

# ABSOLUTE ABSORPTION INTENSITIES OF ALKYL BENZENES IN THE 2250-1700 Å. REGION<sup>1</sup>

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The absolute intensities of absorption of benzene, toluene, ethylbenzene, and the three xylenes, all in *n*-heptane solution in an 0.13-mm. cell, have been measured with a vacuum fluorite spectrograph in the region 2250-1700 Å. Each of the curves follows the basic benzene pattern: there is one electronic transition showing diffuse vibrational structure near 2100 Å., with molar extinction about 8000 and an oscillator strength about 0.14; and there is another transition with a strong broad continuum peaking near 1900 Å., with maximum extinction about 60,000. The total oscillator strength of the two transitions together varies from  $0.79 \pm 0.08$  for benzene (compared to the prediction of 0.71 by Mulliken and Rieke) to about 1.3 for the xylenes. One substituent produces a red shift of about  $1700 \text{ cm.}^{-1}$  and 40 per cent increase in strength; two substituents, about  $2500 \text{ cm.}^{-1}$  and 60 per cent. The *m*-xylene spectrum is further to the red than the mean of the *o*- and *p*-xylenes and is more intense than either.

The spacing of the 2100 Å. bands is about  $950 \text{ cm.}^{-1}$ , the breathing frequency of the ring. Benzene has the most distinct structure in this region; *m*-xylene has the most diffuse structure here, but shows distinct components in its 1900 Å. peak.

## INTRODUCTION

We have recently had an opportunity to continue the studies begun earlier at the University of Minnesota on the absolute intensities of absorption of organic solutions in the vacuum ultraviolet (9, 15, 16, 21). The spectra of some fifty additional compounds have been obtained and will be published in the near future as rapidly as the plates can be reduced. Besides the boron compounds already reported (15), these compounds include the six alkylbenzenes discussed in the present paper, some olefins and dienes, a number of heterocyclics, some polynuclear aromatics, several compounds showing steric hindrance effects, some amino acids, sterols, and other compounds of biological interest, some short-lived metal-organic complexes, and a few saturated hydrocarbons containing chlorine, sulfur, and other substituents.

Unfortunately, there was no chance at this time to make a number of improvements in technique which are greatly needed to increase the accuracy of the

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measurements. The justification for taking advantage of the present opportunity in spite of these deficiencies is that absolute intensity measurements in the important region below about 2200 Å. are so scarce that any quantitative measurement, even though crude, represents a great advance in our information on most of the compounds studied.

The spectrum of benzene in the vapor phase in the vacuum ultraviolet has been reported by a great many investigators (1, 7, 19, 25) but without quantitative intensity measurements. Quantitative measurements have been made on solutions of benzene in non-polar solvents by Henri and his students (4, 8), but have only reached a lower limit of 1900 Å. The intensity of the first very strong transition, near 1840 Å., has thus remained undetermined, though the oscillator strength has been predicted semitheoretically (10, 11) from the observed intensities of similar transitions in dienes and ring compounds in the quartz ultraviolet.

The spectra of toluene and xylene in the vapor phase in the vacuum region have been obtained by Price and Walsh (18); the spectra of the xylenes in *n*-hexane solution to 1980 Å. have been given by Henri (4); and that of ethylbenzene in cyclohexane solution to 1980 Å. has been given by Smakula (24). Otherwise, most previous work on the alkylbenzenes terminates near 2200 Å., where the absorption is just beginning to rise strongly.

Of course, benzene and many of its derivatives have been repeatedly measured in the more accessible 2600 Å. region, under all sorts of experimental conditions and with many different solvents.

#### APPARATUS AND TECHNIQUES

The absolute intensities of absorption of benzene, toluene, ethylbenzene, and the three xylenes, all in *n*-heptane solution in an 0.13-mm. lithium fluoride cell, were determined in the region 2250–1700 Å. The spectrograph used was a Cario-Schmitt-Ott vacuum fluorite instrument kindly loaned to us by the University of Michigan. The techniques used are the same as those described previously (9, 15, 16, 21).

