

## Vibrational Analysis of the 3400 Å Triplet-Singlet Emission of Benzene

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Taking for  $\alpha$  a reasonable value of 2 kcal. we obtain

$$D(C-H) = E_1 = 76 \text{ kcal./mole.}$$

This value corresponds to  $5.10^{13}$  as the frequency factor of the unimolecular constant for the first step of the decomposition of isobutene. It would be expected that this factor should be twice as high as

that for propylene (from statistical reason), and thus the good agreement between the frequency factors found for toluene, the xylenes,<sup>3</sup> propylene, and isobutene provides some justification for the applied approximations.

<sup>3</sup> M. Szwarc, *Nature* **160**, 403 (1947); *J. Chem. Phys.* **16**, 128 (1948).

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## Vibrational Analysis of the 3400A Triplet-Singlet Emission of Benzene\*

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The triplet-singlet emission of benzene at 3400A in a rigid glass-solution has been obtained and measured more accurately than in previous work. An assignment is proposed accounting for all the important bands observed. The analysis of the vibrational structure indicates the presence of the  $703 \text{ cm}^{-1} b_{2g}$  fundamental, showing that in the triplet-singlet transition, the triplet level combines in the same manner as a  ${}^1B_{1u}$  state for electric dipole radiation. This will lead to a definite assignment of the symmetry of this triplet level when the theoretical rules for intercombinations in polyatomic molecules are derived. The analysis supports a hexagonally symmetric planar model for this triplet state.

### INTRODUCTION

THAT the phosphorescence emission observed from many organic molecules was a transition from a triplet to the ground singlet state of the molecule was suggested by Lewis and Kasha.<sup>1,2</sup> Sklar<sup>3</sup> reported finding a weak absorption in the 3400A region (spectrum shown by Lewis and Kasha<sup>2</sup>) which he attributed to one of the triplet levels predicted in his theoretical calculations. It was suggested that this absorption represented the symmetry allowed transition  ${}^1A_{1g} \rightarrow {}^3E_u$  which was predicted at 2120A. Theory, however, predicted an additional transition  ${}^1A_{1g} \rightarrow {}^3B_{1u}$  at 4750A. Inability to find this transition was ascribed to the double forbiddenness of the transition (both spin and symmetry forbidden), whereas the transition  ${}^1A_{1g} \rightarrow {}^3E_u$  is spin forbidden only.

A further calculation of the triplet level was made by Goepfert-Mayer and Sklar<sup>4</sup> using the method of anti-symmetrized products of molecular orbitals. Their calculations showed  ${}^3B_{1u}$  as the lowest triplet level, followed in turn at higher energies by

${}^3E_u$  and  ${}^3B_{2u}$ . The calculated transition  ${}^1A_{1g} \rightarrow {}^3B_{1u}$  was at 8300A. London<sup>5</sup> recalculated these levels including a number of integrals neglected by Goepfert-Mayer and Sklar. The new calculated transition  ${}^1A_{1g} \rightarrow {}^3B_{1u}$  is at 2760A. It should be noted in this recalculation, the singlet levels are in poor agreement with observation, and the relatively good agreement with the lowest triplet level must be regarded as fortuitous.

It is very unlikely that there is a lower triplet level than that involved in this 3400A transition, since the lowest frequency band of the absorption agrees almost exactly with the highest frequency band of the phosphorescence emission.<sup>1</sup> In general emission in polyatomic molecules in condensed media has been observed only from the lowest level above the ground state of a given multiplicity, even though excitation occurs exclusively in higher levels.<sup>6</sup> It is, therefore, more likely that the singlet-triplet absorption at 3400A and its corresponding emission are to be correlated with the lowest triplet level ( ${}^3B_{1u}$ ) predicted by theory. Absorption to the higher triplet levels ( ${}^3E_u$  and  ${}^3B_{2u}$ ) is expected to be hidden by the much more intense singlet-singlet bands.

Roothaan and Mulliken<sup>7</sup> have indicated, however, that previously calculated integrals may be sufficiently in error to reverse the position of the

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<sup>1</sup> G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944).

<sup>2</sup> G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **67**, 994 (1945).

<sup>3</sup> A. L. Sklar, *J. Chem. Phys.* **5**, 669 (1937).

<sup>4</sup> M. Goepfert-Mayer and A. L. Sklar, *J. Chem. Phys.* **6**, 645 (1938).

<sup>5</sup> A. London, *J. Chem. Phys.* **13**, 396 (1943).

<sup>6</sup> Data on this point are not too convincing in the literature. Further evidence to be published soon has been obtained by Dr. M. Kasha of this laboratory.

<sup>7</sup> C. C. J. Roothaan and R. S. Mulliken, *J. Chem. Phys.* **16**, 118 (1948).

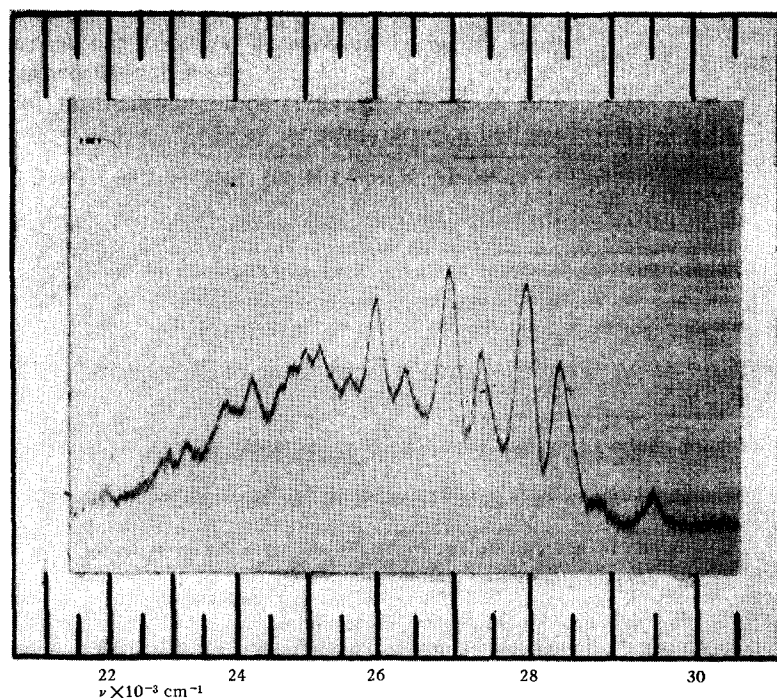


FIG. 1. Microphotometer tracing of the triplet-singlet emission spectrum at a  $2\times$  magnification of the frequency scale of the actual spectrum.

