U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP610

Part of Bureau of Standards Journal of Research, Vol. 11, November 1933

SPECTRAL DIFFERENTIATION OF PURE HYDROCARBONS: A NEAR INFRARED ABSORPTION STUDY [1] [2]

By Urner Liddel [3] and Charles Kasper [4]

ABSTRACT

The spectra of 36 hydrocarbons have been recorded in the near infrared from 5,500 to 9,000 cm^{-1} (2μ to 1μ), using an automatic recording infrared glass spectrograph. Specific absorptive indices have been calculated from the results and plotted against wave numbers (wave lengths per centimeter). Correlations of the spectra of the various compounds have been made in regions associated with three energy transitions in the molecules. Characteristic differentiation of the compounds according to structural types has been indicated.

CONTENTS

I. INTRODUCTION

It was early (1881 to 1905) recognized (1, 2, 3)[5] that certain regions of the infrared absorption spectra of organic compounds might be associated with the presence of various atomic linkages in the mole-

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of project no. 6: The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] This paper was presented before the Petroleum Division of the American Chemical Society at Washington, D.C., Mar. 29, 1933.

[3] Bureau of Chemistry and Soils, U.S. Department of Agriculture.

[4] Research associate representing the American Petroleum Institute.

[5] The arabic numbers in parentheses here and throughout the text refer to the bibliography at the end of the paper.

cules. Later work (4 to 27) (1923 to 1933) has added evidence in favor of this premise, and recent investigation (25) has shown that it may be possible to indicate the general type of the group; e.g., primary, secondary, or tertiary carbon atom combined with a hydrogen atom. If these premises prove applicable, an easy method would be provided for determining the structure of organic molecules, and would be of assistance where chemical methods are very difficult or fail. Careful investigations of the characteristics of these absorptions might lead to quantitative estimations of the amounts of various compounds present in a mixture. With these points in consideration, the generous cooperation of the American Petroleum Institute made possible this study to ascertain the possibility of the usefulness of this method in a study of the constituents of petroleum.

II. EXPERIMENTAL PROCEDURE

The spectrograph, of the Littrow form, is shown in figure 1. The source of continuous radiation is a tungsten ribbon-filament lamp which is enclosed in a water-jacketed cell. The light is collimated through a large brass tube 1 m long, and focused by a concave mirror on the slit of the spectograph. The absorption cell containing the solution or compound under investigation is fixed in the light path between the collimating tube and the slit. The light then goes to a large concave mirror from which parallel rays are reflected through two 60° glass prisms, then reflected by the plane Littrow mirror over the same path, giving four-prism dispersion, and finally focused on a sensitive vacuum thermocouple. Wave length variation is accomplished by rotation of the Littrow mirror which is coupled with the motion of a recording photographic plate by means of a lever system. As the incident energy on the thermocouple actuates the galvanometer, a beam of light reflected from the galvanometer mirror moves across the photographic plate, so that one has recorded a graph of galvanometer deflections with wave lengths, or a plot in arbitrary units of the intensity of transmitted light against frequency. As a check on the constancy of the intensity of emission of the tungsten filament, the cell was withdrawn from the light path by means of a solenoid arrangement moving the cell-holder along a dove-tail slide, thus producing on the recorded photographic plate segments of the curve of the emission of the source not modified by the absorption cell. Likewise, to determine the zero drift of the galvanometer, a shutter was thrown in front of the slit at certain times giving segments of the base line of the curve. The motion of these two auxiliary units was controlled by a breaker circuit operated by a synchronous motor; the motion of the photographic plate was controlled also by a synchronous motor, hence these segments of curves always appeared at the same frequency on the recorded plate, and it was thereby possible to compare the intensity of emission of the source during the recording of one plate with that of another. Thus by recording the transmission of the cell filled with carbon tetrachloride, then the cell containing the solution, it was possible to calculate the transmittancy from which the absorptive indices were derived.

Calibration of the instrument was effected with mercury arc spectra and water-vapor bands, using the wave numbers recorded by McAlister (33) and by Plyler (34). The thermocouple used was a modi-

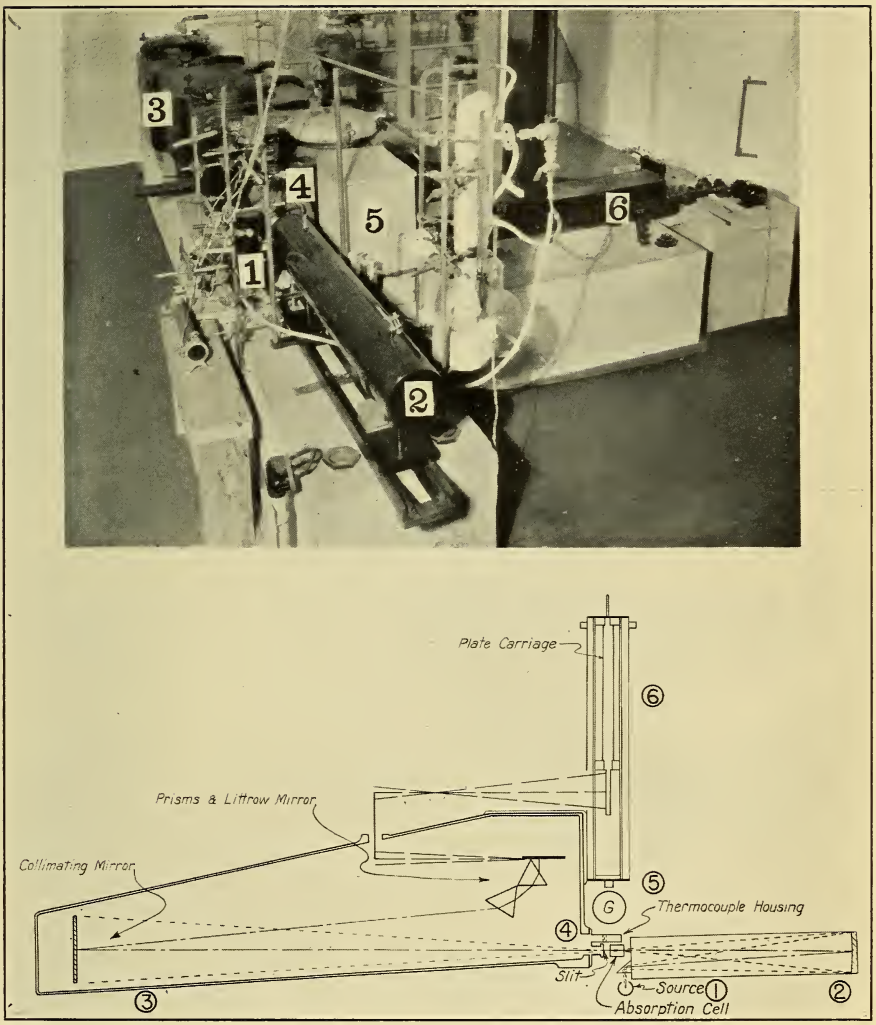


FIGURE 1.—*Photograph and diagrammatic sketch of the recording infrared vacuum spectograph.*

1, Cell containing source lamp; 2, external collimator; 3, spectograph proper; 4, thermocouple housing; 5, galvanometer shield; 6, recording mechanism.

fication of the type of single-junction vacuum thermocouple described by Brackett and McAlister (28). The electrical supply for the source lamp came from a battery of 6 large cells of 1,200 ampere-hour capacity in multiple connection, which held the voltage on the filament constant to within 0.01 volt during the time required for a run. The filament used about 18 amperes of current at 5.75 volts. Since absorption by water vapor is very strong in one of the regions under study, the water was removed by first evacuating the spectrograph casting, and then flushing and filling it to atmospheric pressure with carefully dried nitrogen. The collimating tube was treated in the same manner. Thus, only a very slight amount of water vapor absorption appears on the records and this allows, for the first time, accurate determinations of absorption indices of hydrocarbons in the region of 7,100 cm^{-1}.

Solutions of hydrocarbons were generally used, to enable accurate determination of the concentration of molecules absorbing in the light path. Since pure carbon tetrachloride does not absorb in this region, it was used as a solvent.[6] In stated instances when scarcity or value of the sample required its preservation in the pure state, 1- and 4-mm cells filled with the pure samples were used. The solutions were studied in a 5-cm absorption cell, and approximately 0.5 molar solutions were employed for the regions 6,400 to 7,400 cm^{-1} and 7,900 to 8,900 cm^{-1}, and 0.1 molar for the region 5,400 to 6,400 cm^{-1}.

TABLE 1

	Region 7900–8900	Region 6400–7400	Region 5400–6400	State studied	Purity, percent	Sources[1]	References[2]
	Figure numbers						
AROMATIC HYDROCARBONS							
Benzene	2	11	16	Solution		2	a
Toluene	2	11	17	do		2	a
Ethylbenzene	2	11	17	do		2	a
o-Xylene	3	11	18	do	99.0	1	b
m-Xylene	3	11	18	do	99.9	1	b
p-Xylene	3	11	18	do	99.9	1	b
Hemimellitene	4	11	18	do	99.9	1	c
Pseudocumene	4	11	18	do	99.9	1	c
Mesitylene	4	11	18	do	99.9	1	c
NAPHTHENES							
Cyclohexane	5	11	19	Solution	99.9	2	a
Methylcyclohexane	5	11	19	do	99.9	1	d
Methylcyclopentane	5	11	19	do	98.9	1	e
1, 2-Dimethylcyclopentane	5	11	19	Pure		4	f
1, 2-Dimethylcyclopentane	5	11	19	do		4	f
NORMAL ALIPHATIC HYDROCARBONS							
Pentane	6	12	20	Solution		1 a	g
Hexane	6	12	20	do	98.3	1	h
Heptane	6	12	21	do	99.8	1	d
Octane	6	12	21	do	99.1	1	i
Nonane	6	12	22	do	99.2	1	j
Decane	6	12	22	do	99.9	1	k
Undecane	6	12	22	do		1 a	g
Dodecane	6	12	22	do		1 a	g

See references at end of table.

[6] Commercial C.P. carbon tetrachloride was found to contain small amounts of chloroform which was removed by distillation in the 30-plate still of the Bureau, and fractionated to constant refractive index.

TABLE 1—Continued

ISOMERIC ALIPHATIC HYDROCARBONS

	Region 7900–8900	Region 6400–7400	Region 5400–6400	State studied	Purity, percent	Sources[1]	References[2]
	Figure numbers						
Isopentane	7	13	23	Solution		2	
2-Methylpentane	7	13	23	Pure	95	1	l
3-Methylpentane	8	14	24	Solution	95	1	l
2, 3-Dimethylbutane	8	14	24	do	95	1	l
2, 3-Dimethylpentane	9	15	25	Pure		3	m
2, 4-Dimethylpentane	9	15	25	do		3	m
3, 3-Dimethylpentane	9	15	25	do		3	m
2, 2-Dimethylpentane	9			do		3	m
2, 2, 3-Trimethylbutane	9	15	25	do		3	m
3-Ethylpentane	9	15	25	do		3	m
3-Methylhexane	9	15	25	do		3	m
2-Methylhexane	9	15	25	Solution	99.9	1	n
2, 2, 4-Trimethylpentane	10	15	25	do	99.8	1	o

[1] Sources: 1, American Petroleum Institute; 2, Bureau des Étalons Physico-Chimiques in Brussels; 3 Ethyl Gas Corporation; 4, Professor G. Chavanne.

[2] References:

a. J. Timmermanns et F. Martin, J.chim.phys., vol. 23, p. 747, 1926.
b. J. D. White and F. W. Rose, Jr., Bur. Standards J. Research, vol. 9, p. 711, 1932.
c. B. J. Mair and S. T. Schicktanz, ibid. In press.
d. M. M. Hicks-Bruun and J. H. Bruun, ibid, vol. 8, p. 525, 1932.
e. ibid, vol. 7, p. 799, 1931.
f. G. Chavanne, Extrait des Comptes rendus Congres National des Sciences-Bruxelles, 29 juin-2 juillet, 1930.
g. B. J. Mair, Bur. Standards J. Research, vol. 9, p. 457, 1932.
h. J. H. Bruun and M. M. Hicks-Bruun, ibid, vol. 6, p. 869, 1931.
i. R. T. Leslie and S. T. Schicktanz, ibid, vol. 6, p. 381, 1931.
j. J. D. White and F. W. Rose, Jr., ibid, vol. 7, p. 907, 1931.
k. J. H. Bruun and M. M. Hicks-Bruun, ibid, vol. 8, p. 583, 1932.
l. J. H. Bruun and M. M. Hicks-Bruun, ibid, vol. 5, p. 933, 1930.
m. G. Edgar et al., J.Am.Chem.Soc., vol. 51, p. 1493, 1929.
n. J. H. Bruun and M. M. Hicks-Bruun, Bur. Standards J. Research, vol. 10, p. 465, 1933.
o. J. H. Bruun and M. M. Hicks-Bruun, ibid, vol. 9, p. 269, 1932.