The measure of absorption intensity used here is the molar extinction,

$$\epsilon = \frac{1}{ct} \log_{10} \frac{I_0}{I}$$

$I_0$  being the initial intensity,  $I$  the final intensity,  $c$  the concentration in moles per liter, and  $t$  the cell thickness in centimeters.

For benzene, the extinctions determined from different plates were consistent, and the mean values given here are believed to be accurate, to better than  $\pm 10$  per cent. The consistency was poorer for the other compounds, with the uncertainty increasing to  $\pm 20$  per cent for the xylenes. The reliability may be less below 1800 Å., where the corrections for scattered light in the spectrograph become considerable.

For the xylenes, the intensities in the 2100 Å. bands were determined from only one selected plate apiece, but the remainder of the curves given here were determined on from two to five plates at every point.

With diffuse solution spectra which show no structure, our measurements are usually made at 2260, 2230, 2200, 2160 Å., and so on. However, in the present compounds, maxima and minima could be observed in the bands. These were located by visual inspection to 2 or 3 Å. The plates were then photometered at these positions also, so that the fluctuations shown on the curves here were determined with a relative accuracy which seems to be better than  $\pm 5$  per cent for neighboring bands. The fluctuations are not far from the limit of visual and instrumental discrimination. Some of the maxima observed visually were not justified by the photometry and are marked with a question mark in the tables, but may nevertheless correspond to real components observable visually by virtue of the St. John effect.

#### SOURCE AND PURITY OF COMPOUNDS

The benzene and alkylbenzenes which were studied were samples of API-NBS hydrocarbons. These were made available by the American Petroleum Institute and the National Bureau of Standards through the A. P. I. Research Project 44 on the "Collection, analysis, and calculation of data on the properties of hydrocarbons." The samples were purified at the National Bureau of Standards by the A. P. I. Research Project 6 on the "Analysis, purification, and properties of hydrocarbons," under the supervision of Frederick D. Rossini, from materials supplied by the following laboratories:

Benzene and toluene, by the A. P. I. Research Project 6. Final purity: benzene,  $99.94 \pm 0.03$  mole per cent; toluene,  $99.95 \pm 0.02$  mole per cent.

Ethylbenzene, by the Monsanto Chemical Company, Dayton, Ohio, through the courtesy of G. Åkerlöf. Purity,  $99.86 \pm 0.05$  mole per cent.

*o*-Xylene, by the Standard Oil Development Company, Elizabeth, New Jersey, through the courtesy of William J. Sweeney. Purity,  $99.990 \pm 0.007$  mole per cent.

*m*- and *p*-Xylenes, by the A. P. I. Research Project 45 on the "Synthesis and properties of hydrocarbons of low molecular weight" at the Ohio State University, under the supervision of Cecil E. Boord. Purity: *m*-xylene,  $99.86 \pm 0.03$  mole per cent; *p*-xylene,  $99.94 \pm 0.03$  mole per cent.

#### SPECTRA

Each of the alkylbenzene spectra shows the same basic benzene pattern: there is a strong allowed electronic transition, designated as the  $N \rightarrow V$  transition by Mulliken and Rieke (10, 11), which is characterized by an almost featureless continuum with a peak near 1900 Å.; and there is a weaker transition, which is believed to be a forbidden transition in benzene (3, 22), characterized by a rather flat absorption curve with some diffuse vibrational structure near 2100 Å.<sup>3</sup>

<sup>3</sup> *Note on nomenclature of bands:* The upper electronic state of the 2100 Å. transition in benzene is designated as  ${}^1B_{1u}$  (3,22), that of the 1840 Å. transition as  ${}^1E_u$ ; but the corresponding levels cannot be called by these same symmetry labels in the other compounds, since the symmetry is different for each of the alkylbenzenes and is indeed somewhat indeterminate under free or slightly hindered rotation of the substituent groups.

