314. *The Intensities of the Forbidden Bands of Benzene.*

By (Mrs.) J. K. Thompson and A. D. E. Pullin.

The peak densities of the 1174 cm.$^{-1}$ forbidden band and the peak densities and half-intensity widths of the 851 cm.$^{-1}$ forbidden band of benzene have been measured for solutions of benzene in a variety of solvents. It was found that the peak densities increased smoothly and rapidly with increase of the refractive index of the solvent. The peak density for the carbon disulphide solution was anomalously large. A similar trend was found for the peak densities of the allowed 1033 cm.$^{-1}$ band and could be explained on the basis of decreasing half-intensity width of this band with increasing solvent refractive index. The product of the peak density and half-intensity width of the 851 cm.$^{-1}$ band was taken as a proportionate measure of the area of this band. The product was found to increase with increasing solvent polarisability and decreasing solvent molar volume. Carbon disulphide solution gave the highest value of this product. It is suggested that the large half-intensity widths of the forbidden bands are due to the fact that the transition moment for transitions giving rise to absorption at the wings of the bands is larger than that for transitions giving rise to absorption at frequencies near the band maximum.

It is well known that liquid benzene and solutions of benzene show a number of weak absorption bands at frequencies corresponding to fundamental modes of vibration which are forbidden to be active in absorption by the selection rules for D_{6h} symmetry. Bands at these frequencies might conceivably arise from combination tones or be due to benzene molecules whose mass symmetry is lowered by the presence of ^{13}C. However, considerations of likely allowed combination tones and the comparison made by Halford and Schaefer[1] of the spectra of the liquid and vapour[2] for equivalent absorbing paths rule out both these interpretations, at least as an explanation of the major part of the intensity of these bands. Thus at least nearly all the intensity of these bands must be due to forbidden fundamental vibrations rendered active through the disturbance of the molecule by intermolecular forces.

Following Mair and Hornig's assignment[3] for the two B_{2u} vibrational modes and that of Ingold *et al.*[4] for the remainder, the most prominent of the forbidden bands are: (*a*) A band at 851 cm.$^{-1}$* corresponding to the E_g^- out-of-plane hydrogen bending mode.[5] (*b*) A band at 1175 cm.$^{-1}$ partly overlapped by a weaker band at 1148 cm.$^{-1}$ corresponding respectively to the E_g^+ and the B_{2u} in-plane hydrogen bending modes.

In an attempt to find what solvent properties are important in causing these forbidden bands to appear, we have examined the spectra of a variety of solutions of benzene. The peak densities, and in some cases the half-intensity widths, have been measured for both forbidden and allowed bands, and a dependence of these quantities on the refractive index of the solvent has been established.

Experimental

All the spectra were obtained with a Perkin-Elmer model 21 double-beam spectrophotometer equipped with a sodium chloride prism. Useful solution spectra were obtained with the following solvents: methyl cyanide (1), *n*-hexane (2), ethylidene chloride (3), methylene

---

* Frequencies quoted are those for liquid benzene: corresponding frequencies for the solutions varied slightly with solvent (Fig. 2).

[1] Halford and Schaefer, *J. Chem. Phys.*, 1946, **14**, 141.

[2] A spectrum of liquid benzene obtained at higher resolution than that of Ref. 1. is given in Ref. 3, p. 1239. Liquid and vapour spectra are reproduced by Ingold (*J.*, 1936, 935) and by the American Petroleum Institute Research Project 44, spectra 122 (vapour), 307 and 498 (liquid).

[3] Mair and Hornig, *J. Chem. Phys.*, 1949, **17**, 1236.

[4] Ingold *et al.*, *J.*, 1946, 222 *et seq.*, especially p. 325.

[5] *Idem, ibid.*, p. 231.

chloride (4), *cyclo*hexane (5), *n*-tetradecane (6), carbon tetrachloride (7), phosphorus oxychloride (8), trichloroethylene (9), benzene (10), methylene bromide (11), bromoform (12), carbon disulphide (13), sulphur monochloride (14), methylene iodide (15). The grades or sources of these chemicals were: (7) and (13), " AnalaR "; (1), May and Baker Laboratory Chemicals; (9), Technical: the remainder, B.D.H. Laboratory Reagent. The solvents were used without further purification, except for (14) which was distilled before use. The benzene used was of " AnalaR " quality: preliminary experiments showed that its spectrum remained unchanged when the benzene was subjected to repeated recrystallisation. All solutions of benzene except those in phosphorus oxychloride and sulphur monochloride were made up by volume to 0·8 volume fraction of solvent by adding benzene to 8 ml. of solvent to give a final volume of 10 ml. The weights of the solvent and benzene were noted.

