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THE INFRARED ABSORPTION OF SOME ORGANIC LIQUIDS UNDER HIGH RESOLUTION

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Abstract

For the purpose of comparing the Raman effect with infrared absorption spectra, the following organic liquids have been measured from 3.1μ to 3.6μ: benzene, toluene, ortho-, meta- and para-xylene, ethyl-, butyl-, monochlor-, and monobrombenzene. The spectrometer employed an echelette grating, which had 3600 lines per inch, and which concentrated the energy of a Nernst filament into the region which was investigated. The dispersion of the instrument was such that with the slits each 0.25 mm in width, one "slit width" was approximately 25A". The calibration was obtained in terms of the positions of the 5461 line from an auxiliary Hg arc, and the wave-lengths as given are considered accurate to $\pm 0.003\mu$. In every case the bands in this region, due to the C-H vibration, which have hitherto been reported only under low dispersion have been resolved into many component parts. The 3.25μ band of benzene was resolved into three equally strong components lying at 3.231, 3.253 and 3.291μ respectively. The shifts of these bands caused by the various substitutions were studied, and in no case was a shift of over 0.01μ found.

DURING the past two years much has been said concerning a new method of infrared analysis, the Raman effect. Much importance is attached to it, for it offers a very convenient mode of attacking many problems of molecular structure. However, its usefulness depends upon the accuracy of its theoretical interpretation, and the manner in which this latter agrees with experimental evidence. As a direct result of this, all work previously done in the infrared has taken on an added importance, that of furnishing means of investigating and testing the theory of this effect.

The technique of the Raman effect has developed so rapidly that the photographs taken now, are all made under high resolution and hence show considerable detail. These results must be compared with such infrared measurements as may be found in the literature, and since these latter wavelengths are usually known to a rather low degree of accuracy, such comparisons are not fair and in most cases can be only qualitative. So, in order to obtain any quantitative checks between the two phenomena, it seems necessary that many absorption measurements be made with the highest resolution obtainable.

The complete theory of the Raman effect is contained in the theory of dispersion as outlined by Kramers as early as 1925. Further calculations by Dirac,[1] based upon the more recent form of quantum mechanics lead to the same results as those stated in the papers by Kramers and Heisenberg.[2]

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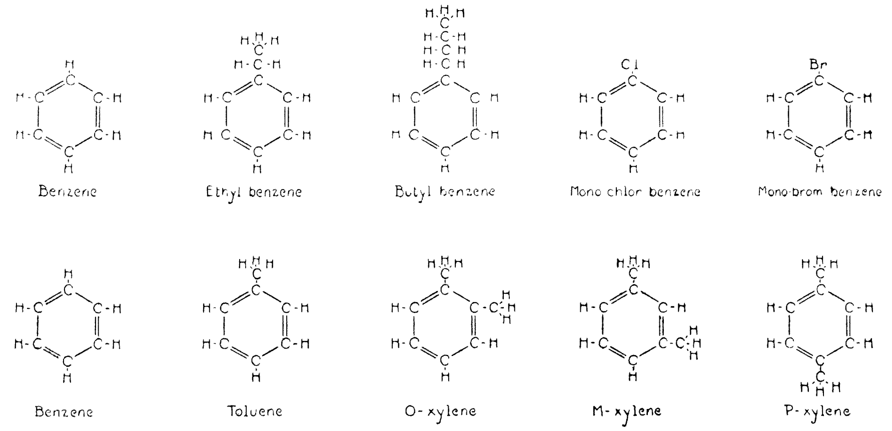
[1] Dirac, Proc. Roy. Soc. **A114**, 710 (1927).

[2] Kramers and W. Heisenberg, Zeits. f. Physik **31**, 681 (1925).

Here we learn that the intensity of a Raman line is determined in an entirely different manner from that of an absorption line. Between any two energy levels, say A_1 and A_2, the presence or absence of an absorption line is completely determined by the value of the transition coefficient (a_{12}). However, in the expression for the intensity of the Raman line, this coefficient does not enter, but in its place the transition coefficients to a third level, say B, which can combine with both A_1 and A_2. Thus it is possible to have, between A_1 and A_2, either an absorption line or a Raman line, or both, depending on the values of the transition coefficients (a_{12}), (a_1b) and (a_2b). Further, in case both exist, the intensities are to be entirely independent of each other. That this interpretation is correct, cannot be doubted in view of the beautiful manner in which it agrees (in the case of the simple molecules) with the experimental results obtained by Rasetti, McLennan and McLeod and Wood. In HCl, Wood finds that the so called "missing line" occurs as a rather strong Raman line. It was shown by Kemble and Hill[3] that this was in perfect accord with the theory. In the case of more complex molecules further corroboration comes from the work of Coblentz[4] on CCl_4, and of many other experimenters.

