59. *Structure of Benzene. Part XV. Experimental Methods for Raman Spectroscopy, including a Micro-method. Revision of the Raman Spectrum of Hexadeuterobenzene.*

By Harry G. Poole.

A general account is given of the methods of Raman spectroscopy which have been applied in the work recorded in this group of papers. A number of developments in technique are described, including an optical system which reduces, by a factor of the order of 20, the quantity of (liquid) experimental material necessary in order to secure a given spectroscopic speed. Using 0·3 c.c. of hexadeuterobenzene, the fundamental Raman frequencies of this molecule have been determined with a probable accuracy of $\pm$ 0·2 cm.$^{-1}$; and a revised list of the higher harmonic frequencies has been prepared, which corrects a number of errors or omissions in the published data.

(1) *Introduction.*

THE Raman spectra of partly deuterated benzenes have been previously studied by Redlich and Stricks (*Monatsh.*, 1936, **67**, 213; **68**, 374) and, considerably more fully, by Langseth and Lord (*Kgl. Danske Vidensk. Selsk.*, 1938, **16**, 6). The present investigations of Raman spectra of deuterated benzenes have already been partly summarised (*Nature*, 1935, **135**, 1023; 1937, **139**, 880; *Z. Electrochem.*, 1938, **44**, 20). They include a

re-examination of the Raman spectrum of hexadeuterobenzene. Certain factors of experimental method, to which considerable attention has been paid, will, it is hoped, have contributed to a relative freedom from errors.

The first is the use of isotopic isomerides of a high standard of purity. Neither Redlich and Stricks nor Langseth and Lord had at their disposal very pure material. They dealt with the situation by discounting any observed frequencies which might have been due to an isotopic impurity. However, the spectra of most of the partly deuterated benzenes are so rich, and the possibilities of approximate coincidence between frequencies of different isotopic forms are so real, that this procedure is not a safe one : an observed and quite authentic frequency may become rejected because its agreement with a frequency of some impurity renders its origin uncertain. The avoiding of this difficulty by the preparation of isomeric benzenes of a high degree of isotopic purity is the central importance of the work described in the three immediately preceding papers.

The other experimental factors are discussed in this paper. One relates to the use of an optical system of relatively high resolving power. The so-called " lines " of a Raman spectrum are vibration-rotation bands of considerable spectroscopic width, and the difficult problem of establishing weak lines which are largely overlapped by strong ones, or of making as sure as possible that such overlapped lines are absent, occurs frequently in the spectra of the partly deuterated benzenes. In most of them also, we find strongly overlapped pairs of lines of nearly equal intensity, and the distinguishing of the resultant photographic effect from that of a single broad line sometimes requires a detailed study of the densitometric contours. Both types of problem necessitate apparatus of considerable resolving power.

Angus, Ingold, and Leckie examined the Raman spectra of benzene and hexadeuterobenzene with the aid of a Hilger E 390 spectrograph (Part III, J., 1936, 925). The dispersion of this standard instrument is adequate, but its limited light-collecting power compels the use in Raman spectroscopy of slit widths great enough to entail a heavy sacrifice of resolving power. Even so, the instrument can cope fairly satisfactorily with the relatively simple spectra of the highly symmetrical benzenes previously studied. But a preliminary survey with the same equipment of the Raman spectra of the less symmetrical, partly deuterated benzenes convinced us that a number of important details in these much richer spectra remained undisclosed. Therefore Messrs. Adam Hilger Ltd. constructed a special spectrograph providing a much increased light-collecting and resolving power. In this connexion we thank Dr. J. W. Perry, who calculated the optical system, for his expert co-operation. This spectrograph and the ancillary apparatus, as well as the general method of working, are described in Section 2.

Another point of method on which we lay stress is the use of filtered light. Like most previous investigators we have used the light from mercury lamps for excitation, and, as many others have done, we have consistently employed filters. These included the usual filters, aqueous sodium nitrite, and iodine dissolved in carbon tetrachloride ; but we have also used other filters (Wood, *Physical Rev.*, 1930, 36, 1421), including the praseo-dymium and cobaltammine filters specified later, for helping to clear the spectra of unwanted radiation, coming either from the lamps or from the scattering substance (cf. Section 2).

Differential filtration of the two principal exciting lines, Hg 4046·56 A. and Hg 4358·34 A., is of great importance in our view, the added certainty thus conferred on the analysis of the spectra being well worth the cost in diminished light intensity and lengthened exposures. As an example we cite the investigation of 1 : 4-di-deuterobenzene by Langseth and Lord, who used unfiltered light. This is almost certainly the reason why they recorded (as a fundamental) a frequency, 1167 cm.$^{-1}$, which does not exist, and missed another (fundamental) frequency, 1309 cm.$^{-1}$, which does : in both cases there is overlap with independently excited frequencies.