$^3B_{1u}$  and  $^3B_{2u}$  levels. It is of interest, therefore, to examine the absorption and emission systems to establish definitely the symmetry of this triplet level.

Since the singlet-triplet absorption has been observed only in samples of liquid benzene with at least a 10-cm optical path ( $\epsilon$  approximately 0.0004), as a series of weak bands superimposed upon the tail of the 2600Å singlet-singlet absorption band, little information may be derived from it concerning the triplet state. There is noticeable in this weak absorption a series of four bands with separations of about  $900\text{ cm}^{-1}$ , and this progression may be assigned to the totally symmetric frequency in the triplet state. This is the more probable since this vibration has been observed to have a frequency of  $992\text{ cm}^{-1}$  in the ground  $^1A_{1g}$  state,<sup>8</sup>  $923\text{ cm}^{-1}$  in the first excited  $^1B_{2u}$  state,<sup>9</sup> and about  $965\text{ cm}^{-1}$  in the

second excited singlet state.<sup>10</sup> Even the absolute position of this absorption observed in liquid benzene may not be used to locate definitely the 0,0 band, since the emission spectrum has been obtained only in a rigid glass-solution, and the absolute positions of the spectra in the two media are not comparable. Further experiments are in progress in this laboratory to attempt the recording of this absorption band in the same rigid medium in which the phosphorescence emission was obtained. It is to be presumed that the same type of absolute correlation could be obtained through the observation of both the emission and absorption of crystalline benzene. The excellent absorption spectra obtained by Kronenberger<sup>11</sup> with crystalline benzene at  $20^\circ\text{K}$  did not include the range of the singlet-triplet absorption, and it is doubtful if large enough single crystals were obtained in this investigation to measure these weak bands.

The triplet-singlet emission spectrum of benzene has previously been reported by Lewis and Kasha<sup>1</sup> and Nauman.<sup>12</sup> All spectra in these investigations were obtained with the use of a wide slit. This slit width, 0.3 to 0.5 mm, is too wide even for the moderate dispersion of the medium Hilger quartz spectrograph used and for the general width of the benzene bands. These investigations, designed merely for qualitative considerations, did not

TABLE I. Observed frequencies of the bands in the 3400Å triplet-singlet emission of benzene.

1. $29,470 \pm 10\text{ cm}^{-1}$	10. 25,555
2. 28,784	11. 25,125
3. 28,460	12. 24,933
4. 28,310	13. 24,743
5. 27,891	14. 24,577
6. 27,308	15. 24,149
7. 26,893	16. 23,735
8. 26,308	17. 23,163
9. 25,916	18. 22,900
	19. 21,850

<sup>8</sup> N. Herzfeld, C. K. Ingold, and H. G. Poole, J. Chem. Soc. (London) 1946, 316.

<sup>9</sup> F. M. Garforth, C. K. Ingold, and H. G. Poole, J. Chem. Soc. (London) 1948, 491.

<sup>10</sup> G. Nordheim, H. Spöner, and E. Teller, J. Chem. Phys. 8, 455 (1940).

<sup>11</sup> A. Kronenberger, Zeits. f. Physik. 63, 494 (1930).

<sup>12</sup> R. V. Nauman, Dissertation, University of California at Berkeley, 1947.

permit accurate analysis because of lack of sufficiently precise calibrations.<sup>13</sup>

### EXPERIMENTAL

A new spectrum of the phosphorescence emission of benzene has been obtained using a much narrower slit (0.10 mm) and, consequently, a much longer exposure (30 hours). Figures 1 and 2 show typical tracings of this new benzene spectrum with the frequency scale magnified 2 $\times$  and 10 $\times$ , respectively. The bands are arbitrarily numbered from the high frequency end. Band 3 is, of course, less accurately measured, but it is included because of the importance of the first few differences in establishing the analysis. Table I lists the frequencies of all the observed bands.

A sample of very pure benzene, crystallized seven times by the method of Lewis and Kasha,<sup>1</sup> was dissolved in EPA (5 parts absolute ether, 5 parts isopentane, and 2 parts absolute ethyl alcohol) and solidified at liquid nitrogen temperatures. The phosphoroscope was essentially that used by Lewis and Kasha with a small rotating can, quartz dewar, and test tube. The source was a hydrogen arc (National Technical Laboratories No. 2230). The

TABLE II. Comparison of frequencies observed in the gas phase (see reference 14) and crystal (see reference 11) absorption and fluorescence spectra of benzene.

Assignment	Gas frequency	Solid frequency
$a_{1g}(B_{2u})$	923 cm <sup>-1</sup>	923 cm <sup>-1</sup>
$e_g^+(B_{2u})$	3085	3099*
$e_g^+(B_{2u}) + 2 \times e_u^+(B_{2u})$	1000	988
$a_{1g}(A_{1g})$	992	990
$e_g^+(A_{1g})$	606	600

\* This value is corrected according to the new interpretation of the  $B_{2u}$  frequencies suggested by C. K. Ingold and F. M. Garforth, *J. Chem. Soc. (London)* 1948, 417. Better agreement is obtained with this interpretation than with that proposed by the SNST analysis (see reference 14).

use of a much smaller quartz dewar and test tube (diameter  $\frac{1}{2}$  inch) enabled the source and the spectrograph slit to be placed very close to the sample tube, eliminating the use of all quartz lenses. The sample was changed approximately once an hour to avoid emission from possible photo-chemical decomposition products.

