

BAND SERIES IN INFRA-RED ABSORPTION SPECTRA OF ORGANIC COMPOUNDS. I

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ABSTRACT

The frequencies of a series of outstanding absorption bands characteristic of organic liquids, previously attributed by the author to vibrations between atoms of a carbon-hydrogen pair, are shown to fit the equation,

$$\nu_n \cdot 10^{-12} = 47.37n - 0.783n^2,$$

where $n = 1, 2, \dots, 10$. Many of the bands of secondary intensity in the spectra of compounds containing a carbon-carbon bond have their frequencies expressed by

$$\nu'_n \cdot 10^{-12} = 10.71n.$$

where $n = 1, 2, \dots, 28$. Practically all other bands observed below 7μ in such spectra can be accounted for by combinations of low frequency members of these two series, $\nu_c = \nu_m + \nu_n'$. Measurements on bands occurring between 2μ and 3μ were made from records obtained with a new registering spectrograph. A number of such spectra are shown.

FOR a decade and a half following the publication by Coblenz¹ of his extensive monograph on infra-red absorption and emission spectra, comparatively little work was done in infra-red spectroscopy, especially in the study of absorption by organic compounds. During this period, however, Weniger² published his results of an investigation of a number of alcohols; Johnson and Spence³ studied a number of aniline dyes, and Stang⁴ investigated the absorption of naphthalene and some of its derivatives dissolved in carbon disulfide and carbon tetrachloride.

The origins of the great number of absorption bands observed in such investigations have remained practically unexplained. Puccianti,⁵ in a short but accurate and important investigation, discovered a band near 1.71μ occurring in all of the fifteen carbon-hydrogen compounds which he had examined, and attributed it to a C-H group. Coblenz¹ had observed a few bands bearing multiple wave-length relationships to be characteristic of groups of compounds, and assigned as the origin

¹ Coblenz, "Investigations of Infra-red Spectra" (1905).

² W. Weniger, Phys. Rev. **31**, 388 (1910).

³ Johnson and Spence, Phys. Rev. **5**, 349 (1915).

⁴ Stang, Phys. Rev. **9**, 542 (1917).

⁵ Puccianti, Nuovo Cim **11**, 141 (1900); Phys. Zeits. **1**, 48 (1899); **1**, 494 (1900).

of such bands groups within the molecule, as the alkyl groups CH_2 and CH_3 .

Interest is again being aroused in the study of absorption spectra of organic compounds with a view to explaining the numerous bands which characterize them. Lecomte,⁶ in a series of short articles, gives results, obtained with a Hilger infra-red wave-length spectrometer, of an investigation of many types of compounds. He concludes that the bands originate from vibrations within the molecule rather than of the molecule as a whole. In particular, he concludes that absorption due to the carbon atoms is but little dependent upon the type of carbon chain. Bell⁷ has recently carefully determined the absorption between 2μ and 12μ of aniline and ten alkyl anilines, and finds that, among the numerous bands which occur, one at 2.8μ is characteristic of the amino group. Two years ago the writer⁸ published in this journal the results of an investigation of the absorption spectra of thirty-one organic liquids to 2.5μ , obtained with a self-registering flint glass spectrograph of high dispersion. The liquids studied were benzene, toluene, p-xylene, mesitylene, pentane, hexane, heptane, octane and several halogen derivatives of methane, ethane, propane and butane. The investigation showed great similarities among these spectra. Márton⁹ has just published the results of an investigation, which he began before the above work was published, in which he independently arrived at some of the author's earlier conclusions, which will be reviewed later in this article.

An examination of the spectrum curves presented in both the early and later investigations reveals two facts which suggest that the absorption bands may be arranged in series originating in the longer wave-length region, whose members suffer gradual diminution of intensity and increasingly shorter wave-length separations as the series progresses toward the limits of the visible spectrum. These facts are:

1. For investigations in the region between 15μ and 3μ best results are obtained when absorbing thicknesses of 0.1 mm or less are used; for the regions between 3μ and 2μ and 2μ and 1μ , cells of 1 mm and 10 mm respectively yield best results; while to bring out clearly the bands between 1μ and the visible red, cells of about 100 mm thickness have to be used.

2. There are relatively fewer bands in the longer than in the shorter wave-length region.

⁶ Lecomte, *Compt. Rend.* **178**, pp. 1530, 1698, 2073 (1924); **180**, 825 (1925).

⁷ F. K. Bell, *J. Am. Chem. Soc.* **47**, 2192 (1925).

⁸ Ellis, *Phys. Rev.* **23**, 48 (1924).

⁹ Márton, *Zeits. f. Phys. Chem.* **117**, 97 (1925).

The complexity of the absorption curves increases more with an increase in the number of distinct types of atoms within the absorbing molecule than with the general complexity, or size, of the molecule itself. This suggests that the origin of the different absorption bands may be traced to definite atoms, or pairs of atoms, as absorbing centers.

A theory of infra-red absorption which would explain all of the bands of very long wave-length as originating from pure rotational effects of the molecule and all of the shorter wave-length bands as due to a combination of rotations and linear vibrations has met with some success in the cases of some relatively simple gas molecules. The series of regularly spaced bands in the long wave-length region of water vapor spectra found by Rubens¹⁰ and Fr. von Bahr¹¹ has been considered an example of the effects of pure rotation of a molecule in the absorption of radiant energy. A second, and more recent, example of a pure rotation spectrum is the series of regularly spaced absorption bands of HCl found by Czerny¹² between 40μ and 80μ . Such rotations have been quantized, and infra-red bands due to them are assumed to originate from discrete changes among the possible states of rotation, the angular momenta of these states bearing integral ratios to one another.

