene	10.06, 10.96
	6-methyl-1-heptene	10.03, 10.94
	1,3-butadiene	9.875, 10.995
	Isoprene*	10.09, 11.03
	<i>cis</i> -1,3-pentadiene*	10.03, 11.035
	<i>trans</i> -1,3-pentadiene*	9.98, 11.10
CHR=CHR**	<i>cis</i> -2-butene	10.245
	<i>trans</i> -2-butene	10.37
	<i>trans</i> -2-pentene	<i>circa</i> 10.35
	2-octene	10.35
	3-octene	10.33
	4-octene	10.33
	<i>cis</i> -1,3-pentadiene*	10.37
	<i>trans</i> -1,3-pentadiene*	10.53
CR ₂ =CH ₂	Isobutene	11.275
	2-methyl-1-butene	11.23
	2-methyl-1-heptene	11.225
	Isoprene*	11.20
CR ₂ =CHR***	2-methyl-2-butene	12.47

* Isoprene and the pentadienes are each included in two categories.

** Omission of statement of *cis-trans* configuration means that as originally prepared this was not known.

*** Further work on this type of molecule indicates much more variability than for the other types.

of Herzberg¹⁸), i.e., involves a dipole change along the intermediate axis of inertia. The approximate fixing of the band center by the intensity distribution leads to a value near 800 cm⁻¹.

In view of the recent interpretation by Gallaway and Barker³ of a series of maxima to the short wave-length side of the 950 cm⁻¹ band as belonging to the previously unobserved ν_9 fundamental frequency (notation of these authors; Herzberg¹⁸ designates this frequency by ν_{10}), there is some difficulty in assigning the band reported here. On Gallaway and Barker's assignment it cannot be explained as an allowable difference band. The possibility that it is an isotope band (ν_{11} of the C¹²—C¹³ molecule) is precluded not only by the lack of a Q_Q branch but also by the fact that, to the harmonic oscillator approximation, the isotopic molecule

frequency differs from ν_{11} of the C¹²—C¹² molecule by less than one percent.

It is suggested here that the 800 cm⁻¹ band is the ν_9 fundamental. The following discussion represents an exploration of the consequences of such an assumption. Table IV shows the fundamentals using this new assignment. The most reasonable explanation of the 2047 cm⁻¹ infra-red band is still $\nu_9 + \nu_{10}$, as assumed by Gallaway and Barker, placing the thus-far-unobserved Raman active fundamental ν_{10} at *circa* 1250 cm⁻¹. This allows the rather strong harmonics observed in the infra-red at 4207.9 and 4324.4 cm⁻¹¹⁹ to be interpreted as $\nu_1 + \nu_{10} = 4240$ cm⁻¹, and $\nu_3 + \nu_8 + \nu_{10} = 4317$ cm⁻¹, respectively, instead of the fourth harmonic combinations necessitated by Gallaway and Barker's assignment.

Application of the Redlich-Teller product rule and use of the $\nu_9 + \nu_{10}$ combination band at 1595 cm⁻¹ in the spectrum of C₂D₄³ leads to probable values of 575 and 1020 cm⁻¹ for ν_9 and ν_{10} , respectively, in this molecule. This assignment allows the 3204 cm⁻¹ band to be interpreted as $\nu_1 + \nu_{10} = 3220$ cm⁻¹ instead of as a fourth harmonic. The band at 3049.0 cm⁻¹ in C₂D₄ cannot be explained on the assignment proposed here. It seems reasonable, however, that this band may be caused by the C—H stretching vibration of C₂HD₃, whose presence was indicated by two other bands. The interpretations offered by Gallaway and Barker for the remainder of the observed harmonic bands in C₂H₄ and C₂D₄ would not be affected by this new assignment, since they do not involve ν_9 or ν_{10} .

TABLE IV. Fundamental frequencies of C₂H₄ and C₂D₄.

