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INFRA-RED ABSORPTION SPECTRA, II.

LIQUIDS AND SOLIDS.

BY W. W. COBLENTZ.

IN the complete account of this work a chapter is devoted to a detailed discussion of each compound studied. In this paper it will be impossible to include more than a brief outline of the more important relations found. For the substances mentioned here the principal results are put in convenient form for reference in Figs. 7, 10 and 11. The lines in these plots represent, in height and in position, the principle absorption bands of some of the compounds studied.

In general the transmission spectrum of each compound shows some interesting property which cannot be correlated with that of a different compound. For example, Friedel,[1] using Tyndall's method of total absorption, found that methyl and ethyl iodide are far more transparent than nitrogen compounds. It will be noticed, Fig. 10, that these iodides have large absorption bands in the region of 10 μ where the radiation from a black body is very weak. They are quite transparent in the region of 2 μ where the black body radiation is strong. Consequently, in measuring their total transmission, the great transparency found by Friedel is not due to the *lack* of absorption bands but to the fact that the absorption bands lie beyond the region of the black body radiation. A more conspicuous example of the reverse effect was found by Drew[2] in his work on vacuum tube

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[1] Friedel, Ann. der Phys., 55, p. 453, 1895.

[2] Drew, PHYS. REV., Vol. XVII., p. 321, 1903.

radiation. He used a cell of CS_2 as an absorbing medium, and found it as opaque as water. This is due to the fact that nearly all of the radiation from the tube is concentrated in a strong emission band at 4.75 μ, which coincides with a strong absorption band of CS_2 at 4.7 μ.

Benzonitrile, C_6H_5CN, is an excellent example of a compound having no strong absorption bands until we arrive at 13.25 μ. This is also the only compound studied which has a series of *small*, narrow, absorption bands extending throughout the spectrum [Fig. 10.]

Eucalyptol, $C_{10}H_{18}O$, is the only compound studied which has a large band of general absorption, extending from 7 μ to 14 μ, beyond which point the substance becomes more transparent the farther one penetrates the infra-red — to 15 μ.

THE SPECTRUM FROM .8 μ TO 2.75 μ.

Puccianti,[1] using a quartz prism and a radiometer, explored the transmission spectra of sixteen liquid compounds. His curves show that all compounds, the molecules of which contain carbon combined directly with hydrogen, present a maximum absorption at 1.71 μ, while all the benzene derivatives have two other maxima in common at 2.18 μ and 2.49 μ. The three alcohols examined by him have a band in common at 2.05 μ.

The results obtained by him seemed so unusual that a continuation of the work was deemed necessary. Accordingly, eighteen new compounds were examined As a whole the results obtained are in excellent agreement with those of Puccianti. The band found by him at 1.71 μ was located at 1.68 μ to 1.7 μ, depending upon the compound. It was found in *all* the carbohydrates studied. The slight shift does not appear to be due to shifting of the apparatus, and is to be found in the more complex compounds, just as is true farther in the infra-red. The 2.18 μ and the 2.49 μ bands of benzene derivatives are also sometimes slightly shifted in the complex derivatives like pinene, eucalyptol, and safrol. As a whole the curves form an interesting study by themselves.

GENERAL DISCUSSION OF THE SPECTRA.

Since the object of this investigation was to determine the effect of molecular weight, of chemical structure, etc., upon the absorp-

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[1] Puccianti, Nuovo Cimento, II., p. 241, 1900.

tion of heat waves, it will simplify matters to discuss each of these topics separately.

A few transmission curves are included to give the reader an idea of their general appearance.

Effect of Structure. — In order to learn what effect a group of atoms in a molecule has upon infra-red absorption spectra, the most logical procedure is to study isomeric compounds in order to determine fully that the phenomenon is intramolecular, and after that attempt to locate the particular group of atoms suspected of causing the disturbance. In many cases the spectra of isomers is very similar until we extend our observations far into the infra-red. The total number studied is so large and varied, however, while the change in the spectra of a pair of isomers is so marked, that there can be no question that this is due to structure rather than impurities. In aniline, $C_6H_5NH_2$, and its isomer, picoline, $C_6H_4N(CH_3)$, Fig. 7, the effect of structure is very marked. The benzene band at 3.25 μ, found in aniline, is entirely obliterated by the one at 3.35 μ in picoline, while in the spectrum of picoline only one band, at 10 μ, is in common with that of aniline. In the sulphocyanites, R-SCN, and the mustard oils, R-NCS, the effect of structure is still more pronounced. The small band of the sulphocyanates at 4.68 μ is com-

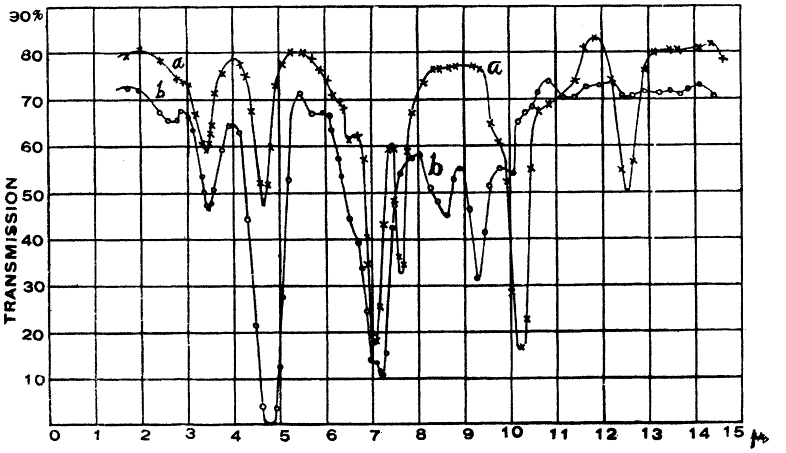

Fig. 5. Methyl Sulphocyanate, CH_3-SCN; Curve *b*, Methyl Mustard Oil, CH_3NCS; $t = .01$ mm.

pletely outclassed by the 4.78 μ band in the mustard oils, Fig. 5. As the band occurring from 3 to 3.4 μ is a characteristic of carbohydrates so is this band a characteristic of the mustard oils. Of all compounds studied, the mustard oils are unique in having an enormous absorption band in the region of shorter wave-lengths, this side of 5 μ. In CS_2 the first strong band occurs at about 6.7 μ, in methyl iodide at 11.35 μ, and in carbon tetrachloride at 13 μ.

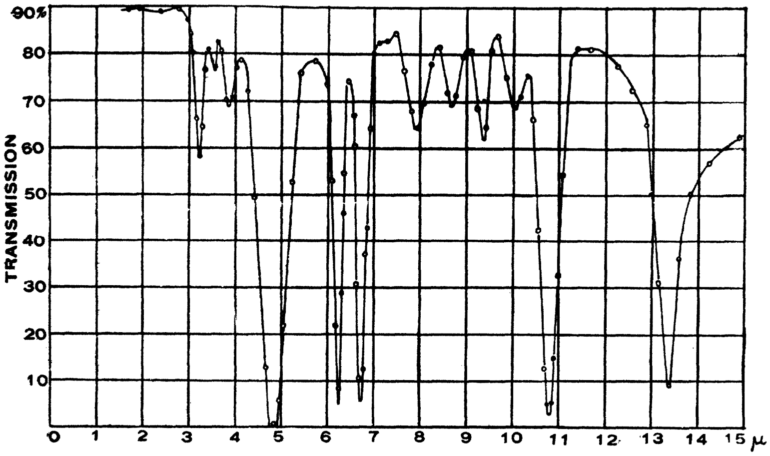

Fig. 6. Phenyl Mustard Oil, C_6H_5NCS; $t = .01$ mm.