The second type of absorption, first proposed by Bjerrum,¹³ predicts that bands in the short wave-length region should be double, and that when studied with a spectroscope of high resolving power each branch should appear made up of equally spaced lines, whose separations should be equal to those of longer wave-length bands of the purely rotational type. Such serrated bands had already been observed by Rubens¹⁰ and Fr. von Bahr¹¹ in the cases of water vapor and HCl gas, but the first precision measurements were made on the former gas by Sleator,¹⁴ and in the case of HCl and also HF and HBr, by Imes.¹⁵ The separation of Czerny's long wave-length bands for HCl are equal to those found by Imes in the fine line structure of the near infra bands, thus confirming, in this case, Bjerrum's theory. Bands of the latter type have recently been measured in the spectrum of ammonia by Spence,¹⁶ and in the spectrum of methane by Cooley.¹⁷

¹⁰ Rubens, *Berliner Ber.*, page 513 (1913).

¹¹ Eva von Bahr, *Verh. d. Deutsch. Ges.* **15**, pp. 731, 1150 (1913).

¹² Czerny, *Zeits. f. Physik* **34**, 227 (Sept. 28, 1925).

¹³ Bjerrum, *Verh. d. Deutsch. Ges.* **16**, 737 (1914).

¹⁴ Sleator, *Astrophys. J.* **48**, 124 (1918).

¹⁵ Imes, *Astrophys. J.* **50**, 251 (1919).

¹⁶ Spence, *J.O.S.A. and R.S.I.* **10**, 127 (1925).

¹⁷ Cooley, *Astrophys. J.* **52**, 73 (1925).

The frequencies of the centers of bands of this type are determined by the discrete modes of vibration of the molecule, and at least in the case of diatomic molecules these bands should appear in series whose members have approximately equal frequency spacings. This has been found to be the case, although but few bands have ever been found for any one gas. Such bands are not exactly equally spaced, but rather have their frequencies expressed by the formula,

$$\nu_n = n\nu_0(1 - nx), \quad (1)$$

where ν_0 and x are constants for a given substance and $n = 1, 2, 3$, etc. This formula has been developed for such cases by Kratzer¹⁸ on the basis of the non-linearity of the law of force which holds between bonded atoms.

An advance has been made in the case of water vapor by Hettner,¹⁹ who has been able to account for the numerous observed absorption bands on the basis of two frequency series and simple additive combinations of members of these series.

It will be noticed that, unlike the ordinary optical spectral series, series of the above type never converge, although their wave-length differences become relatively small, even between members not far from the beginning of the series.

It would seem that we might expect series, similar to the ones characteristic of gases, in the absorption spectra of liquids and solids, although it might be doubtful whether a high resolving power should reveal any duplicity or fine line structure within the bands. The few multiple relations found by Coblenz in his investigations of organic liquids suggest such series. Schaefer and Thomas²⁰ have shown that all crystalline sulfates have four characteristic absorption frequencies which form a linear series, and the author²¹ has found that calcium sulfate has two additional bands which form the fifth and sixth members of such a series.

A C-H SERIES

In an investigation⁸ mentioned above the writer showed that all the organic liquids which he investigated had several absorption bands at approximately the same wave-length values. The average values of these wave-lengths for the thirty-one compounds studied in cells of 11 mm thickness are: 0.913μ , 1.023, 1.171, 1.375 and 1.695. As a con-

¹⁸ Kratzer, *Zeits. f. Physik* **3**, 289 (1920).

¹⁹ Hettner, *Zeits. f. Physik* **1**, 351 (1920).

²⁰ Schaefer and Thomas, *Zeits. f. Physik* **12**, 330 (1923).

²¹ Ellis, *J.O.S.A. and R.S.I.* **8**, 1 (1924).

tinuation²¹ of this study, a number of compounds were also examined in cells of approximately ten times this thickness, and in each case two new bands appeared, the mean wave-length values of which are 0.760μ and 0.835μ . Among the various compounds these seven bands vary slightly in position, although in no case is there a variation from the mean greater than three percent. These bands are the most outstanding ones of the spectra, but in many cases they have superposed, or partially superposed, upon them minor bands which tend to shift their maximum absorption points from their true positions. Consequently, in searching for series relations among such bands their mean values should be used.

It was shown that the corresponding frequency values of these bands could be quite accurately expressed as a non-linear series by means of formula (1), which had been developed for gases by Kratzer from theoretical considerations. The values of n in this instance vary from 4 to 10 inclusively. The constants, ν_0 and ν_0x , were calculated for seven substances. Since this formula was developed upon the assumption that the absorption was due primarily to the oscillations of a pair of atoms, constituting the diatomic gas molecule, it is natural to assume in the case of liquids that the absorption originates from oscillations of a linked pair of atoms within the rather complex molecule. The only type of such a linkage in common to all the substances investigated was a C-H bond, and the above series was attributed to this pair, and may be called a carbon-hydrogen, or C-H series.

Formula (1) may be expressed in terms of two constants, A and B ,

$$\nu_n = An - Bn^2, \quad (2)$$

which is a special form of the general parabolic formula which characterizes many phases of band spectra. A and B have been calculated from the average observed frequencies of all the bands observed in the investigation mentioned above, and have the following values:

$$A = 47.37 \times 10^{12}$$

$$B = 0.783 \times 10^{12}$$

The accuracy with which the formula,

$$\nu_n \times 10^{-12} = 47.37n - 0.783n^2 \quad (3)$$

expresses the observed frequencies is shown in Table I.