TABLE I. STRUCTURAL FORMULAE OF COMPOUNDS STUDIED



Benzene · Ethyl benzene · Butyl benzene · Mono chlor benzene · Mono-brom benzene

Benzene · Toluene · O-xylene · M-xylene · P-xylene

It seems well to emphasize here, the fact that one must not expect to find a one-to-one correspondence between absorption and Raman spectra. In spite of the many theoretical papers on the question regarding the difference between the two, experimentalists frequently refer to the fact that absorption lines "predicted" by the Raman effect do not appear in absorption measurements. Only if we know the energy diagram for a given substance, can we really predict from the Raman spectra just what lines shall occur in the absorption spectra. And in the case of the complex molecule usually studied by Raman investigators, these energy schemes are entirely unknown.

[3] Kemble and Hill, Proc. Nat. Acad. Sci. **15,** 387 (1929).

[4] W. W. Coblentz, Bull. Amer. Phys. Soc. **4,** No. 2 (1929).

It is out of the question therefore to expect, as is very frequently done, that strong Raman lines will be found corresponding to each of the intense absorption lines, and vice versa.

It is clear then, that infrared measurements which can state wave-lengths with the same degree of accuracy as those on Raman photographs, will be of great interest. And so, as a step in this direction, we offer here a study of the C-H vibration in the case of the following nine organic liquids whose structural formulae are given in Table I: benzene, toluene, ortho-, meta- and para-xylene, ethyl- butyl-, monochlor-, and monobrom-benzene.[5] It is hoped that these results will be useful in connection with the Raman study of the same compounds made by Wood,[6] for his plates show that this band is in every case quite complex in its structure.

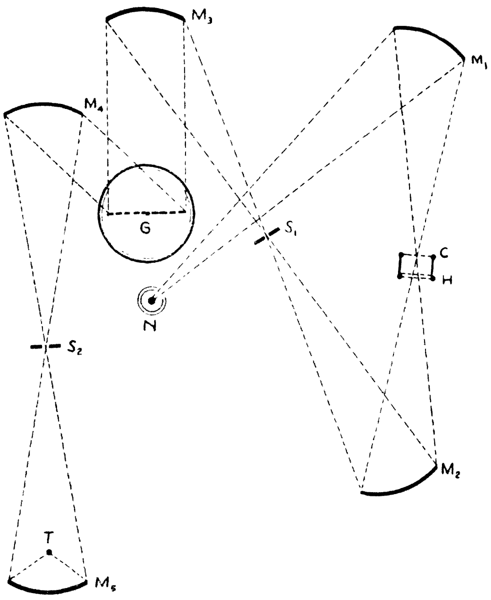


Fig. 1. Plan of apparatus.

Apparatus

A plan of the grating spectrometer, which was used is given in Fig. 1. Radiation from a Nernst glower, operated on a 110-volt storage battery at 0.35 amp., was focussed upon the absorption cell, *C*. After passing through this, it was focussed upon S_1, the first slit. M_3 then collimated the beam and directed it to *G*, the eschelette grating. The diffracted beam was then focussed upon S_2, after which it was finally concentrated upon the thermopile *T*, by the mirror M_5.

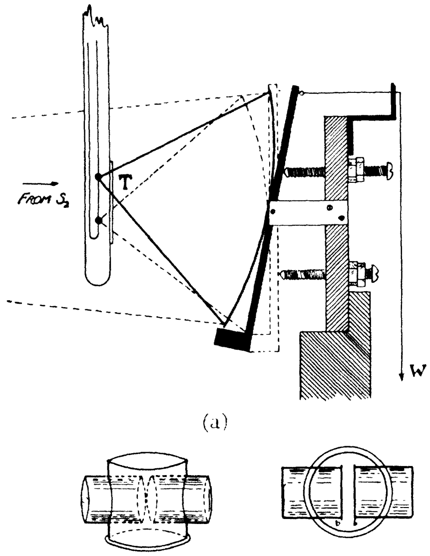
Attention is called to several novel features included in this spectrometer. In the major part of these investigations a new type absorption cell was used,

[5] R. B. Barnes, Nature **124,** 300 (1929), Bull. Amer. Phys. Soc. **5,** 10 (1930).