The errors mentioned in reference 13 were avoided by superimposing a low pressure mercury calibration spectrum directly upon a portion of the emission spectrum of benzene without moving either the slit or the plate holder. A dispersion curve was made from the calibrating lines for each

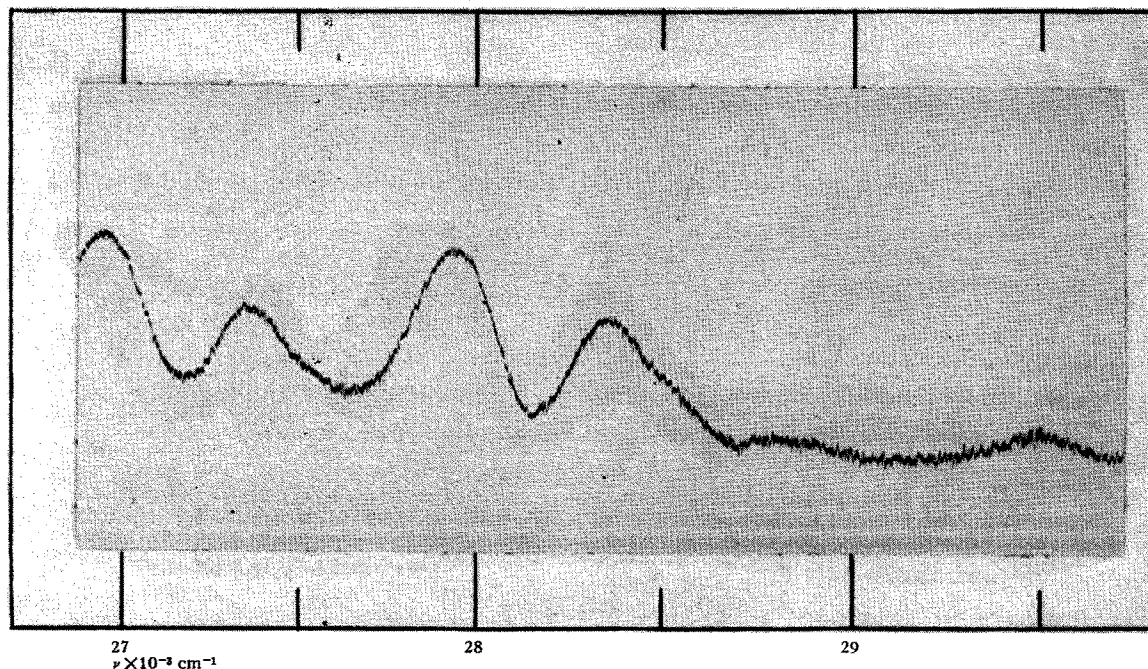


FIG. 2. Microphotometer tracing of the higher energy bands of the triplet-singlet emission spectrum at a 10 $\times$  magnification of the frequency scale.

<sup>13</sup> It was the general practice to move the plate-holder, narrow the slit and place adjacent to the phosphorescence spectrum that of a low pressure mercury arc. A calibration curve was used common for all plates, and spectra were located with respect to this calibration curve through the use of the mercury lines. This procedure introduced three errors: (1) the movement of the plate-holder may have displaced the observed spectrum with respect to the calibration lines, (2) narrowing the slit displaces the spectrum, and the maxima observed with a wide slit do not coincide with those observed with a narrow one, (3) two successive plates placed in the same plate-holder do not necessarily assume the same curvature, and it is important to use a separate calibration curve for each plate. Previously published spectra and frequencies<sup>1,2,12</sup> may therefore be in error up to perhaps 150 cm<sup>-1</sup> notwithstanding smaller limits of error suggested in these papers.

TABLE III. Data of Halford and Schaeffer (see reference 15) on corresponding infra-red bands of benzene in the vapor, liquid, and solid states close to the melting point.

Vapor	Liquid	Solid	Vapor	Liquid	Solid
671	674	676	1755	1760	1764
779	774	766	1811	1822	1836
1032	1033	1037	1880	1880	1890
1243	1247	1252	1954	1965	1982
1385	1393	1396	2215	2210	2220
1483	1478	1485	2620	2600	2600
1615	1614	1616	3085	3065	3070
1655	1650	1650			

individual plate so that no errors were introduced as a result of change in plate curvature. Each plate was traced several times with a Zeiss recording microphotometer with varying slit widths both through a portion of the spectrum upon which the mercury lines had been superimposed and through a portion in which the calibration lines were absent. Measurements were made upon the tracings by the use of a comparator reading to 0.001 mm, and possessing highly accurate ways for both horizontal and vertical motion. Such accuracy was not at all necessary in this work, however, since the nature of the emission spectrum is such that measurements of the maxima can be made only to about 0.1 mm upon a 2 $\times$  tracing. This corresponds to an error of 10  $\text{cm}^{-1}$  in the absolute position of any band. Differences between two peaks, on this basis, may carry an error up to 20  $\text{cm}^{-1}$ . In the analysis of the spectrum, good agreement is considered to have been obtained if the observed frequency difference agrees with the assigned within 30  $\text{cm}^{-1}$ , and in general, if the disagreement between a calculated assignment and the observed difference was more than 50  $\text{cm}^{-1}$ , it was concluded that there was no chance of that particular assignment being correct. In addition, microphotometer tracings were made which magnified the frequency scale of sections of the spectrum by 10 $\times$ . These served to show asymmetries in the band shapes in several places, indicating the presence of further unresolved (or incompletely resolved) bands.

#### ANALYSIS

In comparing the observed values with assigned frequencies, we are assuming that the fundamental frequencies calculated by Ingold *et al.*<sup>8</sup> for the gaseous state are closely applicable to the emission spectrum in a rigid glass-solution at liquid nitrogen temperature. That this is valid is not obvious *a priori*, but several data may be quoted to make it more reasonable. Sponer, Nordheim, Sklar, and Teller<sup>14</sup> in their analysis of the gaseous absorption and fluorescence of benzene also re-examined data

obtained by Kronenberger<sup>11</sup> upon the crystal at 20°K. They found the spectrum shifted by 261  $\text{cm}^{-1}$ , but typical vibrational differences were found relatively unchanged. Some examples are shown in Table II.

