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THE INFRARED SPECTRA OF BENZENE, SYM-BENZENE-d_3, AND BENZENE-d_6

BY

SVEND BRODERSEN AND A. LANGSETH

1742

København 1956
i kommission hos Ejnar Munksgaard

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Erratum.

Equation (4) on page 43 should read:

$$\lambda_3^h (\lambda_{14}^d + \lambda_{15}^d) + \lambda_3^d (\lambda_{14}^h + \lambda_{15}^h) + \lambda_{14}^h \lambda_{15}^h + \lambda_{14}^d \lambda_{15}^d = 2 (\lambda_3^s \lambda_{14}^s + \lambda_3^s \lambda_{15}^s + \lambda_{14}^s \lambda_{15}^s) \qquad (4)$$

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CONTENTS

Synopsis.

The infrared absorption spectra of benzene, sym.-benzene-d_3, and benzene-d_6 have been obtained for the gaseous as well as for the liquid state. The samples used for the investigation were of high chemical and isotopical purity. The measurements cower a spectral range from 400 cm^{-1} to about 6000 cm^{-1} in frequency, and a range of about 1 to 10^5 in relative intensity of the observed bands. The spectra have been analyzed with the following main results:

(1). Of the observed bands about 450 have been assigned. The combination bands showed in general a remarkably low anharmonicity. Except for the well-known cases of resonance perturbation in C_6H_6, only a few instances of weak interactions were observed in spite of the considerable probability for fortuitous degeneracy.

(2). A complete list of assigned, fundamental frequencies for the three isotopic benzenes has been obtained for the gaseous state and the liquid state separately.

(3). The correctness of the assignments has been checked by means of the product rule and the sum rules.

(4). The importance of the higher-order sum rules is pointed out, and expressions for these rules for the present case are given.

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INTRODUCTION

The vibrational problem and the normal coordinate treatment of the benzene molecule have been discussed by numerous authors[1]. Most of these considerations have substantially been based on experimental investigations of the infrared absorption[2] and Raman spectra[2, 3] of benzene and its deuterium derivatives, investigations which are now 10 to 20 years old. In view of the considerable improvement in experimental technique, which has taken place since then, a re-investigation of the molecular spectra of benzene and its isotopic species seemed to be highly desirable.

As a part in this program we report in the present paper on an investigation of the infrared spectra of benzene, sym-benzene-d_3, and benzene-d_6 both in the gaseous and the liquid state. It has been our aim to obtain these spectra as accurate and complete as possible by investigating samples of high chemical and isotopical purity and by use of long path-lengths.

The infrared absorption of *benzene* has been the object of a great number of investigations[4]. The first comprehensive study of the spectrum, undertaken with the explicit object of determining the normal frequencies of the molecule, forms a part of the outstanding work of C. K. Ingold and his collaborators[5]. They investigated a very pure sample of benzene both in the form of vapour and liquid, and were the first to make a careful comparison of the two kind of spectra. Since this work was published no further systematic investigation of the vapour spectrum has appeared in the litterature. The absorption of liquid and crystalline benzene was measured by Halford and Schaeffer[6]. These spectra were re-examined by Mair and Hornig[7] who used a spectrometer with somewhat higher resolving power and extended the temperature range down to −170° C. The most important result of this investigation was a definite and plausible assignment of the hitherto questionable B_{2u} fundamentals.

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[1] See G. Herzberg, Infra-red and Raman spectra of Polyatomic Molecules (D. von Nostrand Co., New York, 1945), p. 362.
E. Bright Wilson, Jr, J. C. Decius, and Poul C. Cross, Molecular Vibrations (McGraw-Hill, 1955), p. 240.
F. A. Miller and B. L. Crawford, Jr. J. Chem. Phys. **14**, 282 (1946); ibid. **17**, 249 (1949).
M. A. Kovner, Zurn. Eksp. i Teor. Fiz. **26**, 598 (1954).
D. H. Whiffen, Phil. Trans. Roy. Soc. (London), A, **248**, 131 (1955).

[2] C. K. Ingold et al., J. Chem. Soc. **1936**, pp. 912—987, ibid., **1946**, pp. 222—333.

[3] A. Langseth and R. C. Lord, Jr., Mat. Fys. Medd. Dan. Vid. Selsk. **16**, no. 6 (1938).

[4] See G. Herzberg, ref. 1.