Most of the hydrocarbons were obtained from the Bureau of Standards, American Petroleum Institute research project no. 6, where they had been isolated from petroleum and carefully purified. The isomers of heptane were lent to us through the courtesy of Dr. G. Calingaert and Dr. Graham Edgar of the Ethyl Gas Corporation and the isomers of 1, 2-dimethylcyclopentane by Prof. G. Chavanne of the University of Brussels.

III. RESULTS

In order to make the results most generally useful, specific absorptive indices (molecular extinction coefficients) have been calculated, permitting direct comparisons between the spectra of any compounds by giving data independent of cell depth and, within certain ranges, of concentration. This last statement of course involves the validity of Lambert's and Beer's laws which has been questioned in previous investigations (23, 24). In the region from 1μ to 2μ, using cells greater than 1 mm in thickness, no deviation from Lambert's law was found, nor any definite deviations from Beer's law in the concentration range studied, roughly 0.03 to 0.8 molar. The slight deviations have always been well within experimental error.

The specific absorptive index is, by definition (31), $\frac{-\log_{10} I/I_0}{cd}$, I/I_0 being the fraction of transmitted light, c, concentration of the

solute in moles per liter of the solution, and d, the cell depth in centimeters.

While the following graphs are continuous curves, enough points have been calculated and critical visual comparisons made with the original records so that presentation of them in this manner seems justified. The accuracy in the wave number (which is proportional to the true frequency) is ± 10 cm^{-1}. The absolute accuracy of the specific absorptive index is ± 0.05 in the region 5,400 to 6,400 cm^{-1}, ± 0.02 in the region 6,400 to 7,400 cm^{-1}, and ± 0.01 from 7,900 to 9,000 cm^{-1}, although the relative accuracy within a given graph is much greater.

Absorption in the regions 5,900 and 8,500 cm^{-1} has generally been interpreted as the first and second overtones of a fundamental frequence around 3,000 cm^{-1}, which has been considered the vibration of the H atom along the valence bond with respect to the carbon atom. Absorption around 7,000 cm^{-1} has been interpreted as a combination frequency of the first overtone (5,900 cm^{-1}) plus another fundamental frequency associated with a "swinging" oscillation. The absorption of the hydrocarbons in each region will be considered separately.

1. ABSORPTION FROM 7,900 TO 9,000 CM^{-1}

(a) AROMATIC HYDROCARBONS

It is seen (fig. 2) that benzene has a strong absorption between 8,700 and 8,800 cm^{-1}. The corresponding absorption by toluene is shifted to slightly lower frequencies, decreased in intensity, and there appears near 8,400 cm^{-1} a band not quite half as intense. The strong component has nearly the same intensity in ethylbenzene but the component of lower frequency has increased approximately two thirds.

The two bands approach equality in the xylenes (fig. 3), intensities and separations of the maxima varying in the three isomers amongst themselves.

In the trimethylbenzenes (fig. 4), the component of higher frequency decreases slightly in intensity and the lower one is appreciably greater than in the xylenes. Separations and intensities of the maxima vary again as in the xylenes, and the lower frequency region is composed of three apparent maxima, as distinguished from the one or two of the xylenes. The high frequency component of mesitylene is considerably sharper than in any of the other methyl derivatives, suggesting that the position of the methyl groups therein places a considerable restraining force on the possible motions of the nuclear hydrogen.

(b) NAPHTHENES

Only a few of this group have been available for study at the present time. Cyclohexane (fig. 5) has a much more complex spectrum than benzene. It and methylcyclohexane exhibit by far the most complex bands observed. The methyl derivative might appear at first to be different in type from cyclohexane, yet if one adds the absorption of a methyl group around 8,350 cm^{-1} to cyclohexane, similarity is obvious. Cyclopentane has not yet been available for study, hence little can be said concerning the methyl compound except that the spectrum is much simpler in character than that of the six-membered ring. The two isomers of 1, 2-di-

methylcyclopentane were studied in the pure state. Little difference is exhibited between the two, as would be expected, yet scrutiny reveals that the low frequency satellite bands are somewhat more apparent in the high boiling compound.

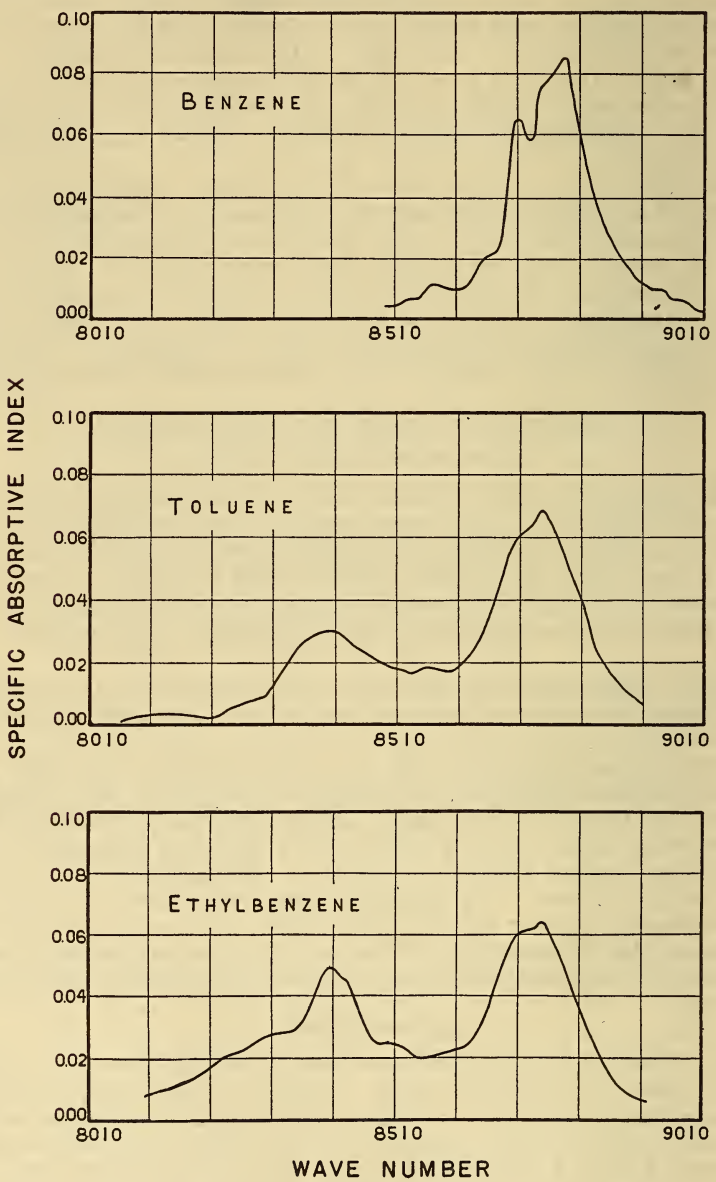


FIGURE 2.

(c) NORMAL ALIPHATIC HYDROCARBONS

The series from pentane to dodecane has been observed (fig. 6). This adds further evidence to Brackett's theory (25) that the absorption at 8,400 cm^{-1} arises from the methyl group, that around 8,250

cm^{-1} from the methylene group, and that the low frequency component shows a shift of the median of absorption to lower frequencies with increasing length of chain.

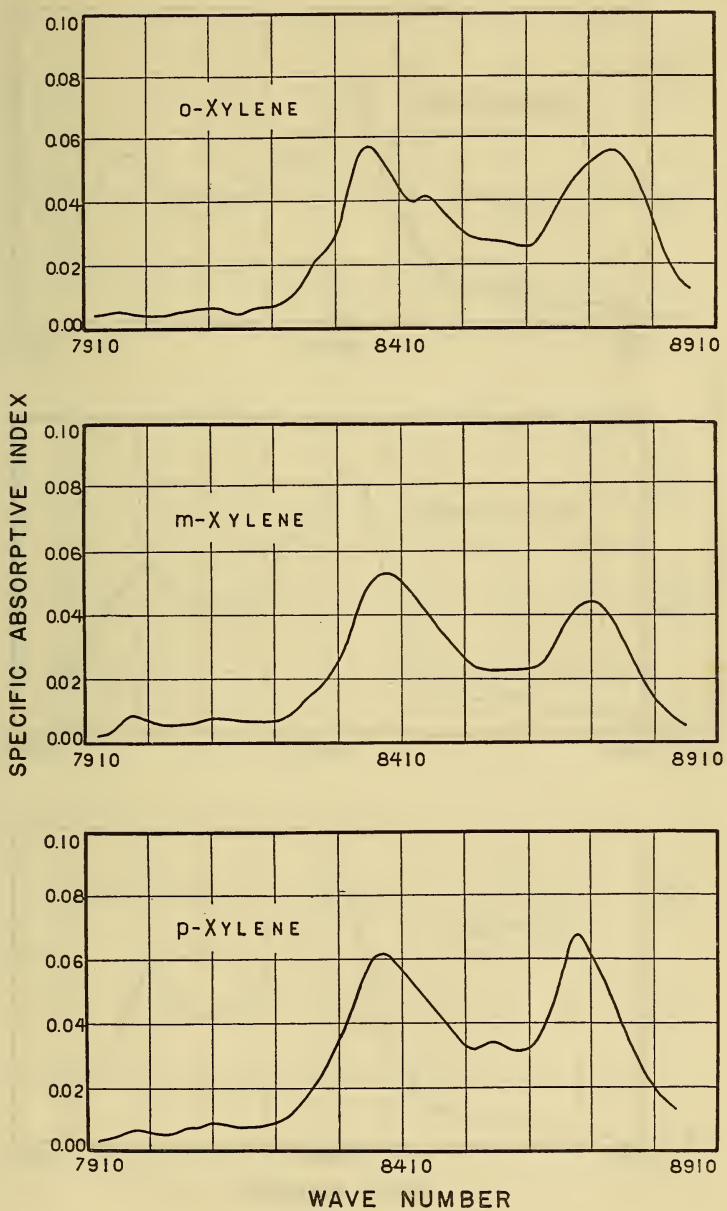


FIGURE 3.

These results, giving intensities of absorption, indicate that the absorption of each CH_2 group is not strictly additive, but nearly so, i.e., the 10 CH_2 groups in dodecane do not absorb as much per unit

as the 4 in hexane. The accuracy of the work does not permit determination of the relation. It may appear to those unfamiliar with this type of absorption that the band which is ascribed to the