In the Raman spectra of most partly deuterated benzenes a number of the active fundamental frequencies appear in pairs, as closely overlapped " lines " of similar intensity, the components of which cannot (or can scarcely) be resolved, still less measured with accuracy, by visual observation. For the analysis of these doublet lines, and many complicated, much-overlapped line-groups, a detailed microphotometric study is essential; and since the grouping in close pairs of certain fundamentals is so characteristic a result of non-trigonal deuterium substitution, a detailed microphotometric study has been made of all the stronger Raman " lines," and certainly of every " line " in which multiplicity was suspected. An illustration of the evidence by which multiplicity was established when it was hardly possible to pick out the separate intensity maxima in the plates is given in Section 2.

Certain of the samples of benzene were too small for satisfactory use in the conventional Wood's tube. Almost the whole laboratory stock of pure hexadeuterobenzene had been sent on loan to the United States of America, and had met with an accident during its travels, with the result that only 0·34 g. remained. A similarly unusual occurrence had reduced our stock of pure pentadeuterobenzene to about 0·9 g. The task of preparing these compounds at the necessary standard of isotopic purity is a very tedious one, and it was decided that the object of the investigation would be more expeditiously attained by developing an optical method for small quantities, than by undertaking the preparation of additional specimens. A new optical method, suitable for quantities of the order of those mentioned, has been developed, and is described in Section 3. It consists essentially of a special cell and an associated optical system, which together enable the cell-contents to provide, from incident light, an amount of useful scattered light that could be obtained only from about 20 times the quantity of substance by means of the usual arrangement.

Finally, in Section 4 a revision of the Raman spectrum of hexadeuterobenzene is recorded. The study of this spectrum could not be left as it had been by Angus, Ingold, and Leckie in Part III (J., 1936, 925) for two

reasons. First, a much greater accuracy could be achieved, with the present methods and apparatus, in the determination of the frequencies of the principal lines than was possible in the earlier investigation : it seemed desirable to raise the study of the Raman spectrum of hexadeuterobenzene to the same standard of precision as that of the spectra of the partly deuterated benzenes. Secondly, the conviction had been growing that the earlier list of weak frequencies contained a number of errors requiring correction, and it was clear that, with the better apparatus and the additional experience, a completely reliable list could be prepared, such as it is essential to have for the purpose of determining the inactive fundamental frequencies of hexadeuterobenzene (Part XXI, this vol., p. 316). Incidentally, the low fundamental frequency of the forbidden E_u^+ class, which could only very doubtfully be distinguished in Angus, Ingold, and Leckie's investigation, was now satisfactorily observed.

(2) *General Methods.*

(a) *Spectrograph.*—A Hilger three-prism glass spectrograph was employed, which was especially designed to have large light-gathering and resolving power. The three prisms were each 11·5 cm. high, the lengths of their refracting faces were 18, 18·5, and 18·5 cm., and those of their bases were approximately 17, 18, and 18·5 cm., respectively. The total deviation produced by the three prisms approached 180°; and the spectrum came to a focus approximately normally to the axis of the camera. The aperture of the collimator lens was about $F/5·5$, and of the camera lens $F/2·2$.

The spectrograph was kept in a thermostated room at 18·6°. It was accurately focussed over the region 4780—4120 A. In this range the dispersion varied from 68 cm.$^{-1}$/mm. at 4130 A. to 134 cm.$^{-1}$/mm. at 4760 A.

The effect of slit-width on intensity and resolving power has been worked out for sharp lines (Schuster, *Astrophys. J.*, 1905, **21**, 197). The "normal" slit, of width $f\lambda/4D$, where f is the focal length and D the diameter of the collimator lens, gives almost the same resolving power as an infinitely narrow slit. On increasing the slit-width, the intensity increases at first rapidly and later more slowly, whilst the resolving power drops at first very slightly but later more rapidly. With a slit-width of 3·67 times the normal, the resolving power is one-half of the maximum, and for sharp lines a further increase of slit-width does not yield any substantial increase of intensity. However, all vibrational Raman lines spread over several wave-numbers, and for these the slit-width beyond which no increase in intensity occurs is considerably greater. The normal slit-width for this spectrograph at 4500 A. is 0·0006 mm., so that for sharp lines a maximum of intensity would be closely approached by a slit-width of 0·0022 mm. For Raman lines we used a slit-width of 0·0125 mm.