[5] C. R. Bailey, I. B. Hale, C. K. Ingold, and J. W. Thompson, J. Chem. Soc. **1936**, p. 931.

[6] R. S. Halford and O. A. Shaeffer, J. Chem. Phys. **14**, 141 (1946).

[7] R. D. Mair and D. F. Hornig, ibid. **17**, 1236 (1949).

The spectrum of *sym-benzene-d*$_3$ vapour has been investigated once only by INGOLD et al.[8]. No measurements of the liquid have been reported.

The infrared spectrum of *benzene-d*$_6$ (vapour and liquid) has been investigated by INGOLD et al.[9]. Quite recently FOIL A. MILLER[10] has obtained rather complete spectra of both vapour and liquid phases in the region 300—3700 cm^{-1}. The analysis of the spectrum confirms MAIR and HORNIG's assignments of the B_{2u} fundamentals in benzene.

II. EXPERIMENTAL

1. Preparations.

In collaboration with NIELS GROVING.

As the ultimate objective of the present spectroscopic investigation was to measure the spectra to the greatest possible completeness and accuracy, we have endeavoured to prepare our samples as pure as possible. Impurities, chemically different from benzene, were carefully removed by means of appropriate conventional methods.

The contamination of the samples with unwanted isotopic species presents a more serious problem. In practice it is of course not possible to carry through a separation of these. In order to identify and eliminate all bands due to deuterium derivatives, alien to the one under investigation, we used the following procedure.

Both sym-$C_6H_3D_3$ and C_6D_6 were prepared by exchange reactions. These were carried through to a point precalculated to be rather close to the pure deuterium derivative. In both cases we prepared two samples with a little different degree of exchange. By comparison of the spectra it was easy to see which bands were diminished in intensity by progressive exchange. Furthermore, we had at our disposal samples of the different deuterated benzenes[11] and were in all cases able to identify the spurious bands with strong bands of lower deuterated species. In the case of sym-$C_6H_3D_3$ the exchange might conceivably result in the formation of small amounts of higher deuterated benzenes. However, no indication of this was observed (enhancement in intensity of bands with progressing exchange).

a. ***Benzene.*** The infrared spectra of some commercial, analytical grade benzenes showed that none of these were pure enough for our purpose. All of them contained either thiophene or/and cyclohexane in varying quantities.

Sample A. For the purification we chose RIEDEL-DE HAËN's Benzene pro analysi as starting-material. It was free from thiophene, but contained some cyclohexane.

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[8] C. R. BAILEY, J. B. HALE, N. HERZFELD, C. K. INGOLD, A. H. LECKIE, and H. G. POOLE, J. Chem. Soc. **1946**, p. 255.

[9] See ref. 2) In a later note by C. R. BAILEY, S. C. CARSON, and C. K. INGOLD, J. Chem. Soc. **1946**, p. 252, new measurements of the 496 cm^{-1} band are reported.

[10] FOIL A. MILLER, J. Chem. Phys. **24**, 996 (1956).

[11] A. LANGSETH and A. KLIT, Mat. Fys. Medd. Dan. Vid. Selsk. **15**, no. 13 (1937).

The purification was accomplished by means of the very efficient method described by Evans, Ormrod, Goalby and Stavely[12]. As the procedure was slightly modified by us we will describe it in detail.

To a solution of 284 g nickel sulfate ($NiSO_4$, $7H_2O$) in 1135 cc cold water were added: first a solution of 141 g potassium cyanide (pro analysi) in 565 cc water, then 1130 cc conc. ammonia water (diluted with 600 cc water), and finally acetic acid (60 $^0/_0$) until just a slight precipitate remained. This mixture was transferred to a 4-l conical flask and 80 cc benzene added. The mixture was stirred vigorously for 2—3 hours. During this time a light-lilac crystal powder was precipitated and the solution discoloured. The crystals were filtered, washed first with water, then with alcohol, and finally left for drying in the air for 24 hours.

We regained the benzene by decomposition of the complex with potassium cyanide. The crystal powder was placed in a separatory funnel, whose stop-cock was greased with silicone grease. A solution of 170 g potassium cyanide in ca. 750 cc water was added little by little, all the while the funnel was shaken and cooled under the water tap. After completion of the decomposition the benzene was transferred to a smaller separatory funnel and thoroughly washed: once with water, three times with 2 molar sulfuric acid, once with water, three times with 2 molar sodium hydroxide, and finally once more with water. The benzene was then dried over P_2O_5 and finally fractionated through a 60 cm column packed with glass helices.