In allyl mustard oil, C_3H_5NCS, using the large spectrometer, this band was found to be complex, being opaque from 4.5 μ to 4.9 μ, with the maximum located at about 4.8 μ. Phenyl mustard oil, C_6H_5NCS, Fig. 6, is still more interesting since it contains the 3.25 μ band as well as several others belonging to benzene and has, in addition, this strong band of the mustard oils, located at 4.8 μ, just as though the CH and the CS ion were vibrating side by side but independently of each other.

Other isomers like pinene and limonene, $C_{10}H_{14}$, have a great similarity until we arrive at 10 μ, while the caproic acids, Fig. 7, are identical to 6 μ and begin to show dissimilarity at 8 μ. Probably the most evident example of the influence of structure is in the aliphatic or chain linked compounds, like octane, and the carbocyclic, or ring compounds, like benzene. If we consider simply the number of atoms in the molecule then the benzene series, C_nH_{2n-6}, can be classed with the chain series, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n+2}. Hence, reasoning from the fact that, in the three groups of chains compounds studied, all the conspicuous bands occur in common, one would, expect at least a few of the bands to occur in the benzene, C_nH_{2n-6}, series. But no such coincidence occurs ; and only after the substitution of CH_3 groups for H atoms in benzene do we find bands, *e. g.*, 3.43 μ, in common with those of the chain compounds. If, then, we had no knowledge of organic chemistry, the evidence presented here would be sufficient to conclude that we are dealing with two distinct classes of compounds.

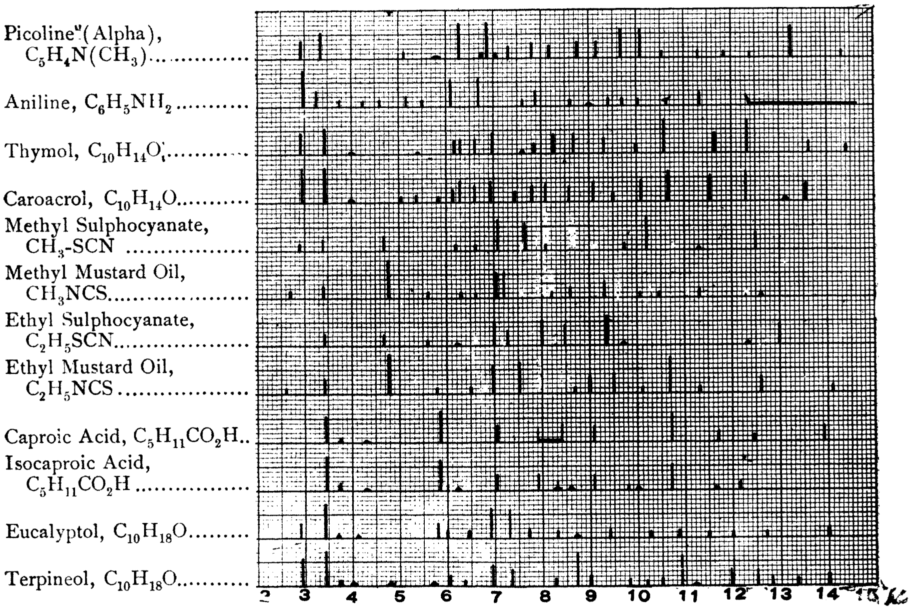

Fig. 7. Isomeric compounds illustrating effect of structure upon absorption. Height of lines indicates depth of bands.

Thymol and carvacrol, Fig. 7, methyl ether and ethyl alcohol, eucalyptol and terpineol, and the three isomeric xylenes are additional examples showing very clearly the marked influence of the arrangement of the chemical atom in the molecule upon the resulting absorption spectrum. In the xylenes the bands occur in groups ; while the location of the maximum of each group seems to occur in the order *para*, *meta*, *ortho*, with increase in wave-length, Fig. 10. In thymol and carvacrol the change in the spectra begins to manifest itself at 5 μ and 6 μ while from 9 μ to 14 μ the spectrum is entirely rearranged. In methyl ether and ethyl alcohol we have the most marked change in the location of the absorption bands, which is noticeable throughout the whole spectrum.

As a whole, the present investigation substantiates the conclusions of Julius (*loc. cit.*) of the influence of structure upon absorption spectra.

Effect of Molecular Weight. — In the present work the results agree with that of Krüss,[1] in so far as it seems permissible to assume that the occurrence of a certain conspicuous absorption band in a different place is a real shift. The benzene derivatives are the most noticeable example. In benzene, C_6H_6, the maximum occurs at 3.25 μ and is shifted to 3.3 μ in toluene, $C_6H_5CH_3$, to 3.38 μ in the xylenes, $C_6H_4(CH_3)_2$, and to 3.4 μ in mesitylene, $C_6H_3(CH_3)_3$ [Fig. 10]. In other words by substituting three CH_3 groups for an H atom we have shifted the maximum from 3.25 μ to 3.4 μ. Of all the compounds studied, excepting the gases, this is the only example where such a supposed shifting occurs. For a shift toward the *shorter* wave-lengths, certain derivatives of benzene containing nitrogen are the most conspicuous, just as found by Krüss. In aniline, $C_6H_5NH_2$, we find the benzene band almost obliterated and the minimum shifted to 2.97 μ, just as in ammonia, while in picoline we have the ammonia band at 2.92 μ and a second band at 3.35 μ. It is to be noticed that in the xylenes and pyridine the benzene band at 3.25 μ has not been entirely obliterated, just as though there were two resonating ions, benzene and CH_3, vibrating side by side. This is more evident in xylidine and the mustard oils.

In xylidine, $C_6H_3(CH_3)_2NH_2$, Fig. 10, which has an NH_2 group and two CH_3 groups, we have the respective bands *found in ammonia*, at 2.95 μ, and in compounds predominating in CH_3 groups at 3.43 μ. The structural formula of aniline indicates that in the original benzene ring an H atom has been replaced by an NH_2 group, while in picoline we have the double benzene ring containing an N atom and a CH_3 group. The absorption spectra support this theory for

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[1] Krüss, Zeit. f. Phys. Chem., 2, 312, 1888.

in the aniline spectrum we have the original benzene band at 3.25 μ and the NH_2 band found in ammonia, xylidine, etc., while in picoline we have the benzene band obliterated and the CH_3 band substituted. The latter band occurs at 3.35 μ, the mean of 3.25 μ and 3.43 μ instead of 3.43 μ. Can we say then that there is a *real shifting* of the 3.38 μ band in the xylenes? It must be remembered that we are integrating through a complex band, which with ordinary dispersion cannot be resolved with a bolometer or a radiometer. Hence, when we find the maximum shifted to 3.3 μ in anisol and to 3.4 μ in mesitylene, and find the separate bands in aniline, etc., it is a difficult matter to decide whether we have a true shifting, or whether we have simply determined the center of gravity of the several bands. An excellent example of this type is thymol, which melts at 44°. The solid film gave a deep band at 3.2 μ. In the melted condition the film was more homogeneous, and two bands were found, at 2.92 μ and 3.42 μ respectively, instead of the mean at 3.2 μ. Other examples have been observed when the layer of liquid under examination was too thick.