Extrapolation of formula (3) to include $n = 3, 2$ and 1 indicates that bands should be found at 2.22μ , 3.28μ and 6.44μ . The last two lie within the region which must be examined with rock salt spectroscopes, and the writer has already pointed out that bands appearing near 3.4μ

TABLE I
 Calculated and observed (average) bands of a C-H series.

| n | $\nu \times 10^{-12}$ (calc.) | $\nu \times 10^{-12}$ (obs.) | λ (calc.) | λ (obs.) |
|-----|----------------------------------|---------------------------------|-------------------|------------------|
| 10 | 395.4 | 394.8 | 0.758 μ | 0.760 μ |
| 9 | 363.0 | 361.5 | 0.827 | 0.835 |
| 8 | 328.8 | 328.8 | 0.913 | 0.913 |
| 7 | 293.4 | 292.8 | 1.022 | 1.023 |
| 6 | 255.9 | 256.0 | 1.172 | 1.171 |
| 5 | 217.5 | 218.1 | 1.379 | 1.375 |
| 4 | 177.0 | 177.0 | 1.695 | 1.695 |
| 3 | 135.2 | | 2.22 | |
| 2 | 91.6 | | 3.28 | |
| 1 | 46.6 | | 6.44 | |

and 6.8 μ in Coblenz's curves are probably to be identified as these bands. Bands near 2.22 μ have usually appeared in most investigations, but the writer has shown in the present study that there are several

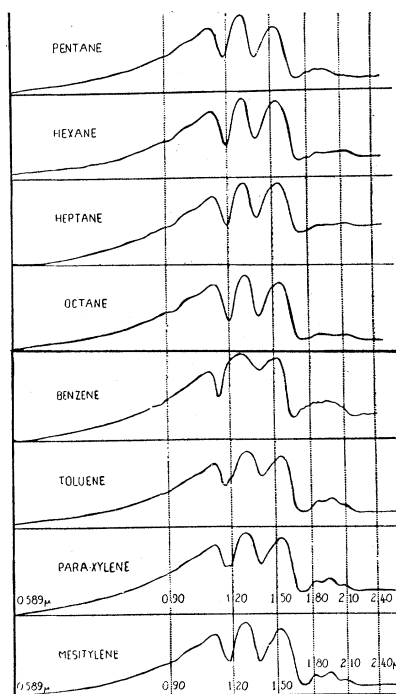


Fig. 1. Absorption spectra to 2.5 μ obtained with a registering glass spectrograph. Thickness of cells was 11 mm.

bands in this region, making the exact location of the third member of the C-H series uncertain.

In his recent report Márton⁹ also concludes that his observed bands are expressible by an equation similar to (1), and points out that the first member should occur near 6.5μ . He makes no attempt, however, to identify this series with any group within the molecule.

A C-C SERIES

Fig. 1 shows the absorption spectra to 2.5μ , previously published in this journal,⁸ of a few relatively simple carbon compounds of both the aromatic and paraffin series. It will be noticed that in addition to the prominent members of the C-H series there are a number of minor bands. These have never been accounted for but an attempt is made in the present work to account for them on the basis of a single-bonded C-C series and simple combinations between this and the C-H series.

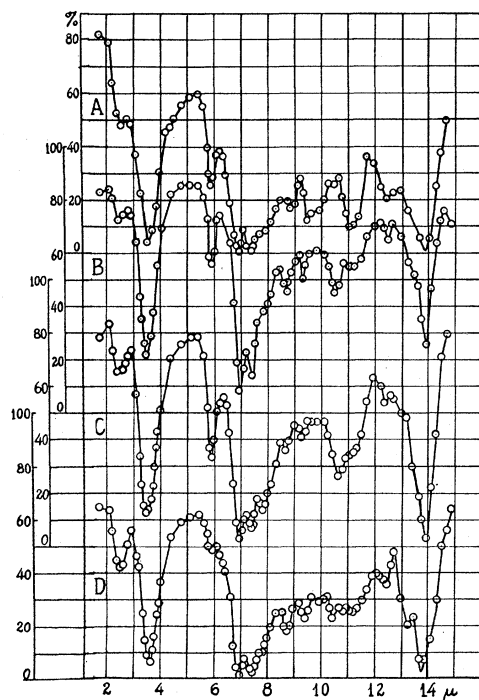


Fig. 2. Spectra obtained by Coblenz with a rock salt spectroscope.

A—0.24mm hexane C—0.15mm dodecane
B—0.15mm octane D—0.15mm hexadecane

Fig. 2 gives a reproduction of some of Coblenz's typical spectra²² of compounds of the paraffin series, while Fig. 3 gives similar spectra for members of the benzene series. After the bands at 3.4μ and 6.8μ common

²² Published by permission of the Carnegie Institution of Washington.

to these substances, probably the most striking feature is a deep band near 14μ . If we take this as the beginning of a C-C series we meet with only partial success in accounting for the numerous secondary bands of the shorter wave-length region. But if we assume that such a series originates at 28.0μ , a region never investigated for such substances, we can account for these bands in a relatively simple manner.

Such a series would predict a number of bands in the region between 2μ and 3μ . To search for these, and others, a new self-registering

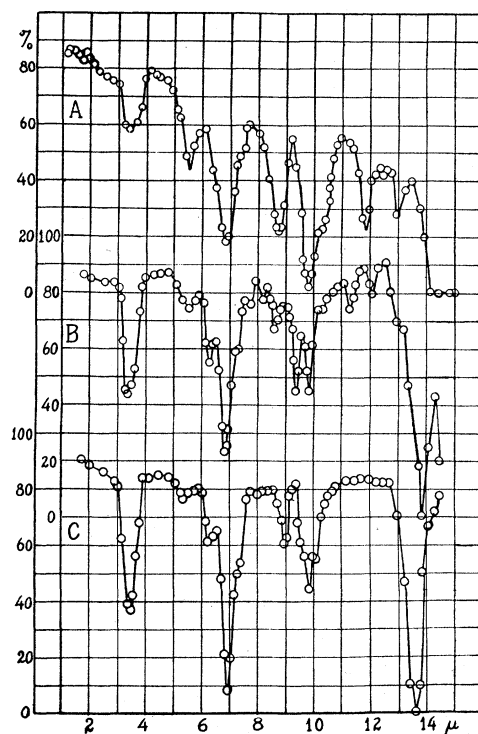


Fig. 3. Spectra obtained by Coblenz with a rock salt spectroscope.