Since the intensities in the two regions are so different, the curves in the vicinity of the allowed transitions have been plotted in figure 1; and in the vicinity of the forbidden transitions in figure 2, on a different scale. Some of the main features of the curves are tabulated in table 1.

The agreement with the older solution measurements is qualitatively good as far as those measurements extend. Gross features, such as the relative red shifts and intensity changes among the xylenes, are confirmed satisfactorily. The *International Critical Tables* (8) peak values for benzene and the xylenes in the 2100 Å. bands are 0–10 per cent higher than ours, but Smakula's peak value for ethylbenzene is about 10 per cent lower than ours.

The structure in the present curves is sharper than in the older results. Perhaps it is exaggerated; but, on the other hand, the I.C.T. curves, especially for the xylenes, are shifted to shorter wave lengths as compared with ours by 5–15 Å. in the 2050–2250 Å. region; and this, together with the indistinctness of the structure, may indicate incomplete separation of the isomers in the earlier work. Smakula's wave-length scale is too cramped to permit comparisons of the ethylbenzene measurements.

A visual estimate indicates that the integrated area under the curves of the 2100 Å. band of a given compound would not differ by more than 5 per cent between the older and newer measurements, if carried to the same short-wave-length cut-off in both cases.

The major differences between the different spectra take the form of the familiar red shift of the bands and an increase of intensity in the  $N \rightarrow V$  peak with alkylation.<sup>4</sup> The first band of the 2100 Å. group and the peak of the  $N \rightarrow V$  band shift about 1600  $\text{cm.}^{-1}$  to the red with the first methyl substitution. On

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This difference (and ambiguity) in terminology points up quite clearly the inadequacy of the symmetry nomenclature when used alone to describe polyatomic electronic states. The corresponding energy levels involved here in the different compounds obviously have almost identical character with respect to term values, vibrational structure or lack of structure, transition probabilities, and, by inference from all of these, electronic wavefunctions. It would be important for our usage and our thinking to have a notation for these states which would *assert* and not deny this identity. These levels in the different compounds are probably more alike than many atomic energy levels in different atoms which are given the same notation.

The Mulliken notation has indeed provided uniform letters,  $E$ ,  $N$ ,  $Q$ ,  $R$ ,  $V$ , and  $Z$ , meeting this need for a number of states or organic compounds and derivatives absorbing in this region. For example, the state like the benzene  ${}^1E_u^-$  state is the  $V$  state in all of these compounds (10, 11) (though it differs in some important respects from the state called  $V$  in the ethylenes). But this notation has not as yet been extended to the states analogous to benzene  ${}^1B_{1u}$ . And there is unfortunately as yet no systematic way of extending this or any other notation to new states as they are found.

A stop-gap suggestion, which will work for a large number of compounds such as alkyl derivatives of a dominant "parent" chromophore, is to write the correct symmetry notation for the "parent" level in brackets, as ( ${}^1B_{1u}$ ) and ( ${}^1E_u^-$ ) for the levels of all of the alkylbenzenes involved here, following this term by such special notations as may be desirable in the particular molecule under discussion.

<sup>4</sup> See references 6, 17, and 20 for discussion of similar effects in the 2600 Å. bands of the alkylbenzenes.

