60. *Structure of Benzene. Part XVI. Experimental Methods for Infra-red Spectroscopy. Note on the Infra-red Spectrum of Hexadeuterobenzene.*

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Preliminary experiments on the Raman spectra of partly deuterated benzenes having shown that, for many of these compounds, fundamental absorption bands were to be expected as far out in the infra-red spectrum as 27 μ, arrangements are described which were instituted to facilitate accurate observation in this long-wave region. Since the long wave (A_{2u}) band of hexadeuterobenzene, although observed, could not be satisfactorily measured in the work which was described in Part IV (1936), the opportunity was taken to repeat the measurement with the new experimental arrangements. The effect of the revision is to reduce the previously stated value of the vibration frequency, improving its agreement with the requirement of the product theorem.

This paper supplements the investigation of Part IV on the infra-red spectra of benzene and hexadeuterobenzene; it also introduces, in their experimental aspect, following papers on the infra-red spectra of certain partly deuterated benzenes.

Bailey, Hale, Ingold, and Thompson studied the infra-red absorption spectra of benzene and hexadeuterobenzene over the complete range of the fundamental vibration frequencies which, for these molecules, are active in the infra-red spectra (Part IV, J., 1936, 921). The prism spectrometer with which the work was done was originally arranged to cover the wave-length interval 1—19 μ, by the use of interchangeable prisms of quartz, fluorite, rock-salt and sylvine. However, with only these four optical systems, difficulty arose over the infra-red parallel band due to the in-phase, out-of-plane, bending vibration of the six hydrogen atoms. In benzene itself this vibration, A_{2u}, has the frequency 671 cm.$^{-1}$, and its infra-red band, in the region of wave-length 15 μ, is readily studied. In hexadeuterobenzene, however, the frequency is lower, and the wave-length is outside the range of the optical systems mentioned. By the substitution of a potassium bromide prism, the A_{2u} band of hexadeuterobenzene was observed around wave-length 20 μ, but it could not be accurately measured because satisfactory optical details had not at that time been worked out. The vibration frequency was given as 503 cm.$^{-1}$, but the difficulty of the measurement was noted. Therefore one of our motives in developing more suitable arrangements for extending the range of spectroscopic observation to beyond the original upper limit of wave-length has been the desire to make more satisfactory observations on the A_{2u} band of hexadeuterobenzene, thus rounding off the experimental work of Part IV. A re-investigation of the band is recorded in this paper.

Our work on partly deuterated benzenes was begun by an examination of Raman spectra; and these spectra at once showed that all benzenes must possess at least one outstandingly low frequency, which, when allowed in the infra-red spectrum, will lie well below the lower limit of possible frequency measurements with our original infra-red equipment. The vibrations concerned were identified as those derived from the non-trigonal, out-of-plane, bending vibration of the carbon ring of benzene (Bailey, Best, Gordon, Hale, Ingold, Leckie, Weldon and Wilson, *Nature*, 1937, **139**, 880; Ingold, *Z. Elektrochem.*, 1938, **44**, 20). For some benzenes the frequency of this vibration can only be observed in the infra-red spectrum; and it was evident from the measured Raman frequencies of other benzenes that the infra-red frequencies we should then have to determine are to be expected near 370—380 cm.$^{-1}$, corresponding to the wave-length region 26—27 μ. This is within, though only just within, the limit of long wave-length attainable by the use of a potassium bromide optical system, and the need to measure these bands provided our second motive for developing the use of this system.

Our spectrometer is a constant-deviation instrument, which is employed as a monochromator, the wave-length of the radiation emerging from the exit slit being controlled by a wave-length drum geared to the rotating prism table. It is possible to use all the prisms with the same prism table and wave-length drum when the readings of the latter have been correlated with wave-length for each prism. It is also possible to set each prism, except the potassium bromide prism, by means of visible light. The method is to set the prism at minimum deviation by means of a special jig, turn the drum to a reading corresponding to the wave-length of, say, the mercury green line, replace the Nernst filament temporarily by a mercury lamp as source of radiation, and then rotate the Wadsworth mirror within the spectrometer until the green light emerges from the exit slit; but with the potassium bromide prism this procedure is impossible owing to the fact that, when this prism is in position, the lowest reading on the drum corresponds to a wave-length in the infra-red. Attempts to set the prism by locating known infra-red bands, using the thermopile in place of the eye as detector, were unsatisfactory, and the following indirect method was therefore devised.