		C ₂ H ₄	C ₂ D ₄
ν_1	B_{3u}	2989.5 cm ⁻¹	2200.2 cm ⁻¹
ν_2	A_{1g}	3019.3	2251.6
ν_3	B_{3u}	1443.9	1077.9
ν_4	A_{1g}	1342.4	981.6
ν_5	B_{2u}	3105.5	2345
ν_6	B_{1g}	3075	2306
ν_7	A_{1u}	(950)*	?
ν_8	A_{1g}	1623.3	1514.7
ν_9	B_{2u}	800*	575*
ν_{10}	B_{1g}	1250*	1020*
ν_{11}	B_{1u}	949.2	720.0
ν_{12}	B_{2g}	943	780

Notation of frequencies same as used by Gallaway and Barker, reference 3. (*) indicates a change from frequency assigned by them.

¹⁸ G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 325–328.

¹⁹ A. Levin and C. F. Meyer, *J. Opt. Soc. Am.* **16**, 137 (1928).

Using the new assignment, the specific heat at 300.0°K was calculated to be 10.58 cal./mole degree, in contrast to the experimental value of 10.39 cal./mole degree.²⁰ The discrepancy is greater by a factor of two or more than the probable experimental error. The high calculated value, arising principally from the two low frequencies ν_9 (800 cm^{-1}) and ν_7 (825 cm^{-1}), would indicate that ν_7 , the torsional frequency, should have a higher value. Indeed, to fit the C_p data, it is necessary to raise ν_7 to *circa* 950 cm^{-1} .

It has recently been suggested by Herzberg¹⁸ that the maxima appearing as a band at 800 cm^{-1} arise from the infra-red inactive A_{1u} torsional oscillation (ν_7) made very weakly active by Coriolis interaction with the infra-red active B_{2u} ν_9 vibration (assumed to be at 995 cm^{-1} as assigned by Gallaway and Barker). The inverse of this explanation can also be applied to account for the 995 cm^{-1} band, assuming the 800 cm^{-1} band to be the ν_9 fundamental. This interpretation offers a better assignment of overtones, as detailed above, but it does not offer a ready explanation of the 1656 cm^{-1} Raman line, which is the source of the value 825 cm^{-1} for ν_7 on Gallaway and Barker's assignment. It is apparent that a more detailed theoretical and experimental study will be necessary to decide the matter.

VI. VIBRATIONAL ASSIGNMENT OF PROPYLENE

The spectrum of propylene (Fig. 2) is in excellent agreement with those of Wilson and Wells⁴ and Avery and Ellis.⁵ Wilson and Wells used a fluorite prism in the range from 6 μ to 9 μ and consequently succeeded in resolving the 7 μ bands somewhat better than was achieved here. In the region from 9 μ to 14.5 μ , however, the instrument used in the present work gave considerably better resolution, so that some further conclusions can be drawn regarding the frequency assignment in this molecule. The strong absorption near 11 μ shows clearly four Q -branch-like maxima, at 9.58 μ , 10.10 μ , 10.84 μ , and 10.95 μ (1044, 990, 923 and 913 cm^{-1}). The 10.10 μ and 10.95 μ peaks were observed by Avery and Ellis⁵ at room temperature. The reality of the weak peak at 10.84 μ is better established than the

TABLE V. Vibrational assignment of propylene, frequencies less than 1300 cm^{-1} . (Frequencies in cm^{-1} .)

Infra-red (vapor, this work)	Raman (liquid, Ananthakrishnan*)	Assignment
7.70 μ 1299(w)	1297(vs, pol.)	CH in-plane wagging. P and R branches at 1285 and 1316
8.17 1224(w)	—	(harmonic or difference) P and R branches at 1215 and 1239
8.39 1190(w)	—	(harmonic or difference)
8.55 1170(w)	—	(CH ₃ in-plane rocking) P branch at 1157
9.58 1044(m)	—	CH ₃ out-of-plane rocking. Diffuse P and R branches near 1015 and 1070.
10.10 990(s)	—	CH (or CH ₃) out-of-plane wagging. Diffuse P and R branches near 950 and 1015
10.84 923(m)	920(s, pol.)	C—C stretching
10.95 913(s)	—	CH ₂ (or CH) out-of-plane wagging. Diffuse P and R branches near 890 and 950 (difference)
12.98 770(vw)	—	(CH ₂ in-plane rocking) P and R branches at 723 and 743
13.68 731(vw)	—	CH ₂ torsion
578(s) ^b	580(w, b, depol.)	C=C—C bending
417(m) ^b	432(m, pol.)	