There are other bands farther out in the infra-red which shift back and forth just as noted above, but here the original benzene bands are more numerous. The most noticeable ones are those of the methyl sulphocyanate at 7.06 μ and 7.61 μ which occur at 6.91 μ and 7.27 μ in ethyl sulphocynate. However, in all the benzene derivatives studied the occurrence of an apparently new band in the derivative does not always seem to be a *new* band, but simply that the derivative has brought about a condition within the molecule such that the original resonating ion has a greater freedom.

In gases there is a more definite shifting of the absorption band lying between 3 and 3.5 μ, as shown in Table I.

TABLE I.

Gases.	Maxima.	Maxima.
Acetylene, C_2H_2	3.08 μ	7.38 μ
Ethylene, C_2H_4	3.28	6.98
Ethane, C_2H_6	3.39	6.85
Butane, C_4H_{10}	3.42	6.85
Methyl ether, $(CH_3)_2O$	3.45	6.88
Ethyl ether, $(C_2H_5)_2O$	3.45	7.00
Methane, CH_4	3.31	7.70

In the region at 6.8 μ to 7.0 μ there is a similar shifting but there is less regularity in the positions of the bands. Ångström[1] has shown that the occurrence of the CO_2 band at 4.28 μ and the CO band at 4.59 μ invalidates the assumption that the position of an absorption band depends upon molecular weight. Ransohoff's[2] work shows that for the alcohols there is no shifting with increase in molecular weight.

Within the experimental errors of observation Puccianti's work for the region of 1.71 μ shows no shifting of the maximum of an absorption band.

In all my work of the different compounds like methyl and ethyl iodide, -nitrate, -cyanide, -aniline, etc., no shifting could be detected.

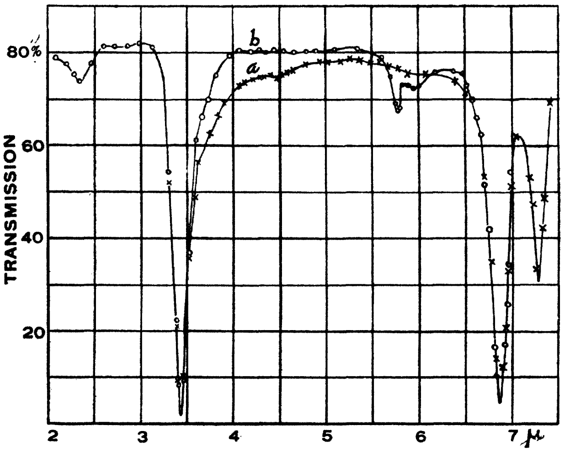

Fig. 8. Octadecylene, $C_{18}H_{36}$; Tetracosylene, $C_{24}H_{48}$, x x x x x x x; $t = .01$ mm.

To make this test conclusive for the marked band at 3.43 μ this region was examined for both compounds (methel and ethyl) before setting the spectrometer for another part of the spectrum. In this manner a slight shift noticed in methyl and ethyl iodide which had been examined on different dates, several months intervening, was found not to exist, showing an instrumental error. This method of testing a series of compounds at one region of the spectrum on the same day is the only way to be certain of slight differences in wave-

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[1] Ångström, loc. cit.

[2] Ransohoff, Inaug. Diss., Berlin, 1896.

length. Through the generosity of Professor C. F. Mabery, who presented me with twenty-five very pure distillates of petroleum belonging to the series C_nH_{2n}, C_nH_{2n-2} and C_nH_{2n+2} a final test was applied to this perplexing question. The absorption spectra of two of these, octadecylene, $C_{18}H_{36}$, boiling point 118°–120°, and tetracosylene, $C_{24}H_{48}$, solid, boiling point 274°–276° (50 mm.), are given in Fig. 8, for which the large spectrometer was used. Curve *a* is $C_{18}H_{36}$.

In these, as well as the intermediate ones, no shifting could be detected, although the greatest efforts were made to do so. This was not a little surprising for according to the measurements on the alcohols by Schönn[1] in the visible spectrum a shift for this greater number of CH_2 groups should have occurred. For, even if we assume that the shifting is least for the infra-red and increases as we approach the ultra-violet, unless the total shift, for this increase of 16 CH_2 groups (octane $C_8H_{18} = CH_3(CH_2)_6CH_3$, tetracosane $C_{24}H_{50} = CH_3(CH_2)_{22}CH_3$), is less than .01 μ it is safe to assume that no shifting occurred. At least, if there is a shifting, it is less than .01 μ which is much smaller than one would anticipate from observations in other regions of the spectrum.

A shift of .01 μ at 3.43 μ is 8″ of arc on the spectrometer circle, and at 6.86 μ it is 12″ of arc, so that it would have been impossible to escape detection — especially in the case of such deep, well defined bands as these. It is to be remembered that a separate examination was made of the 3.43 μ and the 6.86 μ bands for $C_{18}H_{36}$ and $C_{24}H_{48}$, using the large spectrometer [Fig. 8]. This was done to avoid the possibility of a shifting while examining the whole spectrum. Only seven spectrometer settings, at intervals of 1′, were made for each of these two bands. First, the zero of the instrument was determined by means of the sodium flame, then the 3.43 μ region was examined for $C_{18}H_{36}$, the examination being from *right* to *left*, say; the $C_{24}H_{48}$ was then examined going backwards, from *left* to *right*, and then from *right* to *left*, after which the zero was again tested by means of the sodium flame. The 6.86 μ band was examined in the same manner, but in neither case could a shifting of the band be detected, as will be noticed in the curves, Fig. 8. These two bands are so sharp that if a shifting of .01 μ

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[1] Schönn, Ann. der Phys., 6, p. 267, 1879.

had occurred it could have been detected. It is true that these bands vary by .01 μ for some of the other oils, but that is to be ascribed to errors in reading the curves as well as to the fact that the small spectrometer was used, and that in general it was not practicable to make the examinations in the manner just described. A shift of .02 μ was easily observed in the bands of xylene and mesitylene at 3.4 μ.

An interesting fact to be noticed in this connection is that *all* the prominent lines found in the two oils just mentioned are present in all the petroleum oils studied, as well as in many other compounds, like myricyl alcohol, piperidine, etc. For a large dispersion the transparent region at 4 μ to 6 μ remains so for some oils, while in others numerous small bands were found [see Fig. 8].

The difference between the spectra of the oils (aliphatic series) and the benzene spectrum (carbocylic series) has been noticed under the question of structure. The benzene spectrum as well as that of its methyl derivatives is banded, "channeled," *i. e.*, the lines occur in groups just as Pauer[1] found in the ultra-violet [see Fig. 10]. He found the bands of the benzene spectrum, which extend from .267 μ to .235 μ, condensed and shifted toward the visible spectrum for toluene, the xylenes, aniline, etc., and considered it due to increase in molecular weight. If we consider the center of gravity of the benzene bands at about .245 μ and that of the methyl derivatives at about .267 μ this shift amounts to .02 μ while for analine it is about .05 μ.

As a whole there is no evidence of a real shifting of the maximum with increase in molecular weight, if we except the xylenes and the gases mentioned, for the region at 3.1 μ to 3.5 μ, which is not resolved for most compounds. The condition is similar to that in Kayser and Runge's work on the emission spectrum of the elements, in which they observed that, for the alkali metals, the violet lines shifted toward the longer wave-lengths with increase in atomic weight; but they could not establish[2] this relation for all the elements.

Effect of Temperature. — There is little to be said on this subject

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[1] Pauer, Ann. der Phys., 61, p. 363, 1897.