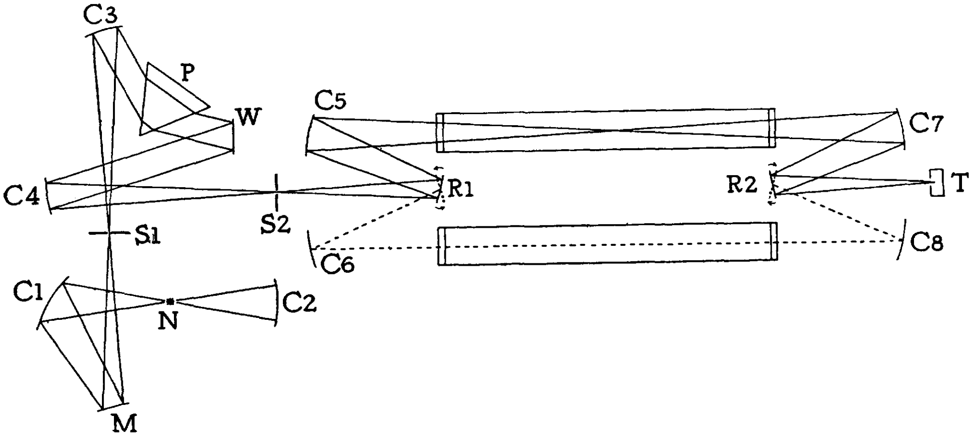
The drum was set at the reading 11·95, corresponding, for the potassium bromide prism, to a wave-length of 26·55 μ. From tables it can be ascertained that radiation of this wave-length is deviated by 31° 46′ 22″ on passing through a potassium bromide prism, of angle 60°, set at minimum deviation. The fluorite prism was then inserted, and set, not with its own jig, but with the jig belonging to the potassium bromide prism. This fixes the incident light on the prism at an angle of 48° 21′ 22″, and it can easily be calculated that the wave-length of radiation, which, if incident on the fluorite prism at this angle, would be deviated by 31° 46′ 22″, is the wave-length of the mercury green line. Therefore, with a mercury lamp illuminating the entrance slit of the spectrometer, the Wadsworth mirror was turned until the green line emerged from the exit slit. The fluorite prism was then removed, and the potassium bromide prism inserted. The values recorded by Korth (*Z. Physik*, 1933, **84**, 677) for the refractive index of potassium bromide were used to calculate the calibration curve connecting drum reading with the wave-length of the emergent radiation given by the potassium bromide prism.

In regions of comparatively long wave-length, the main difficulty with a spectrometer of the type of ours is to concentrate sufficient radiation on the detecting apparatus. In our apparatus the radiation was received on one of a pair of 20-junction, silver–bismuth thermopiles, coupled in opposition, and connected to a sensitive Zernicke galvanometer, the deflection of which (1 mm. at 1 m. = 10^{-11} amp.) was magnified by means of a photo-relay operating a second similar galvanometer. To some extent, the falling off with increasing wave-length of the energy in the spectrum of a hot filament can be countered by utilising the circumstance that for larger wave-lengths the slit-width can be increased without loss of resolving power. However, full advantage could not at first be taken of this fact, because, with our original arrangement, radiation from either of two alternative directions became received obliquely by the thermopile, the guards and containing gas-tight case of which limited the size of image which could thus be focussed on the thermo-elements. Under the restriction imposed by this oblique focussing the galvanometer deflections were so small as to be quite unreliable for wave-lengths of 25 μ and greater.

The focussing system was accordingly modified to the form shown diagrammatically in Fig. 1. Radiation from the source *N*, focussed by the plane mirror *M* and the concave mirrors *C*1 and *C*2 on the entrance slit *S*1, after collimation by the concave mirror *C*3, refraction by the prism *P*, reflection by the Wadsworth mirror *W*, and focussing by concave mirror *C*4, emerges as a monochromatic beam from the exit slit *S*2, and is then deflected by a rotatable, plane mirror *R*1 towards either of two collimating concave mirrors *C*5 and *C*6. Two similar absorption cells, with potassium bromide end-plates, one cell evacuated, and the other containing the vapour of the substance to be studied, are in the paths of the alternative collimated beams. The alternative beams, after passing through the cells, are focussed by concave mirrors *C*7 and *C*8, and the focussed beams are then directed normally on the thermopile *T* by a properly oriented, rotatable, plane mirror *R*2. With this arrangement we were able to carry the measurements up to about 27 μ, the limit to which the refractive index of potassium bromide is accurately known.