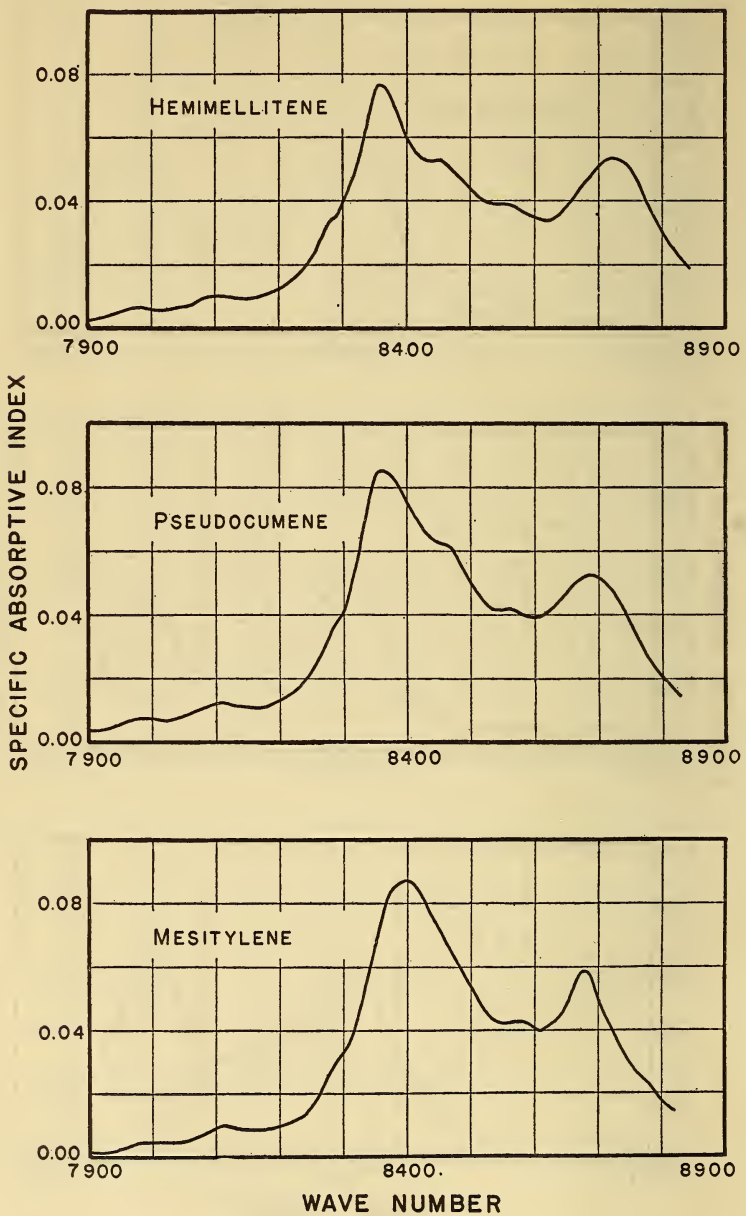
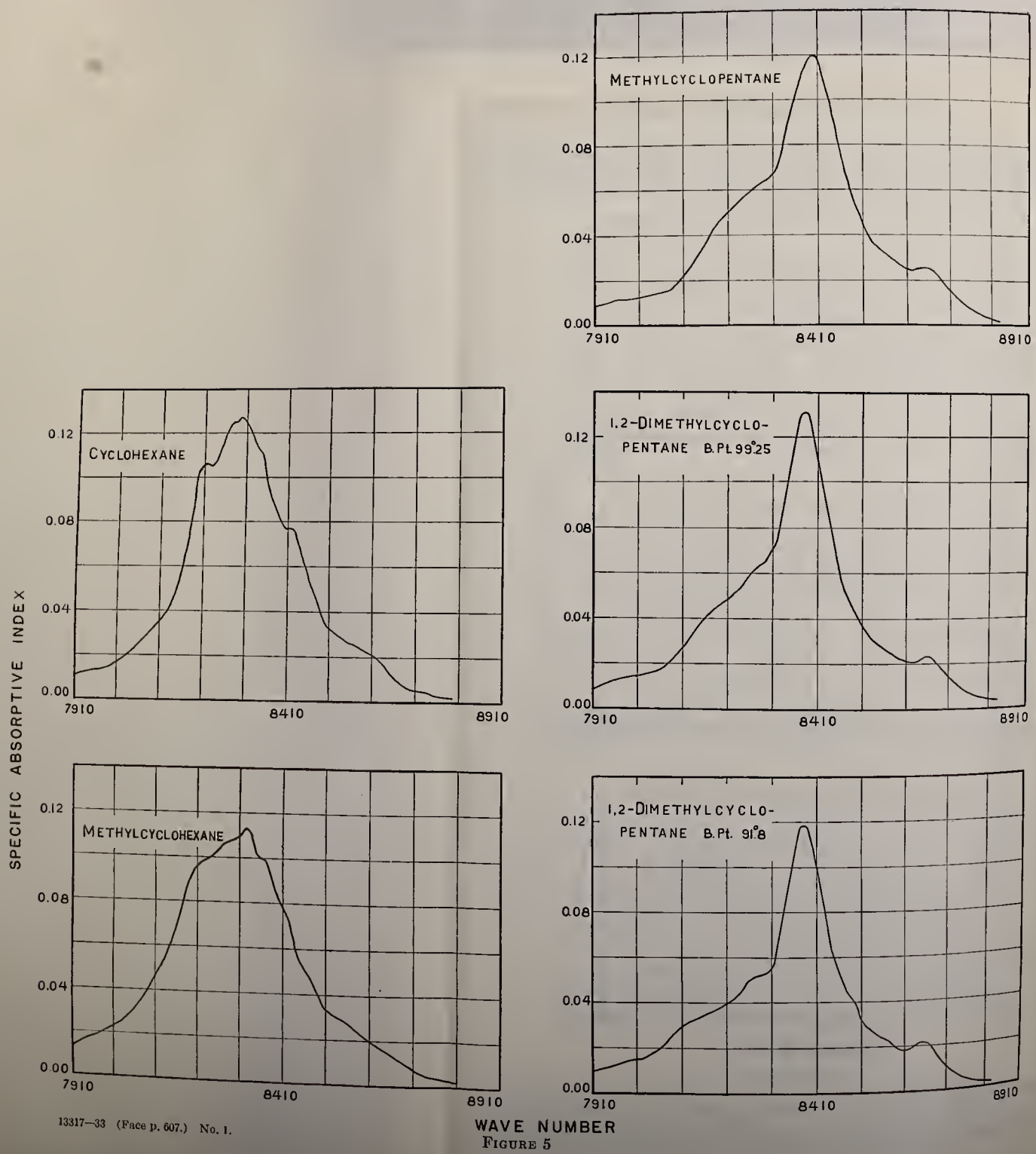


FIGURE 4.

methyl group is increasing in intensity in the longer chains, which is not true. It must be realized that these are integrated curves and that the separation of the maxima is insufficient to determine the



13317—33 (Face p. 607.) No. 1.

FIGURE 5

true intensity of each component, so that as the CH_2 absorption becomes more and more intense, the CH_3 maximum is carried up on the side of the curve. Possibly, it should be emphasized here that this is a true overlapping of bands. The lack of further resolution is not due to the apparatus used, but is an inherent characteristic of these large molecules which possess such large moments of inertia

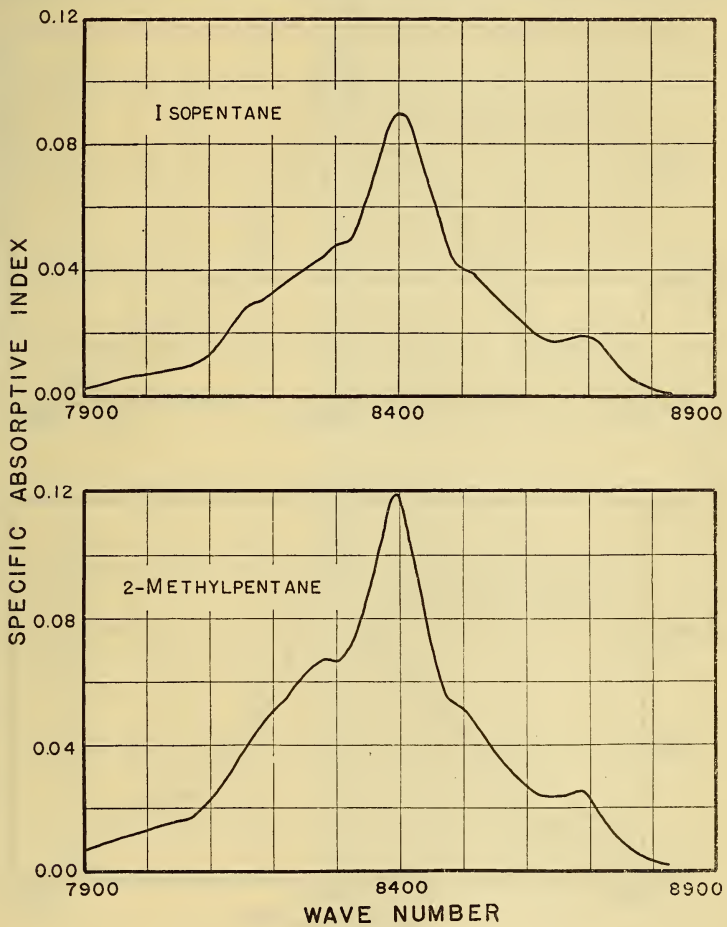
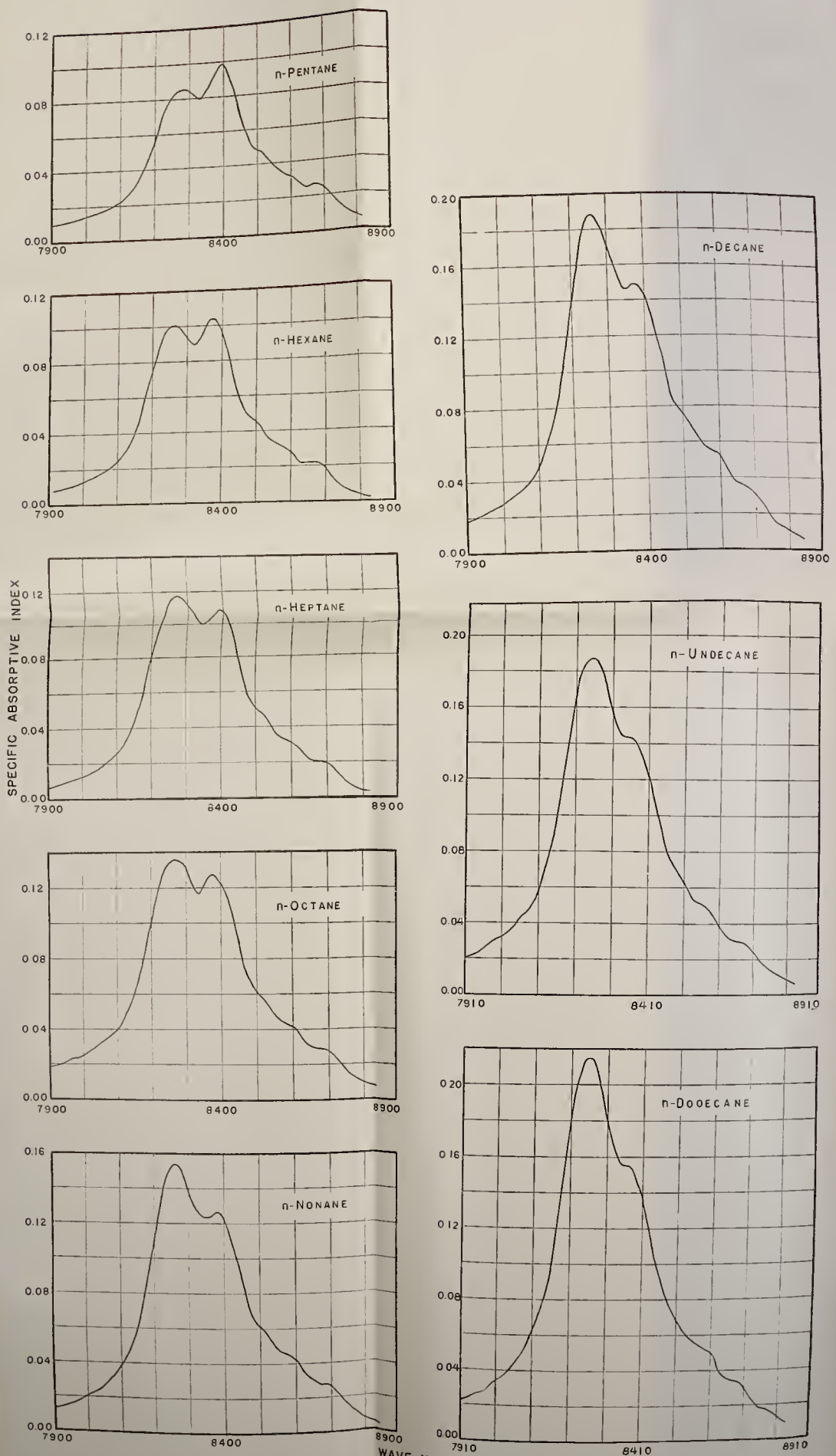


FIGURE 7.

that the separation of the rotation lines is far too small to be observed experimentally by any apparatus known.

An interesting observation is that the frequency of the maximum attributed to the methyl groups varies slightly between the odd- and even-numbered carbon atom chains, the variation decreasing with length of chain and becoming indistinguishable after decane. The other maximum shifts very slightly. This may be correlated with other known alternations in the properties of these compounds.



13317—33 (Face p. 607.) No. 2.