[2] Kayser's Spectroscopie, II., p. 591.

for no effect due to rise of temperature of about 20° has been observed. As already mentioned, the absorption cell was between the spectrometer slit and the Nernst heater, with the double sheet iron asbestus shutter intervening. It was necessary to have the heater close to avoid loss of radiation. Consequently, in the course of a series of observations, lasting four hours, the cell would unavoidably become warmer, due principally to the raising of the shutter in making observations. This was first noticed in thymol, melting point 44°, which in the course of examination as a solid film became a liquid. It is quite crystalline in a solid film, hence more opaque due to scattering of the rays, so that it became more transparent on melting. This is the only compound found to behave thus.

It was an easy matter to repeat the observations on several sharp absorption bands, after finishing the exploration of the whole spectrum, to see whether the transparency remained the same as in the beginning; and in *no case* was there a change observable excepting for the solid thymol just mentioned.

This fact that the cell became warmer was utilized in examining several compounds with low melting points, *e. g.*, phenol and menthol, in their liquid state. It was only necessary to melt them before placing them upon the spectrometer arm, then keep the shutter raised longer than usual. This made possible the examination of several solid compounds which would have been too opaque because of their scattering effect.

The Effect of Certain Characteristic Groups of Atoms. — Having shown that infra-red absorption spectra depend upon the internal structure of the molecule and that their maxima are not influenced by molecular weight (of the molecule as a whole, *e. g.*, the petroleum distillates) the next step is to determine, if possible, what groups of atoms, or ions, have the power of absorbing heat waves. This is of considerable importance since many recorded phenomena have been credited to "the resonance[1] of the

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[1] Marx, Potentialfall und Dissociation in Flammengasen, Drude's Ann., 2, p. 795, 1900 (also on Electromagnetic Resonance, Wied. Ann., 66, p. 600, 1898). After a lengthy discussion concludes that although it is a plausible assumption it has not been proven that electrolytic dissociation in a flame depends upon the effect of the electromagnetic resonance of the OH ion upon the infra-red radiation.

OH ion in the molecule." Aschkinass[1] found the absorption bands of water at the wave-lengths 1.51 μ, 3.06 μ and 6.1 μ. Although he says little about the sequence of the maxima subsequent writers have laid considerable stress upon it, as showing harmonics, *i. e.*, electromagnetic resonance. Marx[2] in finding the dielectric constants of water for electrical waves finds a double harmonic relation for the electrical region. Ransohoff (*loc. cit.*) studied six alcohols and found the bands harmonic at 1.71 μ (3.0 μ) and 3.43 μ, although the alcohols were "chemically pure" that is a different question from the one of having them "water free," which he does not consider, and the 3.0 μ and 6.06 μ bands may be due to water. The higher alcohols, like glycerine, even if they could be freed from water are so hydroscopic that they are difficult to investigate. In the present work alcohols were not investigated because of their great opacity beyond 7 μ as well as on account of the difficulty in freeing them from water. Only one alcohol was studied, viz., myricyl, $C_{30}H_{61}OH$, which is a solid obtained from beeswax [Fig. 9]. Its maxima occur at 1.71 μ, 2.95 μ, 3.43 μ and 5.8 μ. The water bands were found at 2.95 μ and 6.0 μ so that if the alcohol bands are due to the OH group then one would expect the 5.8 μ band to coincide with that of water, at 6.0 μ.

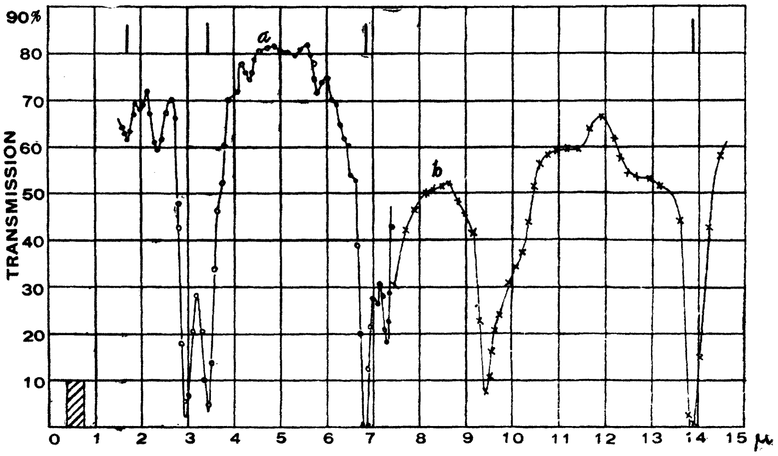

Fig. 9. Myricyl Alcohol, $C_{30}H_{61}OH$; *a* = large spectrometer.

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[1] Aschkinass, Ann. der Phys., 55, p. 401, 1895.

[2] Marx, *l. c.*

TABLE II.

Compounds.	Maxima.	Remarks.
Water, HOH	2.95 μ	Depth is 70 per cent. as found with larger spectrometer.
Thymol Carvacrol $C_{10}H_{13}OH$	2.92	
Eugenol, $C_{10}H_{11}O\text{-}OH$	2.89	
Methyl salicylate, $CH_3OOC\text{-}C_6H_4OH$	3.1	Depth 70 per cent., probably the mean of the 3.25 μ and 2.95 μ bands.
Menthol, $C_{10}H_{19}OH$	3.0	50 per cent., comparison spectrum of H_2O at 2.95.
Phenol, C_6H_5OH	2.97	60 per cent.
Ammonia, NH_3	2.92	30 per cent.
Pyridine, C_5H_5N	2.95	30 per cent.
Picoline, $C_5H_4N(CH_3)$	2.92	Band shallow, 3 per cent.
Piperidine, $C_5H_{11}N$	3.00	30 per cent.
Aniline, $C_6H_5NH_2$	2.97	70 per cent., very sharp.
Xylidine, $C_6H_3(CH_3)_2NH_2$	2.95	50 per cent.
Pyrrol, $C_4H_4(NH)$	2.95	70 per cent.
Eucalyptol $C_{10}H_{18}O$	2.90	30 per cent., oxide, does not contain an OH group.
Terpineol	2.93	30 per cent.

In Table II. it will be noticed that ammonia also has a band near that of water, and at a slightly less wave-length. Considerable time was spent in showing that it is not due to water vapor. The gas was fractionally liquefied and distilled and then placed in a gas pipette containing freshly heated calcium oxide over mercury, for eight days. At the end of this time the absorption band coincided exactly with the one previously found showing that the band is characteristic of ammonia. Furthermore, it will be noticed that the compounds containing the amido, NH_2, group and certain ones containing nitrogen have a characteristic band in this region. These compounds were dried with potassium carbonate which would have removed traces of water. Other compounds like the aldehydes and fatty acids *do not* show this band. Commercial ethyl ether contains about 3 per cent. of water, but there is only a slight depression in the absorption curve at 2.95 μ. The fatty acids, *e. g.*, caproic stearic, etc., are of interest, because they have no band at 2.95 μ. In electrolysis the alcohols are separated into ethyl and OH ions while in the fatty acids instead of the OH ion we have simply an H ion. Hence, reasoning from this analogy one would not expect a band at 2.95 μ for the fatty acids. In the other compounds having an OH group, *e. g.*, eugenol, thymol, menthol and phenol, strong bands are to be found shifting from 2.87 μ to 3.0 μ. They show *no* bands at 6 μ. Can we assume then that the bands at 2.9 μ to 3.0 μ are due to OH? The evidence is not very favorable.