For measurements of the forbidden bands the following procedure was adopted. Spectra compensated for solvent absorption were obtained with the solution and solvent in Hilger variable-path cells set at 0·200 and 0·160 mm., respectively. By making up the solutions on the basis of a constant volume of solvent one setting of the variable-path cells could be used throughout and only small corrections needed to be made to the observed intensities to refer them to a constant weight (taken as 1·76 g.) of benzene in 10 ml. of solution. For solutions in phosphorus oxychloride and sulphur monochloride a similar procedure was followed except that a solvent volume fraction of 0·714 was used in conjunction with fixed-thickness cells of 0·140 and 0·100 mm. Comparison spectra of pure benzene were obtained in two ways: first by obtaining a " solvent-compensated " spectrum with the variable-path cells both filled with pure benzene; and, secondly, with a single variable-path cell set at 0·040 mm. For all the solvents employed the spectrum of the compensating cell alone filled with the solvent was obtained. Spectral regions of the solution, solvent-compensated spectrum in which the solvent absorption exceeded 50% were not further considered.*

Because of the dependence on medium of the frequency, shape, and intensity of solvent absorption bands, the bands of the solvent are modified by the presence of the benzene in the solution, so that, apart from volumetric inaccuracies, compensation of solvent absorption cannot be quite exact. (A shift of solvent band position shows up on the solvent-compensated solution spectrum as sharp twinned upward and downward peaks like an anomalous dispersion curve: this effect was most noticeable in the spectra of solutions in bromoform, carbon disulphide, and methylene iodide.) To avoid errors arising from inexact solvent compensation, solute peak intensities were measured only if the solvent absorption at the solute band peak was less than 30% and remained less than 50% for a distance of 20 cm.$^{-1}$ on either side.

Further errors arise from the estimation of the base line for zero benzene absorption. This was estimated from regions of the spectrum between 4000 and 2000 cm.$^{-1}$ which were free from absorption bands due to either solvent or benzene. Other procedures, such as assigning a suitable small constant value to the optical density at the minimum of absorption on the low-frequency side of the 1970 cm.$^{-1}$ benzene band would have given essentially the same results. To allow for these and other errors, lines are drawn through the points in Figs. 4 and 5, representing, in optical density units, $\pm$(0·003 plus 5% of the solvent optical density at that frequency).

Because both the 851 and the 1174—1148 cm.$^{-1}$ band are considerably overlapped by the wings of neighbouring bands it is not possible to measure the band areas accurately. Where possible, approximate half-intensity widths have been measured and in these cases the product of half-intensity width and peak density ($\log_{10} I_0/I$) has been used as a proportionate measure of band area. Because of the width of forbidden bands, no correction for finite slit width need be applied. To check that large concentration errors were not occurring, the band areas of the 1819 and the 1970 cm.$^{-1}$ combination bands were measured approximately from the same spectra as the forbidden bands. The former remained within $\pm$10% of a mean value for all the solvents employed; a variation probably mainly arising from errors in measuring the half band widths. The constancy of the spacing of the variable path cells was checked obtaining the interference spectra of the empty cells.

Measurements of the peak densities and half-intensity widths of the allowed benzene band at 1033 cm.$^{-1}$ were also made for solutions of benzene in a number of the solvents listed above. (The 1033 cm.$^{-1}$ band arises from an in-plane E_u^- hydrogen bending mode.[5]) For these measurements solutions of the same concentration as before were used, but owing to the greater intensity

---

* The spectrum of pure benzene obtained by the first method was an exception to this.

of this band the variable-path cells were set at 0·040 and 0·032 mm. The products of the half-intensity band width and peak density were found to vary by less than 10% from a mean value for the solvents used.