FIGURE 6

(d) ISOMERIC ALIPHATIC HYDROCARBONS

Perhaps the most valuable part of the work lies in the observation of the spectra of various isomers. In isopentane (Fig. 7) the secondary absorption has dropped very appreciably from that found in *n*-pentane and tertiary absorption appeared near 8,150 cm^{-1}. It was very interesting to note whether substitution of a methyl group in

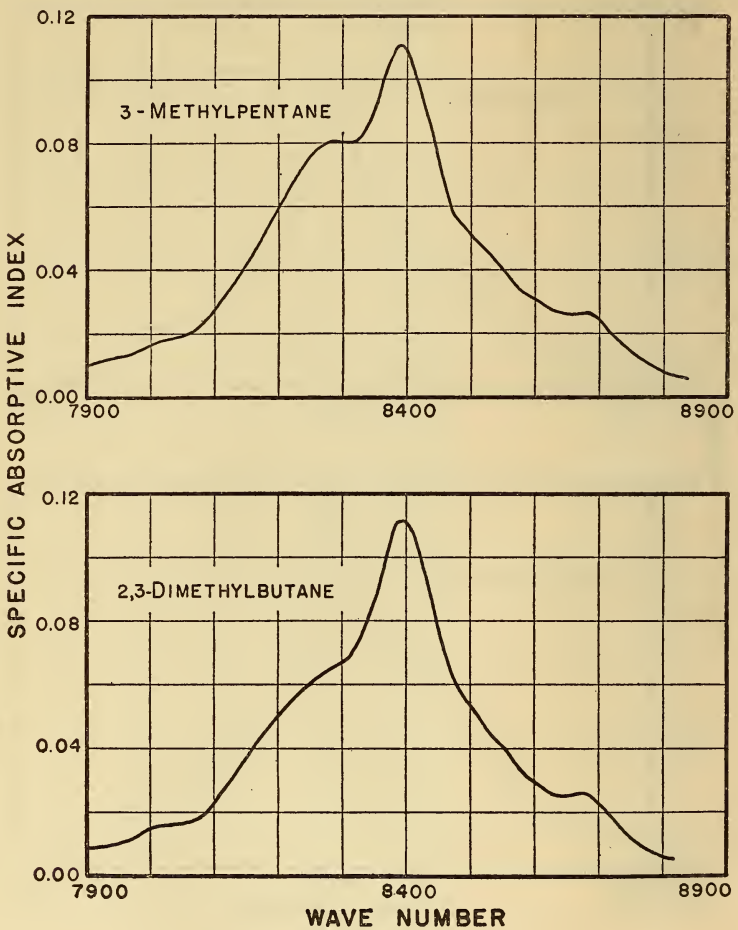
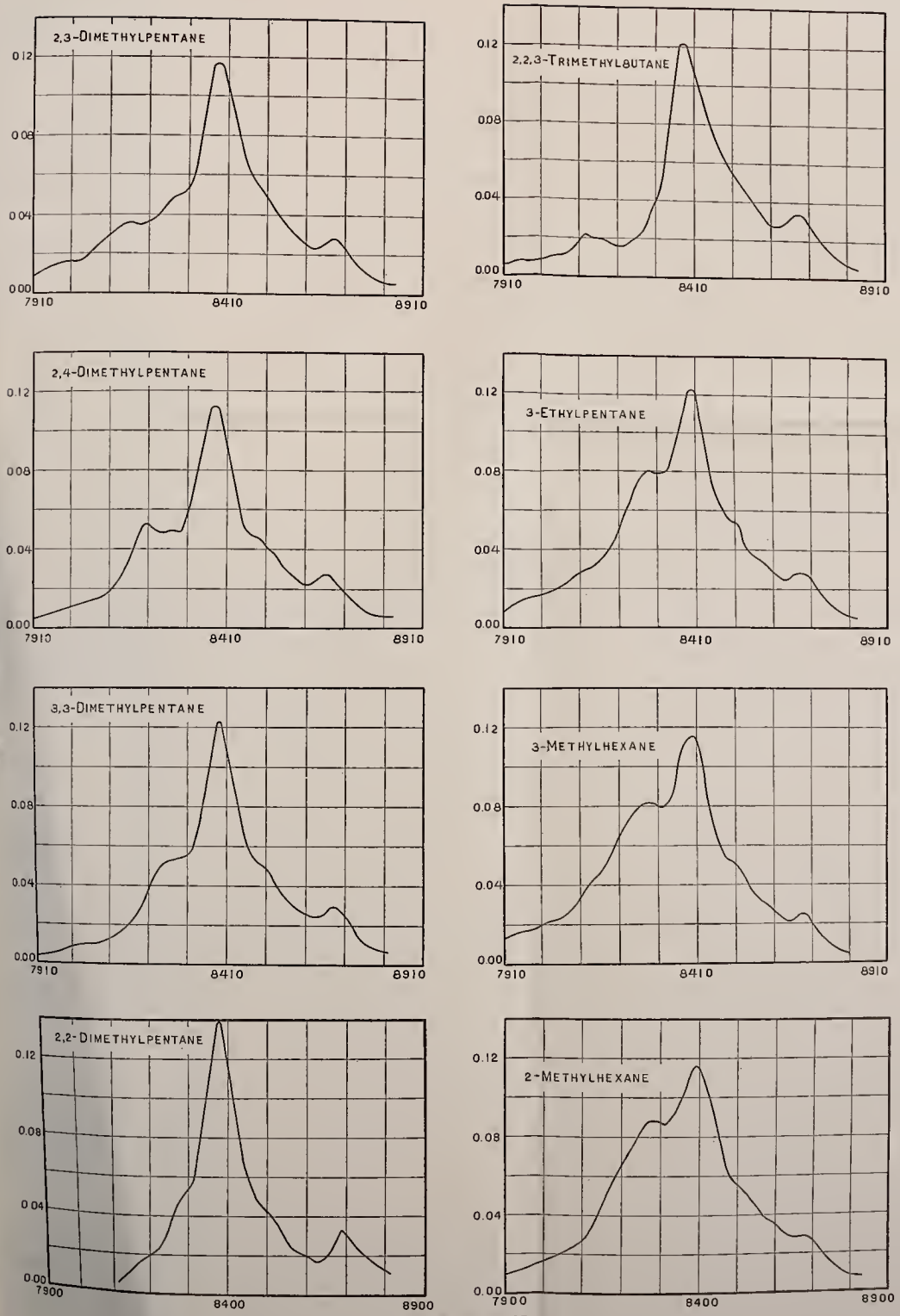


FIGURE 8.

various positions along the chain produced any differences in the absorption. 2-Methylpentane and 3-methylpentane (fig. 8) offer a good example of this. Minute differences cannot be stressed, since 2-methylpentane was observed in the pure state and the values are not so dependable. However, it appears that the maximum of the 2-isomer is sharper than that of the 3-isomer and certainly the ratio of primary to secondary absorption is greater in the 2-form than the 3-form. 2, 3-Dimethylbutane consists of 4 primary groups and 2 tertiary groups, and no secondary absorption appears in the spectrum. It must be pointed out that, while the general slope of the



13317—33. (Face p. 608.)

FIGURE 9.

curve might lead one to suspect the presence of secondary groups, the maximum, if completely resolved, would be of a nearly symmetrical character. Possibly adjacency of the methyl groups plays some part in the 2, 3-isomer. An unexpected difference appears in the spectra of 2, 3-, and 2, 4-dimethylpentane; unexpected since both molecules are composed of the same number of each type of carbon groups. In these curves the absorption of primary, secondary, and tertiary hydrocarbon linkages is clearly evidenced. 3, 3-, and 2, 2-Dimethylpentane are another interesting pair, and it is indeed unfortunate that no reliability can be placed on the results of the 2, 2-isomer since it was only available before accurate measurements could be made. It is included merely for comparison of frequencies and for rough ratios of intensities.

2-Methyl- and 3-methylhexane show the least difference of any two compounds that were studied in this region. Again, it was not

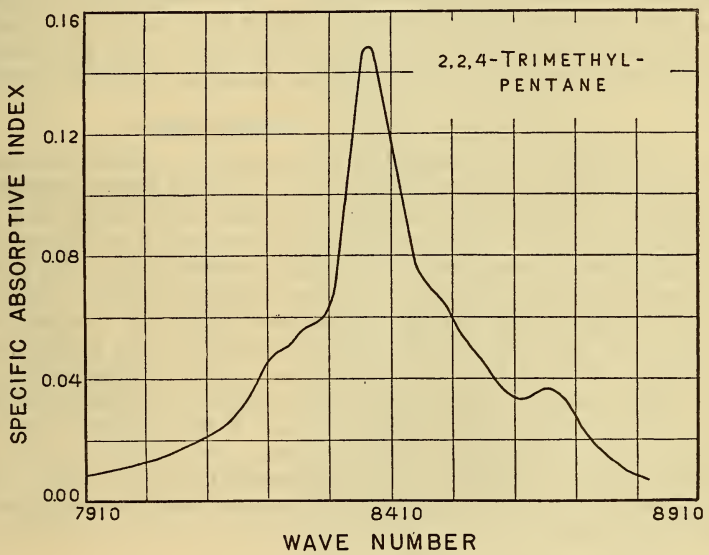


FIGURE 10.

possible to study them both in the same state, which may make a difference. 2, 2, 3-Trimethylbutane, being composed of 5 primary and 1 tertiary groups, has the distinct type of bands to be expected, as does 3-ethylpentane with 3 primary, 3 secondary, and 1 tertiary groups.

2. ABSORPTION FROM 6,400 TO 7,400 CM^{-1}

(a) AROMATIC HYDROCARBONS

The absorption by benzene (fig. 11) in this region is characterized by its weak intensity and multiplicity of structure. The addition of a methyl group to the nucleus considerably increases the intensity of absorption through the whole region and wipes out part of the apparent structure, as does the addition of an ethyl group. The absorption increases again in the xylenes, certain differentiating characteristics between the three isomers appearing. Similar remarks apply to the three trimethylbenzenes. A characteristic of the absorption

in this region seems to be that the aromatic linkages absorb much less than the aliphatic, i.e., per C-H bond; the reverse of this is true in the other two regions.

(b) NAPHTHENES

These curves show the presence of two relatively strong maxima with many satellite bands on the low frequency side. A more obvious similarity of these curves to bands around 5,700 cm^{-1} is apparent in the case of naphthenes than in the case of the preceding aromatic hydrocarbons.

(c) NORMAL ALIPHATIC HYDROCARBONS

The normal aliphatic hydrocarbons (fig. 12) show less apparent structure here than the naphthenes, although the relation of these two groups is more easily seen in this region than in the foregoing. Two strong maxima appear, increasing in intensity in a regular manner with increasing length of chain. The distinction of primary and secondary absorption is not as evident here as in the preceding region; possibly the weak band around 7,350 cm^{-1} is to be associated with the methyl groups, the two intense maxima with the secondary groups.

(d) ISOMERIC ALIPHATIC HYDROCARBONS

It is not felt that space should be taken here to consider the absorption of each of these in detail (figs. 13, 14, 15), it being sufficient for the purposes of this paper to point out that each compound is individual in character of absorption, and to suggest that it seems from the alternations in intensity of the bands absorption of the primary group occurs around 7,350 cm^{-1}, of the secondary group at 7,075 and 7,175 cm^{-1}, and of the tertiary group near 6,950 cm^{-1}, which is not to be confused with the band near 6,975 cm^{-1} found in the normal compounds. This is not to be taken as a rigid classification until further work has been done, since there are a few apparent discrepancies. One peculiar observation is that, if two maxima are to be associated with secondary groups, the one near 7,075 cm^{-1} is much more affected by substitution in the molecule than the other in which the intensity is the same throughout the isomers and the corresponding normal compounds.

3. ABSORPTION FROM 5,400 TO 6,400 CM^{-1}

(a) AROMATIC HYDROCARBONS

Benzene (fig. 16) exhibits two sharp, intense maxima with many satellite bands. Physical analysis shows that some of these bands are combinations of the main absorption with known low-frequency bands of benzene such as those found by Kettering and Sleator (32). Substitution by a methyl group, as in toluene (fig. 17), greatly decreases the intensity and slightly decreases the frequency of the main peak, and introduces three bands around 5,700 cm^{-1}. The absorption curve of ethylbenzene exhibits even more structure.

The frequencies of the main maxima decrease still further in the xylenes (fig. 18), each isomer varying in intensity of absorption and exhibiting characteristic bands. The three bands seen first in toluene around 5,700 cm^{-1} are present here with considerably greater intensity, which is even greater in the trimethyl substituted compounds, hence may be associated with the presence of side chains in the