[6] R. W. Wood, Phil. Mag. **7,** 858 (1929).

instead of the customary one of rock-salt. As is shown in Fig. 2(b), this cell consisted of a brass cup so designed that the layer of the liquid to be examined would be contained between the two microscope cover glasses, *b* and *b'*. This thickness could be varied at will, and very easily measured, for a metal "thickness gauge" could be temporarily inserted between the plates, while the horizontal tubes were being sealed in place with sodium silicate. Such a cell has a high uniform transparency in this region, and eliminates the inconveniences caused by evaporation of the solution and fogging of salt plates. The use and design of this new cell was suggested by Dr. Pfund.

The grating was a chromium plated echelette[7] ruled in this laboratory, and concentrated most of the energy in the desired region. Having 3600 lines per inch, and being 3 inches wide, it had a theoretical resolving power of over 10,000, as compared with about 170 for a 3-inch salt prism, the type usually used in this region. Since a grating, however, superposes orders, the effect of the second order 1.5μ radiation had to be determined. A water cell, which had zero transmission beyond 3μ was used. This had a transparency of about 70 percent at 1.5 to 2.0μ. By making measurements with and without this shutter in place, the second order effect was readily detected and due allowance made for it in the calculations.



(a)

(b)

Fig. 2. Absorption cell and thermocouple mounting.

The thermocouple was a compensating one made of Hutchings alloys.[8] This was used in series with a high-sensitivity Leeds and Northrup galvanometer of 5 sec. period. The scale distance was about 5 m, and the deflections

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[7] R. W. Wood, Phil. Mag. **7,** 742 (1929).

[8] A. H. Pfund, J.O.S.A. **15,** 69 (1927).

were read to 0.5 mm. By means of the arrangement shown in Fig. 2(a) a double deflection method, somewhat analogous to that used by Pfund,[9] was employed. By raising the weight, W, the radiation was focussed upon the lower junction of the thermocouple instead of the upper junction, and a deflection in the opposite direction was obtained. Readings were taken of deflections to the right, left and again to the right, thus eliminating the troublesome zero shift and at the same time realizing a double sensitivity and a greater accuracy.

The calibration was obtained by placing a mercury arc in front of S_1 and observing the positions of the grating as the first eight orders of the 5461 line fell upon S_2. The grating settings were determined by observing the image of a lamp filament, reflected by a small mirror which rotated with the grating. By plotting the grating settings against the respective wave-lengths a perfectly straight calibration curve was obtained. Before and after each set of absorption measurements were made, this was checked at two points. In no case did the image of the filament fail to fall at its appointed place by as much as 0.5 mm, where a distance of 1 mm indicated a change of wave-length of 0.0028μ. The accuracy of the calibration was therefore better than 0.0014μ.

For each setting of the spectrometer we recorded a set of galvanometer deflections, C, for the radiation passing through the absorption cell; a set for transmission through an empty cell, E; and finally a set while the water shutter H, was in place. By dividing (C-H) by (E-H) we obtained directly the percentage transmission for the wave-length indicated by the grating setting.

Results and Discussion

The wave-lengths as stated below are believed to be accurate to less than $\pm 0.003\mu$. Throughout most of the work the two slits were kept at a separation of 0.25 mm. The mercury yellow lines in the 6th order were separated on the face of S_2 by 1.2 mm, which indicated that the "slit-width" must have been very nearly 0.0025μ. Except in regions where a more careful check upon the location of some particular band was desired, readings were taken at intervals of 0.0070μ. Even when these intervals were halved, the author realizes that much of the band structure has been missed.