RESULTS

The band areas or integrated intensities of the 851 cm.$^{-1}$ band and the 1174—1148 cm.$^{-1}$ pair in different solvents should be used as a measure of the perturbing power of the different solvents. However, because of the width of the forbidden bands and consequent overlapping with neighbouring more intense bands, direct measurement of their band areas is difficult. For cases where reliable half-intensity widths could be obtained the product of half-intensity width and peak density has been taken as an approximately proportional measure of band area. Half-intensity widths of the forbidden bands definitely varied with the solvent, though precise measurement was difficult. In order of increasing half-intensity width the solvents were;

FIG. 1. *Benzene spectra for equivalent absorbing paths :* 1450—750 *cm.*$^{-1}$. *A, Liquid benzene,* 0·040 *mm. layer. B, Carbon disulphide solution of benzene. C, Methylene iodide solution of benzene. Spectra B and C are successively displaced downward; the horizontal lines represent* 100% *transmission for spectra B and C.*

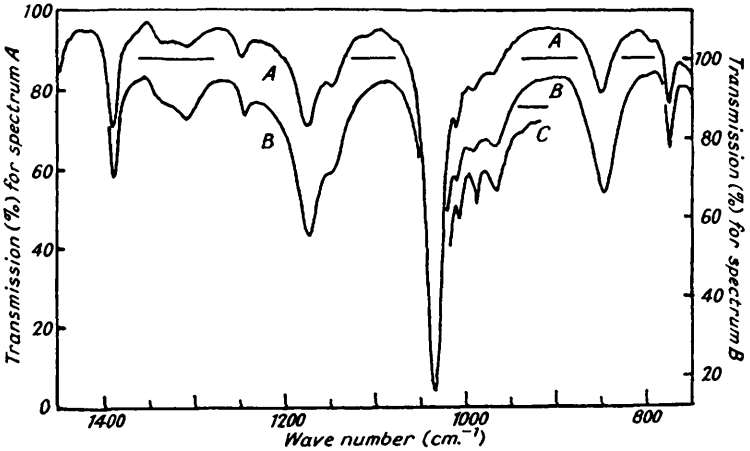


FIG. 2. *Benzene solution spectra for equivalent absorbing paths :* 900—750 *cm.*$^{-1}$. *The solvents are : A,* n-*tetradecane; B, methylene bromide; C, methylene iodide; D, carbon disulphide. Vertical lines represent* 10% *absorption.*

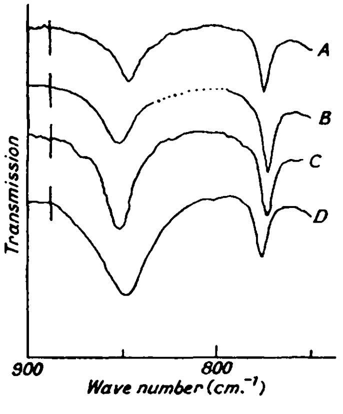
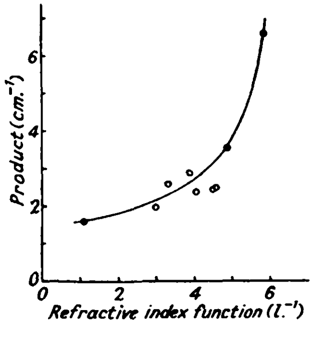


FIG. 3. *Plot of the product of peak density and half-intensity band width for the* 851 *cm.*$^{-1}$ *band against the solvent function* $(n^2 - 1)/(n^2 + 2)V$. *In increasing value of the abscissae, the points are for the solvents* 6, 3, 10, 12, 1, 11, 14, 15, 13.



n-tetradecane, sulphur monochloride, and methylene iodide, 19 cm.$^{-1}$; bromoform, 22 cm.$^{-1}$; methylene bromide 24 cm.$^{-1}$; ethylidene chloride, 25 cm.$^{-1}$; benzene, 28 cm.$^{-1}$; carbon disulphide, 33 cm.$^{-1}$; methyl cyanide, 35 cm.$^{-1}$. These are probably correct to ± 2 cm.$^{-1}$. Half-intensity widths of the 1819 and 1970 cm.$^{-1}$ allowed combination bands show a similar solvent order, except in carbon disulphide solution, in which these bands are among the narrowest. The experimental findings may be summarised as follows:

(*a*) Even excluding the carbon disulphide solution of benzene, there appears to be a much greater dependence of the integrated intensities of the 851 cm.$^{-1}$ band than is found for the 1033 cm.$^{-1}$ band, or for allowed bands generally (Figs. 1 and 2).