For calibration purposes a series of iron-arc spectra, some with superposed mercury spectra, were photographed. We used Hg 4347·50 A. as origin for distance measurements on the plates. The weaker Hg 4343·64 A. was found to be a convenient secondary origin. Fifteen iron lines, from 4134·681 to 4736·780 A. inclusive, were selected as fixed points for interpolation, and their distances from Hg 4347·50 A. were measured to 0·002 mm. They were used in overlapping sets of three to calculate the constants of Hartmann formulæ, valid to 0·002 mm., for the several spectral regions, and the formulæ were then employed in the construction of a graph (scale, 1 mm. = 0·2 cm.$^{-1}$, 1 mm. = 0·002 mm.) connecting wave-number with distance on the plate from Hg 4347·50 A. An iron-arc spectrum was put on every Raman plate, so that the calibration could be checked when desired.

The specimen, normally about 6 c.c., was enclosed in a Raman tube of the type introduced by Wood. The tube was charged by non-ebullient distillation in a vacuum from phosphoric oxide, and sealed. The specimen naturally had to be cooled for the sealing, and there was danger that, as the frozen material became warm again the window of the tube would be cracked by the expansion. To avoid this, the carbon dioxide freezing mixture was placed only round the top part of the specimen, which was afterwards thawed carefully from the top downwards.

The tube was set vertically on a total-reflexion prism in front of the slit. Liquid light filters were kept in annular vessels co-axial with the Raman tube. One or two mercury lamps were used for illumination, the effective intensity of which was increased by means of mirrors. A forced draught kept the apparatus cool, and removed the formed ozone.

(b) *Filters.*—For the selective removal of Hg 4046·56 A. we used, as is usual, a 1 cm., or 2 cm., thickness of saturated sodium nitrite. Rough absorption measurements showed that 1 cm. transmits about 2% of Hg 4046·56 A., about 10% of Hg 4077·8 A., and about 75% of Hg 4358·34 A. For reducing the intensity of Hg 4358·34 A. we employed Wood's filter, a 1-cm. thickness of a saturated solution of iodine in carbon tetrachloride; but as this filter transmitted only about 10% of Hg 4046·56 A., the exposures had to be considerably lengthened. The continuous radiation from the lamps was reduced, where desirable, by a 1-cm. thickness of a concentrated aqueous solution of praseodymium chloride or of an M/20-aqueous solution of cobaltic chloride in excess of ammonium thiocyanate. The former filter is very effective between 4400 and 4520 A. and is of some value on the long-wave side of 4630 A. The latter is mainly useful on the long-wave side of 4500 A. The praseodymium filter transmits almost 100% of Hg 4046·56 A. and about 80% of Hg 4358·34 A. The cobalt filter transmits roughly 50% of each of these lines. Fluorescent products of photochemical decomposition, formed within the Raman tube, were another source of background in the spectra. This trouble was avoided by removing the chemically active light by means of a sheet of Crookes's glass A, which transmitted about 60% of Hg 4046·56 A. and about 75% of Hg 4358·34 A. When a nitrite filter was used, this glass filter was unnecessary.

Most of the spectrograms were taken on Ilford Special Rapid plates, previously sensitised by means of mercury vapour. Measurements were carried out with a microscope reading to 0·001 mm.

(c) *Microphotometer.*—Only some Raman lines are suitable for direct measurement; others are too broad or too weak; or their structure is complex, and the eye is no adequate judge of the maxima of their components. In these cases it is necessary to determine frequencies from microphotometer records.

A Zeiss recording microphotometer was used for this purpose. A section of the spectrum to be examined was illuminated, and a cross-section, never more than 0·04 mm. wide and often narrower, was selected, after magnification, by a slit. The light passing this slit fell on a photo-cell, the output of which was fed to the fibre of a Wülf unifilar electrometer. As the spectrogram was slowly moved by a motor-driven mechanism past the slit, the movement of the fibre was recorded photographically. The magnification ratio, *i.e.*, the ratio of the dispersion on the record to that on the spectrogram, was variable, being governed by an adjustment on the transmission arm linking the motion of the table bearing the Raman plate with the motion of the record-holder.

In the examination of doublets or more complex line-groups, the microphotometer slit-width had often to be set by trial, sometimes without much permissible margin of deviation from the optimum, so that it would be fine enough to cope with the problem of resolution in hand, and yet not so fine that a real resolution would be masked by fluctuations of photographic density due to the finite size and random distribution of the developed grains of the plate. The technique by which some of the more difficult resolutions were effected is illustrated by the four microphotometer records, printed together in Fig. 1, of the doublet representing the nearly degenerate, planar ring-bending vibration of 1 : 4-dideutero-benzene. The separation of the maxima amounts to 4·3 cm.$^{-1}$, and the only record, of the four shown, which could be

used in the measurement of this value (*i.e.*, which had *both* maxima sharp) is that taken with a microphotometer slit-width equivalent to a spectral width of 2·1 cm.$^{-1}$.