FIG. 1.

General arrangement of apparatus.



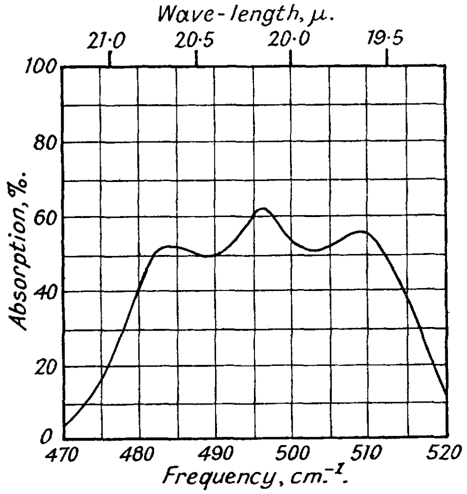
KEY
N = *Nernst filament.*
M = *Fixed plane mirror.*
W = *Wadsworth mirror.*
P = *Prism.*

C1 *to* C8 = *Concave spherical mirrors.*
R1, R2 = *Rotatable plane mirrors.*
S1, S2 = *Slits.*
T = *Thermopile.*

As a check upon the setting of the prism, the calibration of the drum, and the general accuracy of observation, Dennison and Wright's measurements on the long-wave fundamental band of carbon disulphide (*Physical Rev.*, 1931, **38**, 2077) have been repeated. These authors located the main intensity maximum of the band at wave-length 25·2 μ, corresponding to frequency 396 cm.$^{-1}$, whilst, with satisfactory consistency, we find wave-length 25·1 μ, corresponding to frequency 398 cm.$^{-1}$.

FIG. 2.

The A_{2u} band of hexadeuterobenzene.



Length of cell = 45 *cm.*
Vapour pressure = 0·8 *cm.*

Infra-red Spectra of Benzene and Hexadeuterobenzene Vapour from 19 μ to 27 μ. The A_{2u} Fundamental Band of Hexadeuterobenzene.

The infra-red specta of these substances as vapour were examined over the range of wave-length stated. In the spectrum of benzene no bands were found within this range. The spectrum of hexadeuterobenzene showed the already known, strong band around wave-length 20 μ; but no other bands were found in the region studied.

The contour of the 20 μ band of hexadeuterobenzene has been re-examined, using an absorption tube, 45 cm. long, containing the vapour at various pressures less than 1 cm. The band exhibits a prominent Q-branch, as well as P- and R-branches of the usual form, as is shown in Fig. 2. Numerical particulars relating to the observed intensity maxima are as given in Table I.

The separation of the rotational branches of this band shows it to be of the parallel type. The PR-separation calculated for a parallel band from the atomic masses and molecular geometry of hexadeuterobenzene is approximately 24 cm.$^{-1}$, and the observed PR-separation confirms the assignment of the band to the only fundamental vibration of the molecule, the vibration A_{2u}, which should produce a parallel band in the infra-red spectrum.

TABLE I.

The A_{2u} Fundamental Band of Hexadeuterobenzene.

Branch.	Wave-length, μ.	Frequency (cm.$^{-1}$).	% Absorption (l = 45 cm.; p = 0·8 cm.).	PR-separation (cm.$^{-1}$).	Vibration frequency (cm.$^{-1}$).
P	20·68	484	51	25	496·5
Q	20·14	496·5	62		
R	19·63	509	56		

The corrected vibration frequency, 496·5 cm.$^{-1}$, when correlated with the well-established frequency of the corresponding vibration of ordinary benzene, 671 cm.$^{-1}$, gives a much improved agreement with the requirements of the product theorem of Teller and Redlich :

$$\frac{\Pi\, A_{2u}(C_6H_6)}{\Pi\, A_{2u}(C_6D_6)} = \frac{671}{496\cdot5} = 1\cdot351 \text{ (harmonic value } 1\cdot362)$$

The calculated value is derived on the assumption that the forces are strictly harmonic, and, since the usual effect of anharmonicity is to reduce the value of the ratio, the agreement between the found and calculated ratios can be considered satisfactory.

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