Halford and Schaeffer<sup>15</sup> took the infra-red spectrum of benzene in the solid, liquid, and vapor states close to the freezing point of benzene. Their data may be examined for the effect of state of aggregation upon the vibrational frequency, but not of the temperature, since the latter variable was not changed significantly in this particular investigation. Typical examples of corresponding bands in the three states are assembled in Table III. From inspection of the spectra these may easily be identified as corresponding bands. The differences observed are in most cases hardly more than the errors in the determination of the vapor phase frequencies themselves, involving as they do, the assumption of harmonic vibrations. Halford and Schaeffer conclude that "the molecular vibrations retain their individualities in the condensed phases to a very high degree."

The close agreement of the easily observed totally symmetric frequencies in the phosphorescence emission with that in the gas phase as shown below is a final indication of the validity of using the complete set of gas phase fundamentals in this analysis. Because of possible errors in these fundamental frequencies themselves and because of possible slight changes in passing to the solid, 30  $\text{cm}^{-1}$  has been used as the limit of disagreement allowed even though the error in measurement of the frequency differences has been indicated as only 20  $\text{cm}^{-1}$ .

Since the emission was observed at liquid nitrogen temperature, the emitting triplet state is most probably in a non-vibrating state. This follows from the long lifetime of the state and the low temperature. The long lifetime, 7 sec.<sup>16</sup> allows ample time for excess vibrational energy to be drained off by the medium. At the temperature of the experiments, 77°K, the Boltzmann factor for as low an energy as 200  $\text{cm}^{-1}$  is only 0.02. In the lowest excited singlet state the lowest vibration is 243  $\text{cm}^{-1}$ ,<sup>9</sup> and the lowest vibration in the triplet state should probably be in the same range. The analysis presented in detail below makes it unlikely that such a low vibrational level of the triplet state is involved, and consequently the weakness of the first few bands may not be attributed to a Boltzmann distribution in low vibrational levels of this state. The weakness of bands 1, 2, 3, and any others in this series concealed by the remainder of

<sup>15</sup> R. S. Halford and O. A. Schaeffer, J. Chem. Phys. **14**, 141 (1946).

<sup>16</sup> D. S. McClure, Dissertation. University of California at Berkeley, 1948.

<sup>14</sup> Sponer, Nordheim, Sklar, and Teller, J. Chem. Phys. **7**, 207 (1939).

the spectrum, does set them apart from the remaining bands, and any adequate analysis should have at least a qualitative explanation of this fact. Since it is concluded that the initial state is the lowest vibrational level of the triplet molecule, all differences observed must be characteristic of the ground state. This is an important factor contributing to the simplicity of the spectrum.

A final assumption is made for the purpose of the analysis that the symmetry selection rules for this intercombination transition are the same as for singlet-singlet transitions. That this may not be the case is shown by some examples in diatomic molecules. The use of this assumption will lead, however, to a correct choice of the symmetry of the singlet level which interacts with this triplet level to make the transition observed.

A glance at the spectrum immediately suggests that bands 4, 6, 8, 10 and bands 5, 7, 9 (11 or 12), form two series. Calculation of these differences shows that, excepting 8-10 which will be discussed later, they do indeed fall very nicely into line, and that they correspond to expected series of totally symmetric vibrations. The differences are: 4-6, 1002  $\text{cm}^{-1}$ ; 6-8, 1000  $\text{cm}^{-1}$ ; 5-7, 998  $\text{cm}^{-1}$ ; 7-9, 977  $\text{cm}^{-1}$ ; 9-12, 983  $\text{cm}^{-1}$ . The average of these, 992  $\text{cm}^{-1}$ , is to be compared with the  $a_{1g}$  fundamental of 992  $\text{cm}^{-1}$ . In addition similar differences appear between other bands which may possibly be linked to this vibration, but not in any long series. Examples are: 10-14, 11-15, 13-16, 15-17 with values 978, 976, 1008, 986  $\text{cm}^{-1}$  respectively, averaging 987  $\text{cm}^{-1}$ . For the further analysis of the spectrum, two possibilities must be considered. Either band 1 is the 0,0 band or it is not the 0,0 band. In the former case, the 0,0 band may be assumed observable either because the transition is permitted under the symmetry selection rules or because the close environment of the rigid medium perturbs the otherwise forbidden transition and makes it weakly observable. First we may consider the assumption that band 1 is the 0,0 band.

Under this assumption, the differences between band 1 and the next few bands must most likely represent fundamental frequencies of the ground state. It is not considered likely that combination frequencies will be important relative to the fundamental vibrations. The 1-2 difference, 686  $\text{cm}^{-1}$ , may be ascribed within the above mentioned limits of error either to 671 ( $a_{2u}$ ) or 703 ( $b_{2g}$ ). Also 1010 (1-3, less accurately known) is in the region of 970 ( $e_u^+$ ), 985 ( $b_{2g}$ ), 992 ( $a_{1g}$ ), 1010 ( $b_{1u}$ ), and 1039 ( $e_u^-$ ). Difference 1-4 of 1160  $\text{cm}^{-1}$  is close only to 1178 ( $e_g^+$ ), and 1-5 of 1579  $\text{cm}^{-1}$  is close only to 1596 ( $e_g^+$ ). Since the latter two bands are each identifiable only with a single fundamental frequency, both of which are of the same symmetry type, and since these two bands are the first two

TABLE IV. Fundamental frequencies of benzene from Ingold (see reference 8) (column 2) and the same plus the 1-2 observed difference of 686  $\text{cm}^{-1}$ .

Symmetry	Fundamental Frequency	Fundamental + 686
$e_u^+$	405	1091
$e_g^+$	606	1292
$a_{2u}$	671	1357
$b_{2g}$	703	1389
$e_g^-$	849	1535
$e_u^+$	970	1656
$b_{2g}$	985	1671
$a_{1g}$	992	1678
$b_{1u}$	1010	1696
$e_u^-$	1039	1725
$b_{2u}$	1110	1796
$e_g^+$	1178	1864
$a_{2g}$	1326	2012
$e_u^-$	1485	2171
$e_g^+$	1596	2282
$b_{2u}$	1648	2334
$e_g^+$	3047	3733
$b_{1u}$	3060	3746
$a_{1g}$	3062	3748
$e_u^-$	3080	3766

of the high intensity group, we are led to the suggestion that the transition is a forbidden one, but appears weakly due to perturbations by the medium, and more strongly when perturbed by vibrations of  $e_g^+$  symmetry.