- A—0.16mm benzene
- B—0.01mm toluene
- C—0.01mm o-xylene

spectrothermograph, recently described by the author,²³ has been assembled. This is equipped with quartz prisms, the combined refracting angles of which are equivalent to 180° . This instrument, although the prisms are small, has a fairly high dispersion.

Figs. 4 and 5 show the spectra of several compounds obtained for the region between 2μ and 3μ with this machine. The dotted tracing

²³ Ellis, J.O.S.A. and R.S.I. 11, (December 1925).

above the absorption curve of p-xylene is an approximation of the original distribution of energy. The atmospheric carbon dioxide band

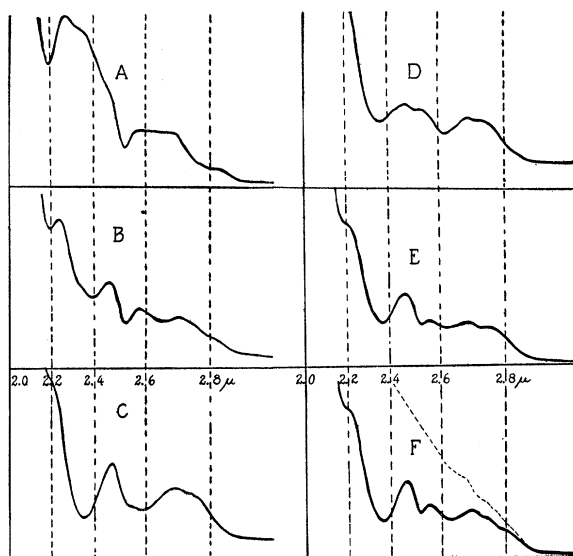


Fig. 4. Absorption spectra obtained with a registering quartz spectrograph.

A—0.05mm benzene D—0.05mm o-xylene
 B—0.05mm toluene E—0.05mm m-xylene
 C—0.05mm mesitylene F—0.05mm p-xylene

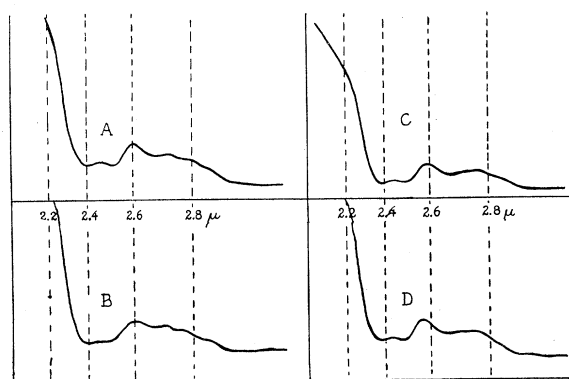


Fig. 5. Absorption spectra obtained with a registering quartz spectrograph.

A—0.05mm pentane C—0.05mm octane
 B—0.05mm hexane D—0.05mm decane

at 2.73μ and the water vapor band at 2.66μ always appear in such a distribution curve.²⁴

²⁴ Ellis, *Phys. Rev.* **26**, 469 (1925).

This method of recording spectra has the disadvantage of not always indicating the relative intensities among the various bands. When the energy curve has a steep slope, a band of considerable intensity may be manifest only by a point of inflection in the absorption curve. Nevertheless, repeated records show that great reliance may be placed upon the details of such curves. Thus, numerous minor bands, of importance in identifying members of a series, especially in the region between 2μ and 3μ have been revealed. As an example, there is no doubt in the writer's mind but the two points of inflection in the spectrum of benzene occurring in Fig. 4 between 2.18μ and 2.52μ represent bands at approximately 2.32μ and 2.44μ . In toluene these have merged together into a broad band with maximum absorption at 2.38μ , yet the duplicity of this band is still apparent. In the higher homologues, the xylenes and mesitylene, this combination band has been so deepened as to partially include the one at 2.18μ .

If we assume a linear series of bands expressible by the formula,

$$\nu_n' \times 10^{-12} = An = 10.71n, \tag{4}$$

or
$$\lambda_n' = 28/n \tag{4'}$$

we seem to be able to trace the series to include about twenty-eight members, in the spectra of compounds of both the chain and the ring type. There are, however, numerous cases in which the bands become partially, or wholly, superposed upon members of the C-H series. In many cases, as heretofore explained, these are manifested by distinct points of inflection; while in other cases, although not capable of detection, these help to account for the abnormal depth of the C-H

TABLE II
Agreement between calculated wave-lengths of the C-H series and corresponding values observed in the spectra of various compounds.