(*b*) The forbidden bands are symmetrical but much broader than the allowed bands. [Compare the allowed combination bands at 774, 1250, and 1394 cm.$^{-1}$ with the forbidden fundamental bands at 851 and 1174 cm.$^{-1}$ (Fig. 1).]

(*c*) The present rather limited results suggest that the integrated intensities of the forbidden bands increase fairly steeply with some function of the solvent refractive index *n* and solvent molar volume *V*, such as $n/V^{1/3}$ or $(n^2 - 1)/(n^2 + 2)V$ (Fig. 3) (n_{α}^{20} values have been used throughout).

FIG. 4. *Plot of peak densities against solvent refractive index for the* 851 *cm.*$^{-1}$ *band. Solvents, in order of increasing refractive index, are:* 1—4, 6, 8, 10—15.

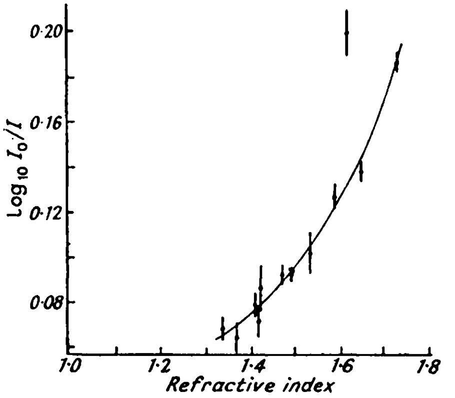
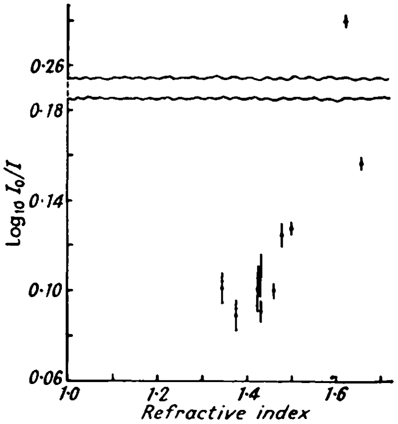


FIG. 5. *Variation of peak density of the* 1174 *cm.*$^{-1}$ *band (uncorrected for overlap by the* 1148 *cm.*$^{-1}$ *band) with solvent refractive index. Solvents, in order of increasing refractive index, are:* 1, 2, 4, 5 (*lower point*), 6, 7, 9, 10, 13, 14.



(*d*) Excluding the peak solution of benzene in carbon disulphide, the peak density of the 851 cm.$^{-1}$ band increases smoothly with the refractive index of the solvent (Fig. 4). Corresponding data for the 1174 cm.$^{-1}$ band are less complete but the results are broadly similar (Fig. 5). Introduction of a factor involving the molecular volume, as in (*c*), would give a much greater scatter to the points.

(*e*) The peak densities of the 851 and the 1174 cm.$^{-1}$ band maintain an approximately constant ratio for the solvents studied.

(*f*) The behaviour of carbon disulphide solutions differs in several respects from those of the other solvents. The point for carbon disulphide can only with difficulty be accommodated on the band area–solvent property curve (Fig. 3) and as shown in Figs. 4 and 5 the peak densities of the 851 and the 1174 cm.$^{-1}$ band are off the peak density–refractive index curve established by the other solvents. The half-intensity widths of the benzene forbidden bands in benzene are also irregular as in the other solvents a high value of the peak density of the 851 cm.$^{-1}$ band is associated with a low half-intensity width (*e.g.*, in bromoform, sulphur mono chloride, and methylene iodide) while in carbon disulphide solution the 851 cm.$^{-1}$ band is one of the broadest. In the case of the allowed bands examined (those at 1970, 1818, and 1033 cm.$^{-1}$) the bands in carbon disulphide solution were narrower than for most other solvents.