For combinations with an  $A_{1g}$  ground state, only four types of states may be associated with  $e_g^+$  vibrations. These are  $B_{2u}$ ,  $B_{1u}$ ,  $E_u^+$ , and  $E_u^-$ . Furthermore, it may be shown group theoretically that all of these transitions are associated only with  $g$  vibrations (a consequence of the electric moment operator having only  $u$  characteristics). Hence, if differences 1-4 and 1-5 are to be identified with  $g$  vibrations, so must also differences 1-2 and 1-3. This limits the interpretation of difference 1-2 to the 703 ( $b_{2g}$ ) vibration, and 1-3 to either the 985 ( $b_{2g}$ ) or 992 ( $a_{1g}$ ) vibration.

Of the four states mentioned above as associated with  $e_g^+$  vibrations, only two may also be associated with  $b_{2g}$  vibrations. These are  $B_{1u}$  and  $E_u^+$ . Since benzene has an even number of electrons, the wave-function for each state must be symmetric with respect to the plane of the ring. This condition eliminates  $E_u^+$ , leaving  $B_{1u}$  as the symmetry of the perturbing singlet state.

We must consider now all other reasonable possibilities in order to determine if any of the remainder are as satisfactory in accounting for the first five bands as this one which considers the 1-2 difference as the  $b_{2g}$  703  $\text{cm}^{-1}$  fundamental. There is no possible fit if we consider the 1-2 difference as the 671  $a_{2u}$  vibration. For transition to the ground  $A_{1g}$  state, this choice would imply that the lowest triplet was perturbed by a state of symmetry  $E_g^-$  or  $A_{1g}$ . The former state is eliminated because it is antisymmetric to the benzene plane. If  $A_{1g}$ , the vibrations allowed would be of symmetry  $a_{2u}$  or  $e_u^-$ ,



having frequencies of 671 ( $a_{2u}$ ), 1039, 1485, 3080 ( $e_u^-$ ). Difference 1-4 of 1160  $\text{cm}^{-1}$  can hardly correlate with any of these or with the possibility of  $671+992=1663 \text{ cm}^{-1}$ . One is led to the conclusion, then, that if band 1 is the 0,0 transition, band 2 is certainly due to the 0,1 transition involving one quantum of 703  $\text{cm}^{-1}$   $b_{2g}$ .

We next must examine the possibility that the 0,0 band is not observable because of the forbidden character of the transition. It is then presumed that the spectrum observed is due to perturbation of the symmetry by certain vibrations with resulting violation of the selection rules. The band differences observed should then be found to agree with differences in fundamental frequencies, especially for the first band. In Table IV, therefore, appear all the fundamental frequencies of benzene in column 2, and in column 3 these frequencies plus the observed 1-2 difference of 686  $\text{cm}^{-1}$ . Where coincidences are found between column 2 and column 1 there is the possibility that the 0,0 band is as many wave numbers above band 1 as the lower of the two frequencies concerned. This new 0,0 position may then be used for a band analysis in the same manner as when band 1 was considered as the 0,0 band.

Being slightly liberal with the 30  $\text{cm}^{-1}$  error suggested, six coincidences are found. Three of these correspond to the impossible situation of a  $g$  and a  $u$  vibration arising from the same electronic level. These are the coincidences 671 ( $a_{2u}$ )+686=1357 with 1326 ( $a_{2g}$ ); 985 ( $b_{2g}$ )+686=1671 with 1648 ( $b_{2u}$ ); 992 ( $a_{1g}$ )+686=1678 with 1648 ( $b_{2u}$ ). There remain three coincidences which must be examined in more detail. These are 405 ( $e_u^+$ )+686=1091 with 1110 ( $b_{2u}$ ); 606 ( $e_g^+$ )+686=1292 with 1326 ( $a_{2g}$ ); 970 ( $e_u^+$ )+686=1656 with 1648 ( $b_{2u}$ ).

First, consider the possibility that the 0,0 band is 405  $\text{cm}^{-1}$  above the band 1. Then the frequency differences between the 0,0 band and the first five bands observed are: 405, 1091, 1415, 1565, 1983. The  $e_u^+$  vibration 405  $\text{cm}^{-1}$  and the 1110  $b_{2u}$  vibration (1091), imply an electronic state of symmetry  $B_{1g}$  or  $E_g^+$ . If the latter, the totality of allowed vibrations are 405, 970, 1010, 1039, 1110, 1485, 1648, 3060, 3080. The observed 1415 may be correlated with  $405+992=1397$ , but there is no possible correlation for the 1565 band. 1983 could not possibly be correlated with  $1110+992=2102$  and this leaves the first two strong bands with no theoretical counterpart. Therefore, an  $E_g^+$  state at this frequency seems out of the question. The  $B_{1g}$  symmetry is unsuitable because it does not satisfy the requirement of being symmetric with respect to the molecular plane.

The second case places the 0,0 band 606  $\text{cm}^{-1}$  above band 1, and the new differences between this and the observed bands are 606, 1292, 1616, 1766,

2185. Since 606 is of symmetry  $e_g^+$  and 1292 corresponds to 1326 of symmetry  $a_{2g}$ , the only symmetry allowing vibrations of these two types is  $E_u^-$ . Transitions between  $E_u^-$  and  $A_{1g}$ , however, are allowed. It seems unlikely that this possibility is correct, for the suggestion of an  $E_u^-$  symmetry was arrived at only with the supposition that the transition was forbidden. Even so, the vibrations might also be considered. The totality of allowed vibrations are 606, 849, 992, 1178, 1326, 1596, 3047, 3062. The first three observed differences may be correlated with 606, 1326, 1596, but there are no possibilities for the next one. The combination  $849+992=1841$  cannot be used for 1766, but  $1178+992=2170$  agrees well with 2185. Since the first important band is still unaccounted for, and the selection rules do not follow any normal pattern, this is also considered an unlikely possibility.