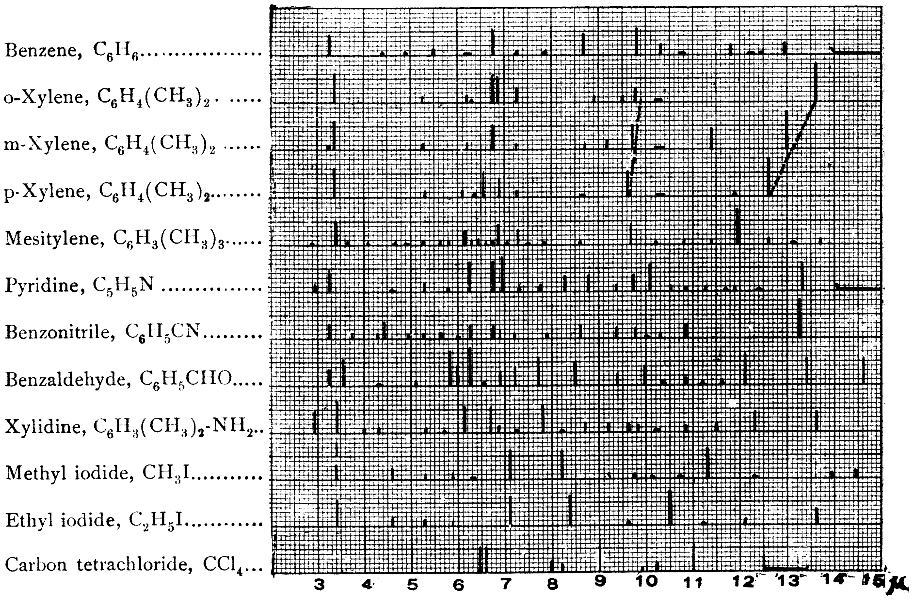

Fig. 10. Illustrating the persistence of the benzene bands at 3.25 μ and 6.75 μ in the spectra of its derivatives.

Considering the bands of ammonia and of the compounds containing NH_2, or certain ones containing nitrogen, the coincidence appears to be somewhat accidental. Farther in the infra-red we have numerous cases of the coincidence of absorption bands.

As a whole the most definite conclusion we can draw, at present, is that the alcohols have a characteristic band at about 2.95 μ just as the band at 4.78 μ is characteristic of the mustard oils.

The CH_3 group of atoms is probably the most important to be considered but only a few cases can be noticed here. The most noticeable effect is in benzene derivatives [Fig. 10]. It was shown under the discussion of the effect of structure that the benzene group, C_6H_6, although it appears as a series C_nH_{2n-6} is entirely different from the chain compounds like C_nH_{2n-2}, etc. But a substitution of several CH_3 groups completely absorbs the 3.25 μ benzene band, and the 3.43 μ band, characteristic of all compounds containing CH_3, takes its place. Whether the 3.25 μ band has actually disappeared is an open question. In mesitylene there is still a trace of the 6.75 μ band of benzene, showing that the benzene "ion" has not been destroyed by the substitution of 3 CH_3 groups. In the xylenes the 6.75 μ band is least effected while the 3.25 μ suffers the most and the whole strengthens the belief mentioned in the beginning that certain vibrating ions always seem to be present but that their effect in absorbing heat waves seems to depend upon their surroundings. Thus the effect of substituting an NH_2 group for an H atom, forming aniline, has the least effect on the benzene, 3.25 μ band, while those from 6 μ to 7 μ have disappeared entirely. In benzaldehyde, C_6H_5CHO, the 3.25 μ band is not seriously influenced by a more intense absorption band at 3.55 μ, while in benzonitrile, C_6H_5CN, and in monobrombenzene, C_6H_5Br, the 6.25 μ band suffers no change.

As a whole, the substitution of a CH_3 or NH_2 group has a great effect on the resulting absorption spectrum. In the benzene derivatives these groups form new bands which occur beside the benzene bands, *showing that the original benzene vibration has not been destroyed.* Such examples as these would indicate that the new bands are due to the groups of atoms substituted. But how are we to establish this with certainty, especially when in the myricyl alcohol the evidence is contradictory for the direct effect of the OH group?

Total Absorption.— This is not so well illustrated here as in the work of Friedel (*loc. cit.*) and of Zsigmondy[1] who used the undispersed radiation. The present work agrees with theirs in showing that compounds having sulphur and the halogens are more transparent than H, O, OH or N which they have replaced. But *not all* the nitrogen compounds are highly opaque, *e. g.*, nitromethane. The present work illustrates best the question of the location of the

[1] Zsigmondy, Ann. d. Phys., 57, p. 639, 1896.

regions of greatest absorption. Thus in pyridine and picoline a layer 0.16 mm. in thickness is almost opaque beyond 6 μ while methyl cyanide is quite transparent. Methyl iodide is quite transparent, since its large absorption bands lie in the region where the radiation from a black body is very weak, while the 3.4 μ band is shallow so that its great transparency, observed by Friedel, as compared with nitrogen compounds is apparently due to the lack of absorption bands in the region of intense radiation [Fig. 10]. As a whole the work agrees with that of Friedel and of Zsigmondy in showing that the absorption of radiant heat depends upon the manner of the bonding of the atoms in the molecule, as well as upon the kind of compound in which the atoms of an element are united.

Friedel and Zsigmondy (*loc. cit.*) found that total absorption does not depend upon the size of the molecule. In the present instance we have noticed that the number and intensity of the absorption bands does not depend upon molecular weight, *e. g.*, in the petroleum distillates. In the present work on dextro-pinene and lævo-pinene the maxima of the bands coincide, showing that the shape of the molecule has no influence on absorption spectra.

Grouping Spectra. — Abney and Festing,[1] say their results indicate "without much doubt that the substances we have examined agree on the whole with that adopted by chemists." In other words certain great groups of compounds have characteristic absorption spectra. This is just what Hartley and Dobbie[2] observed for the alkaloids, in which the ultra-violet absorption spectra vary only in minor details.

These observations apply to the present work. For example, the terpene group of compounds has a series of bands which is common to *all* of the compounds belonging to this group. In the same manner the general trend of their absorption curves is similar. The petroleum distillates have all the principal bands in common, Fig. 11. The spectra of the fatty acids are conspicuous for the lack, but great depth, of their absorption bands, Fig. 7. Having observed that certain groups of spectra are similar, one would naturally search for

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[1] Abney and Festing, Phil. Trans., 172, p. 887, 1882.

[2] Hartley and Dobbie, Phil. Trans., 77, p. 846. Also Dobbie and Lawder, Chem. Soc. Jour., 83 and 84, pp. 605 and 626, 1903.

certain characteristic absorption bands; and, reasoning from this standpoint, we may possibly be able to locate the group of atoms which causes the band. Thus, the 2.95 μ band and the OH group of atoms are characteristic of alcohols, while the 4.78 μ band and the NCS radical are characteristic of the mustard oils. But this avails us little for a great many other facts, besides the group of atoms, serve as characteristics of these groups of compounds.