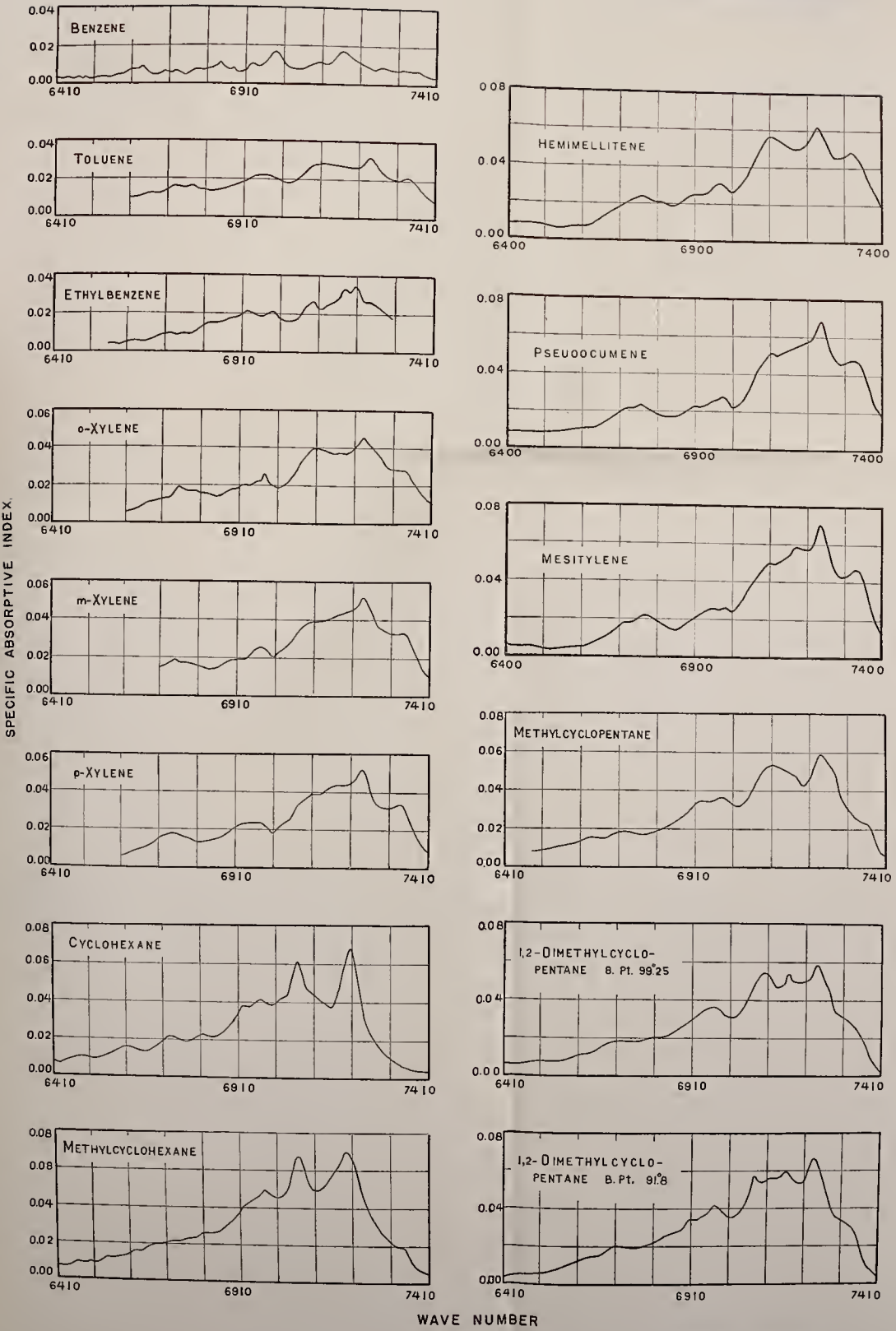


FIGURE 11.

12317—33 (Face p. 610.) No. 1.

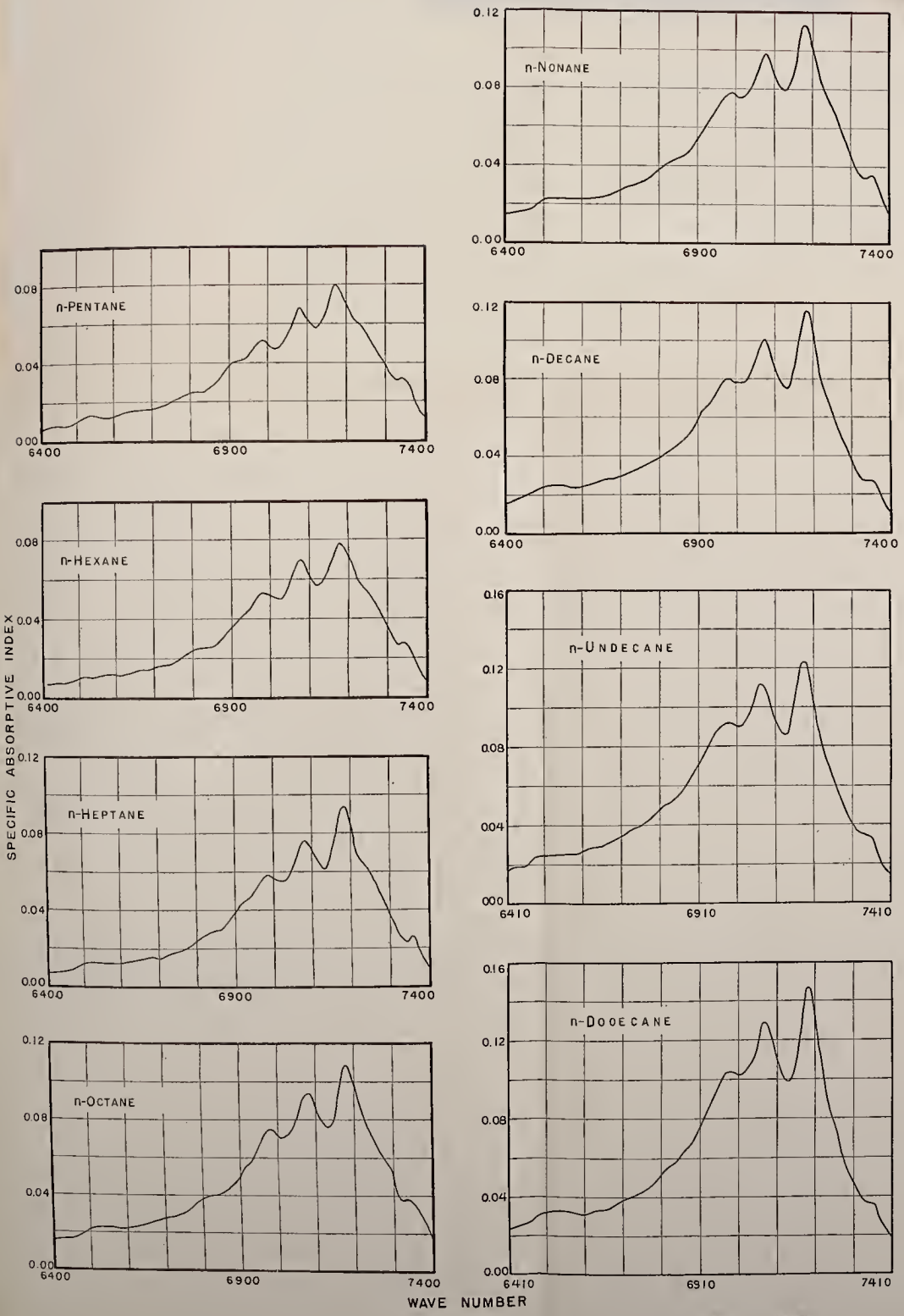

n-NONANE
n-PENTANE
n-DECANE
n-HEXANE
n-UNDECANE
n-HEPTANE
n-DODECANE
n-OCTANE
SPECIFIC ABSORPTIVE INDEX
WAVE NUMBER

FIGURE 12.

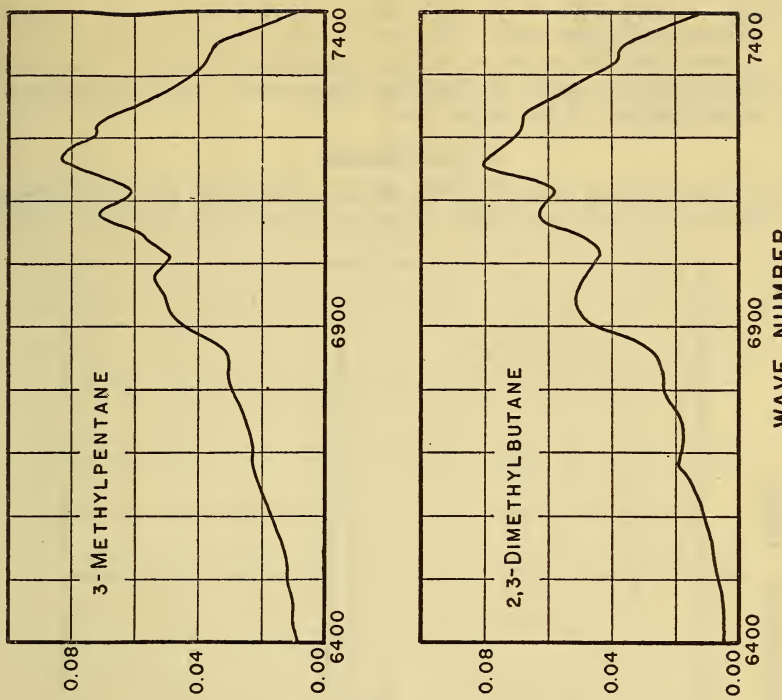


FIGURE 14.

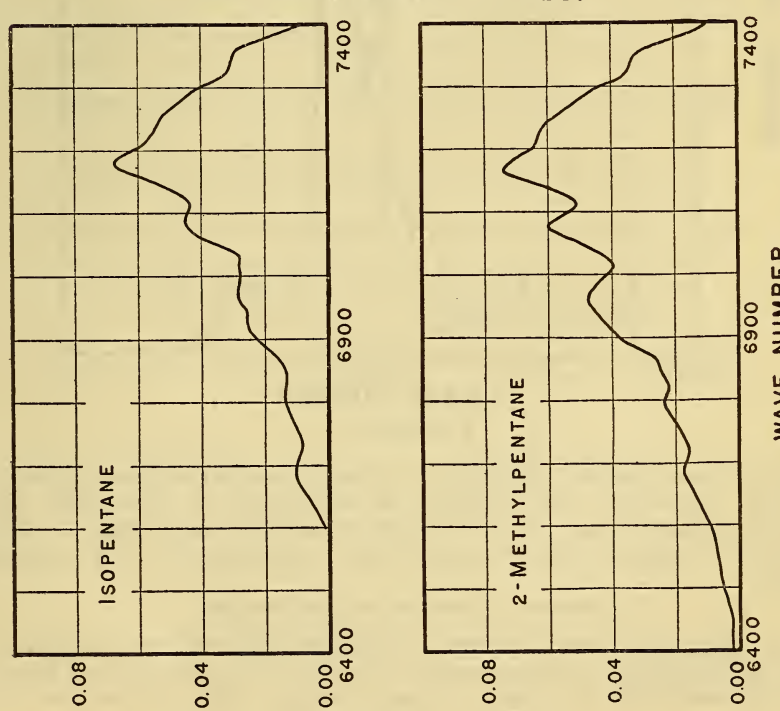
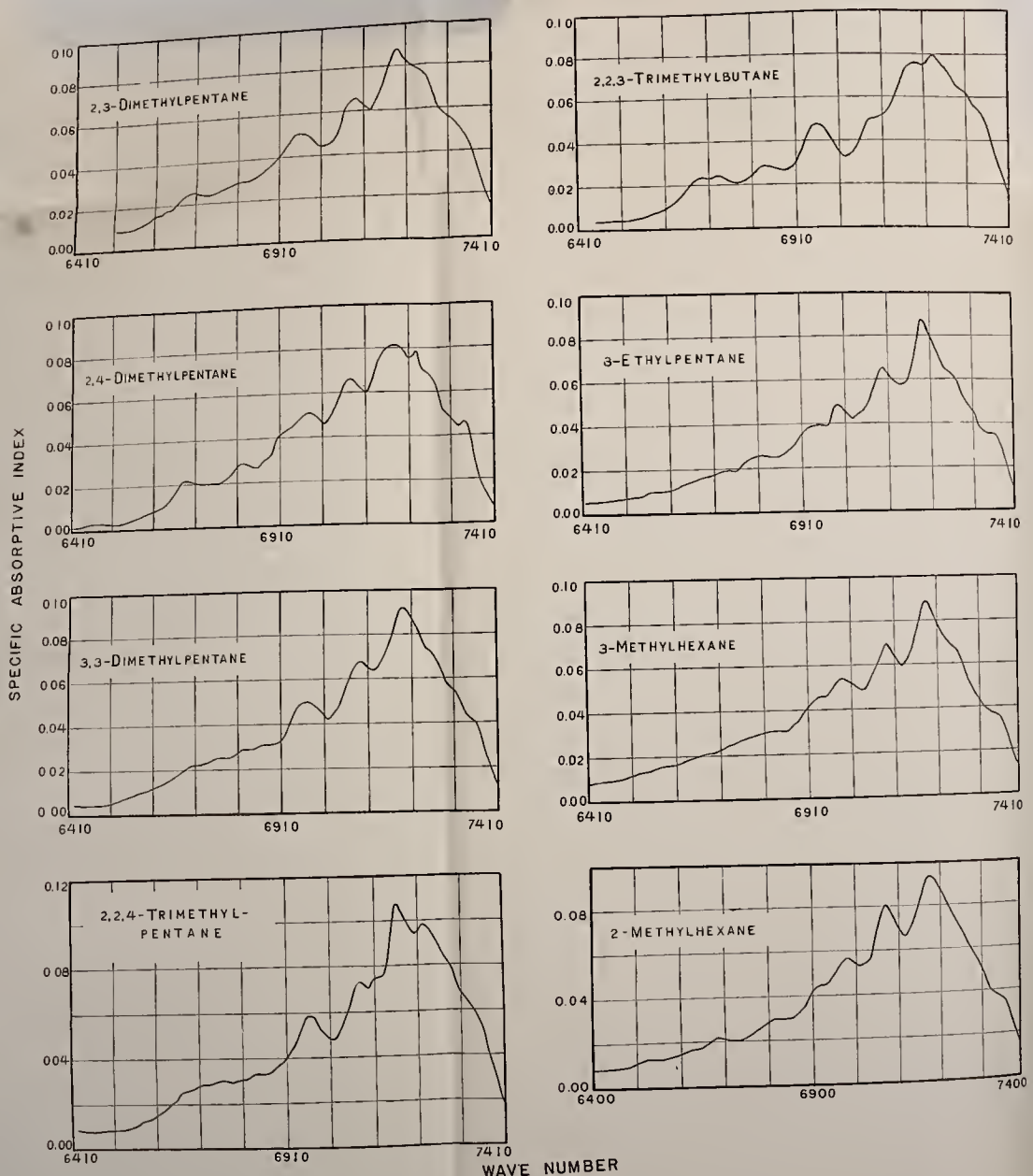


FIGURE 13.