Fig. 3 shows a comparison of the absorption of benzene and four methyl substitutions. In Fig. 4 we have compared benzene with ethyl-, butyl-, chlor- and brom-benzene. In these curves we have plotted as ordinates the percentage transmission, and while the numerical values are not given, as the curves are each based upon a different zero line, the percentages run in each curve from about 95% to 25 or 30%. The structural formulae of the various compounds, showing the position of the C-H linkages, are given in Table I. Table II gives a list of all the observed bands. The samples used in every case are the same as those used by Dr. Wood in his Raman work, and are of a very high degree of purity.

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[9] A. H. Pfund, Pub. of Allegheny Observatory **111**, No. 6 (1913).

TABLE II. *Wave-lengths of observed bands.*

Benzene	Toluene	O Xylene	M Xylene	P Xylene	Ethyl-Benz	Butyl-Benz.	Mono-Chlor Benzene	Mono-Brom Benzene
*3.036μ	*3.163μ	*3.193μ	*3.193μ	*3.186μ	*3.186μ	*3.178μ	*3.156μ	*3.133μ
*3.096	3.238	3.261	3.276	3.231	3.238	3.238	*3.186	*3.163
*3.163	3.261	3.283	3.291	3.291	3.261	3.261	3.253	*3.186
*3.186	3.276	3.313	3.313	3.308	3.298	3.298	3.268	3.261
3.231	3.298	3.366	*3.328	*3.328	*3.328	*3.328	3.298	3.298
3.253	*3.343	3.396	3.381	3.366	3.366	3.381	*3.328	*3.328
3.291	*3.358	3.418	3.396	3.396	3.411	3.411	3.366	3.396
*3.351	3.388	3.456	3.426	3.411	3.456	3.501	3.426	3.426
3.456	3.426	3.473	3.441	3.426	3.478	3.546	3.441	3.478
3.501	3.478	3.501	3.486	3.486	3.568	—	3.456	3.493
—	3.583	3.666	3.658	3.658	—	—	3.478	—

* Bands due to the absorption of water vapor in the atmosphere. More recent investigations, in which better resolution was obtained, have revealed the fact that several of the bands listed in Table II, and which occur in Figs 3 and 4 as very small minima, are due to atmospheric absorption. It is possible also, that in regions where the C-H bands are of about the same intensity as the water-vapor bands, there may be some little uncertainty as to the exact locations of the former due to imperfect resolution. However, in the cases of the stronger C-H bands which I discussed above, this effect plays a negligible role. A complete account of this more recent work is very soon to be published.

In this series of benzene derivatives, we have an excellent opportunity to study and observe the effects of various substitutions and of molecular arrangement and symmetry in causing a shift in the frequency of particular bands. Since benzene is the parent of all of the compounds studied we call especial attention to its characteristic bands.

The C-H band of benzene is always reported at 3.25μ in the literature.[10] In this work we have it clearly resolved into three components of approximately the same intensity lying at 3.231μ, 3.253μ and 3.291μ respectively. We shall follow these bands throughout all of these compounds. Benzene shows other weaker bands as can be seen from Table II. In this discussion however, we shall deal only with the strongest bands in each of the compounds.

In the case of toluene, we find in the literature[10] a single band at 3.34μ, indicating a shift, due to the substitution of the methyl group of 0.09μ. From curve (*b*) of Fig. 3 it can be seen that this is not at all the case. All three of the benzene C-H vibrations persist, each having been shifted by 0.007μ only, and are found at 3.238μ, 3.261μ and 3.298μ respectively. The intensities of the two bands of shorter wave-length have been noticeably decreased, while the band at 3.291μ is still quite strong. The vibrations of the C-H within the methyl group have apparently introduced rather strong bands at 3.276, 3.343, 3.428 and 3.478μ besides other weaker ones. These facts suggest that the presence of the other two H atoms in the CH_3 group makes possible several modes of C-H vibration other than those possible in benzene.

In the xylenes we find many interesting changes. Orthoxylene is very unsymmetrical with respect to benzene, and so we expect the substitution

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[10] W. W. Coblentz, Astrophys. J. **20,** 207 (1924); Carnegie Inst. of Wash, No. **35,** 1 (1905).

to have a greater effect on the benzene vibrations than in the case of toluene. In the meta form, the effect should be smaller, and in paraxylene we would expect it to be nearly the same as that in toluene, or possibly less. By examining curves (*c*), (*d*), and (*e*) of Fig. 3 this is seen to be the case. In orthoxylene there is only one band which closely checks the benzene vibrations, the 3.253μ band occurring here at 3.261μ again. In paraxylene on the other hand, we find the 3.231μ and the 3.291μ bands recurring with no shift at all.