TABLE I  
Main features of spectra

	BENZENE	TOLUENE	ETHYLBENZENE	<i>o</i> -XYLENE	<i>m</i> -XYLENE	<i>p</i> -XYLENE
A. Forbidden transition						
Onset of absorption* . . . . .	{ 2,080 A. 48,050 cm. <sup>-1</sup>	2,160 46,300	2,170 46,000	2,190 45,600	2,210 (?) 45,200	2,225 45,000
Peaks of component bands . . . . .	49,000 49,800 50,900 51,700 (?)	47,300 47,800	47,000 48,000 48,900	46,500 47,400 48,500 49,500 (?)	46,200	46,000 47,200 48,000(?)
Maximum molar extinction ( $\epsilon_{\max}$ ) . . . . .	6,900	8,100	7,400	8,100	10,500	8,100
Remarks . . . . .	Components most distinct				Components most diffuse	Narrow irregular maxima
Approximate oscillator strength, $f'$ (to arbitrary cut-off, see text) . . . . .	0.10 (1950 A.)	0.12 (2000 A.)	0.11 (2000 A.)	0.11 (2040 A.)	0.18 (2030 A.)	0.14 (2030 A.)
B. Allowed transition						
Peak . . . . .	{ 1,835 A. 54,500 cm. <sup>-1</sup>	1,885 53,000	1,890 52,900	1,905 52,500	1,930 51,800	1,925 52,000
Maximum molar extinction ( $\epsilon_{\max}$ ) . . . . .	46,000	55,000	57,000	59,000	76,000	62,000
Components . . . . .	53,700 (?) 54,500 55,400 (?)	52,400 (?) 53,300 (?)	52,000 (?) 53,200 (?) 54,300 (?)†	†	51,000 51,800 52,800†	51,300 52,500 53,800 (?)†
Remarks . . . . .	Components doubtful			No components	Components distinct	
Total oscillator strength, $f$ . . . . .	0.79	1.09	1.11	1.22	1.46	1.23

\* Probably the 0-0 band, except in benzene.

† Curves flatten out at 1750 A., with  $\epsilon$  about 18,000, before the next absorption. The *m*-xylene curve has an actual peak at 1730 A. with  $\epsilon_{\max} = 19,000$ .

replacing methyl by ethyl, there seems to be an additional shift to the red of perhaps  $200\text{ cm.}^{-1}$ , but this is not certain; the toluene and ethylbenzene curves coincide within experimental error at almost every point. On adding a second methyl to toluene, a further red shift of about  $900\text{ cm.}^{-1}$  occurs, subject to some variation among the xylenes.