| | Calc. λ | ben- zene C_6H_6 | tol- uene C_6H_5 CH_3 | p-xy- lene C_6H_4 $(CH_3)_2$ | mesity- lene C_6H_3 $(CH_3)_3$ | pen- tane C_5H_{12} | hexane C_6H_{14} | hep- tane C_7H_{16} | octane C_8H_{18} |
|----------------|--------------------|--------------------------|------------------------------------|---|---|-----------------------------|-----------------------|-----------------------------|-----------------------|
| λ_1 | 6.44 μ | 6.8 μ | 6.85 μ | 6.85 μ | 6.85 μ | † | 6.86 μ | † | 6.87 μ |
| λ_2 | 3.28 | 3.25 | 3.45 | 3.45 | 3.45 | † | 3.43 | † | 3.43 |
| λ_3 | 2.22 | 2.18* | 2.19* | 2.20** | 2.20** | ** | ** | | ** |
| λ_4 | 1.695 | 1.66* | 1.70* | 1.705* | 1.70* | 1.705* | 1.72* | 1.72* | 1.72* |
| λ_5 | 1.38 | 1.39* | 1.375* | 1.38* | 1.37* | 1.375* | 1.38* | 1.38* | 1.385* |
| λ_6 | 1.172 | 1.145* | 1.155* | 1.155 | 1.18* | 1.185* | 1.195* | 1.19* | 1.195* |
| λ_7 | 1.022 | 1.03* | 1.025* | 1.02* | 1.015* | 1.015* | 1.03* | 1.035* | 1.035* |
| λ_8 | 0.912 | 0.885 | 0.915 | 0.915* | 0.915 | 0.915 | 0.925 | 0.925 | 0.930 |
| λ_9 | 0.826 | † | † | † | 0.825 | † | † | 0.835 | † |
| λ_{10} | 0.758 | † | † | † | 0.750 | † | † | 0.765 | † |

* Has another band superposed upon it.
** Occurs as a point of inflection only.
† No measurements recorded.

band. A good example of the latter occurs near 1.18μ , in which region the twenty-third, twenty-fourth and twenty-fifth members of the series of formula (4) become superposed upon the sixth member of the C-H series. It has also been stated that such superpositions cause an apparent shift of members of the C-H series to slightly different wavelength positions; but there are doubtless real shifts in the positions of these bands as well. However, the molecule as a whole has a surprisingly small effect upon these spectra. The agreement of the observed wavelength values of the C-H bands of a number of substances of the two types mentioned above with the values calculated from formula (1) is shown in Table II.

Table III shows the agreement between the observed bands attributed to a C-C series in the spectra of benzene and its simple methyl derivatives and their corresponding members calculated from formula (4). Table IV gives a similar agreement in the case of liquids of the paraffin series.

TABLE III
Calculated and observed wave-lengths in a
C-C series for benzene and its homologues.

| | Calc. $\nu' \times 10^{12}$ | Calc. λ | ben- zene C_6H_6 | tol- uene C_6H_5 (CH_3) | o-xy- lene C_6H_4 $(CH_3)_2$ | m-xy- lene C_6H_4 $(CH_3)_2$ | p-xy- lene C_6H_4 $(CH_3)_2$ | mesity- lene C_6H_3 $(CH_3)_3$ |
|-----------------|--------------------------------|--------------------|--------------------------|--------------------------------------|---|---|---|---|
| λ'_1 | 10.7 | 28.0 μ | ## | ## | ## | ## | ## | ## |
| λ'_2 | 21.4 | 14.0 | 14.1 μ | 13.85 μ | 13.55 μ | 12.95 μ | 12.55 μ | 11.95 μ |
| λ'_3 | 32.1 | 9.35 | * | 9.3 | 9.2 | 9.0, 9.6 | 9.65 | |
| λ'_4 | 42.8 | 7.00 | ** | 7.3** | 7.3** | 7.3** | 7.3** | 7.3** |
| λ'_5 | 53.5 | 5.60 | 5.5 | 5.5 | 5.35 | 5.35 | 5.4 | 5.5 |
| λ'_6 | 64.2 | 4.67 | | | | | | |
| λ'_7 | 74.9 | 4.00 | | | | | | |
| λ'_8 | 85.6 | 3.50 | * | * | * | * | * | * |
| λ'_9 | 96.3 | 3.11 | * | * | * | * | * | * |
| λ'_{10} | 107.1 | 2.80 | 2.8 | 2.8 | 2.82 | | 2.78 | 2.8 |
| λ'_{11} | 117.8 | 2.545 | 2.52 | 2.53 | 2.54 | 2.52 | 2.52 | 2.54 |
| λ'_{12} | 128.5 | 2.33 | 2.32 | 2.32** | 2.33** | 2.33** | 2.33** | 2.33** |
| λ'_{13} | 139.2 | 2.15 | 2.18* | 2.19* | 2.20* | 2.20* | 2.20** | 2.20** |
| λ'_{14} | 149.9 | 2.00 | 2.05* | 2.03* | 2.0* | 2.0* | 2.03* | 2.02* |
| λ'_{15} | 160.6 | 1.865 | 1.855 | 1.86 | 1.86 | 1.86 | 1.86 | 1.86 |
| λ'_{16} | 171.3 | 1.75 | 1.74 | 1.70* | 1.75** | 1.75** | 1.75 | 1.75 |
| λ'_{17} | 182.0 | 1.645 | 1.66* | 1.70* | 1.64** | 1.64** | 1.705* | 1.70* |
| λ'_{18} | 192.7 | 1.555 | | | ** | ** | | |
| λ'_{19} | 203.4 | 1.475 | 1.47 | 1.475** | 1.46** | 1.46** | 1.47** | 1.47** |
| λ'_{20} | 214.0 | 1.400 | 1.39* | 1.375* | 1.40** | 1.40** | 1.38* | 1.37* |
| λ'_{21} | 224.8 | 1.335 | 1.33* | 1.375* | 1.33** | 1.33** | 1.38* | 1.37* |
| λ'_{22} | 235.6 | 1.270 | | | | | | |
| λ'_{23} | 246.3 | 1.215 | ** | ** | 1.21** | 1.21** | 1.195 | 1.18* |
| λ'_{24} | 257.0 | 1.165 | 1.145* | 1.155* | 1.17** | 1.17** | 1.155* | 1.18* |
| λ'_{25} | 267.8 | 1.120 | 1.145* | 1.155* | 1.11** | 1.11** | 1.155* | 1.18* |
| λ'_{26} | 278.5 | 1.075 | | | 1.06** | 1.06** | | |
| λ'_{27} | 289.3 | 1.035 | 1.03* | 1.025* | 1.03** | 1.03** | 1.02* | 1.015* |
| λ'_{28} | 300.0 | 1.000 | 1.03* | 1.025* | 1.0 | 1.0 | 1.02* | 1.015* |

* Superposed upon another band.