13317—33. (Face p. 611.)

FIGURE 15.

molecule. There seem to be three main components in the absorption of hemimellitene near 5,900 cm^{-1}. In pseudocumene, one of these is considerably stronger, with appreciable decrease of another. Mesitylene exhibits only one intense sharp peak, with almost complete subordination of the other two.

(b) NAPHTHENES

The quite striking characteristic of the absorption by cyclohexane (fig. 19) here as compared with absorption around 8,300 cm^{-1} is its

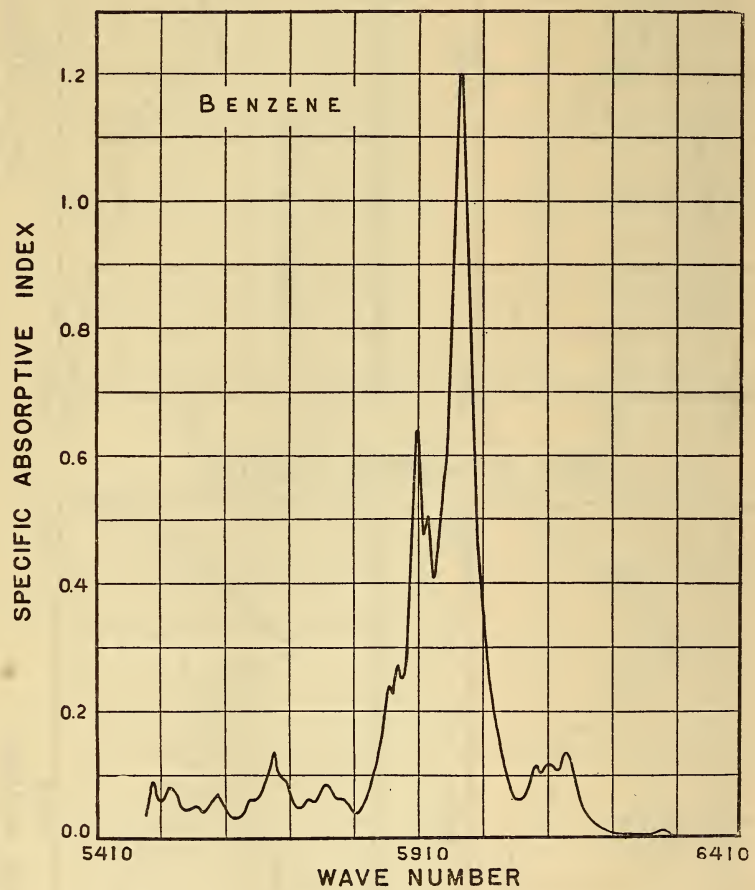
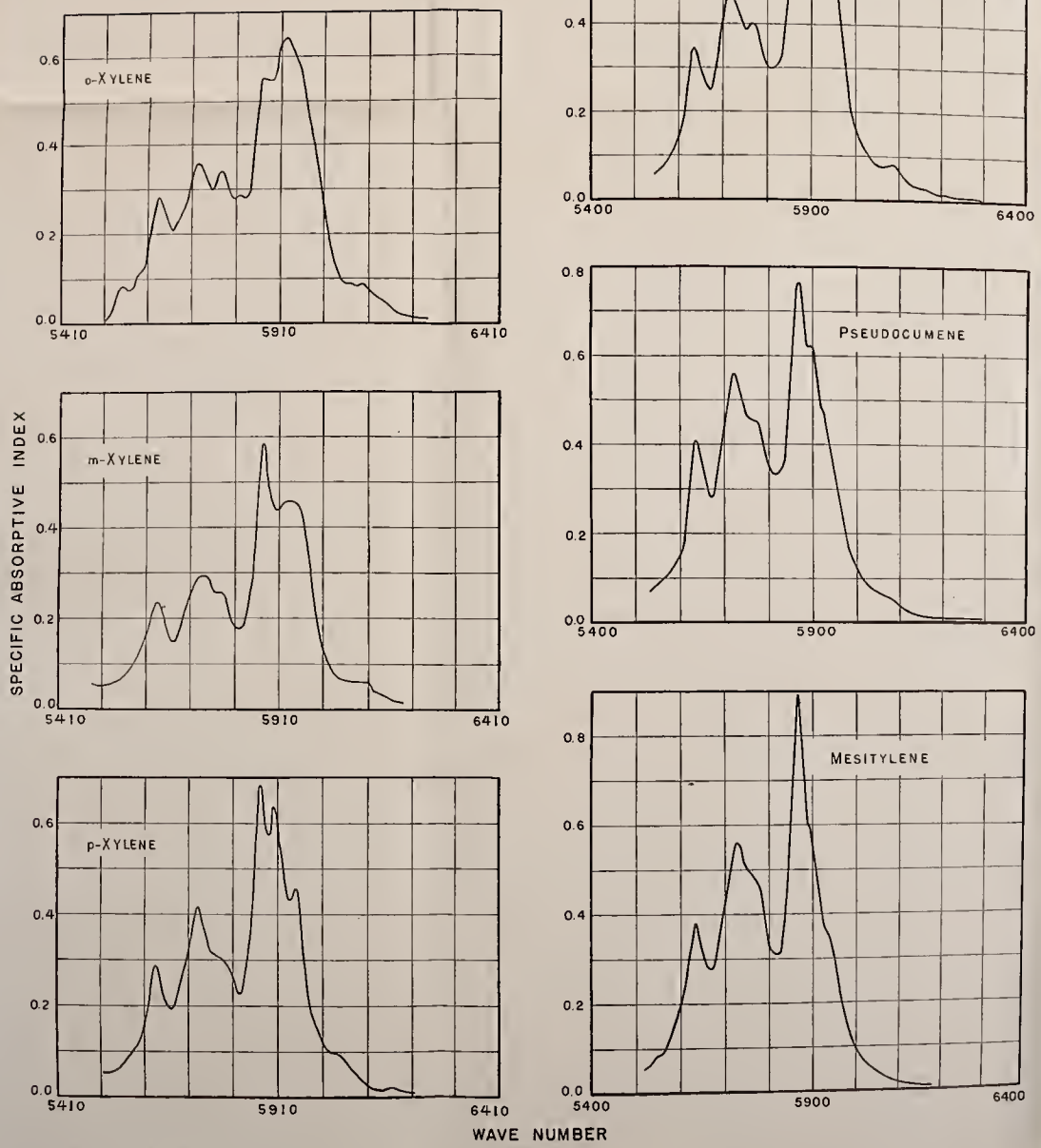


FIGURE 16.

simplicity and distinct similarity to that of normal aliphatic hydrocarbons. However, the intensity of absorption is more than 50 percent greater than that of *n*-hexane in this same region. No pertinent remarks may be made now concerning the rest of this group.

(c) NORMAL ALIPHATIC HYDROCARBONS

Here (figs. 20, 21, and 22) one may suggest that the two maxima at 5,670 and 5,790 cm^{-1} are associated with secondary groups, and those at 5,860 and 5,900 cm^{-1} with primary groups. This is based on the



13317—33. (Face p. 613.) No. 1.

Figure 18.

observation that the first two increase with increasing length of chain and the last do not. In character these bands are almost identical

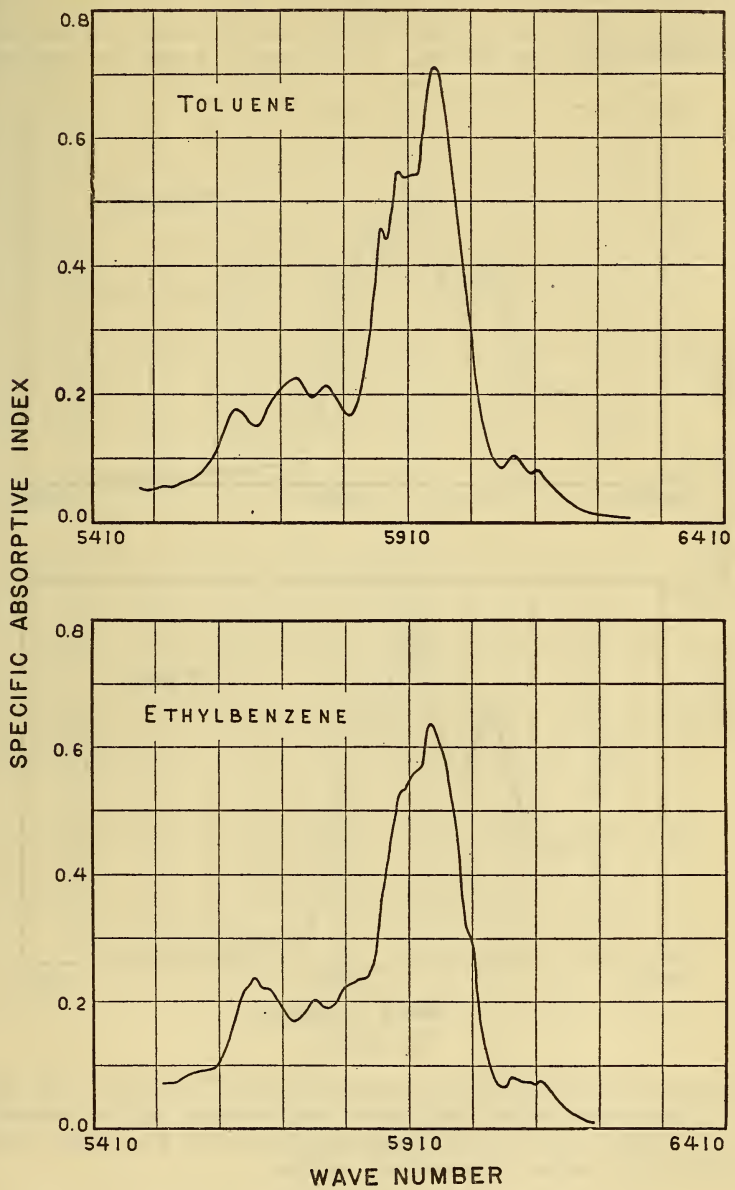
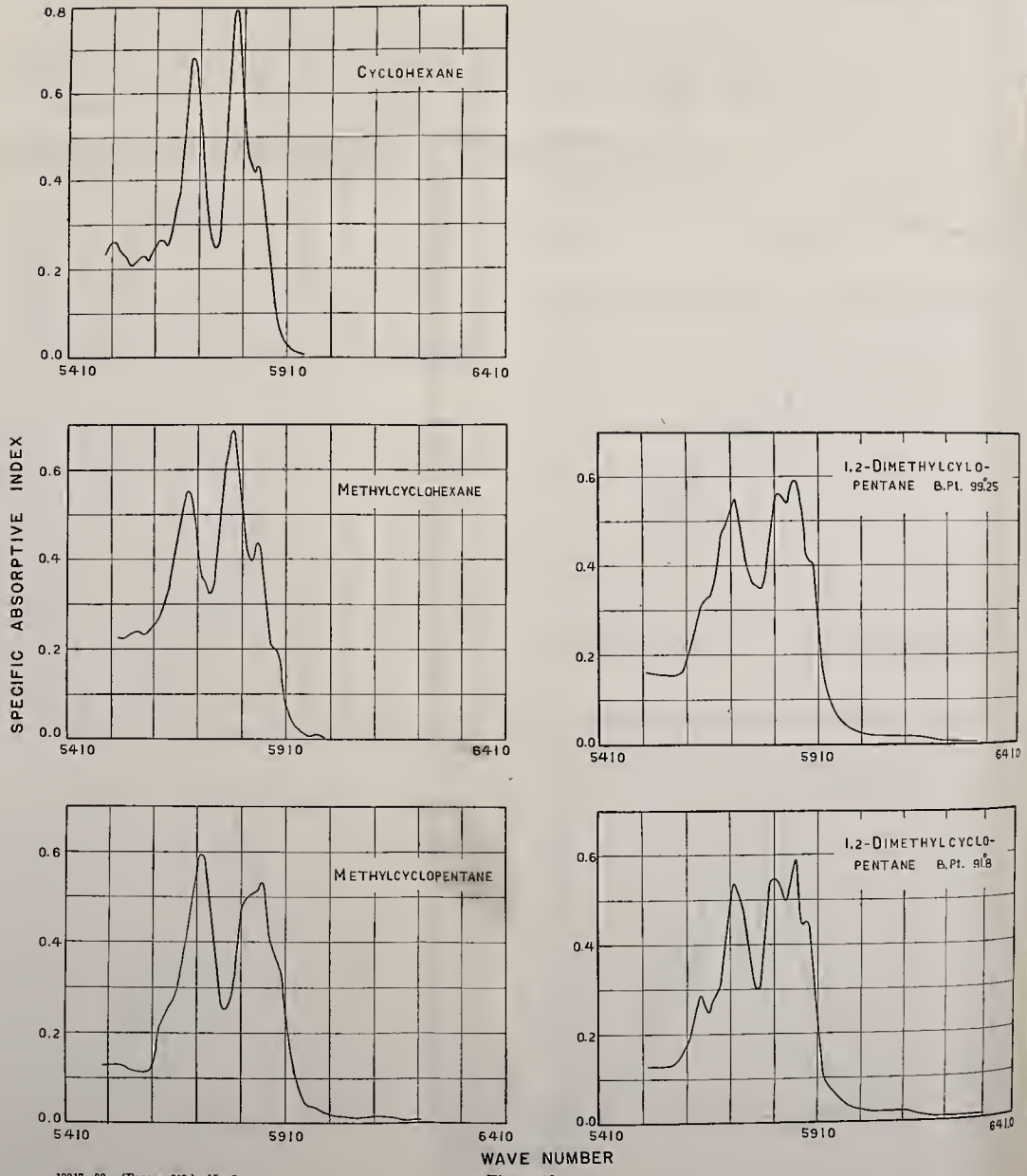


FIGURE 17.

with those around 7,100 cm^{-1} but are several times as intense, as would be expected.