Characteristics of the Spectra of Carbohydrates.—Puccianti (*loc. cit.*) found that in all cases where the carbon atom was joined directly to the hydrogen atom in the molecule, the absorption spectrum showed a band at 1.71 μ. This has been verified in the present work, where the band was found oscillating between the values of 1.68 μ benzene to 1.74 μ for caproic acid, for ethyl succinate, and for methyl acetate. From this point to 3 μ there are numerous small bands of minor importance. Somewhere between 3.1 μ and 3.43 μ a band is found for *every* carbohydrate studied, oscillating from 3.25 μ in benzene to 3.43 μ in the alcohols and compounds rich in

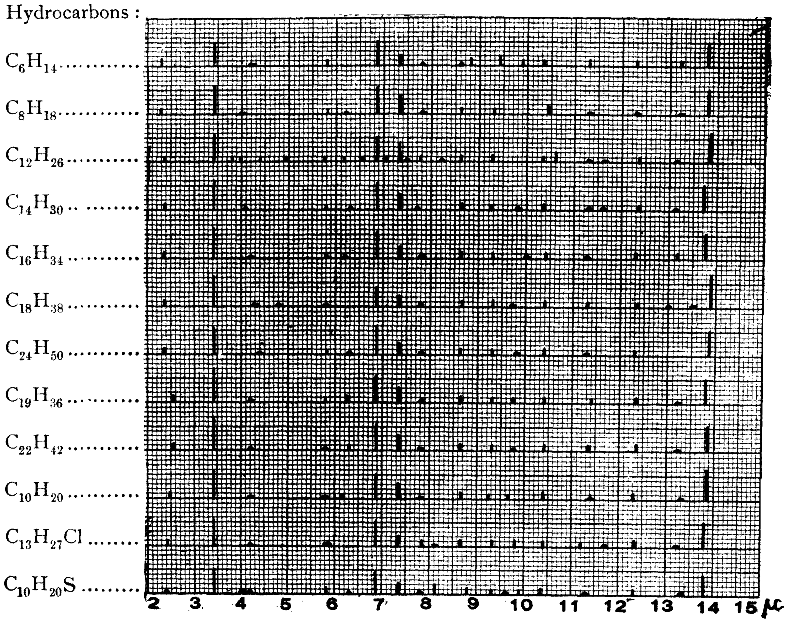

Fig. 11. Petroleum distillates.

CH_3 groups. In the region extending from 4 μ to 5 μ there is great transparency (except in the case of the mustard oils), and for the more complex compounds, *e. g.*, the petroleum distillates, there are generally no lines even with the large dispersion used. Beyond 5.5 μ the transmission curve decreases, often very abruptly, terminating in strong absorption bands, varying from 6.75 μ in benzene, 6.86 μ in aliphatic compounds [Fig. 10] to 7 μ in terpenes. Beyond this point the bands become stronger, while the transmission curve varies from great transparency to complete opacity. The region at 12 μ is often lacking in absorption bands, and finally we come to a region of frequently great absorption, with bands occurring from 13.6 μ to 14.2 μ. Beyond this point it is difficult to penetrate, but all observations made indicate the existence of similar conditions as in the region investigated.

In addition to the general characteristics of the spectra of carbohydrates it will be noticed, Fig. 6, that the characteristic bands of benzene derivatives are at 3.25 μ, 6.25 μ, and 6.75 μ; that of the aliphatic compounds, *e. g.*, the petroleum distillates, at 3.43 μ, 6.86 μ, and 13.6 μ to 13.8 μ; that of carbon tetrachloride at 13 μ; that of compounds having N or NH_2, at 2.95 μ, and at 6.1 μ to 6.2 μ; that of the fatty acids at 3.45 μ and 5.86 μ; that of the alcohols at 2.95 μ and 3.43 μ; and that of the mustard oils at 4.78 μ, see Table III. The region of great transparency from 4 μ to 5 μ is also to be noticed since the larger dispersion failed to show the presence of strong lines [Fig. 8].

Occurrence of Harmonics. — In discussing the question of the presence of simple relations among the spectral lines in the optical region, Cornu[1] shows that it is useless to search for harmonic overtones since the case is relatively rare. He adds that the law of vibration in whole numbers is applicable only to a particular form of sounding bodies of which the type is a cylindrical column, whose length is great in comparison to the cross-section. In any other type, except this special one, the relations between the vibration numbers of the successive tones is very complex. In Kayser's Spectroscopy, it is remarked that such a search is delusive, and Grünwald's mathematical spectrum analysis[2] is cited as an example

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[1] Cornu, Compt. Rend., 100, p. 1181, 1885.

[2] Grünwald, Wien. Ber., 96 to 101, 1887 to 1892.

in which all wave-lengths of the so-called compound spectrum of hydrogen can be converted into corresponding wave-lengths of the water vapor spectrum by multiplying by 0.5. Since then more exact measurements on these lines show that no such relations exist.

Schuster[1] speaks of the iron spectrum which has two lines which are in the ratio of 2 to 3, while hydrogen has lines in the ratios of 20 : 27 : 37. He demonstrates that in accordance with the theory of probability a certain number of coincidences between lines of two spectra might be expected to occur even if the spectra be quite unrelated. Furthermore, there appears to be a tendency for functions formed by two lines to *cluster around harmonic ratios* and "most probably some law hitherto undiscovered exists which in special cases resolves itself into the law of harmonic ratios." Of course, as is well known now, the nearest approximation to such a law is Balmer's Law and the numerous other convergent series formulæ used by Kayser and Runge, and by others. Nevertheless, in spite of these warnings, and fully realizing the danger from lack of dispersion, experimental errors, etc., I venture to call attention to certain marked absorption bands which occur so frequently, in positions which so closely fulfill this relation, that it is necessary to examine more fully into the probable significance.

Abney and Festing (*loc. cit.*) found that compounds having CH_3 groups have a band at 0.74 μ and another between .907 μ and .942 μ, while benzene and CH_3 compounds have a band at .867 μ. Puccianti (*loc. cit.*) found a band at 1.71 for all compounds in which the C atom is joined directly to the H atom in the molecule. Aschkinass (*loc. cit.*) found the absorption bands of water at 1.51 μ, 3.06 μ and 6.1 μ, while Paschen (*loc. cit.*) found them at from 2.916 μ to 3.024 μ, and at 6.06 μ, values which are closely harmonic. Ransohoff (*loc. cit.*) found closely harmonic bands for alcohols at 1.71 μ and 3.43 μ.

In the present work, using a quartz prism, the first band occurs at from .83 μ to .86 μ, while the second one oscillates between the values 1.66 μ for thiophene to 1.73 μ in ethyl succinate. The next disturbance is in the region of 3.4 μ, the maximum being at 3.25 μ

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[1] Schuster, Proc. Roy. Soc., 31, p. 337, 1881.

for benzene, and 3.43 μ for compounds rich in CH_2 or CH_3 groups.

The next region where there is a constant recurrence of bands is at 6.75 μ for benzene, and 6.86 μ for other compounds rich in CH_2 or CH_3 groups. In discussing the sources of errors it is shown that the 6.86 μ band is quite accurately known.

Beyond 13.6 μ there is a band of frequent recurrence. In this region, however, it is difficult to locate the bands with great accuracy because of the weakness of the radiation. As a whole, however, the bands at 1.71 μ, 3.43 μ, 6.86 μ and 13.6 μ to 13.8 μ are closely harmonic, *e. g.*, in the petroleum distillates and myricyl alcohol, Figs. 9 and 11, and taken with the .867 μ band of Abney and Festing (.83 to .86 μ in present work) would seem to indicate a vibration about a fixed point (Schuster's clustering). Even if in the future this relation should be found false, the constant recurrence of these bands, in so many compounds, cannot be without meaning. These bands are so sharp and symmetrical that it is difficult to conceive how with greater dispersion they can be resolved into lines which are very unsymmetrically placed about the present centers of gravity.