** Occurs as a point of inflection only.

Region never investigated.

In these tables the values for the second, third, fourth and fifth members are taken from Coblenz's data, the values for the tenth to the thirteenth members inclusive from the records of the present investigation, while those for the last fifteen members, with the exception of ortho- and

TABLE IV
Calculated and observed wave-lengths in a
C-C series for paraffin compounds.

| | Calc. $\nu' \times 10^{-12}$ | Calc. λ | pentane C ₅ H ₁₂ | hexane C ₆ H ₁₄ | heptane C ₇ H ₁₆ | octane C ₈ H ₁₈ | decane C ₁₀ H ₂₂ |
|-----------------|---------------------------------|-----------------|---|--|---|--|---|
| λ'_1 | 10.7 | 28.0 μ | †† | †† | †† | †† | †† |
| λ'_2 | 21.4 | 14.0 | † | 13.9 | † | 13.83 | † |
| λ'_3 | 32.1 | 9.35 | † | 9.4 | † | 9.3 | † |
| λ'_4 | 42.8 | 7.00 | † | 7.35 | † | 7.35 | † |
| λ'_5 | 53.5 | 5.60 | † | 5.8 | † | 5.75 | † |
| λ'_6 | 64.2 | 4.67 | † | | † | | † |
| λ'_7 | 74.9 | 4.00 | † | | † | | † |
| λ'_8 | 85.6 | 3.50 | † | * | † | * | † |
| λ'_9 | 96.3 | 3.11 | † | * | † | * | † |
| λ'_{10} | 107.1 | 2.80 | 2.8 | 2.8 | † | 2.8 | 2.8 |
| λ'_{11} | 117.8 | 2.545 | 2.5* | 2.5* | † | 2.5* | 2.5* |
| λ'_{12} | 128.5 | 2.33 | 2.33** | 2.33** | † | 2.33** | 2.33** |
| λ'_{13} | 139.2 | 2.15 | ** | ** | † | ** | ** |
| λ'_{14} | 149.9 | 2.00 | 2.02 | 2.02 | 2.0 | 2.0 | 2.0* |
| λ'_{16} | 160.6 | 1.865 | 1.83 | 1.83 | 1.83 | 1.83 | 1.90* |
| λ'_{16} | 171.3 | 1.75 | 1.75* | 1.75* | 1.75* | 1.75* | 1.73* |
| λ'_{17} | 182.0 | 1.645 | 1.705* | 1.72* | 1.72* | 1.72* | 1.64** |
| λ'_{18} | 192.7 | 1.555 | | | | | ** |
| λ'_{19} | 203.4 | 1.475 | ** | ** | ** | ** | 1.47** |
| λ'_{20} | 214.0 | 1.400 | 1.38* | 1.38* | 1.38* | 1.385* | 1.40** |
| λ'_{21} | 224.8 | 1.335 | 1.38* | 1.38* | 1.38* | 1.385* | 1.34** |
| λ'_{22} | 235.6 | 1.270 | | | | | |
| λ'_{23} | 246.3 | 1.215 | 1.195* | 1.195* | 1.19* | 1.195* | 1.18* |
| λ'_{24} | 257.0 | 1.165 | 1.195* | 1.195* | 1.19* | 1.195* | 1.18* |
| λ'_{25} | 267.8 | 1.120 | 1.195* | 1.195* | 1.19* | 1.195* | 1.18* |
| λ'_{26} | 278.5 | 1.075 | | | | | 1.08 |
| λ'_{27} | 289.3 | 1.035 | 1.015* | 1.035* | 1.035* | 1.035* | 1.03* |
| λ'_{28} | 300.0 | 1.000 | 1.015* | 1.035* | 1.035* | 1.035* | 1.0 |

* Superposed upon another band.
 ** Occurs as a point of inflection only.
 † No measurements recorded.
 †† Region never investigated.

meta-xylene and decane, are taken from the writer's curves previously published. The short wave-length values for ortho-and meta-xylene and decane are taken from the new curves of this investigation recorded in Fig. 6.

It has been pointed out that extrapolation of the C-H series indicates that the first member should occur at 6.44 μ . The mean value actually observed by Coblenz for these compounds is about 6.85 μ , giving a discrepancy of about +0.4 μ . There is a discrepancy of +0.3 μ between the observed and calculated values for the fourth member of the C-C series at 7 μ . Furthermore, in the case of the open chain compounds there seems to be a corresponding error of about 0.2 μ in the fifth member

at 5.8μ . These errors, if real, indicate a progressive error in the positions of bands between 3μ and 8μ which reaches a maximum value between 6μ and 7μ and which disappears beyond 9μ . If this error exists, it is doubtless due to inaccurate values of the refractive indices of rock-salt rather than to experimental errors, since measurements by various investigators are fairly consistent in this region. The writer is cognizant of the fact, however, that these indices have been determined by investigators skillful in the technique of infra-red spectroscopy.

There seems to be no detectable deviation from linearity in the case of this latter series, although according to Kratzer the members of the

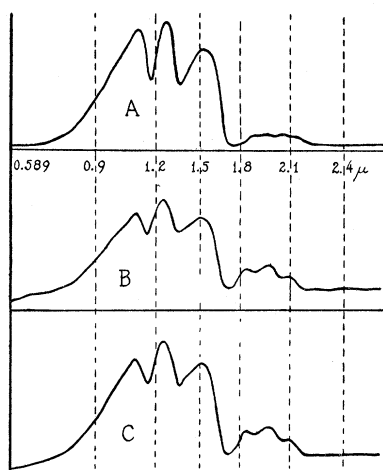


Fig. 6. Absorption spectra obtained with a registering quartz spectrograph.

