

The Far Infrared Absorption of Benzene

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The absorption of benzene has been studied from 40–135 μ under high resolution. Five weak bands, interpreted as difference bands, have been found in the liquid. The observations lend strong support to the plane symmetrical hexagonal model for benzene.

ALTHOUGH the infrared, ultraviolet and Raman spectra of benzene have been extensively studied¹ no general agreement yet exists concerning the equilibrium structure and vibrational states of this important molecule. Accordingly we have examined its absorption in the hitherto unexplored far infrared region (40–135 μ). The work of Shapiro, Gibbs and Johnson has demonstrated the existence of a low frequency vibrational interval (160 cm^{-1}) in the ground state of the molecule. If benzene has a structure of low symmetry this frequency, or one related to it, might appear in the far infrared spectrum as an active fundamental.

The spectrometer used has been described recently.²

In this investigation we first used a cell 3 cm length, with windows of crystal quartz 0.3 mm in thickness. When filled with benzene vapor at the saturation vapor-pressure at room temperature, no absorption was found from 40–110 μ . It was then filled with liquid benzene (Kahlbaum's thiophene free, carefully dried over sodium, but otherwise not further purified). Absorption was now practically complete in this region. Reduction of the layer of benzene to 3.5 mm thickness gave good relative transmissions throughout the region. The transmission curve is given in Fig. 1. The slit-width was 2 μ , and two points were taken per slit width. The absorption is seen to be fairly constant throughout the region, with no out-

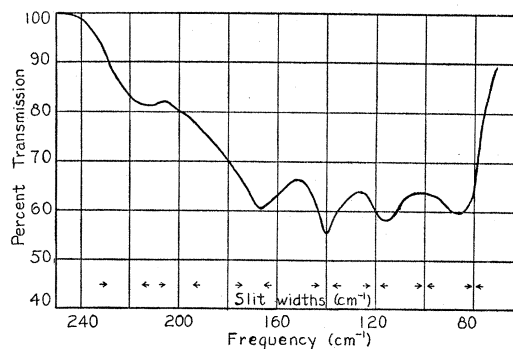


FIG. 1. Far infrared transmission of benzene.

standing structure, but with maxima at 87, 117, 140, 168 and 216 cm^{-1} . These maxima we interpret as Q branches of individual vibrational transitions and the remaining absorption as due to overlapping of the undefined P and R branches. Comparison with the results of Leberknight and Silverman, who worked with comparable resolving power in the near infrared, shows that this is the expected band structure in liquid benzene. In the vapor the P and R branches stand out more distinctly. It is, of course, not excluded that other weaker bands, in addition to the five named, may be present.

DISCUSSION

The absence of any absorption in the vapor, or with thin layers of liquid, would seem to prove the absence of a fundamental vibrational frequency in the region studied. A thickness of 0.01 mm of liquid is sufficient to give the fundamental band at 6 μ . Even after making allowance for the ν -factor in the expression for absorption intensities, our bands are seen to be associated with transitions 15–40 times less probable than the 6 μ fundamental. The number and irregularity of the bands observed precludes the possibility of

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¹ Infrared: Silverman, *Phys. Rev.* **41**, 486 (1932); Leberknight, *Phys. Rev.* **43**, 969 (1933); Kettering and Sleator, *Physics* **4**, 39 (1933).

Ultraviolet: Shapiro, Gibbs and Johnson, *Phys. Rev.* **38**, 1170 (1931); Kistiakowsky and Nelles, *Phys. Rev.* **41**, 595 (1932).

Raman: Grassmann and Weiler, *Zeits. f. Physik* **86**, 321 (1934).

Correlation: Dietz and Andrews, *J. Chem. Phys.* **1**, 62 (1933); Wilson, *Phys. Rev.* **45**, 706; **46**, 146 (1934).

Also references to earlier work therein cited.

² R. Bowling Barnes, *Rev. Sci. Inst.* **5**, 237 (1934).

their all being overtones or combinations of very low frequencies, as there can, on any reasonable choice of force constants, be only two such frequencies, associated with puckering of the benzene ring, and one of these is doubtless 160 cm^{-1} . Our bands must therefore be interpreted as difference bands; and the four strongest maxima are immediately seen to correspond each with the difference of a Raman and an infrared fundamental. Table I shows the assignment, the

TABLE I. *Assignment of frequencies.*

Raman	Infrared	Calculated	Observed
1605 $\left\{ \begin{array}{l} \nu_8 \\ \nu_1 + \nu_6 \end{array} \right\}$	1483 ν_{19}	122 101	117 87
1178 ν_{10}	1038 ν_{11}	140	140
849 ν_9	672 ν_{18}	177	168

frequencies being numbered following Wilson.

The agreement is satisfactory, particularly as the Raman frequencies have been observed in the liquid and the infrared in the vapor.

These results lend convincing support to Wilson's assignment of the frequencies on the basis of the plane symmetrical hexagonal model (symmetry group D_{6h}). The observed differences are in all cases allowed by the selection rules and no other allowed differences between observed frequencies would fall in this region. The following other differences, involving inactive Raman and infrared bands, whose approximate positions can however be calculated from Wilson's formulae, might appear in our region: $\nu_{12} - \nu_6$; $\nu_7 - \nu_{12}$; $\nu_5 - \nu_{17}$; $\nu_8 - \nu_{17}$; $\nu_8 - \nu_{14}$; $\nu_5 - \nu_{14}$. Of these, the first

two are most probable, involving the lowest frequencies. An assignment such as $\nu_{12} = 693$ would place both these bands in reasonable observed positions, 87 and 156 cm^{-1} but, lacking data of comparable accuracy on the weak combination bands in the nearer infrared, such assignments are risky.

On any model of less symmetry, the possible number of difference bands observable would be much greater: if there were no center of symmetry, differences of two Raman bands, such as $849 - 606 = 243$ would be expected to appear rather strongly; our data agree with the whole body of Raman and infrared data in excluding this possibility. If the ring is puckered (symmetry D_{3d} , as postulated by Dietz and Andrews) the number of possible differences is not prohibitively increased and this model might possibly be made to fit previously existing data. However, on this model the *ungerade* ring-puckering vibration (Wilson's ν_{16}) would be active. If the 160 cm^{-1} observed by Shapiro, Gibbs and Johnson is ν_4 , as seems highly probable,³ ν_{16} must lie in our region. There is a faint possibility that $\nu_{16} < 80\text{ cm}^{-1}$, but in that case $\nu_4 + \nu_{16}$ would fall in our region and should appear strongly. Hence the non-appearance of any band of sufficient intensity to qualify as a fundamental or first combination provides a decisive spectroscopic proof of the plane model for benzene.

³ If the *upper* state of the ultraviolet absorption system is puckered, all vibrational differences involving *gerade* puckering frequencies of the *lower* state may appear, according to the Teller-Herzberg selection rules, *Zeits. f. physik. Chemie* **B21**, 410 (1933); if both states are plane, only even overtones of the lower state fundamentals are allowed. Thus 160 may be ν_4 or, less probably in our opinion, $2\nu_4$.