For recording, Kodak Recording Paper R.P.15 was used. This showed a practically uniform shrinkage of about 0·4% on processing. Errors in frequency measurement due to irregularity in the shrinkage of recording paper did not exceed 0·05 cm.$^{-1}$, and were therefore negligible. Two methods were employed for the evaluation of the frequencies of Raman lines from microphotometer records. In the first, at least two " key " lines, which had been accurately measured directly on the plate, had to be included in each magnified record. Measurement of these lines on the record gave the magnification ratio (relating to distances on the processed record), by means of which the distances from these lines of any others measured on the record could be converted into corresponding distances on the plate, thence into distances on the plate from the zero-line of the calibration, and thence into wave-numbers; a cathetometer was used for the measurement of records. A second and better method of evaluation was devised, which could be used even if only one key line, accurately measured on the plate, were included in each magnified record. For this method, each record was

FIG. 1.

Spectral width of photometer slit (cm.$^{-1}$).

4·2

3·1

2·1

1·6
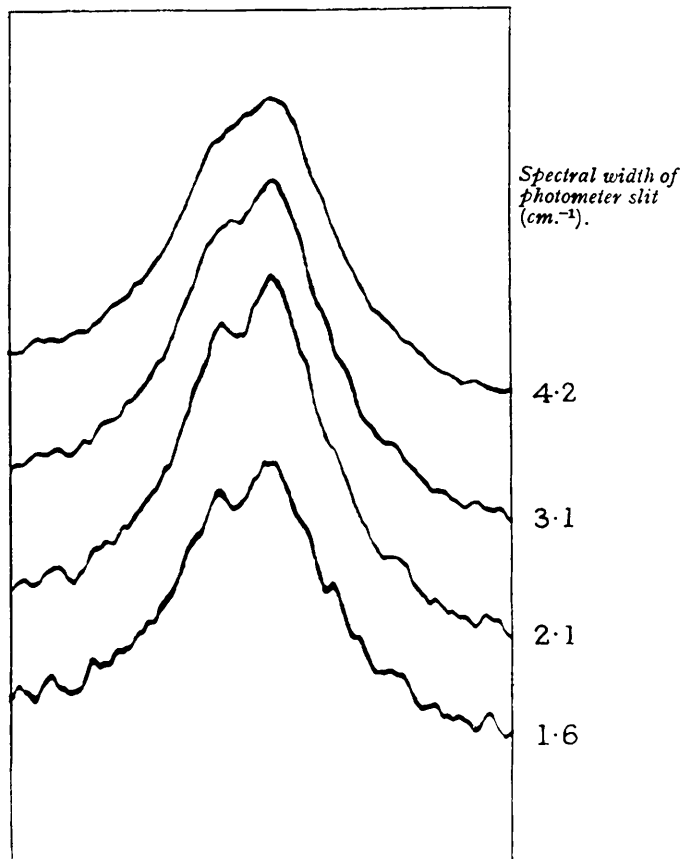
Resolution of the Raman doublet 596·6/600·9 cm.$^{-1}$ of 1 : 4-dideuterobenzene. The best microphotometer slit-width corresponds to a spectral width of 2·1 cm.$^{-1}$. With wider slits the resolution is incomplete, and with narrower slits it is overlaid by effects due to the granular structure of the photographic image.

over-printed with a grid of known dimensions, thus enabling a shrinkage correction factor to be determined. Distances (relating now to the unprocessed record) from a single reference line were then readily obtainable by measurement and correction of only the short distances from the nearest grid marks; the shrinkage corrections were thus reduced to values corresponding to about 0·2 cm.$^{-1}$ on the average, *i.e.*, just on the threshold of significance. The magnification ratio (also relating to the unprocessed records) was determined by taking, with the same setting of the transmission arm, a similarly over-printed record of a calibrating graticule. Hence the distances on the plate could be determined, and converted by the usual stages into wave-numbers.

The final preferred technique involved the measurement of even the key lines by this second method, thus entirely obviating the use of the microscope. Each key line was now included in the records of two adjacent regions of the spectrum, so that their distances from the zero line were obtained successively by summation. The spectrum was usually covered by four records. The longer distances were thus affected slightly by the accumulated errors of successive measurements, but this is more than offset by the greater certainty of location of the intensity maxima. This method was used in the re-examination of the hexadeuterobenzene spectrum described below.