A—8mm decane
B—8mm o-xylene
C—8mm m-xylene

series originate from a cause which should also cause them to depart from a true multiple relationship, namely, the non-harmonic motion of the bonded atoms arising from the non-linearity in the law of force acting. However, in the case of the C-C pair we have a symmetry which is lacking in the C-H group. There probably is a greater amplitude of vibration in the latter case because of the relative lightness of the hydrogen atom, and hence we should expect a greater departure from true harmonic motion than occurs in the oscillations of a C-C pair.

COMBINATION FREQUENCIES

Kratzer's theory is built upon a quantum theory basis, the absorption frequencies arising from successive integral changes in the rates of

TABLE V

Combination bands of C-H and C-C series.

| | calc. $\nu \times 10^{-12}$ | calc. λ | ben- zene | tol- uene | o-xy- lene | m-xy- lene | p-xy- lene |
|------------------|--------------------------------|--------------------|--------------|--------------|---------------|---------------|---------------|
| $\nu_1 + \nu'_1$ | 57.2 | 5.23 | ** | 5.2 | 5.35* | 5.35* | 5.35* |
| $\nu_1 + \nu'_2$ | 68.2 | 4.40 | 4.4 | | | | |
| $\nu_1 + \nu'_3$ | 78.7 | 3.81 | * | * | * | * | * |
| $\nu_1 + \nu'_4$ | 89.5 | 3.35 | * | * | * | * | * |
| $\nu_1 + \nu'_5$ | 100.0 | 3.00 | * | * | * | * | * |
| $\nu_1 + \nu'_6$ | 110.5 | 2.71 | 2.75 | 2.72 | 2.72 | 2.72 | 2.72 |
| $\nu_1 + \nu'_7$ | 122.0 | 2.46 | 2.44* | 2.38* | 2.37* | 2.37* | 2.37* |
| $\nu_1 + \nu'_8$ | 132.0 | 2.27 | 2.18* | 2.19* | 2.20* | 2.20* | 2.20* |
| $\nu_2 + \nu'_1$ | 102.5 | 2.93 | | | | | |
| $\nu_2 + \nu'_2$ | 113.0 | 2.65 | | 2.66 | 2.63 | 2.63 | 2.63 |
| $\nu_2 + \nu'_3$ | 124.0 | 2.42 | 2.44* | 2.38* | 2.37* | 2.37* | 2.37* |
| $\nu_2 + \nu'_4$ | 134.5 | 2.23 | 2.18* | 2.19* | 2.20* | 2.20* | 2.20* |
| $\nu_2 + \nu'_5$ | 145.0 | 2.07 | 2.05* | 2.03* | 2.05* | 2.05 | 2.03* |
| $\nu_2 + \nu'_6$ | 156.0 | 1.925 | 1.89 | 1.86* | 1.86* | 1.86* | 1.86* |
| $\nu_3 + \nu'_1$ | 145.5 | 2.06 | 2.05* | 2.03* | 2.05* | 2.05* | 2.03* |
| $\nu_3 + \nu'_2$ | 156.5 | 1.915 | 1.89* | 1.86* | 1.86* | 1.86* | 1.86* |
| $\nu_3 + \nu'_3$ | 167.0 | 1.795 | 1.79* | 1.70** | 1.86* | 1.86* | 1.70* |
| $\nu_3 + \nu'_4$ | 178.0 | 1.685 | 1.66* | 1.70* | 1.70* | 1.70* | 1.70* |
| $\nu_3 + \nu'_5$ | 188.5 | 1.59 | 1.66* | 1.70* | 1.70* | 1.70* | 1.70* |
| $\nu_4 + \nu'_1$ | 187.5 | 1.60 | 1.66* | 1.70* | 1.70* | 1.70* | 1.70* |
| $\nu_4 + \nu'_2$ | 198.5 | 1.51 | | | | | |
| $\nu_4 + \nu'_3$ | 209.0 | 1.435 | 1.39* | 1.375* | ** | ** | 1.38* |
| $\nu_4 + \nu'_4$ | 219.5 | 1.365 | 1.39* | 1.375* | 1.36* | 1.36* | 1.38* |

Combination bands of C-H and C-C series.