(*g*) Quantitative examination of the other forbidden bands was not attempted. A group of three partly resolved bands on the low-frequency side of the strong 1033 cm.$^{-1}$ band is present in the spectrum of liquid benzene and of solutions, but not in the spectrum of the vapour. As before, these must be ascribed to forbidden fundamental modes. The spectra strongly suggest that they show solvent effects similar to those discussed; in particular, the greater resolution of these three bands in solvents of higher refractive index resulting from decreased band width and increased peak density, is quite striking (Fig. 1). Two weak and barely resolved bands appear at 1312 and 1339 cm.$^{-1}$. There are no binary allowed combination tones that could account for these and, as before, other evidence points to their being forbidden modes. It is reasonable to suppose that they are the B_{2u} (C) mode observed by Mair and Hornig[3] in the spectrum of the solid at 1311 cm.$^{-1}$ and the A_{2g} mode observed by Ingold *et al.*[4] as a forbidden fundamental in the Raman spectrum of the liquid. Alternatively, the 1339 cm.$^{-1}$ band might be the (forbidden) first overtone of the 671 cm.$^{-1}$ fundamental. The 1312 cm.$^{-1}$ band is noticeably intensified in carbon disulphide solution. The other forbidden fundamentals were not examined.

Discussion

Fundamental modes forbidden to be active in absorption have been observed in gases and mixtures of gases at high pressures.[6] Mizushima[7] discussed the case of pressure-induced absorption of symmetric diatomic gases in terms of distortion arising from the field due to the quadrupole moment of the surrounding molecules, and obtained an expression for the integrated absorption intensity in terms of the molecular quadrupole moment, polarisability, and distance of closest approach R_0. In this expression the polarisability and anisotropy of polarisability occur as squared terms and R_0 occurs as an inverse fifth power. Later, Bird[8] discussed the pressure-induced absorption in hydrogen, deuterium, and hydrogen–helium mixtures in terms of an atomic distortion effect produced by overlap of the atoms of the perturbing molecule considered separately, and the quadrupole distortion effect. As in the present work the bands were observed in the liquid state, a fresh factor should be taken into account. The forbidden bands occur because the symmetry of the vibrating molecule is lower in the liquid state, which results in a finite value of the oscillating dipole moment associated with the vibrational transition. However, because the molecule is immersed in a dielectric medium effects connected with electrical displacements in a dielectric then intervene, to enhance the absorption intensity resulting from the original oscillating moment. The magnitude of this enhancement has been discussed by Chako.[9] There is some doubt about the exact correction to be applied, but it appears to be small compared with the observed changes of the integrated intensity of the 851 cm.$^{-1}$ band. Furthermore, only small changes of the integrated intensity, of less than 10%, were found for the 1033 cm.$^{-1}$ allowed band, for the same solvents.

In benzene, finite absorption may arise from causes similar to those discussed by Mizushima and Bird, that is electrical distortion, or through distortion of the geometrical form of the normal mode under the influence of molecular collisions. The latter type of distortion may be described by saying that the inactive fundamental becomes mixed with an active vibrational mode. Thus admixture of either of the infrared active vibrational modes E_u^- or A_{2u} with the inactive modes E_g^+ and B_{2u} will confer activity on these, the A_{2u} out-of-plane hydrogen bending mode at 671 cm.$^{-1}$ being particularly effective as it gives rise to the strongest infrared absorption band in the benzene spectrum.

The importance of the electronic polarisability of the solvent in determining the intensity of the forbidden bands (Fig. 3) suggests that the major part of the intensity comes from distortion of the electron distribution rather than from change in the form of the vibrational mode. The high intensity of the 1174 cm.$^{-1}$ band in carbon disulphide solution discussed below almost certainly excludes the possibility that the intensity of this band arises mainly from distortion of the vibrational mode through admixture of E_u^-

---

[6] Chisholm and Welsh, *Canad. J. Phys.*, 1954, **32**, 291.
[7] Mizushima, *Phys. Rev.*, 1949, **76**, 1268; 1950, **77**, 150.
[8] Bird, *Physica*, 1951, **17**, 953.
[9] Chako, *J. Chem. Phys.*, 1934, **2**, 644.

character. The dependence of the band area on the solvent function $(n^2 - 1)/(n^2 + 2)V$ (or some similar function) might arise from a dependence on the product of the molar polarisation of the solvent $(n^2 - 1)V/(n^2 + 2)$ and $1/r^6$, where r, the molecular radius of the solvent molecules, is proportional to $V^{1/3}$, making the dependence of integrated intensity similar to that found by Mizushima [7] for the less complicated case of highly compressed symmetrical diatomic gases.