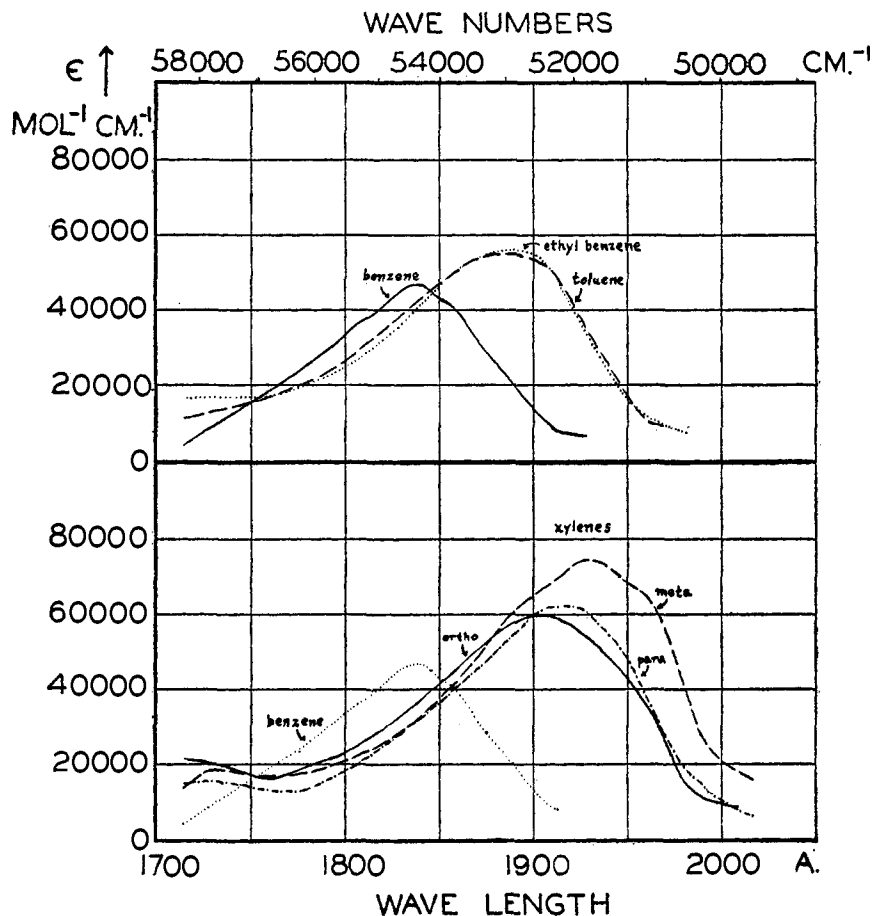


FIG. 1. Transitions near 1900 A. in alkylbenzenes

The first substitution increases the  $N \rightarrow V$  peak intensity of benzene about 20 per cent; and it increases the total area under the curve, which is the index of the oscillator strength of the transitions, by 40 per cent. The second substitution produces roughly an additional 20 per cent increase in both quantities.

These shifts of band position and intensity in going from toluene to the xylenes are of about the same size as those found in going from a singly substituted ethylene, such as 1-octene, to a doubly substituted one, such as *cis*- or *trans*-2-octene (14). For the *cis* form, the red shift is  $1800\text{ cm.}^{-1}$  and the intensity increase is 0 per cent; for the *trans* form,  $1000\text{ cm.}^{-1}$  and 20 per cent. (The more extensive data of Carr and Stücklen on the polymethylethylene vapors (2) cannot

be used in the comparison, because the shifts with alkylation in the vapor phase seem to be much larger than those in solution.)

The changes in position and intensity in the  $N \rightarrow V$  bands with substitution throw light on the related changes of intensity found in the 2600 Å. bands of the alkylbenzenes.<sup>4</sup> In benzene, the latter bands are forbidden, but still occur weakly