In carbon tetrachloride, Fig. 10, and tetrachlor-ethylene it was found that this group of compounds is conspicuous for the absence of absorption bands except at 6.5 μ and 13 μ (harmonics) where there are large bands, each of which is evidently complex.

An explanation of the significance of these relations is not attempted and it will be sufficient to add that any such harmonic relation would seem to indicate the resonance of a definite group of atoms, or "ions," to which these lines are solely due. But to attribute a given line to a certain group of chemical atoms is dangerous; for it has already been shown in the case of the mustard oils that the manner of grouping of the atoms is not the only characteristic of this group of compounds. Thus, the physical properites of benzene and thiophene are so similar that these two compounds are readily confounded,[1] yet their absorption spectra are entirely different. It might be added that in the gases, where one would naturally expect such harmonic relations, only acetylene at 3.7 μ and 7.4 μ and methyl ether at 3.45 μ and 6.9 μ have bands satisfying this condition.

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[1] Smith's (Richter) Org. Chemie, Vol. 2, p. 47.

Whether this relation will ultimately be proved absolutely true, remains to be seen. To determine this question a very much larger dispersion will have to be employed than has yet been available. This means a far more sensitive recording apparatus than has yet been devised.

In dismissing this question, it will be sufficient to add that after a year's struggle with it, to prove or disprove it, the result has been a closer agreement in the values first obtained, especially for the bands at 3.43 μ and 6.86 μ, Fig. 8. The agreement is as close as one would expect from our present knowledge of the infra-red dispersion of rock-salt. It is quite possible that the 3.43 μ, 6.86 μ and 13.8 μ bands belong to a slowly converging "spectral series," in which case there ought to be a discrepancy in the above harmonic at 13.8 μ.

Absorption of Solids in Solution. — In the ultra-violet Hartley and Dobbie (*loc. cit.*) have studied the absorption spectra of solids dissolved in water. They found that groups of chemically related compounds have similar absorption spectra. In the visible spectrum we also find absorption bands, especially when the solute is a colored substance. Iodine is an example of this type. But in the infra-red the writer found iodine transparent beyond 1.1 μ. As far as is known to the writer, only one other substance, sulphur in CS_2, has been examined far out in the infra-red. This was done by Julius (*loc. cit.*) who found that S had no appreciable effect upon the transparency of the CS_2.

That a solid in solution should be transparent to infra-red radiation seemed doubtful. It would indicate a resonance of small particles, in the optical region, as distinguished from the intra-molecular resonance of the solvent.

After studying so many compounds it seemed imperative to consider this question more thoroughly.

It was suspected that this transparency is simply due to the thin cell used, and to the slight solubility of the solids. For example, assuming that .05 gr. of iodine per c.c. are dissolved in CS_2, using a cell .3 mm. thick, this would be sufficient to form a solid film only .03 mm. It seemed that the proper method of answering this question would be to select a solid having a *strong* absorption band in a region of the spectrum where the solvent has *no absorption bands.*

DIPHENYL, $C_{12}H_{10}$.

The curves of carbon tetrachloride, CCl_4, showed no marked bands up to 6.5 μ. Accordingly this liquid was selected for a solvent. The sample used with diphenyl showed the water band at 2.9 μ and a second band at 4.5 μ. A saturated diphenyl solution showed an additional large band at 3.25 μ which is the characteristic band of the benzene nucleus. This is of considerable interest since diphenyl, $C_6H_5—C_6H_5$, is a double benzene ring. The curve, Fig. 12, shows that solids in a solution do absorb heat waves, and that the selective absorption of a solid in solution and that of the solvent are identical.[1] It also shows that the *benzene vibration still exists*, and that solids in solution can be studied in the infra-red as in the ultra-violet.

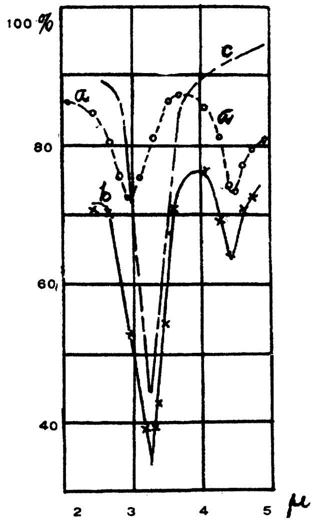

Fig. 12. Curves: $a = CCl_4$; $b =$ sol. diphenyl, $C_{12}H_{10}$, in CCl_4; $c =$ transmission through $C_{12}H_{10}$.

However, in the infra-red we have no transparent solvents, as is true of the ultra-violet. Water is the most common solvent; but, of all substances examined, it is the most opaque to infra-red radiation. Crystalline solids are not applicable because of their scattering effect, so that many solid compounds of interest on account of their structure cannot be studied because of the lack of a suitable solvent.

NAPHTHALENE, $C_{10}H_8$.

Naphthalene was also examined at 3.25 μ. Its solubility in CCl_4 is unusually great, *e. g.*, the present solution contained .25 gr. per cubic centimeter of CCl_4. This is sufficient to make a homogeneous solid film .28 mm. thick (sp. gr. = 1.15, cell = .6 mm.).

This compound is of considerable importance since its molecule is formed by the condensation of two benzene nuclei. As a result

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[1] In my preliminary communication on Infra-red Absorption Spectra, Astrophys. Jour., XX., p. 215, 1904, it appeared to me that there might be a difference.

the cismical properties are quite different from that of benzene; but its absorption spectrum, Fig. 13, shows the 3.25 μ band of benzene, with which it is also comparable in general transmission. As a whole, for the region investigated, this compound shows that the vibration of the benzene nucleus has not been disturbed.

AZOBENZENE, $C_6H_5 — N = N — C_6H_5$.

This compound is also quite soluble in CCl_4 so that a saturated solution contained about .2 gr. per c.c. of the liquid. As with the preceding compounds the rock salt cell was .6 mm. thick.

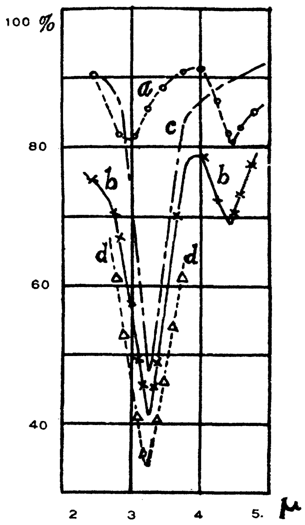

Fig. 13. Curves: $a = CCl_4$; $b =$ Napthalene, $C_{10}H_8$, in CCl_4; $c =$ transmission through $C_{10}H_8$; $d =$ Azobenzene in CCl_4.

The curve *d*, Fig. 13, shows the 3.25 μ benzene band, indicating that the presence of the N atoms does not disturb the vibration of the benzene nucleus. This solution is far more opaque than the preceding, showing the effect of the introduction of the N atoms, just as in other compounds containing nitrogen.

Moreover, this solution is of a reddish-brown color, showing an absorption band in the visible spectrum, as well as in the infra-red. This shows that both are due to an intramolecular disturbance and disapproves the idea of a resonance of small particles (of molar dimensions, as for example, Kosonogoff's butterfly scales and Wood's metal films) in the optical region, as distinguished from the intramolecular resonance in the infra-red. Of course, one might say that the infra-red band, *e. g.*, the 3.25 μ band, is also a resonance effect. Possibly it is but the evidence of a resonance of small electrically charged particles, whose capacity and hence whose periods (like a condenser) depend upon their proximity to similarly charged particles (the closer the particles, the greater the capacity, hence, the slower the period and, hence, the farther is the absorption band shifted toward the longer wave-lengths) is somewhat contradictory in the infra-red.