The boiling point was constant (± 0.05° C) during the whole distillation. The first fraction (ca. 10 c.c.) was discarded as the infrared spectrum revealed traces of NH_3. The middle fraction (ca. 60 c.c.) was used for the spectroscopic investigation. No traces of cyclohexane could be detected.

Sample B. In order to reduce the possibility of the presence of some unknown impurity we prepared a sample of benzene from aniline.

Aniline, pro analysi (Riedel-de Haën), was dissolved in ether and transformed into the hydrochloride by passing HCl into the solution. As the precipitate was slightly coloured it was re-crystallized from constant-boiling hydrochloric acid. The anilin hydrochloride was then diazotized and reduced exactly as described by Best and Wilson[13]. The benzene formed was washed with water, 2 molar sulfuric acid, water, 2 molar sodiumhydroxide, and water. It was then dried over P_2O_5 and fractionated exactly as described for sample A. The boiling point was constant (± 0.05° C) during the whole distillation. The middle fraction (ca. 70 $^0/_0$) was collected as sample *B*.

A comparison of the infrared spectra of the two samples, *A* and *B*, showed that they were identical.

b. ***Sym-benzene-d_3*.** Except for slight modifications we followed the method developed by Best and Wilson[13]. This is based on the observation[14] that an exchange

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[12] J. Chem. Soc. **1950**, p. 3346.

[13] A. P. Best and C. L. Wilson, J. Chem. Soc. **1946**, p. 239.

[14] C. K. Ingold, Raisin, and C. L. Wilson, J. Chem. Soc. **1936**, p. 1637; ibid. **1938**, p. 28.

reaction takes place when anilin hydrochloride is dissolved in heavy water, and furthermore in such a way that the ortho-para-hydrogen atoms are the only nuclear positions which participate in the reaction. The resulting 2,4,6-anilin-d_3 is then de-aminated to sym-$C_6H_3D_3$.

For the preparation we started from two portions (of each 20 g) of aniline hydrochloride prepared as described for benzene, sample B. The two reaction vessels used for the exchange reaction were of a type as shown in Fig. 1. For reasons to be explained below it was found necessary to insert a glass-filter plate between the reflux condenser and the stopcock. The anilin hydrochloride was put into the 50 cc bulb before the glass-filter was sealed on to the reflux condenser. The system was then evacuated and the stopcock closed. 14 cc heavy water (99.84 °/₀ D_2O) was filled into the upper end of the glass tube, and by cautious opening of the stopcock allowed to flow into the apparatus without admitting the atmospheric air. The system was now filled with nitrogen and the bulb heated by means of an infra-heater. When the boiling started the stopcock was opened just to equalize the pressure. The closed vessel was then left refluxing for 18—20 hours in order to reach equilibrium of the exchange reaction. The exchanged heavy water was now distilled off quantitatively in vacuum. Towards the end of this distillation it could not be avoided that small crystals of the aniline hydrochlorid by the stream of water vapour were blown up through the condenser. It was the purpose of the glass-filter to keep back these crystals. When a new portion (14 cc) of heavy water was introduced, the powder was dissolved and washed down into the bulb again and a new exchange was started. The exchanged water from vessel no. 1 was used for further exchange in vessel no. 2, after which it was discarded. In this way 7 exchanges were carried through in vessel no. 1 (*Sample A*) and 6 in vessel no. 2 (*Sample B*). According to an approximate calculation the deuterium content in the 2, 4, 6-positions of the aniline should then be ca. 99.5 °/₀ for sample *A* and ca. 96.5 °/₀ for sample *B*. We decided to stop the exchange at this stage because of the risk of introducing deuterium in the 3- and 5-positions also.

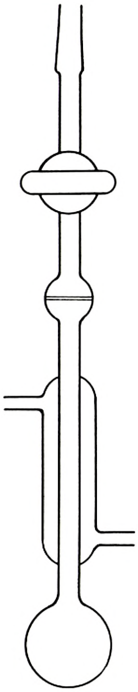

Fig. 1.

Isotopic normalization of the amino-hydrogen was for each sample carried out by dissolving the hydrochloride in 500 cc cold water which immediately afterwards was distilled off in vacuum at ordinary temperature. This was repeated three times.

The de-amination and purification of the sym-benzene-d_3 was carried out as described above for benzene, *Sample B*. Yield for both samples: 7 cc of pure sym-benzene-d_3.