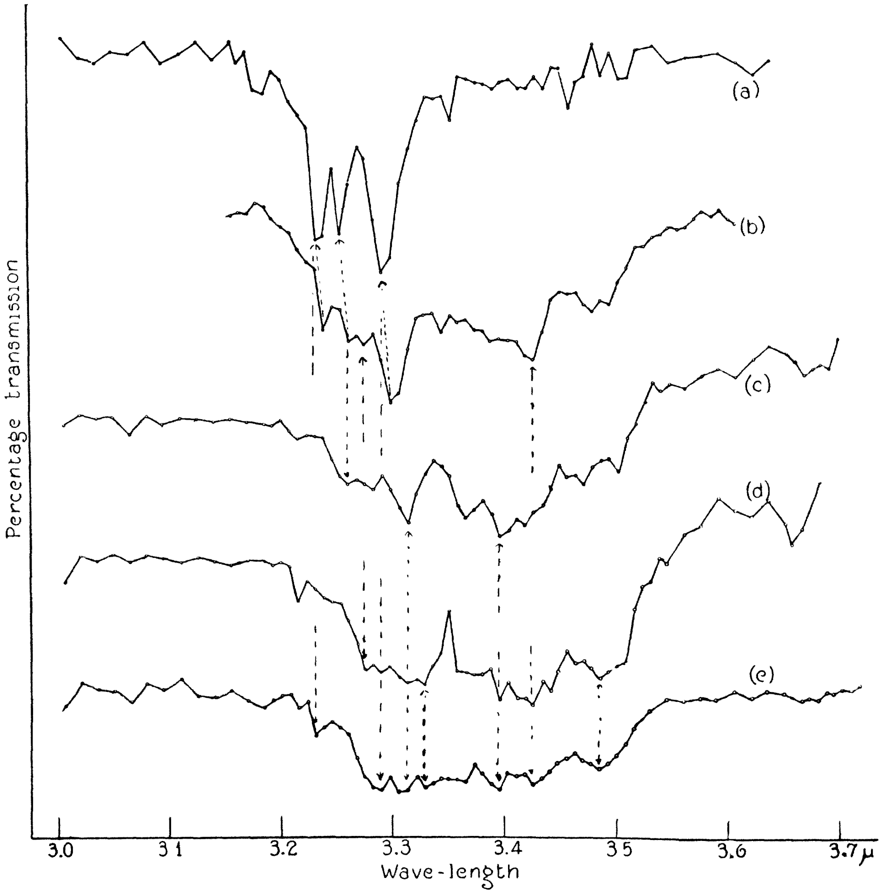

Fig. 3. Absorption curves. (a) benzene (b) toluene (c) orthoxylene (d) metaxylene (e) paraxylene. Thickness, 0.05 mm.

Since the strong 3.426μ band of toluene, does not appear in orthoxylene, while it does in the meta- and para- forms, we are inclined to look for a mutual effect of the two neighboring CH_3 groups. We find bands at 3.313μ, 3.396μ and 3.486μ occurring almost exactly in all three forms of xylene, while they are entirely absent in toluene, or to say the least, they occur in entirely new locations, again seeming to point to a mutual effect of the two groups.

The cases of ethyl- and butyl- benzene are somewhat similar. In each, we find the three benzene bands each shifted by 0.007μ. Their intensity changes are relatively the same as in the case of toluene. Just as we expected, the other bands, occurring in these two compounds, which are apparently due to the C-H vibrations within the ethyl- and butyl groups, are found at