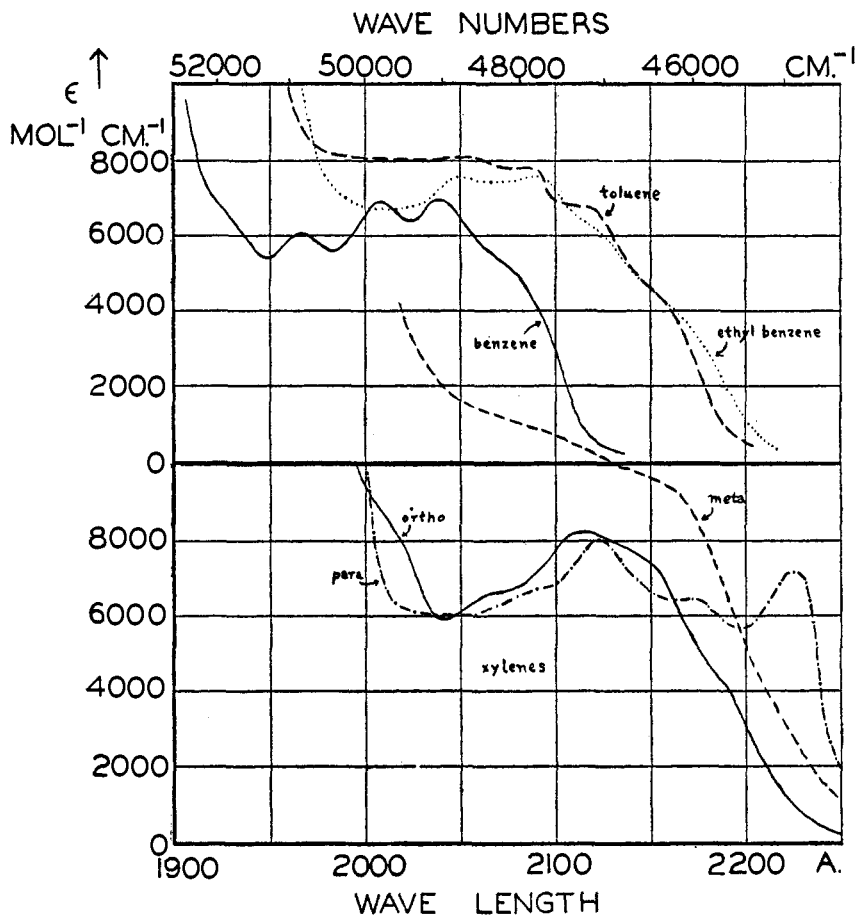


FIG. 2. Transitions near 2100 Å. in alkylbenzenes

because of perturbations of the Herzberg-Teller type by which they "steal" intensity from the  $N \rightarrow V$  transition (10, 11). The intensity acquired by means of this mechanism should be proportional to the  $N \rightarrow V$  intensity itself, and inversely proportional to the square of the separation of the upper states.

Now in going from benzene to the substituted benzenes, the present measurements show that the  $N \rightarrow V$  intensity increases and the separation of the upper states decreases. There should result considerable increases of intensity in the 2600 Å. bands of these compounds from this cause alone, even if all the other parameters affecting the perturbations remained constant.

Thus, in going from benzene to toluene, the  $N \rightarrow V$  changes should produce an

increase of intensity in the 2600 Å. bands by a factor of 1.5; in going to *m*-xylene, a factor of 2.2. Experimentally, the increases are by factors of 2.0 and 2.9, respectively (23); the discrepancies are scarcely larger than experimental error.

Theorists have made much out of these changes of intensity in the 2600 Å. bands, attributing them to breaking down of the selection rules by loss of symmetry, to charge migration, and so on. In the case of *p*-xylene these additional considerations may be necessary, since the 2600 Å. changes of intensity are much greater than can be accounted for solely by the  $N \rightarrow V$  changes. But for the other compounds it appears that the  $N \rightarrow V$  changes must first be explained, and after that the 2600 Å. changes will largely follow without further assumptions.

This emphasizes the remarks on the symmetry notation made in a footnote above. The surprising thing is not that the loss of symmetry with substitution breaks down the selection rule of the 2600 Å. bands and makes them "more allowed," but rather that the breakdown is in most cases so very small.

#### VIBRATIONAL STRUCTURE

The vibrational components which are seen in the 2250–1700 Å. region are very diffuse and symmetrical, and in appearance are not at all like the narrow and strongly shaded 2600 Å. bands of these compounds.

Nevertheless, there are differences between the various curves as regards the distinctness of these components. The differences seem not to depend on the extent of alkylation, but rather to be correlated with the symmetry. Thus, the most distinct structure in the 2100 Å. bands occurs in benzene, and the next most distinct in *p*-xylene, but the most diffuse is in *m*-xylene. In the  $N \rightarrow V$  bands, on the other hand, the clearest components occur in *m*-xylene, next clearest in *p*-xylene, and after that in benzene; and the other components suggested for these bands in table 1 may be imaginary. Diffuse components have been indicated for the  $N \rightarrow V$  band of benzene in the vapor phase in some previous reports (1). (In benzene in the vapor phase, very sharp absorption bands with vibrational structure are also seen overlying this  $N \rightarrow V$  band. These are regarded as members of a Rydberg series (1, 19). No such bands were found in the present work. Probably they are smeared out in solution, because their Rydberg electronic orbitals are so large.)

A complete explanation of these changes in distinctness among the spectra would require information on the strength and overlapping of all of the strong vibrational series which must be present. Since such information is not available, one can only say that the frequency which dominates the spacing of most of the observed bands is about 950  $\text{cm}^{-1}$  and is the same within experimental error as the totally symmetric benzene breathing frequency of 920  $\text{cm}^{-1}$  which dominates the 2600 Å. bands in all of these compounds. On theoretical grounds the vibrational frequencies in the 2600, 2100, and 1900 Å. bands are expected to be about the same, because only one of the six unsaturation electrons is supposed to be excited; its contribution to the binding is small and furthermore is probably about the same in each of the upper states of these transitions.