(3) *Method for Small Quantities.*

(a) *Principles.*—The nature of the method by which the economy of material is effected will first be explained by means of the following simplified comparison with the procedure followed when quantities of the order of

6 c.c. are available. In this case a Wood's tube was employed. A cylindrical body of liquid is thus illuminated, but the useful scattered light comes from within the frustrum of a cone, whose apex is at the slit and whose apical angle is fixed by the aperture of the collimating lens of the spectrograph (Fig. 2a). This was about

FIG. 2a.

Wood's tube system (diagrammatic).
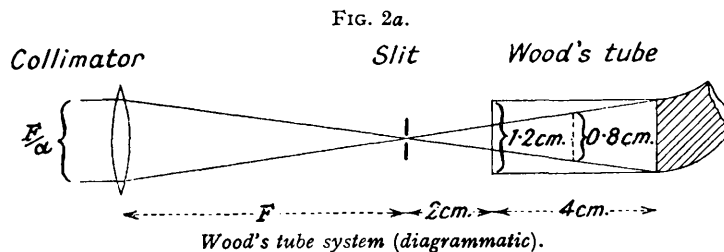
$F/5\cdot5$, but, since its value was not very exactly known, we assumed $F/5\cdot0$ (in order to be safe) when calculating cell dimensions (below). Owing to the reflecting prism, and for other optical and mechanical reasons, the optical distance of the slit from the end of the illuminated cylinder nearest the slit was about 2·0 cm. The cylinder itself was usually about 4·0 cm. long. The assumed aperture then determines the minimum diameter of the cylinder, 1·2 cm., necessary to include the whole of the frustrum. The illuminated cylindrical volume is 4·5 c.c., but, of course, an additional 1—1·5 c.c. of liquid is required to fill the bend in such a Wood's tube. If $I dv d\Omega$ is the amount of light scattered within a solid angle $d\Omega$ from an element of volume dv, the amount of useful scattered light coming from a circular slice of the cylinder, of thickness dL, is easily shown to be $\pi I hw dL/4\alpha^2$, where h and w are the height and width of the slit, and F/α is the aperture (assumed $\alpha = 5\cdot0$). Thus circular slices, if of constant thickness, independently of their position, make the same contribution to the total useful light $\pi I hw L/4\alpha^2$, which accordingly is directly proportional only to the *length* of the cylinder, provided that it is wide enough to include the whole of the frustrum. The amount of useful scattered light provided by a slice of constant thickness will come from a greater or smaller part of that slice, depending on its position. Thus if the slice is taken in the middle of the illuminated cylinder the useful scattered light will emanate from a central portion 0·8 cm. in diameter.

Now consider the effect of interposing between the slit and the cell a lens of sufficiently large aperture to pass all light that can be accepted by the collimating system, the cell being displaced to such a position that if the slit were a source of light its image would be found in the centre of the cell (Fig. 2b). Let H and W be

FIG. 2b.

Micro-system (simplified illustration).
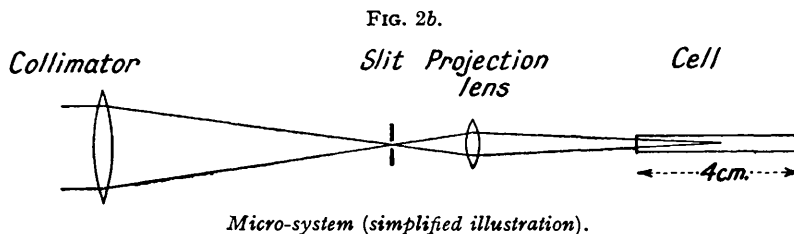
the height and width of this image, and consider once again a central slice of thickness dL. The only portion of this slice which contributes useful scattered light will now be the portion of area HW, and thickness dL, marked out by the geometrical image of the slit. It can easily be shown that the amount of the useful scattered light contributed by this portion, and therefore by the whole slice, is $\pi I hw dL/4\alpha^2$—exactly the same as in the system with the Wood's tube and without the lens. But now all this light comes from a much smaller volume; for, with a slit of any ordinary dimensions, the area HW will be much smaller than that of a circle of diameter 0·8 cm. This consideration permits a reduction in the area of cross-section of the cell, without any loss of useful light. The optimal shape of cross-section, from the point of view of economy, will not now be a circle, but a tall, narrow rectangle.

Actually, the cross-sectional dimensions of the cell must be greater than H and W, because, if the centre of the cell is focussed on the slit, other cross-sections will not be so focussed, and allowance must be made for material which, though out of focus, could supply some light to the slit. And rays from the focussed section must be allowed to diverge sufficiently to flood the effective aperture of the lens. In a quantitative calculation, refraction at the front window of the cell has also to be taken into account.