SUMMARY.

The infra-red absorption spectra of organic compounds have been studied, the majority to 15 μ, using a radiometer, two mirror spectrometers and rock salt prism. Out of a total number of at least 135 compounds examined with the rock salt prism, 131 have been recorded in this paper. They include solids, liquids, and gases. In addition to this, 19 compounds were examined to 2.7 μ, using a quartz prism.

The following are some of the results obtained:

1. A study of isomeric compounds shows that the arrangement or bonding of the atoms in the molecule, *i. e.*, its structure, has a great influence upon the resulting absorption spectrum, which agrees with Julius.

This is of considerable significance, and is in marked contrast with stereomeric compounds, like dextro- and lævo-pinine, which were found to have identical spectra, showing that the spacial arrangement of the atoms, *i. e.*, the configuration of the molecule, had no effect upon the resulting absorption spectrum.

2. No shifting of the maxima with increase in molecular weight, "Kundt's Law," could be detected, except in the case of the band lying between 3.1 μ and 3.5 μ, for gases. Instead of a shifting of the band in certain compounds there occurs a new band beside the original one when a methyl- or amido-group is substituted for a hydrogen atom, the new band lying toward the longer wave-lengths when a methyl-group is substituted, and toward the shorter wave-lengths when the hydrogen atom is replaced by an amido-group. This disagrees with investigations of Krüss in the optical region, where *only the new band* was observed.

3. A rise in temperature of 20° had no effect upon the transparency of the compound, nor upon the position of its maxima.

The effect of replacing an H atom by certain groups of atoms like NH_2 and CH_3 is very marked, and usually shows new bands, *e. g.*, 2.96 μ and 3.43 μ, in the resulting absorption spectrum. In the spectra of certain benzene derivatives, however, the bands of the

benzene spectrum are usually present, showing that the vibration of the benzene nucleus has not been destroyed. However, the writer does not consider this sufficient evidence to consider the new bands to be due to the groups of chemical atoms substituted.

5. Total absorption is not influenced by the size of the molecule; while compounds having sulphur or halogens are more transparent than those having H, O, OH or N which they have replaced, just as found by Friedal and by Zsigomondy.

6. The spectra of groups of compounds are similar and are characteristic of the grouping adopted by chemists, as found by Abney and Festing, for the region of 1 μ.

7. Carbohydrates have a characteristic spectrum, with absorption bands at .83 μ to .86 μ, 1.67 μ to 1.72 μ, 3.25 μ to 3.43 μ, 6.75 μ to 6.86 μ, and 13.6 μ to 14 μ. The first large absorption band in carbohydrates occurs in the region of 3.2 μ, which is in general followed by a *transparent* region from 4 μ to 5 μ. The work of Puccianti, in which he found that all carbohydrates have an absorption band at 1.71 μ while benzene derivatives have two additional bands, at 2.18 μ and 2.49 μ respectively, has been confirmed on 18 new compounds. The 1.7 μ band deserves especial notice.

8. In addition to the characteristic carbohydrate spectrum, certain bands in it occur in positions which are close harmonics, the maximum wave-length of each succeeding band being twice the preceding. The question whether this is merely a coincidence or whether it is an exact relation is not fully determined. To decide this question a larger dispersion will be necessary, while the spectrum will have to be explored to 27.6 μ for the next harmonic. In the same manner more pairs of bands will have to be located in the ammonia spectrum in order to show that the constant difference of the wave numbers found is not merely a coincidence, hence, that there is a true spectral series present.

8. The three isomeric xylenes have banded, "channeled," spectra in which the most important line, in each group, lies farthest toward the long wave-lengths, in the order: *ortho*, *meta*, *para*. In other words the *ortho*, in which the CH_3 groups are the closest together in the benzene ring, has the "head" of each group of bands lying farther toward the infra-red than are the heads of the corresponding bands of the meta- and para-compounds.

10. In many compounds numerous bands are in coincidence, which would no doubt be found in different positions, when using a larger dispersion. Other bands, like the one at 3.25 μ in benzene, in benzaldehyde, and in pyridine, or the 3.43 μ and 6.86 μ bands found in aliphatic compounds, seem to point to a specific group of atoms or to some "ion" or "nucleus" common to them, as their source.

The most marked example of this type is phenyl mustard oil in which the vibration characteristic of the mustard oils, at 4.78 μ is *superposed* upon the vibration of the benzene "nucleus" or "ion" which has its maxima at 3.25 μ, 6.75 μ etc. In some compounds there is evidence that certain bands, *e. g.*, the 3.43 μ band, are due to a definite group of atoms, *e. g.*, the CH_3 groups in the chain compounds and terpenes; in other compounds the evidence is just as strongly in favor of the manner of bonding of the atoms, *e. g.*, the methylene hydrocarbons of the petroleum distillates; other compounds, *e. g.*, benzene and its derivatives, especially phenyl mustard oil, in which we have the characteristic vibration of the mustard oils superposed upon the vibration of the benzene nucleus, show that both the groups of atoms and their manner of bonding with other atoms, as well as the kind of atom, have a great influence upon the absorption curve.

TABLE III.

Compounds Having the Following Groups:	Show Characteristic Absorption Bands at:		
CH_2 or CH_3	3.43	6.86	13.6–13.8 and 14 μ
NH_2	2.96	6.1 to 6.15 μ	
C_6H_6	3.25 μ	6.75 8.68 9.8 11.8 12.95	
NO_2		7.47? 9.08	
OH	2.95		
NCS		4.78	

In the present work the spectra have been discussed from the standpoint that, since compounds of the same chemical composition (isomers) have different spectra, the source of the disturbance is intramolecular. If we had assumed ignorance of the composition of the compounds, we would have expected, from our knowledge of the spectra of the elements, that each compound ought to have a different spectrum. This has been found to hold true, except for certain lines in them. There would be no reason for deciding whether the cause is inter- or intra-molecular. The compounds might then be grouped according to the marked absorption bands which they have in common, *e. g.*, those having a band in common at 3.25 μ, at 3.43 μ or at 4.78 μ. One compound (phenyl mustard oil) would then be placed in the 3.25 μ and in the 4.78 μ group. Another (xylidine) would belong to the 2.95 μ group and to the 3.43 μ group. This would then suggest a disturbance common to both groups, and we are brought to the point arrived at, by the other line of argument ; viz., there is a something, call it " particle," " group of atoms," " ion," or " nucleus," in common with many of the compounds studied, which causes absorption bands, characteristic of the great groups of organic compounds, but we do not know what that " something " is.

The presence of these groups of " ions," each group having its own free period of vibration, is in accord with the present conceptions of absorption and anomalous dispersion. To assign the cause of the absorption bands, given in Table III., to a particular group of chemical atoms rather than to a less definite, ultra-atomic, source, does not elucidate matters very much, although it is true that these bands do *not* appear until these groups of atoms are introduced into the compound.

This investigation has placed the writer under obligations to numerous persons, to all of whom he is very grateful for services rendered. In particular would he mention Professor E. L. Nichols and E. Merritt, of the Dept. of Physics ; Professors L. M. Dennis, W. R. Orndorff and Dr. J. R. Teeple, of the Dept. of Chemistry ; Professor A. C. Gill and H. Reis, of the Dept. of Geology, and Professor C. F. Mabery, Case School of Applied Science, who through advice or the loan of materials have furthered the work.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY,
January, 1905.