The infrared spectra of both samples were investigated and by comparison the spurious bands located. These could all be identified as due to meta-$C_6H_4D_2$ and C_6H_5D. No trace of $C_6H_2D_4$ or C_6HD_5 could be detected.

c. ***Benzene-d_6*.** This was prepared according to LANGSETH and KLIT[15] by passing a stream of DCl through benzene in the presence of $AlCl_3$.

Assuming a pure statistical distribution of the D-atoms between DCl and C_6H_6, a calculation shows that the deuterium content in the benzene will not approach closely to 100 % until almost all the benzene has evaporated, if the exchange reaction is carried out at ordinary temperature. If, however, the DCl is passed through several exchange vessels arranged in series, the benzene will evaporate in the first vessel only, all the while the deuterium concentration will increase in all the following ones.

Fig. 2 shows a diagram of one of the 4 exchange units used. The DCl was passed into the benzene through a capillary tube going down close to the bottom of the vessel. In order to keep the DCl-bubles as small as possible the end of the tube was sharpened by grinding. It will be seen that the construction is so that the benzene can not accidentally be sucked back into the neighbouring vessel. All 4 exchange vessels were placed in a water bath, the temperature of which was kept just above the freezing point of benzene (ca. 4° C).

The DCl was prepared from benzoyl chloride and heavy water[16]. A large excess of benzoyl chloride was used in order to keep the benzoic acid and its anhydride, formed by the reaction, in solution and thus preventing these from subliming up into the reflux condenser of the reaction flask. We used 3 kg benzoyl chloride (ca. 21.5 mol) and ca. 75 g D_2O (99.84 %) for the total exchange. The DCl was passed through a trap (kept at $-80°$ C) before entering the 4 exchange vessels each of which contained 15 cc benzene (purified as described above) and ca. 50 mg freshly sublimed $AlCl_3$. As the exchange reaction is extremely fast, the DCl may be passed through the vessels as quickly as the practical conditions allow.

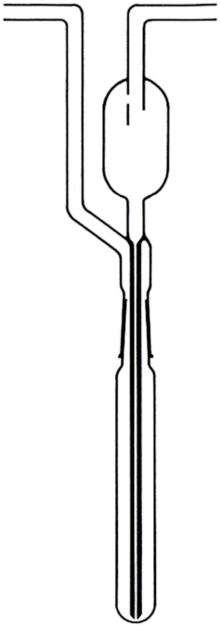

Fig. 2.

When all benzene in the first vessel and half of the benzene in the second had evaporated the exchange was stopped. The benzene was separated from $AlCl_3$ (and most of the DCl) by distillation in vacuum, washed once with water, three times with molar NaOH, and once more with water. It was then dried over P_2O_5 and distilled.

Two samples, *A* and *B*, from the second and the third exchange vessel respectively, and therefore of a little different isotopical purity, were used for the spectroscopic investigation. The infrared spectrum showed sample *A* (7 c.c.) to be very pure C_6D_6 (99.9 % D). Spurious bands were located by comparison with the spectrum of sample *B* (15 c.c.) and the bands identified in the usual way as due to lower deuterated species.

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[15] A. LANGSETH and A. KLIT, Zeitschr. phys. Chem. A. **176**, 65 (1936).

[16] H. C. BROWN and C. GROUT, J. Amer. Chem. Soc. **64**, 2223 (1942).

2. Instrument.

The spectra were obtained with a slightly modified *Beckman IR3* spectrometer. The principal features of this instrument are the following:

(1) The instrument has a double monochromator, effectively eliminating all stray light. As each half is equipped with one prism in Littrow-mounting the instrument has a dispersion and a resolving power corresponding to 4 prisms.

(2) The entire light path can be evacuated thus eliminating atmospheric absorptions.

(3) It is a single-beam instrument operated by means of a memorizing system. The spectral range is traversed twice. During the first run (with empty absorption cell) the slits are automatically adjusted to give constant light output, the movements of the slits being memorized on a tape-recorder. This record masters the movements of the slits during the second run (with the sample in the cell), giving a spectrum linear in transmission.

(4) The movement of the recorder paper is mastered by a special control film in such a manner that the spectrum is recorded linear in wave-numbers.

(5) The spectrum is scanned at a speed proportional to the geometrical slit width and the time constant of the noise filter. This is correct to a good approximation.