In Fig. 2c, the arrow marked $w/2$ represents half the slit-width. In air, its geometrical image, of length $W/2$, formed by a projection lens of focal length f and effective diameter d, distant v from the slit, would lie at Z, distant u from the lens and x from the front surface of the cell contents; but refraction by the cell contents, of refractive index u, displaces the image to Z', the mid-point of the cell, of internal length L'. Now let the arrow $W/2$ be regarded as the object, and let m be the magnification factor (less than unity) for the formation of its image at the slit by the projection lens (which will here be treated as a thin lens). We have $v/d = \alpha$ (taken as 5·0); also $L'/2x = \mu$; and $m = w/W = v/u$; also we have the thin-lens formula $v = f(1 + m)$.

Part of the necessary width of the cell is W.   The other part is twice the distance marked $a/2$ in Fig. 2c, and this is given by the geometrical relation $a/(W + d) = x/u$.   Eliminating u, v, and d from amongst these equations,

FIG. 2c.

Micro-system (optical diagram).

we may express the minimum permissible width, $W' = W + a$, of the cell in terms of the focal length and magnification factor as follows :

$$W' = w\left\{\frac{1}{m} + \frac{L'}{2\mu f(1 + m)}\right\} + \frac{L'm}{2\mu\alpha}.$$

In practice the term independent of w is the more important.   A similar formula gives the minimum height of the cell,

$$H' = h\left\{\frac{1}{m} + \frac{L'}{2\mu f(1 + m)}\right\} + \frac{L'm}{2\mu\alpha},$$

but in this case the term proportional to h is the more important.

The interior of the cell is represented in Fig. 2d, showing the region from within which comes all of the useful scattered light.

(b) *Cell Construction.*—Several cells based on these principles were built,* and more than one lens was employed.   Particulars will be given of the system used for hexadeuterobenzene.

It should first be explained that, owing to the slight curvature in the spectral lines, we never used a greater

FIG. 2d.

Interior of cell (diagrammatic).

length of line than 0·7 mm. for the taking of microphotometer records.   In order to utilise to the best advantage the small amount of hexadeuterobenzene available, it was now arranged to produce spectral lines only 0·6 mm. long, and this necessitated a slit-length, h, of 1·2 mm.   The cell dimensions were calculated for this slit-length, and for a slit-width, w, of 0·0125 mm.   The projection lens employed had an aperture $F/3\cdot1$ (more than sufficient for the purpose), and a focal length of 54 mm.   The optical system was arranged to give the magnification factor $m = 1/5$.   The length of the cell, the dimension on which the intensity of the useful scattered light essentially depends, was planned to be 40 mm., the same as the cylindrical length illuminated in the Wood's tubes which were employed when sufficient material was available.   The refractive index, μ, of the cell contents was taken as 1·5.   The above equations then gave $W' = 0\cdot60$ mm. and $H' = 6\cdot8$ mm.   The cell was actually constructed to be slightly wider and taller, in order to leave some latitude for error in lining up.   Its width, as measured after construction, was 0·84 mm., its height 8·32 mm., and its length 39·4 mm.   Its internal volume was thus 0·28 c.c.

The cell was made of silica, the joints being welded.   Two clear silica plates, 4·5 mm. thick, were prepared to form the vertical sides of the cell.   They were separated by spacing strips of silica ground to the correct thickness (0·83 mm.).   The strip along the bottom was continuous, whilst the two upper strips left a central gap (Fig. 3a).   The assembly was then sealed externally with the blowpipe along the strips at the top and bottom of the cell.   Next the silica filling tube, the end of which had been thickened and ground flat, was sealed on externally over the gap between the upper spacing strips.   Finally, front and back plates, also 4·5 mm. thick, and optically flat and polished, were prepared and sealed on.   When sealing on these plates a slight positive pressure was maintained in the cell (with the aid of the already attached filling tube) in order to prevent any silica vapour from entering and condensing on the important interior optical surfaces.   One of the large side plates

* The first was made, to specification, by Adam Hilger, Ltd., of silica by adhesion.   Later, it was found quite easy (and much speedier) to make one's own cells of silica by welding.

was then silvered on the outside in order to increase the intensity of irradiation, whilst those remaining parts of the external surface through which light was not intended to pass were blackened.