13317—33. (Face p. 613.) No. 2.

Figure 19.

(d) ISOMERIC ALIPHATIC HYDROCARBONS

In a general manner these curves (figs. 23, 24, 25) bear out the suggestions in the preceding paragraph. There are small fluctuations in the frequencies of the maxima and variations in intensities which differentiate the isomers. The remarks made concerning the

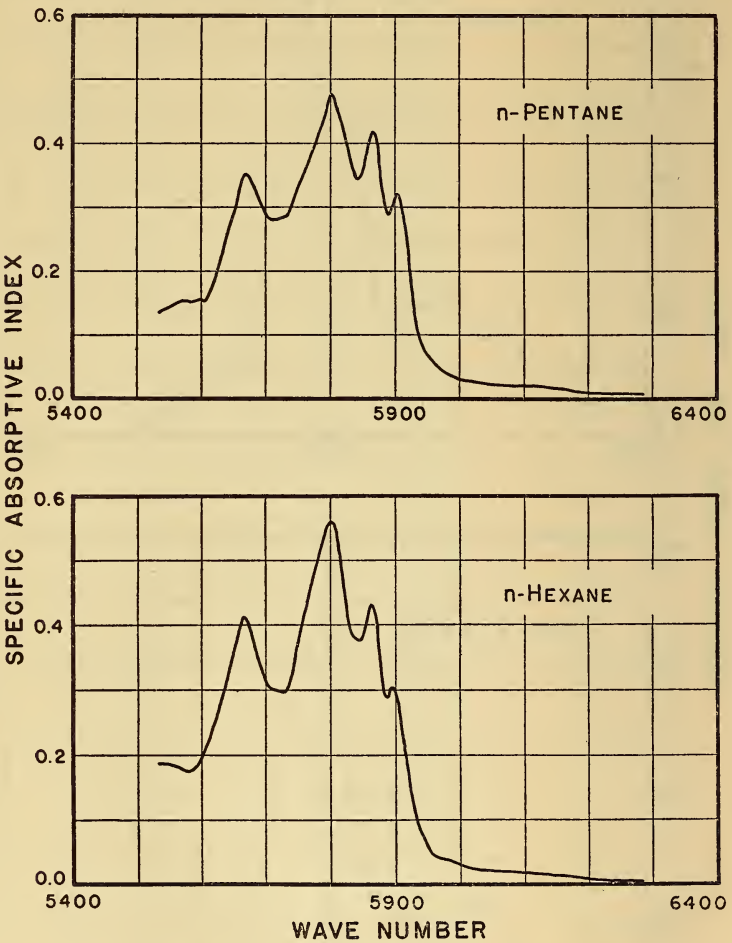


FIGURE 20.

alternation in intensity of the maxima around 7,100 cm^{-1} also apply here. It therefore seems that one of the maxima may be connected with the length of the carbon chain and the lower frequency component with the number of secondary groups.

IV. DISCUSSION OF RESULTS

For many years it has been considered that the complete infrared absorption spectrum of any compound is a unique characteristic of that compound, even among isomers. Experimental technique required, however, makes it rather difficult to obtain the spectrum of

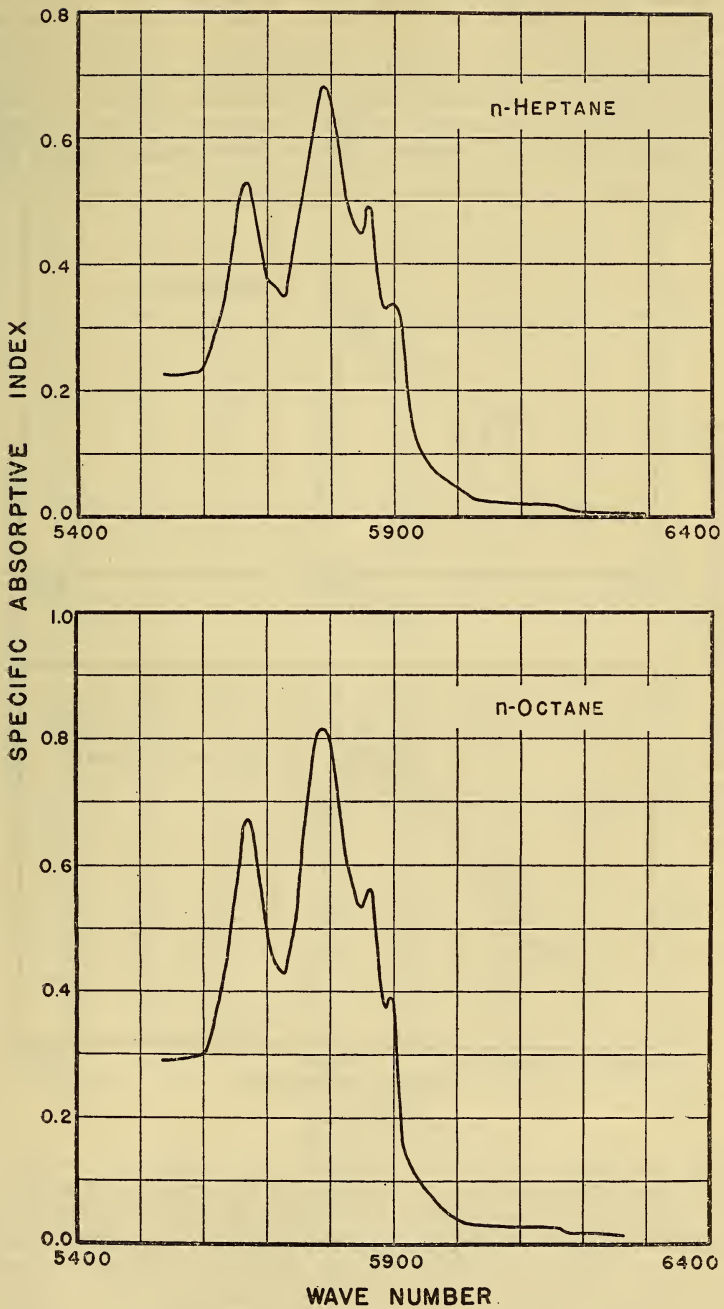
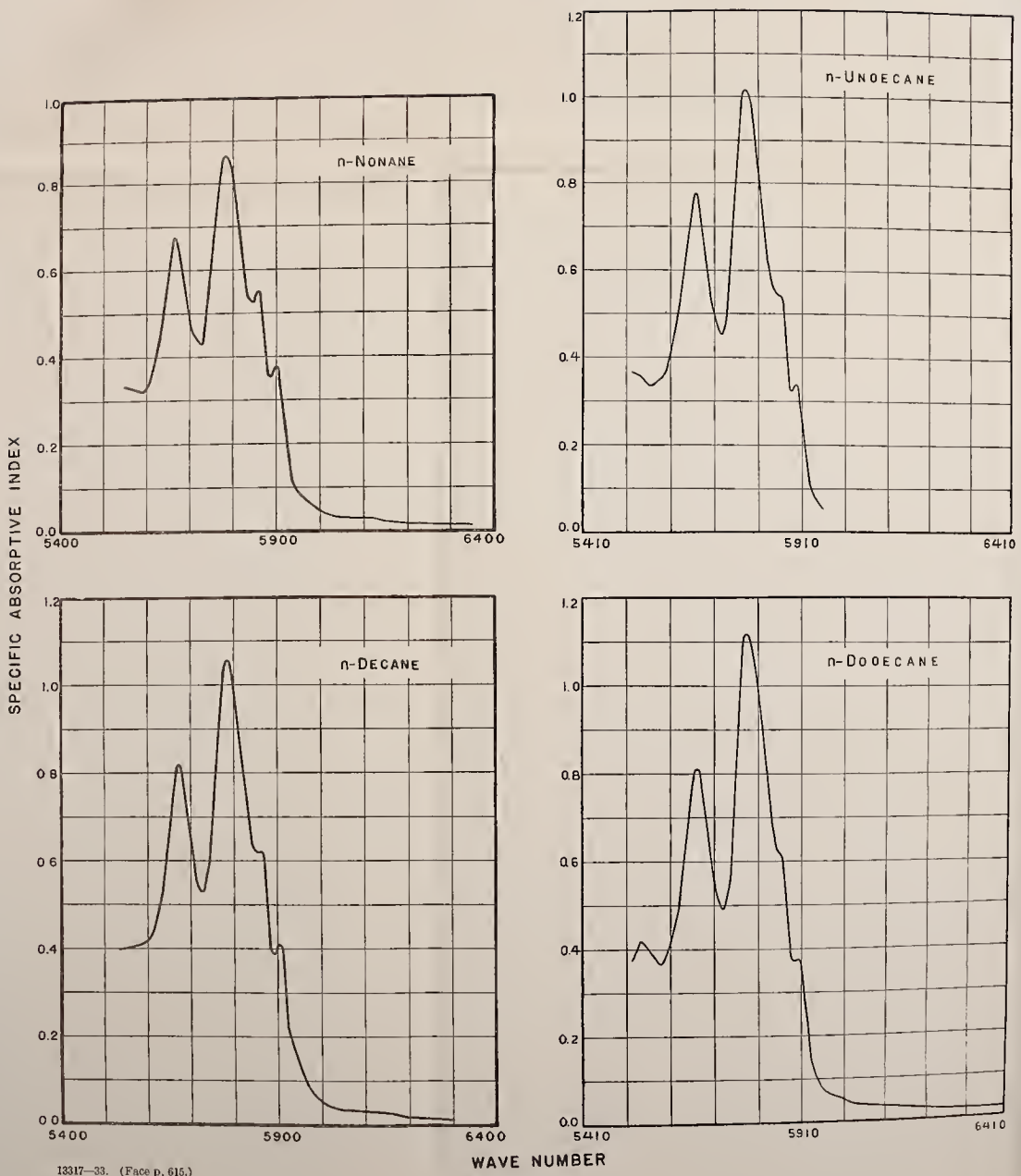

n-HEPTANE
n-OCTANE
SPECIFIC ABSORPTIVE INDEX
0.0
0.2
0.4
0.6
0.8
1.0
5400
5900
6400
WAVE NUMBER

FIGURE 21.



13317—33. (Face p. 615.)