The principal modifications of the instrument introduced by us are the following:

(1) An electronic delay unit is inserted in the marker circuit giving a time delay equal to the delay of the signal caused by the noise filter[17].

(2) The thermostate controller has been mounted inside the monochromator near the prisms, ensuring a better control of the temperature of the prisms.

(3) An arrangement has been installed which allows the use of a direct coupling between chart paper and Littrow-mirrors. In this way the errors in frequency determination caused by the control film (about ± 0.3 cm^{-1}) may be eliminated, which can be of importance in special cases.

(4) The instrument is originally equipped with liquid cells and a 10 cm gas cell only. In order to get longer path-lengths for gasses, necessary for our purpose, a multiple-pass cell was constructed, according to the principle of White[18] as modified by Herzberg and Bernstein[19].

A photograph of the arrangement is shown in Fig. 3. The vertical cell has a length of 50 cm and a volume of ca. 6 liters. By means of a micrometer screw, introduced vacuum-tight through the upper end plate of the cylinder, the path-length can be varied in 2-m-steps between 2 and 20 meters. The optical arrangement, necessary for bringing the multiple-pass cell into the light path of the instrument, is shown schematically in Fig. 4. The light from the glower is normally focused on the entrance slit of the monochromator. With the long cell in use the light is reflected by the plane mirror A and now brought to a focus just off the concave mirror B. After reflections

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[17] Svend Brodersen, J. Opt. Soc. Am. **43**, 1216 (1953).

[18] J. U. White, J. Opt. Soc. Am. **32**, 285 (1942).

[19] H. J. Bernstein and G. Herzberg, Journ. Chem. Phys. **16**, 30 (1948).

back and forth the light leaves the cell just off the opposite side of mirror B, which means that the beam has been displaced sidewards from its plane. By means of the nearly vertical, plane mirror C and the concave mirror D it is brought back to the original plane, and after reflection from the backside of the thin mirror A (which is aluminized on both sides) finally re-focused on the entrance slit.

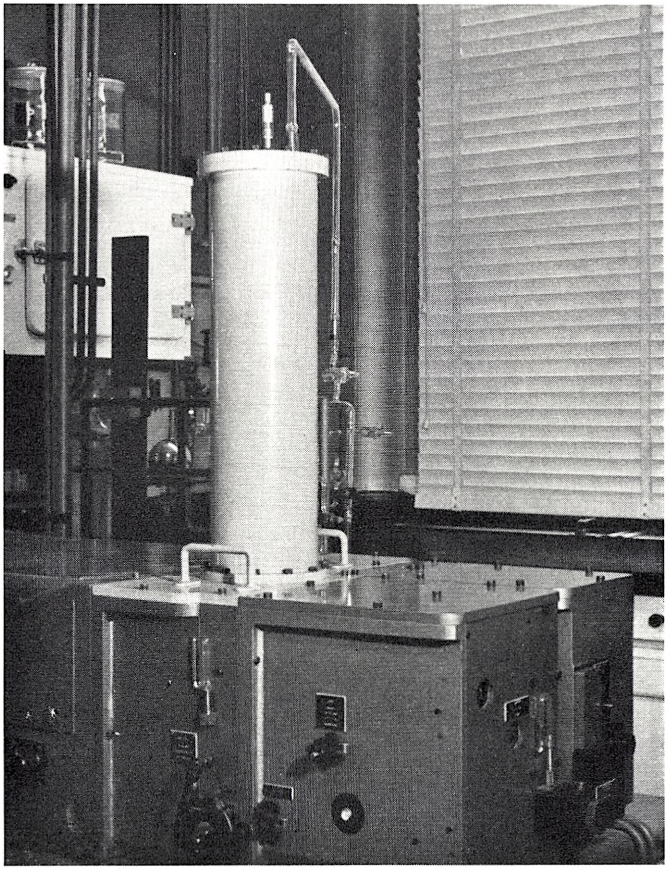

Fig. 3.

The multiple-pass cell as well as the mirrors A and C are mounted on an auxiliary cover for the gas cell compartment in order to allow an easy interchange of this cell and the 10 cm cell.