(c) *Mode of Operation.*—Since the introduced hexadeuterobenzene had to be frozen at a low temperature in order to permit the final sealing of the filling tube, and since the material, if frozen in the cell itself, could scarcely have been thawed again without breaking the cell, a bulb, several times larger than the sample (0·33 c.c.), was attached to the filling tube (Fig. 3*b*). The hexadeuterobenzene was first transferred to this bulb by non-ebullient distillation in a vacuum; it was then strongly cooled, and, with the vacuum still maintained, the filling tube was sealed. By gently warming the bulb, the hexadeuterobenzene could be melted and transferred by distillation to the cell, filling it completely.

During the taking of a Raman spectrum, the filling tube and bulb had to be heated gently by means of an electrical winding so that this part of the apparatus should be slightly hotter than the cell. Otherwise the cell became the warmer end of the system, by reason of its proximity to the mercury lamp, and the hexa-deuterobenzene distilled from the cell into the bulb during the exposure.

Care was necessary in lining up. A holder was made to grip the cell securely, and also support the liquid filters, which were now, of course, contained in rectangular vessels; and a mounting was made for the holder, in which the three degrees of translational freedom, and the three of rotational freedom, were all provided by screw adjustments. This mounting, as well as a simpler mounting, with adjustments, which supported the projection lens, were secured to a rigid extension to the chassis of the spectrograph. The cell holder was so made that the back window of the cell could be obscured by a removable soot-coated dark-slide (a few mm. behind the cell window, in order to avoid direct illumination of the blackened surface). In lining up, this slide was withdrawn, and a lamp was placed in the position of the plate holder of the spectrograph. The light emerging from the slit was focussed to an image in the centre of the cell, and the position of the latter in relation to all its translational and rotational degrees of freedom was so adjusted that the beam passed through the front and back windows without touching any side or edge of the cell. As expected, the cell gave Raman spectrograms with approximately the same speed as did Wood's tubes filled with about 6 c.c. of material. An unexpected characteristic of the spectrograms was the remarkably low level of continuous background; it had been anticipated that there would be a serious amount of scattered light coming from the soot-blackened slide.

FIG. 3.

(a)

(b)

Cell construction.

The small latitude in lining up permitted by the dimensions of the cell described necessitated the use of a well-corrected lens. For cells of greater width (1·5 mm. was permissible with our sample of pentadeutero-benzene), conditions were less stringent, and a lens taken from a microscope eye-piece was found to be quite satisfactory; also a much wider slit could be used with such cells, if desired.

(4) *Raman Spectrum of Hexadeuterobenzene.*

(a) *Observations.*—The revised list of frequencies is given in the first row of figures in the table below. The second row contains qualitative indications of intensity on the same basis as that employed in the following papers in connexion with other Raman spectra (ww, very weak; w, weak; mw, moderately weak; m, moderate intensity; ms, moderately strong; s, strong). No new quantitative intensity and polarisation measurements have been made, and therefore the values previously recorded (Part III, *loc. cit.*) are given in the third and fourth rows for completeness. The last row distinguishes fundamental frequencies (F) from overtones (o) and combination tones (c): a complete assignment is given in Part XXI (this vol., p. 316).

(b) *Discussion.*—Reference is made in Part III (*loc. cit.*) to all the observations on the Raman spectrum of hexadeuterobenzene which had been published up to 1936. Since then, Langseth and Lord (*loc. cit.*) have recorded new values of the seven active fundamental frequencies. For the five fundamental frequencies which
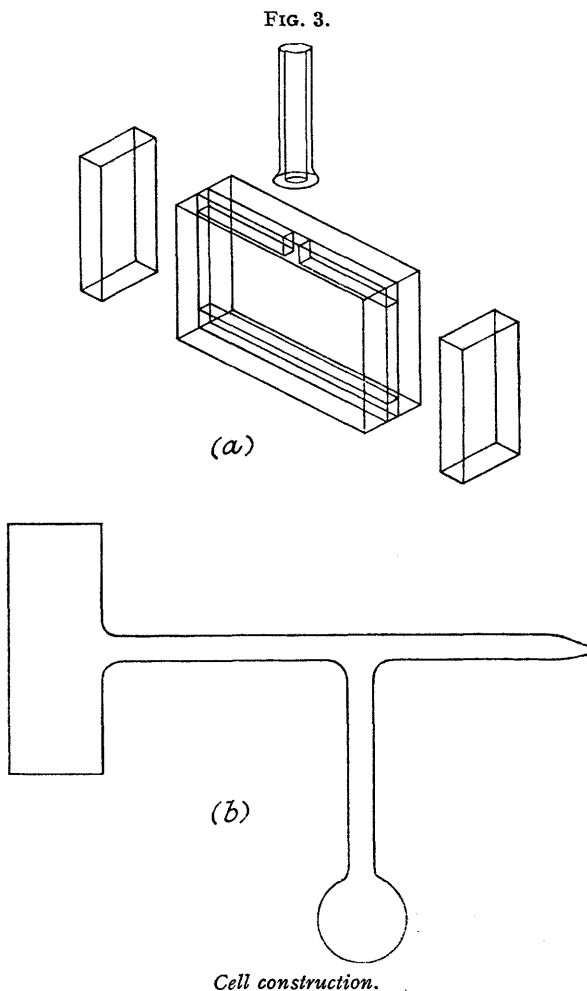
lie below 2000 cm.$^{-1}$, Langseth and Lord's values are almost exactly 1·8 cm.$^{-1}$ higher than those now recorded, whilst for the two highest fundamental frequencies, their values are 0·7 cm.$^{-1}$ higher than the present figures. The deviations from the values given in Part III are more casually distributed, though most of them are within 1 cm.$^{-1}$. The present values are believed to be good to within 0·1 or 0·2 cm.$^{-1}$. This does not apply, of course, to the weak frequencies, which may be in error by several wave-numbers.