The final case for consideration places the 0,0 band 970  $\text{cm}^{-1}$  above band 1. The new differences then become 970, 1656, 1980, 2130, 2549. If 1656 is the 1648  $b_{2u}$  vibration then the perturbing level is either of symmetry  $E_g^+$  or  $B_{1g}$  as in case 1 above and the allowed vibrations are 405, 970, 1010, 1039, 1110, 1485, 1648, 3060, 3080. None of the remaining three bands may be correlated with fundamentals. Difference 1980 is closely  $970+992=1962$ , and 2130 just falls within the range of  $1110+992=2102$ , but 2549 has no counterpart. Hence this analysis is also discarded.

Thus, careful analysis of all the reasonable possibilities shows there is but one satisfactory way of accounting for the first five bands observed. This will henceforth be considered as the correct choice in the following discussion.

Returning to this choice, the 1-2 difference has been settled as corresponding to the 703  $b_{2g}$  vibration. There are two possibilities for the 1-3 difference. As may be seen from the tracings, this is a relatively inaccurately measured shoulder and the value 1010  $\text{cm}^{-1}$  could correspond either to the 985  $b_{2g}$  or 992  $a_{1g}$  vibration. The latter might be expected to appear to about the same intensity as the 1 band because of perturbations by the rigid medium. There is no obvious reason why the 985 band should either be present or absent other than its being of appropriate symmetry. Thus it is equally hard to explain why the 606  $e_g^+$  vibration prominent in the fluorescence and singlet absorption spectra does not appear here at all. Its absence is most logically ascribed to the Franck-Condon principle. Differences 1-4 and 1-5 were explained by the appropriate  $e_g^+$  vibrations, while 6, 7, 8, 9, and 12 were accounted for on the basis of  $a_{1g}$  progressions. It would not be surprising if some of the higher bands and shoulders were hard to account for, as there are undoubtedly many bands of varying intensities superimposed, and the max-

ima measured may not accurately represent true maxima of the component bands.

Band 10, however, is moderately sharp and the measurement of its position should be fairly accurate. When the differences between it and preceding bands are considered, no correlation with fundamentals of appropriate symmetry is possible. From the tracing it appears generically to belong to the series 4-6, 6-8, 8-10, but the 8-10 difference is only  $753\text{ cm}^{-1}$ , far from the expected  $992\text{ cm}^{-1}$ . This band must come from higher combinations. Since it is fairly intense, it is logical to suggest that it is the result of a combination band superimposed upon bands 4, 5, 6, or 7. It is unlikely that such intensity could be gained by superimposing combinations upon the weaker series of bands 1, 2, or 3.

For this reason, a complete survey was made of all binary combination possibilities of benzene. Difference 4-10 is  $2755\text{ cm}^{-1}$ , and the combinations within  $40\text{ cm}^{-1}$  of this value are

$$\begin{aligned} 1110 (b_{2u}) + 1596 (e_g^+) &= 2706 (e_u^+), \\ 1110 (b_{2u}) + 1648 (b_{2u}) &= 2758 (a_{1g}), \\ 1178 (e_g^+) + 1596 (e_g^+) &= 2774 (a_{1g}, a_{2g}, e_g^+). \end{aligned}$$

The latter two are of appropriate symmetry for the combination since superimposed upon  $e_g^+$  vibrations may be expected only  $a_{1g}$  vibrations (although some other types may possibly appear according to group theory). The last one is the more likely since involved in it are vibrations already known to be excited.

The combinations corresponding to the difference 5-10 of  $2336\text{ cm}^{-1}$  are

$$\begin{aligned} 671 (a_{2u}) + 1648 (b_{2u}) &= 2319 (b_{1g}), \\ 703 (b_{2g}) + 1596 (e_g^+) &= 2299 (e_g^-), \\ 703 (b_{2g}) + 1648 (b_{2u}) &= 2351 (a_{1u}), \\ 849 (e_g^-) + 1485 (e_u^-) &= 2334 (a_{1u}, a_{2u}, e_u^+), \\ 985 (b_{2g}) + 1326 (a_{2g}) &= 2311 (b_{1g}), \\ 992 (a_{1g}) + 1326 (a_{2g}) &= 2318 (a_{2g}), \\ 1010 (b_{1u}) + 1326 (a_{2g}) &= 2336 (b_{2u}), \\ 1039 (e_u^-) + 1326 (a_{2g}) &= 2365 (e_u^-), \\ 1178 (e_g^+) + 1178 (e_g^+) &= 2356 (a_{1g}, a_{2g}, e_g^+). \end{aligned}$$

Only the last one has symmetry  $a_{1g}$ , and once again this involves a vibration known to be excited (for band 4).

6-10 has a difference of  $1753\text{ cm}^{-1}$  to which correspond the following combinations.

$$\begin{aligned} 405 (e_u^+) + 1326 (a_{2g}) &= 1731 (e_u^+), \\ 606 (e_g^+) + 1110 (b_{2u}) &= 1716 (e_u^-), \\ 606 (e_g^+) + 1178 (e_g^+) &= 1784 (a_{1g}, a_{2g}, e_g^+), \\ 671 (a_{2u}) + 1110 (b_{2u}) &= 1781 (b_{1g}), \\ 703 (b_{2g}) + 1039 (e_u^-) &= 1742 (e_u^+). \end{aligned}$$

There is once again one of the appropriate symmetry involving  $e_g^+$  vibrations. This time, however, there is involved the 606 vibration which did not

appear in the early bands. It can thus be seen that there is no lack of combinations from which to choose, and no certain choice may be made among them.

Particularly suggestive, however, is the combination of two units of 1178 added onto one of 1596 to give band ten, for it is found that two units of 1596 added onto one of 1178, a total of 4370 corresponds fairly well to 4345, the hitherto unexplained 1-11 difference. Allowing 10-14 (978 observed) 11-15 (976 observed), and 15-17 (986 observed) as  $a_{1g}$  vibrations, this leaves bands 13, 16, 18, and 19 as yet unaccounted for. Of these 13 and 16 are connected by what is possibly an  $a_{1g}$  vibration (1008 observed). The 1-13 difference of 4727 observed is not too far away from three units of  $1596 = 4788$ . Further speculation on these weak bands of uncertain position is not profitable at this time. Table V summarizes the analysis.