Assignments in parentheses are uncertain but plausible.

* R. Ananthakrishnan, Proc. Ind. Acad. Sci. 3A, 527 (1936).

^b From Wilson and Wells, reference 4.

curve of Fig. 2 indicates, since it has been found also in several other spectra at different pressures. Avery and Ellis⁵ show also the spectrum of solid propylene at -195°C , in which there appear bands corresponding to all four of the bands noted above, at wave-lengths 9.59 μ , 10.06 μ , 10.68 μ , and 10.96 μ . A series of weak maxima were found in the present work between 13 and 14 μ , which were observed by Wilson and Wells as a weak structureless band. The maxima seem to indicate two bands with origins (Q branches) at 12.98 μ and 13.68 μ (770 cm^{-1} and 731 cm^{-1}).

In accordance with the discussions given by Wilson and Wells⁴ and by Herzberg²¹ of the vibrational assignment in propylene, the CH₃ and CH₂ bending frequencies in the 7 μ (1400 cm^{-1}) region, the CH in-plane wagging frequency at 7.70 μ (1299 cm^{-1}), the carbon-skeleton bending frequency at 417 cm^{-1} and the torsion about the double bond at 578 cm^{-1} (the latter two found by Wilson and Wells with a KBr prism) are all fairly clear-cut. Thus there remain two CH₃ rocking, two CH₂ rocking, the out-of-plane CH wagging, and the C—C stretching vibrations to be assigned to the bands between 8 μ and 15 μ . There are observed here a complex of bands near 8.5 μ , probably consisting of three bands with Q

²⁰ E. J. Burcik, E. H. Eyster, and D. M. Yost, J. Chem. Phys. 9, 118 (1941).

²¹ G. Herzberg, reference 18, pp. 354, 355.

branches at 8.17μ , 8.39μ , and 8.55μ (1224 , 1190 , and 1170 cm^{-1}), and the six bands noted above.

From the discussion given earlier of the strong olefin bands in the 10 to 12μ region, the strong bands at 10.10μ and 10.95μ (990 and 913 cm^{-1}) represent the CH_2 and CH out-of-plane wagging vibrations. The Raman line at 920 cm^{-1} is to be taken as the $\text{C}-\text{C}$ stretching frequency from its intensity,⁴ and hence is to be correlated with the 10.84μ (923 cm^{-1}) infra-red peak.

From analogy with other molecules and from the normal frequency calculation of Wilson and Wells,⁴ the two methyl rocking frequencies are to be expected near 1000 cm^{-1} . The peak at 9.58μ (1044 cm^{-1}) is therefore in all probability one of these. The other one and the CH_2 in-plane rocking are still uncertain. A plausible guess is

that one of the bands near 8.5μ , the 8.55μ (1170 cm^{-1}) band for instance, represents the second methyl rocking frequency, since many methyl-containing compounds exhibit methyl rocking bands near this position. The other two bands in the 8.5μ region (8.17μ and 8.39μ) would then have to be explained as harmonic or difference bands. The CH_2 in-plane rocking frequency, in accordance with the ethylene assignment postulated above, should be found below 800 cm^{-1} , and may be the cause of the very weak 13.68μ (731 cm^{-1}) band. The weak band at 12.98μ (770 cm^{-1}) must be interpreted as a difference band, probably from the low methyl torsion frequency near 200 cm^{-1} .

Table V lists this frequency assignment for frequencies less than 1300 cm^{-1} .