| | calc. $\nu \times 10^{-12}$ | calc. λ | mesity- lene | pentane | hexane | octane | decane |
|------------------|--------------------------------|--------------------|-----------------|---------|--------|--------|--------|
| $\nu_1 + \nu'_1$ | 57.2 | 5.23 | 5.35* | # | | | # |
| $\nu_1 + \nu'_2$ | 68.2 | 4.40 | ** | # | ** | | # |
| $\nu_1 + \nu'_3$ | 78.7 | 3.81 | * | # | * | * | # |
| $\nu_1 + \nu'_4$ | 89.5 | 3.35 | * | # | * | * | # |
| $\nu_1 + \nu'_5$ | 100.0 | 3.00 | * | # | * | * | # |
| $\nu_1 + \nu'_6$ | 110.5 | 2.71 | 2.72 | 2.72 | 2.72 | 2.72 | 2.72 |
| $\nu_1 + \nu'_7$ | 122.0 | 2.46 | 2.36* | 2.38* | 2.38* | 2.38* | 2.38* |
| $\nu_1 + \nu'_8$ | 132.0 | 2.27 | 2.20* | 2.38* | 2.38* | 2.38* | 2.38* |
| $\nu_2 + \nu'_1$ | 102.5 | 2.93 | | | | | |
| $\nu_2 + \nu'_2$ | 113.0 | 2.65 | 2.63 | 2.65 | 2.65 | 2.65 | 2.65 |
| $\nu_2 + \nu'_3$ | 124.0 | 2.42 | 2.36* | 2.38* | 2.38* | 2.38* | 2.38* |
| $\nu_2 + \nu'_4$ | 134.5 | 2.23 | 2.20* | 2.38* | 2.38* | 2.38* | 2.38* |
| $\nu_2 + \nu'_5$ | 145.0 | 2.07 | 2.02* | 2.0* | 2.0* | 2.0* | 2.08* |
| $\nu_2 + \nu'_6$ | 156.0 | 1.925 | 1.86* | 1.9* | 1.9* | 1.9* | 1.90* |
| $\nu_3 + \nu'_1$ | 145.5 | 2.06 | 2.02* | 2.0* | 2.0* | 2.0* | 2.08* |
| $\nu_3 + \nu'_2$ | 156.5 | 1.915 | 1.86* | 1.9* | 1.9* | 1.9* | 1.90* |
| $\nu_3 + \nu'_3$ | 167.0 | 1.795 | 1.70* | 1.75* | 1.75* | 1.75* | 1.80 |
| $\nu_3 + \nu'_4$ | 178.0 | 1.685 | 1.70* | 1.705* | 1.72* | 1.72* | 1.72* |
| $\nu_3 + \nu'_5$ | 188.5 | 1.59 | 1.70* | 1.60* | 1.72* | 1.72* | ** |
| $\nu_4 + \nu'_1$ | 187.5 | 1.60 | 1.70* | 1.60* | 1.72* | 1.72* | ** |
| $\nu_4 + \nu'_2$ | 198.5 | 1.51 | | | | | |
| $\nu_4 + \nu'_3$ | 209.0 | 1.435 | 1.37* | 1.375* | 1.38* | 1.385* | ** |
| $\nu_4 + \nu'_4$ | 219.5 | 1.365 | 1.37* | 1.375* | 1.38* | 1.38* | 1.37* |

* Superposed upon another band.
 ** Occurs as a point of inflection only.
 # No measurements recorded.

vibration within the molecule. It would seem probable that if a carbon atom is bonded both to a hydrogen and another carbon atom that a new frequency ν_c would be absorbed provided that

$$\nu_c = \nu_m + \nu_n' \quad (5)$$

where ν_m and ν_n' are low frequency members of the C-H and C-C series respectively. This means that a quantum of energy would be divided between the two absorbing centers.

Table V shows the new absorption frequencies to which such a phenomenon would give rise, and an attempted identification of their corresponding wave-lengths with bands actually observed in the curves of Figs. 1-6. The two series, with these simple combinations, seem to satisfactorily account for practically all of the bands, up to about 7μ , observed in the spectra of the simple hydrocarbons. In no case do these series demand a band of major intensity which cannot be accounted for. The bands predicted by formulae (4) and (5) between 3.5μ and 5.5μ do not appear in the ordinary spectra, probably because of the unusually low dispersion of rock salt in this region and the thinness of absorption cell used. In the instances where Coblentz used a large spectrometer, of greater resolution, many of these bands appeared. Their values have been included in Tables III, IV and V. The numerous bands occurring more or less regularly between 8μ and 15μ , for all substances, and the rather prominent band at 6.2μ in the spectrum of benzene and its derivatives, are not accounted for by such series.

It also seems that the conditions would be appropriate for a division of an energy quantum between two C-H groups sharing the same carbon atom. This would cause the second member of the C-H series to appear with unusual intensity. This phenomenon is observed, especially in the spectra of the paraffin compounds, as may be seen in Fig. 2.

Methane, CH_4 , should have a very simple spectrum, since it has only bonds of the C-H type. Coblentz's curve shows it to have but three absorption bands, at 7.7μ , 3.31μ and 2.35 , which may be identified as the first three members of the C-H series, in spite of the shift of the first member toward longer wave-lengths. In the spectrum of ethane, C_2H_6 , these three bands appear, with the first member in the position which it occupies in the spectra of the higher liquid members of the paraffin series to which this gas belongs. It is impossible to identify any members of a C-C series, although there is an undefined group of bands at 12μ . In the spectrum of butane, C_4H_{10} , we have the three C-H bands as in ethane, and in addition there are bands at 14μ and

5.65 μ which may be identified as the second and fifth members respectively of a C-C series.

In the spectra of the ring compounds there is a considerable variation in the position of the 14 μ band. This band shifts progressively toward a shorter wave-length value with successive substitutions of a methyl group, CH₃. In the spectra of the xylenes, C₆H₄ · (CH₃)₂, the position of this band also depends upon the positions of such substituted groups. Table VI shows the displacements of this band. Its average value for all the compounds examined by Coblenz is about 13.7 μ . The shorter wave-length spectra of the compounds of Table VI are quite similar.

TABLE VI

Displacement of the 14 μ band in the spectra of the benzene derivatives.

| | |
|------------|------------|
| benzene | 14.1 μ |
| toluene | 13.85 |
| o-xylene | 13.55 |
| m-xylene | 12.95 |
| p-xylene | 12.55 |
| mesitylene | 11.95 |

If C-C and C-H pairs of atoms give rise to linear, or approximately linear, series of absorption bands, then we should expect other bonded pairs within the molecule to behave in a similar manner. In a later paper it will be shown that the shorter wave-length bands occurring in addition to the members of the C-H series in the spectra of simple halogen derivatives of the benzene and paraffin series can be accounted for on the basis of carbon-halogen series starting near 17 μ , and combinations between such series and the carbon-hydrogen series.

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