## DISCUSSION

The analysis leads to the conclusion, therefore, that the 3400A triplet-singlet emission is observed because of mixing with the triplet level of a singlet level of symmetry  $B_{1u}$ . This will lead to a definite decision as to the symmetry of the lowest triplet level when the intercombination selection rules are fully understood. At the present time, it is not clear whether  $B_{1u}$  singlet states will mix with  $B_{1u}$  or  $B_{2u}$  triplet states, and a final choice must wait until this point is clarified. In diatomic molecules  $^3\Sigma^+$  states act like  $^1\Sigma^-$  states when they combine with singlet states, and this situation may also

TABLE V. Proposed assignment of bands for the triplet-singlet emission of benzene at 3400A. In each case the transition is from the 0 vibrational level of the triplet state to the level of the ground state indicated.

Band (x)	Vibrational Level of $^1A_{1g}$ State	Difference $1-x$	
		Calc'd.	Obs'd
1	0	0	0
2	1 of 703 ( $b_{2g}$ )	703	686
3	1 of 985 ( $b_{2g}$ ) or 1 of 992 ( $a_{1g}$ )	985 or 992	1010
4	1 of 1178 ( $e_g^+$ )	1178	1160
5	1 of 1596 ( $e_g^+$ )	1596	1579
6	1 of 1178 ( $e_g^+$ ) + 1 of 992 ( $a_{1g}$ )	2170	2162
7	1 of 1596 ( $e_g^+$ ) + 1 of 992 ( $a_{1g}$ )	2588	2577
8	1 of 1178 ( $e_g^+$ ) + 2 of 992 ( $a_{1g}$ )	3162	3162
9	1 of 1596 ( $e_g^+$ ) + 2 of 992 ( $a_{1g}$ )	3580	3554
*10	1 of 1596 ( $e_g^+$ ) + 2 of 1178 ( $e_g^+$ )	3952	3915
*11	1 of 1178 ( $e_g^+$ ) + 2 of 1596 ( $e_g^+$ )	4370	4345
12	1 of 1596 ( $e_g^+$ ) + 3 of 992 ( $a_{1g}$ )	4572	4537
*13	3 of 1596 ( $e_g^+$ )	4788	4727
*14	1 of 1596 ( $e_g^+$ ) + 2 of 1178 ( $e_g^+$ ) + 1 of 992 ( $a_{1g}$ )	4944	4893
*15	1 of 1178 ( $e_g^+$ ) + 2 of 1596 ( $e_g^+$ ) + 1 of 992 ( $a_{1g}$ )	5362	5321
*16	3 of 1596 ( $e_g^+$ ) + 1 of 992 ( $a_{1g}$ )	5780	5735
*17	1 of 1178 ( $e_g^+$ ) + 2 of 1596 ( $e_g^+$ ) + 2 of 992 ( $a_{1g}$ )	6354	6307
18	Not assigned	—	6570
19	Not assigned	—	7620

\* Assignment of these bands is less certain.



occur in polyatomic molecules.<sup>17</sup> In that case a  $B_{1u}$  singlet state would perturb a  $B_{2u}$  triplet state. A  $B_{2u}$  assignment for the lowest triplet state would not agree with previous theoretical calculations.<sup>3,4</sup>

Several final points may be brought out. First, the present analysis very nicely accounts for the weakness of the first few bands. The 0,0 band 1 appears only because of perturbations of the medium. Band 2 might be expected to have higher intensity since it involves the addition of a perturbing vibration that makes the transition allowed. That it does not do so may be attributed to the absence of any other nearby electronic level for which the transition moment to the ground state is polarized in the  $Z$  direction. Thus the 2600Å benzene band's weakness relative to the 2000Å band has been attributed to the proximity of the latter to the allowed 1800Å  $E_u^- \rightarrow A_{1g}$  transition.<sup>10</sup> The observations indicate that the band series observed for both these singlet forbidden bands involve an electric moment in the plane of the ring. No transitions are known at all in which polarization perpendicular to the ring may be expected, nor are any calculated by the molecular orbital treatment. It would seem logical, therefore, to believe that band 2 and possibly the shoulder 3 would not appear at all because of the absence of a suitable transition from which to "borrow," except for the perturbing influence of the medium. This would, therefore, account for the observation that bands 1 and 2 (and possibly 3) are of almost identical intensity. Bands 4 and 5, of course, from this viewpoint are much stronger since in this case there is a nearby electronic transition from which they can borrow some intensity.

This immediately suggests that the fluorescence of benzene should be re-examined under similar conditions in a rigid medium. Sponer, Nordheim, Sklar, and Teller<sup>14</sup> made no mention of finding either the 703 or 985  $b_{2g}$  vibrations, but the plates of Radle and Beck<sup>18</sup> should be re-examined for them. The absence of these vibrations in the gas phase, however, does not preclude their appearance in the rigid medium, where they are much more likely to be found, judging from the phosphorescence analysis above.

Examination of Kronenberger's<sup>11</sup> data on crystalline benzene at liquid hydrogen temperature indicates the possible presence of the  $b_{2g}$  vibration which is 985  $\text{cm}^{-1}$  in the  $A_{1g}$  state but 775  $\text{cm}^{-1}$  in the lowest excited singlet state.<sup>9</sup> Assuming the assignment of the 0,0 band at 37,828  $\text{cm}^{-1}$ ,<sup>14</sup> the theoretical position of this  $b_{2g}$  vibration would be at 38,603  $\text{cm}^{-1}$ . Kronenberger reports a weak band at 38,600  $\text{cm}^{-1}$ , which may possibly be thus

assigned. There is no evidence of the 703  $b_{2g}$  vibration which drops to 365  $\text{cm}^{-1}$  in the excited state. If this assignment were found to be correct, the lowest excited singlet state would have to be redesignated as  $B_{1u}$ . The fact that this reported band is much weaker than the forbidden 0,0 band in this transition, however, makes the assignment unlikely.