A number of the weak frequencies given in Part III are fictitious, owing mainly to erroneous assignments of the Raman lines to their excitation frequencies, though in some cases the lines themselves could not be confirmed. Two Raman frequencies (844·5 and 1161 cm.$^{-1}$) have been observed which were not recorded in Part III as separate vibration frequencies, though the frequency 844·5 cm.$^{-1}$, which has a moderate intensity, is clearly visible on the original plates belonging to the authors of that paper; it was, however, overlapped by a stronger line, and not nearly as well resolved as is possible with the present equipment. It was missed by Wood, but was recorded by Klit and Langseth (cf. Part III, *loc. cit.*). Satisfactory observations, and fairly

TABLE I.

Revised Raman Frequencies of Hexadeuterobenzene.

Frequency (cm.$^{-1}$)	350	577·4	661·7	844·5	867·3	943·2	974
Intensity	ww	ms	ms	m	ms	s	ww
Intensity (Part III)	—	1·2	1·4	—	2·3	10·0	—
Polarisation (Part III)	—	0·76	0·87	—	0·81	0·08	—
Assignment	F *	F	F	c	F	F	C$_6$HD$_5$
Frequency (cm.$^{-1}$)	998	1161	1329	1522	1551·5	1575	1923
Intensity	mw	ww	w	mw	ms	mw	w
Intensity (Part III)	—	—	—	—	2·0	—	—
Polarisation (Part III)	—	—	—	—	0·82	—	—
Assignment	o	c	o or F *	c	F	o	o
Frequency (cm.$^{-1}$)	2129	2139	2264·9	2292·6	2567	3050	3098
Intensity	mw	mw	ms	s	w	ww	ww
Intensity (Part III)	—	—	6·1	10·6	—	—	—
Polarisation (Part III)	—	—	0·7	0·35	—	—	—
Assignment	c	c	F	F	c	C$_6$HD$_5$	o

(*F* * = Forbidden fundamental.)

satisfactory measurements, have been made on the line of low frequency (350 cm.$^{-1}$), only doubtful traces of which had been seen by the authors of Part III. The table contains all the 21 Raman frequencies which have been established in these experiments, although it will be noted that two of them are assigned to pentadeutero-benzene, 1·8% of which was present in the hexadeuterobenzene employed (Part XIII, this vol., p. 243). The necessity for these assignments has been pointed out by Lord (cf. Part III; cf. Langseth and Lord, *loc. cit.*).

The better values of the fundamental frequencies lead to the following revised product ratios :

$$\frac{\Pi A_{1g}(C_6H_6)}{\Pi A_{1g}(C_6D_6)} = \frac{991·6 \times 3061·9}{943·2 \times 2292·6} = 1·404 \text{ (calculated value 1·414)}$$

$$\frac{\Pi E_g^+(C_6H_6)}{\Pi E_g^+(C_6D_6)} = \frac{605·6 \times 1178·0 \times 1596 \times 3046·8}{577·4 \times 867·3 \times 1551·5 \times 2264·9} = 1·970 \text{ (calculated value 2·000)}$$

$$\frac{\Pi E_g^-(C_6H_6)}{\Pi E_g^-(C_6D_6)} = \frac{848·9}{661·7} = 1·283 \text{ (calculated value 1·285)}$$

The calculated values are those given by the product theorem of Teller and Redlich, which assumes harmonic forces. (In the succeeding papers, such calculated values will be termed harmonic values.) Since the effect of anharmonicity is usually to reduce the value of the ratio, the agreement is to be regarded as satisfactory.

SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
              UNIVERSITY COLLEGE, LONDON, W.C. 1.