FIGURE 22.

the whole region. In this study using high resolution, further evidence is given that the fine structure of certain bands in the near infrared, obtainable with rather simple technique, give quite as definite information concerning the identity of the molecules. Certain characteristics of these bands seem to be intimately connected with the structure of the molecule, as previously stated; i.e., the positions of certain maxima seem to be connected with the presence in the molecule of primary, secondary, and tertiary hydrocarbon linkages, also distin-

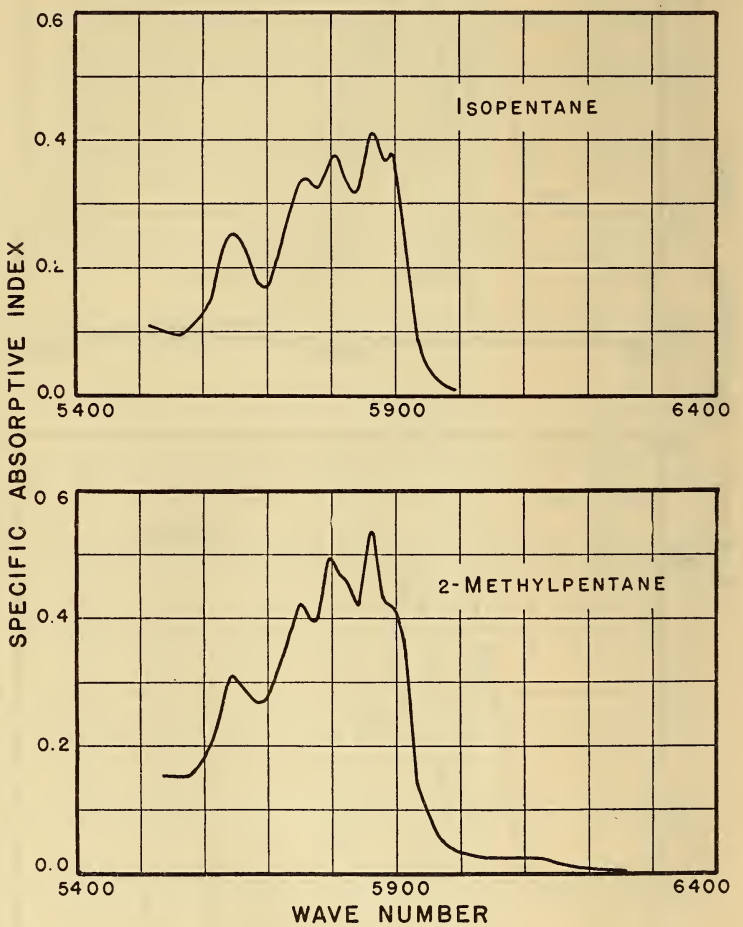


FIGURE 23.

guishing between the types aromatic and aliphatic compounds. With further classification of the bands observed and study of a greater number of compounds, it is probable that the structure of an unknown pure compound can be almost positively predicted. Also, if Beer's law is valid and there is no interaction between the compounds in solution, a quantitative estimate of the amount of each component present in a mixture can be made. No results are given herein in support of this last statement, but two experiments have been made in which it proved valid. Further work not possible

at the present time is necessary. However, analysis of a mixture of three similar components is very difficult, and of a greater number practically impossible.

In the high frequency region, it is seen that the absorptions of aromatic and aliphatic linkages are widely separated, and that variations of the type of absorption indicate the manner in which the groups are bound together. Confirmation of this indication comes from a study of the other two regions. These last two regions might well be used for first considerations except that they are considerably

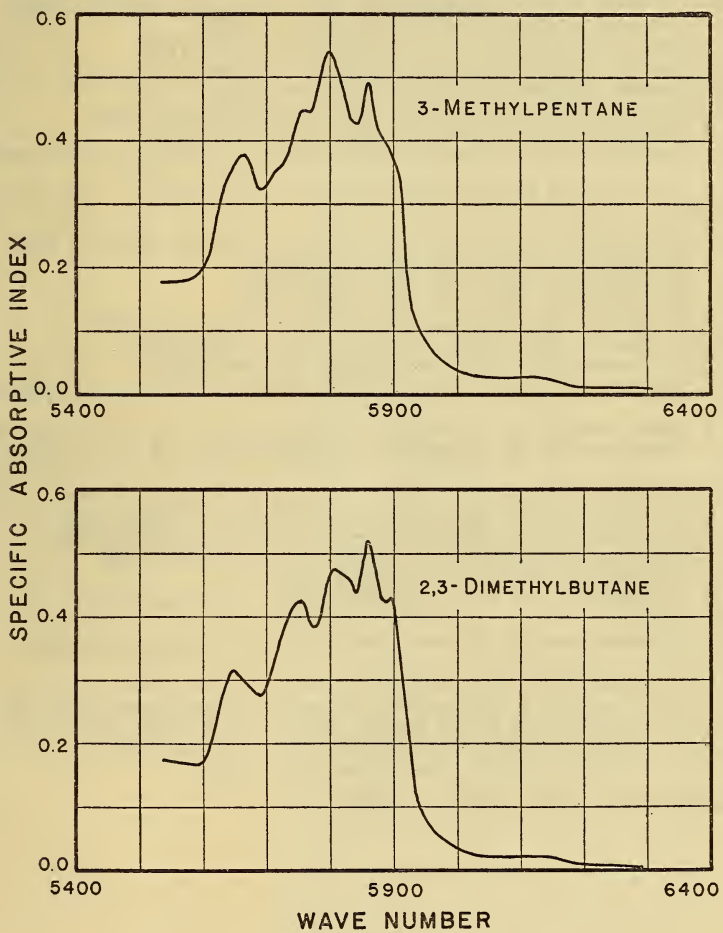


FIGURE 24.

more complex, arising from different transitions in the energy levels of the molecules and being contaminated with transitions of weaker intensity other than the main series under consideration.

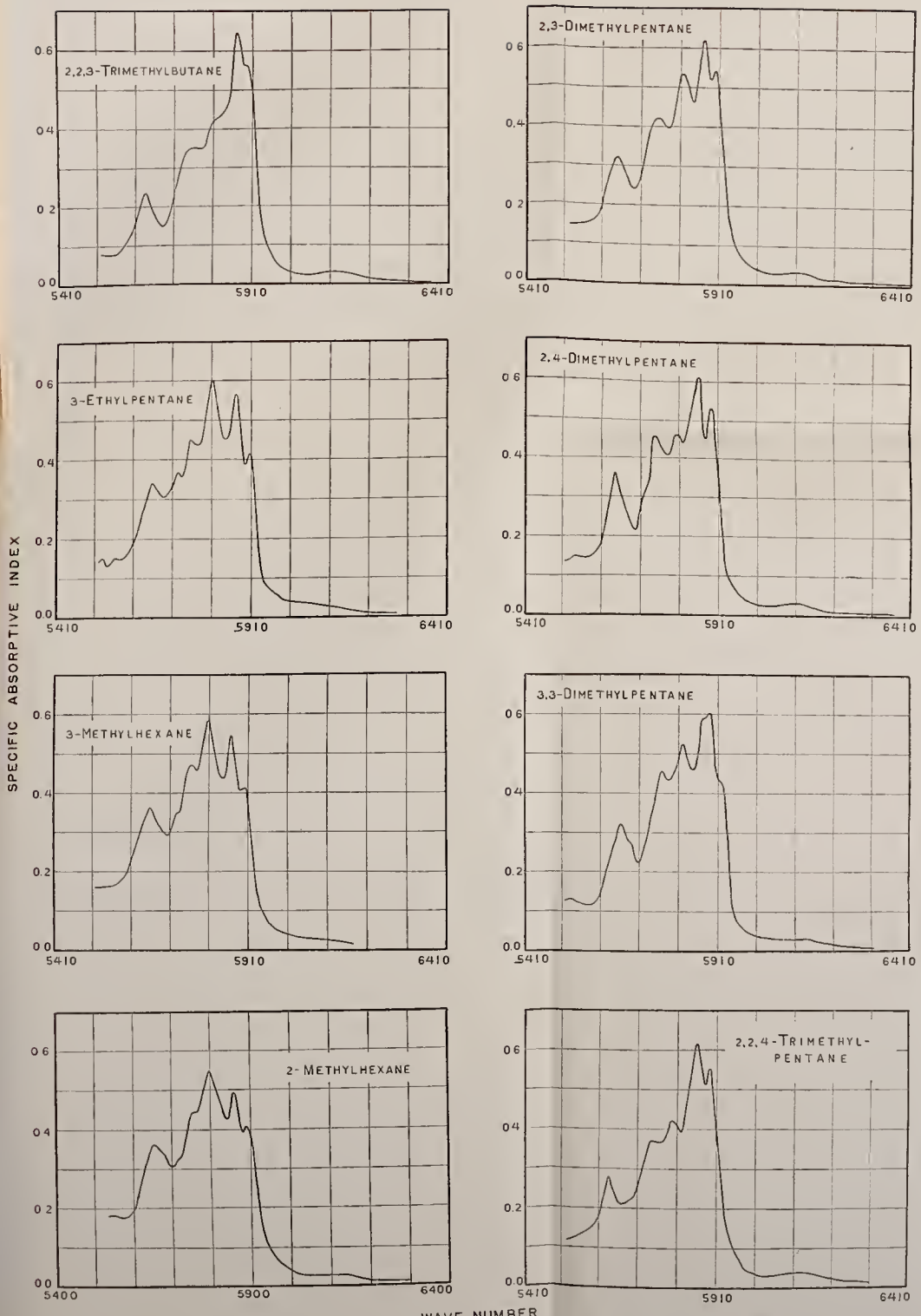
It is not to be understood that this method will ever find universal application in analytical organic chemistry. There undoubtedly are specific examples the study of which would be impossible. It is merely offered as an additional aid to other forms of technique and as such should prove very valuable.

This work was initiated at the suggestion of Dr. E. W. Washburn, whose assistance and cooperation has made it possible. F. W. Rose, Jr., has aided materially in preparing the illustrations of this paper.

V. BIBLIOGRAPHY

1. W. Abney and B. Festing, Phil. Trans., vol. 172, p. 887, 1881; Proc. Roy. Soc. (London) (A), vol. 31, p. 416, 1881.
2. H. Julius, Verhandel Akad. Wetenschappen Amsterdam, Deel i, no. 1, 1892.
3. W. W. Coblentz, Investigations of Infrared Spectra, Pub. No. 35, Carnegie Inst., Washington, 1905.
4. J. E. Purvis, Proc. Cambridge Phil. Soc., vol. 21, pp. 556–565, 1923.
5. Th. Dreisch, Z. Physik, vol. 30, pp. 200–216, 1924.
6. L. Marton, Z. physik. chem., vol. 117, pp. 97–128, 1925.
7. J. Lecomte, Compt. rend., vol. 178, pp. 1530, 1698, 2073, 1924.
8. J. Lecomte, Le Spectre Infra Rouge, Paris, 1928.
9. J. Lecomte, Trans. Faraday Soc., vol. 25, pp. 864–876, 1929.
10. J. Lecomte, Compt. rend., vol. 194, pp. 2037–2040; 1932.
11. P. Lambert and J. Lecomte, Compt. rend., vol. 194, pp. 77–79, 960–962, 1932.
12. P. Lambert and J. Lecomte, Ann. combustibles liquides, vol. 6, pp. 1001–1083, 1931.
13. P. Lambert and J. Lecomte, Ann. phys., vol. 18, pp. 329–390, 1932.
14. J. W. Ellis, Phys. Rev., vol. 23, p. 48, 1924.
15. J. W. Ellis, Phys. Rev., vol. 27, p. 298, 1926.
16. J. W. Ellis, Phys. Rev., vol. 32, p. 906, 1928.
17. J. W. Ellis, Trans. Faraday Soc., vol. 25, pp. 888–898, 1929.
18. R. B. Barnes, Phys. Rev., vol. 35, pp. 1524–1532, 1930.
19. R. B. Barnes, Phys. Rev., vol. 36, pp. 296–304, 1930.
20. J. Barnes and W. H. Fulweiler, J.Am.Chem.Soc., vol. 49, pp. 2034–2037, 1927.
21. J. Barnes and W. H. Fulweiler, J. Am.Chem.Soc., vol. 50, p. 1033, 1928.
22. J. Barnes and W. H. Fulweiler, J.Am.Chem.Soc., vol. 51, pp. 1750–1752, 1929.
23. G. B. Bonino, Gazz. chim. ital., vol. 53, p. 267 et seq. 576 et seq., 1923.
24. G. B. Bonino, Trans. Faraday Soc., vol. 25, pp. 876–888, 1929.
25. F. S. Brackett, Proc. Natl. Acad. Sci., vol. 14, pp. 857–864, 1928.
26. R. Freymann, Compt. rend., vol. 194, pp. 1471–1474, 1932.
27. R. Freymann, Thesis, Univ. of Paris, 1933.
28. F. S. Brackett and E. D. McAlister, Rev. Sci. Instruments, vol. 1, pp. 181–193, 1930.
29. C. Schaefer and F. Matossi, Das Ultrarot Spektrum, Springer & Co., Berlin, 1931.
30. E. O. Salant, Proc. Natl. Acad. Sci., vol. 12, p. 370, 1926.
31. R. Davis and K. S. Gibson, Bur. Standards Miscellaneous Pub. No. 114.
32. C. F. Kettering and W. W. Sleator, Physics., vol. 4, pp. 39–49, 1933.
33. E. D. McAlister, Phys. Rev., vol. 34, pp. 1142–1147, 1929.
34. E. K. Plyler, Phys. Rev., vol. 39, pp. 77–82, 1932.

Washington, D.C., July 19, 1933.



13317—33. (Face p. 618.)

FIGURE 25.