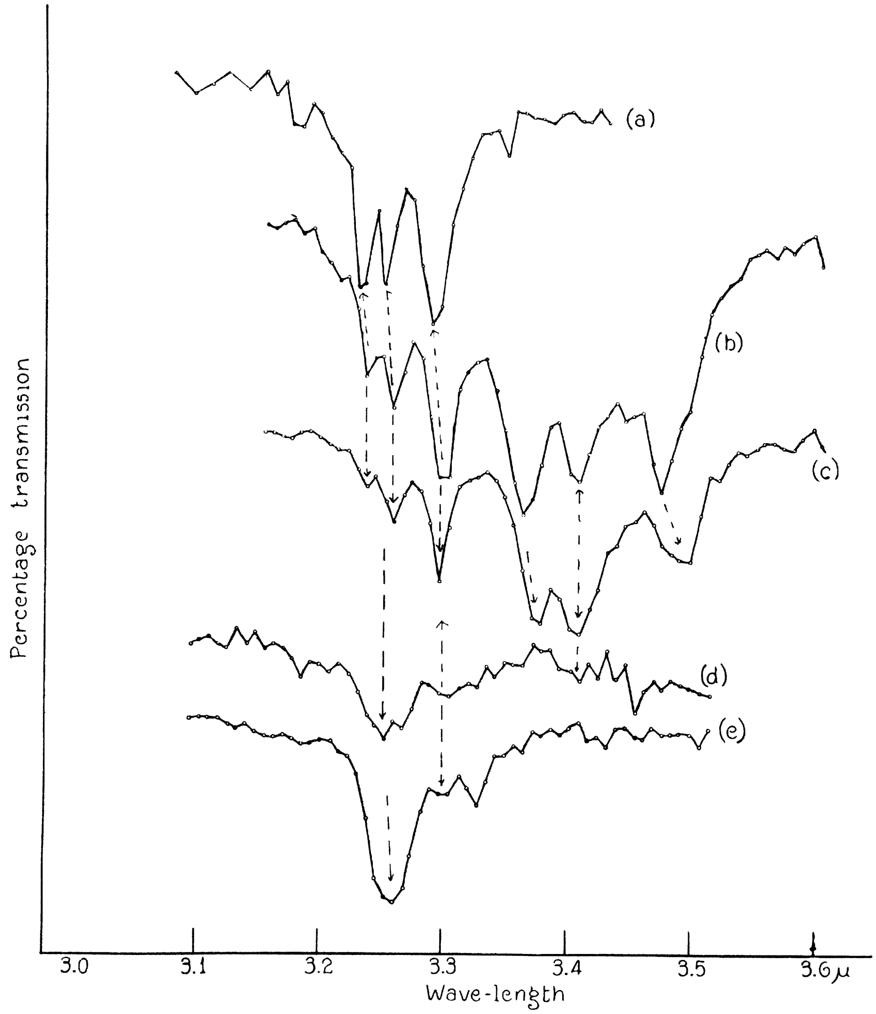

Fig. 4. Absorption curves. Thickness 0.05 mm. (a) benzene (b) ethyl benzene (c) n-butyl benzene (d) monochlor benzene (e) mono-brombenzene.

entirely different wave-lengths in the two cases. This is probably due to a different mutual effect in the two cases.

It is interesting to note that in methyl-, ethyl- and butyl-benzene, whose molecular weights are respectively 92, 106 and 134, the vibrations of the C-H bond in the benzene radical, have been shifted by the same amounts, namely

0.007μ. It must be remembered that 0.007μ is the interval between the spectrometer readings and so the actual shift might even be slightly less than that indicated.

In chlor- and brom- benzene we have a different type of substitution-namely, a single heavy atom instead of a group of C's and H's. Here, the 3.23μ band is absent entirely; the 3.253μ band occurs in each; the 3.291μ vibration appears in each at 3.298μ, and for the first time has its intensity very greatly decreased. Literature[10] gives for each one single band at 3.25μ, with that for brom-benzene being much the stronger of the two, in close agreement with these results.

CONCLUSIONS

If we notice in every case the combined effect of the intensity changes and of the new vibrations introduced by the substitutions, we find that the result is just that necessary to cause the center of the absorption region to agree nicely with the wave-lengths given in the lower resolving power work recorded in literature.[10]

Apparently we can follow a particular band through the series of substitutions, noting the shifts and intensity changes which it suffers. We can see the mutual effect of the neighboring atoms upon the C-H radicals, and we can note distinct changes, dependent upon the symmetry of the molecule, as we progress for instance from benzene through toluene, ortha- and metaxylene to paraxylene.

It is thought that from these results, supplemented by further experimental data on temperature effects which we are at present assembling, we shall be able to work out the energy levels of these compounds.

The author wishes to express his sincere appreciation to Dr. Pfund, Dr. Herzfeld, and Professor Wood, who have been very helpful in aiding this work.