The integrated intensities of the forbidden bands are surprisingly large. Some approximate values are given below for the integrated absorption intensity A, defined by:

$$A = (2{\cdot}303/cl)\int \log_{10}(I_0/I)\,d\nu$$

where c is the concentration in moles/l., l the path length in cm., and ν in cm.$^{-1}$. $\pi/2$ times the product of peak density and half-intensity width has been used [10] as an approximation for $\int \log_{10}(I_0/I)\,d\nu$.

Integrated absorption intensities for the 851 *cm.*$^{-1}$ *band.*

Solvent	Carbon disulphide	Methylene bromide	n-Tetradecane
$10^{-2} A$	5·3 cm.$^{-1}$	2·0 cm.$^{-1}$	1·3 cm.$^{-1}$

The 1174—1148 cm.$^{-1}$ pair is most intense in carbon disulphide so that overlap from neighbouring bands is least troublesome in this solvent. Decomposition of the 1174—1148 cm.$^{-1}$ pair was effected on the basis of Lorentz-type band shapes [10] of equal half-intensity widths, and approximate integrated absorption intensities calculated as before for the 1174 cm.$^{-1}$ band. The integrated absorption intensity was also calculated for the 1033 cm.$^{-1}$ band for carbon disulphide solution, a small correction being made for the effect of finite slit width. Values of $10^{-2}A$ are: 1174 cm.$^{-1}$ band, 6·1 cm.$^{-1}$; 1033 cm.$^{-1}$ band, 15 cm.$^{-1}$. Because the forbidden 1174 cm.$^{-1}$ band is about three times as wide as the allowed 1033 cm.$^{-1}$ band, the absorption coefficients [defined as $(2{\cdot}303/cl) \log (I_0/I)$] of these two bands become about equal at frequencies 20—30 cm.$^{-1}$ from their respective band maxima. (On the high-frequency side of these bands, the experimental measurements on which these comparisons are based need only small corrections for overlapping of neighbouring bands; on the low-frequency side the comparison rests much more strongly on the reliability of the band shapes found to fit these bands.)

Little is known about the origin and variation of band widths in solution. The widths and shapes of liquid and solution bands probably depend on two main factors: first, the superposition of molecular librational energy changes on the main vibrational energy change, similar to the superposition of rotational energy changes on the main vibrational energy change which is responsible for vapour-phase band contours; and, secondly, perturbations of the energies of the vibrational levels caused by intermolecular forces. For one polyatomic molecule evidence for rotational changes in the liquid similar to those in the vapour has been obtained. Crawford *et al.*[11] examined the Raman spectrum of liquid methane and found wide bands without fine structure, the contours of which could be fitted to the vapour-phase band structures calculated for the same temperature if individual rotational lines were given widths of approximately 55 cm.$^{-1}$. (Individual rotational lines are 21·5 cm.$^{-1}$ apart in the wings of these bands so that at least a greater width than this was necessary to account for absence of rotational structure.) Crawford *et al.* also found greater relative intensity in the Q branch, suggesting that there was a higher proportion of vibrational changes without concomitant rotational changes in the liquid than in the vapour. However, for most substances liquid-phase bands are considerably narrower than the corresponding vapour-phase bands, and a wide variety of molecules, showing diverse rotational band contours, has been found to give bands approximating to a Lorentz band shape in solution or in the liquid phase. These facts suggest that

---

[10] Cf. Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

[11] Crawford, Welsh, and Harold, *Canad. J. Phys.*, 1952, **30**, 81.

rotation in solution or in the liquid is inhibited or replaced by librational motions and that the energetic contributions from the librational motions are random. This is a reasonable supposition for a molecule such as benzene which has moments of inertia more than twenty times larger than that of methane, with correspondingly greater periods of rotation, and for which the intermolecular forces, judged by heats of vaporisation, are 3—4 times larger than for methane. However it is also possible to account for the band widths by perturbations of the energies of the vibrational levels involved. This may be the major cause of the band width of the 1033 cm.$^{-1}$ band in benzene, which has, for a variety of solutions, an average half-band width of about 10 cm.$^{-1}$. This band is approximately half as wide again as the 1485 cm.$^{-1}$ band belonging to the same symmetry class. By analogy with rotation-vibration bands the effect on the vibrational band shape and width of superposed librational energy changes might be expected to depend mainly on the symmetry of the levels involved and only to a small extent on the other details of the vibrational modes, whereas if the disturbance of the vibrational levels by intermolecular forces is the major cause of the band width the effect would be expected to be bigger for the 1033 cm.$^{-1}$ band, the frequency of which is determined by the forces controlling the motion of the hydrogen atoms on the periphery of the ring, than for the 1485 cm.$^{-1}$ vibration the frequency of which is mainly determined by the forces controlling the motion of the more shielded carbon atoms.