It is easy to see qualitatively that the structure should be clearest in the most symmetrical molecules, benzene and *p*-xylene, where the breathing vibration is



the main totally symmetrical frequency; and it should generally be more obscure in less symmetrical molecules, where other totally symmetric frequencies may produce strongly overlapping bands. This explanation however does not account for the apparent sharpness of the *m*-xylene components in the  $N \rightarrow V$  peak nor for the fact that the ethylbenzene 2100 Å. structure is as clear as—or, if anything, a little clearer than—the toluene structure.

The 2100 Å. *p*-xylene structure seems visually to be more narrow and irregular than that of the other xylenes, just as in the 2600 Å. bands, indicating that the same totally symmetric vibrations of this molecule are probably present with about the same relative intensity in both groups of bands.

#### OSCILLATOR STRENGTHS

Oscillator strengths for the transitions were computed from the integrated areas under the curves, by the familiar equation (11, 13):

$$f = 4.32 \times 10^{-9} \int \epsilon_{\nu} d\nu$$

where  $\nu$  is the frequency in  $\text{cm.}^{-1}$ . No correction is made for the effect of solution on the  $f$ -values, since it has been shown (5, 12) that, in cyclopentadiene and cyclohexadiene at least, the classical corrections do not fit the data for the allowed transitions, and it is not certain what corrections should take their place.

The values of  $f'$  given in the first section of table 1 are approximate oscillator strengths for the 2100 Å. bands. They were determined by integrating the areas under the curves up to an arbitrary short-wave-length limit. This limit was chosen to lie in the center of the last clear minimum between the two electronic transitions, when such a minimum existed. Though arbitrary, this procedure is straightforward and definite. It was used because there is no unique way of ascertaining the extent of overlapping of the two transitions; such a notion may even be meaningless.<sup>5</sup>

A quantity of more significance than the strength of each transition is the total oscillator strength,  $f$ , of the two transitions together, which is also tabulated in table 1. The 2100 Å. bands, like the 2600 Å. bands, are supposed to be forbidden in benzene (3, 22), appearing only because of interaction with the  $N \rightarrow V$  transition. The same is true, or almost true, for the other compounds, as the similarity of the spectra bears witness. The  $N \rightarrow V$  intensity is then divided between these two transitions (a negligible part going into the 2600 Å. bands), and their combined oscillator strength is the best measure of what the  $N \rightarrow V$  intensity would be if no interaction were present.

This quantity has been computed theoretically by Mulliken and Rieke (11). They apply a correction factor of 0.3 to bring their purely theoretical values into line with observed intensities in the ring dienes, and on this basis predict an oscillator strength of 0.71 for the  $N \rightarrow V$  transition in benzene. This agrees within experimental error with the observed value of 0.79 given in the last row of table 1. No calculations have been made on this intensity in the substituted

<sup>5</sup> Some recent unpublished work of Dr. W. C. Price in this laboratory on these same compounds shows that there is usually a clear gap between the two transitions in the vapor phase, which would validate the procedure adopted here.

benzenes. It seems surprising for them to have oscillator strengths so much greater than unity. Sklar (23) expected the allowed transition intensities to be very little influenced by non-chromophoric substitutions.

Part of the large  $f$ -number of the alkylbenzenes, as well as the excess in benzene itself over the predicted value, if this excess is significant, may be due to the contributions to the absorption from the first Rydberg series members which lie in this wave-length region. The observed series bands in the vapor (1, 19) are narrow and line-like, but may be strong enough to contribute appreciably to the integrated intensity. No theoretical computations have been made on their oscillator strengths, and no accurate way of measuring their intensity separately has been worked out as yet.

The spectrum of benzene has been compared previously (15) with that of borazole or triborinetriamine,  $B_3N_3H_6$ , which it strongly resembles.

We are indebted to Professor R. S. Mulliken for helpful discussions of the interpretation of these spectra. Technical assistance was supplied by Howard Carter, Dorothy Iker, and George Rotariu. The work would have been impossible without the extended loan of the spectrograph from the University of Michigan. Grateful acknowledgement is made to the American Petroleum Institute and the National Bureau of Standards for the loan of the samples measured in this investigation.

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