Redlich and Holt,<sup>19</sup> using a classical analysis upon previous inaccurate data, arrived at the conclusion that their calculations supported a quinoidal model of the triplet state as proposed by Lewis and Kasha.<sup>2</sup> It should be pointed out that the latter proposed a non-planar model while Redlich and Holt's best model was planar. In fact, they definitely ruled out a non-planar model. Part of the evidence for the non-planar model proposed by Lewis and Kasha was the prominent 400  $\text{cm}^{-1}$  difference in their data, which they ascribed to the 405  $e_u^+$  out-of-plane vibration of benzene. The present analysis has shown that a reasonable assignment may be made with the assumption of retention of  $D_{6h}$  symmetry in the triplet state. The previous assumptions attributing the weakness of the first few bands to the Franck-Condon principle have been found unnecessary. In view of the success of analyzing the 2600Å singlet-singlet absorption and fluorescence bands<sup>14</sup> and, in the present case, the triplet-singlet emission on the basis of hexagonally symmetric excited states, it would seem likely that this configuration is the most probable one.

Sponer, Nordheim, Sklar, and Teller<sup>14</sup> pointed out that in the totally symmetric progressions observed by them in the analysis of the lowest excited singlet state, the usual case was that the second member was the most intense, while the first and third were of about equal intensity but somewhat lower. It is apparent from the tracings that the same is true of the phosphorescence emission spectrum, and the considerations applied by these authors may be applied equally well here. These suggested that the increase in the ring size was of the order of magnitude of 0.1Å, showing that despite disturbance of the  $\pi$  bonds, the molecule is rather securely held by its  $\sigma$ -bond framework.

Ingold *et al.*<sup>20</sup> have succeeded in setting up an approximate potential function for the lowest excited singlet state as a result of their assignment of most of the vibrational frequencies of this state. They conclude from consideration of the relationships between force constants and bond lengths that the increase in size for this singlet state is

<sup>19</sup> O. Redlich and E. K. Holt, *J. Am. Chem. Soc.* **67**, 1228 (1945).

<sup>20</sup> F. M. Garforth, C. K. Ingold, and H. G. Poole, *J. Chem. Soc. (London)* **1948**, 508.

<sup>17</sup> The author is indebted to Professor R. S. Mulliken for pointing this out.

<sup>18</sup> W. F. Radle and C. A. Beck, *J. Chem. Phys.* **8**, 507 (1940).

about  $2\frac{1}{2}$  percent or 0.04Å in the C—C bond. It is likely that the change in size of the molecule in passing to the triplet state is of the same order of magnitude. That there are, however, some fundamental differences in the shape of the lowest

triplet and lowest excited singlet states is shown by the prominence of the 1178 and 1596  $\text{cm}^{-1}$   $e_g^+$  vibrations in the triplet emission, whereas the 606 and 1596  $e_g^+$  vibrations are prominent in the singlet emission.

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## The Configuration of Real Polymer Chains\*

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The average configuration of polymer molecules in solution is markedly influenced by the obvious requirement, ordinarily disregarded in problems relating to molecular configuration, that two elements of the molecule are forbidden from occupying the same location in space. The influence of spatial "interferences" between different segments of the molecule on its average configuration has been investigated by statistical and thermodynamic methods.

It is shown that if the average linear dimension of a polymer chain is to be taken proportional to a power of the chain length, that power must be greater than the value 0.50 previously deduced in the conventional "random flight" treatment of molecular configuration. This power should approach 0.60 for long chain molecules in good solvents. With increase in size of the solvent molecule, the influence of

interference on molecular configuration diminishes, vanishing entirely in the extreme case of a solvent which is also a high polymer. The effect of a heat of interaction between solvent and polymer may also be incorporated quantitatively in the theory. A positive heat of mixing (poor solvent) tends to offset the expansive influence of interference, and the exponent referred to above tends to approach 0.50. The results are of foremost significance in the interpretation of the intrinsic viscosity and its dependence on the polymer constitution and on the solvent. It is pointed out that the spatial dimensions of the irregularly coiled polymer molecule cannot be correlated directly with hindrance to rotation about chain bonds, unless the expansion of the configuration due to interference and the effects of the heat of dilution are first of all taken into account.

### INTRODUCTION

THE spatial configuration of randomly coiled chain polymer molecules is customarily treated in the "random flight" approximation, according to which each element, or "segment," of the chain is considered to be free to choose any orientation with respect to its predecessor, independent of the locations of all other segments of the same molecule. Impossible configurations which would require two segments to occupy the same element of volume are not excluded from consideration. The effects of short range "interferences" of this nature between two segments situated in close proximity along the chain are readily taken into account approximately by merely enlarging the effective segment length somewhat, the form of the equation expressing the nature of the chain configurations being unaltered.<sup>1</sup> The influence of long range interferences between remotely related segments of the same chain is not so easily disposed of, however.

The average "density" of polymer within the region occupied by a chain of a thousand segments may be of the order of only one percent. The chance

that a given segment will seek to occupy the site occupied by some other remotely connected segment will be relatively rare. It must not be inferred, however, that long range interferences are inconsequential under these conditions. A given "random flight" configuration for the molecule will be acceptable only in case *none* of its segments is assigned to a site occupied by another segment. The probability of compliance with this condition will be of the order of  $e^{-5}$  for a molecule of a thousand segments distributed at an average density of one percent. Only a very small fraction of the "random flight" configurations tacitly assumed in previous theories may be realized by the actual chain molecule. Interferences will be fewer on the average in more expanded configurations. Hence, a relatively larger fraction of the latter will be acceptable to the actual polymer chain and the average size of the randomly coiled molecule will be greater than that calculated by the usual procedures.

This fairly obvious influence of interference of actual chain molecules having finite lateral dimensions has been pointed out on various occasions<sup>2-4</sup> in the past, but it has not been investigated quantitatively. Direct treatment of the configuration problem in terms of the space coordinates for

\* The greater portion of the theoretical development presented in this paper was carried out during the author's tenure as George Fisher Baker Non-Resident Lecturer in Chemistry at Cornell University for the spring term of 1948.

<sup>1</sup> W. Kuhn, *Kolloid Zeits.* **87**, 3 (1939).

<sup>2</sup> W. Kuhn, *Kolloid Zeits.* **68**, 2 (1934).

<sup>3</sup> M. L. Huggins, *J. App. Phys.* **10**, 700 (1939).

<sup>4</sup> R. Simha, *J. Polymer Sci.* **3**, 227 (1948).