Accordingly it will be assumed that in solution each vibrational mode differs slightly in its energy from molecule to molecule, that is, the molecules show a distribution of values depending on the perturbation momentarily affecting each molecule. For allowed bands the transition moment is probably very nearly constant for all but a very small fraction of the molecules contributing to the absorption band, as generally the frequency width of the band is small compared with its frequency. On these assumptions the band contour of allowed bands represents also the distribution of energy separations of the upper and lower vibrational states of the molecules. For forbidden bands it is clearly not permissible to assume that the transition moment is constant over the frequency range of the band, and the band area has a different meaning from that for allowed bands. These ideas can be applied to compare the half widths and intensities of the 1174 and the 1033 cm.$^{-1}$ band of benzene in CS_2 solution as follows. It seems reasonable to assume, from the similarity of the normal co-ordinates [5] that the distribution of the perturbations of the energy levels of these vibrations in solution will be approximately the same: that is, for both the 1174 and the 1033 cm.$^{-1}$ band approximately the same fraction of molecules will have their ground and their first excited vibrational level so perturbed that they give rise to a vibrational transition x cm.$^{-1}$ from their respective band maxima. If this is so, it follows from the near equality of absorption coefficients when x equals 20—30 cm.$^{-1}$ that the perturbed E_g^+ vibration has there a transmission moment nearly equal to the uniform value of the transition moment for the 1033 cm.$^{-1}$ vibration. On this interpretation, the greater width of the forbidden band springs, not from a greater perturbation of the vibrational states in solution, but from a transition moment that increases outward from the band maximum. Also the value of the variable transition moment for transitions giving rise to the major part of the intensity of this band is comparable with that for the allowed E_u^- band. In view of the relatively small changes of frequency involved (20—30 cm.$^{-1}$ from the band maximum) compared with the frequency separation (140 cm.$^{-1}$) of the 1033 and 1174 cm.$^{-1}$ bands, the major part of the intensity of the 1174 cm.$^{-1}$ band cannot be ascribed to admixture of E_u^- hydrogen bending character.

The plot of peak densities of the 851 and 1174 cm.$^{-1}$ bands against refractive index of the solvent is shown in Figs. 4 and 5. For the 851 cm.$^{-1}$ band the steep increase of peak density with refractive index is due to both the increase in band area and a decrease in half-intensity width with increasing refractive index. The peak densities of the 1033 cm.$^{-1}$ band increase rather similarly with increase in refractive index, but the value for carbon disulphide was in line with the other solvents. The steep increase of peak density was not continued for solvents of higher refractive index, *viz.*, bromoform and methylene iodide. The cause of this was at least partly that the band half-intensity widths for these solvents are too small compared with the spectral slit widths that could be used. For the 1033 cm.$^{-1}$ band the increase in peak density arose almost entirely from a corresponding decrease in half-intensity width.

Although the high values of the peak densities and band areas found for solutions of benzene in carbon disulphide suggest that some special interaction might be operative, the vapour-pressure data [12] show that such interaction, if present, must be small. The ultraviolet absorption spectrum of 10 μ layers of 1 : 4 and 4 : 1 solutions of benzene in carbon disulphide have been measured and no new bands such as might be expected if charge-transfer interaction were taking place were found at 2600—4000 Å. The authors are indebted to one of the Referees for indicating the need to consider the effect of librational motion on band widths.

THE QUEEN'S UNIVERSITY, BELFAST.

[*Received, November* 19*th*, 1956.]

---

[12] Hildebrand and Scott, "The Solubility of Nonelectrolytes," Reinhold Publ. Corp., New York, 1950, p. 215.