The monochromator is equipped with KBr, NaCl, and LiF prisms, which can easily be interchanged. The effective slit width (effective resolving power) is calculated in the following way[20]. The effective slit width, s_0, corresponding to zero geometrical slit width is calculated by adding the contributions from: (1) diffraction effect (*Ray-*

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[20] Svend Brodersen, J. Opt. Soc. Am. **43**, 877 (1953).

leigh limit), (2) mismatch of slit curvature, and (3) spherical aberration. This instrument has pure spherical aberration only, because the two halves of the double monochromator are symmetrical. Contributions from misadjustment and imperfections of optical parts are neglectable. The obtained values for s_0 versus frequency are shown as dotted curves in Fig. 5. The effective slit width, s_{eff}, for actual values of the geometrical slit width, s_g, is now obtained from the relation:

$$s_{eff}^2 = s_0^2 + s_g^2.$$

With normal gain the values indicated in Fig. 5 are obtained for the 10 cm gas cell, and for the long cell using 2 m and 20 m path-length. For the liquid cell the slit widths are slightly smaller than for the 10 cm gas cell.

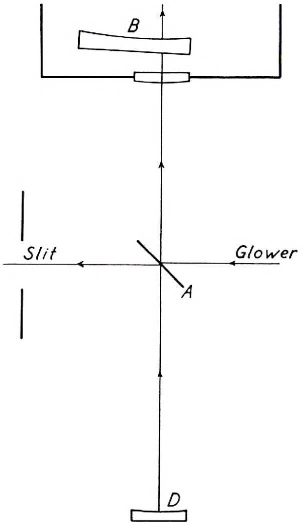

Fig. 4.

It is possible to use narrower slits and thereby to reduce s_{eff}, according to the above formula. But this requires the use of larger time-constants and of proportionally reduced scanning rates in order to keep the noise within reasonable values. At the most the geometrical slit width can be reduced to about 30 % of its normal value, but in this case extremely long scanning times must be used.

The frequency calibration was carried out by the interferometer method[21]. Uncoated KBr plates were used with separations giving 'periods' of 10 cm^{-1} rsp. 25 cm^{-1}. The fundamentals and first overtones of HCl and CO were used as standards. In this way an accuracy of ± 0.2 cm^{-1} was obtained for the region 400—4500 cm^{-1}, decreasing to about ± 1 cm^{-1} at 8000 cm^{-1}.

[21] Svend Brodersen, J. Opt. Soc. Am. **46**, 255 (1956).

The reproducibility of the frequency measurements using the direct paper coupling is about ± 0.1 cm^{-1}. Some difficulties in exact replacement of the exchangeable prisms have, however, slightly increased the errors in the frequencies presented in this paper. For this reason, and because we consider a higher accuracy to be insignificant for unresolved bands, the frequencies are given without a decimal. They are, however, believed to be correct within ± 0.5 cm^{-1} as far as this has any meaning for the band in question.

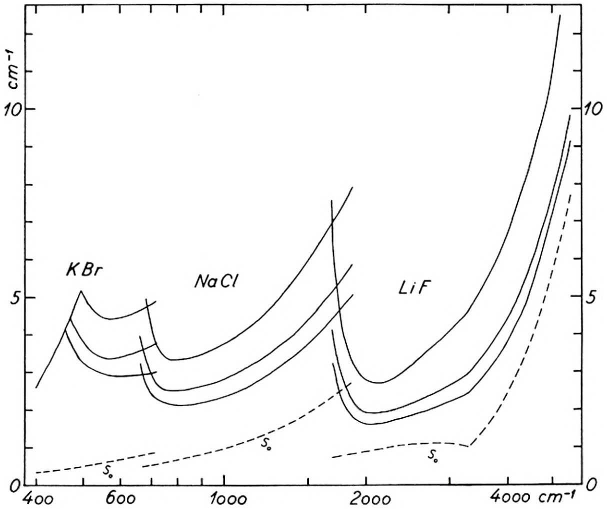

Fig. 5. Effective slit width versus frequency for the 10 cm gas cell (lower heavy curve) and for the multireflexion cell using 2 m and 20 m path length (middle and upper curve respectively).

3. Measurement of the Spectra.

Each of the 6 samples: C_6H_6 (*A* and *B*), sym-$C_6H_3D_3$ (*A* and *B*), and C_6D_6 (*A* and *B*), were measured both in the liquid and in the vapour state. The following technique was used. The spectra of the liquids were obtained with cell lenghts of 0.03, 0.3, and 3 mm and normal gain. Consequently, the effective slit widths for all cell lenghts were slightly smaller than the values plotted in Fig. 5 for the 10 cm gas cell. There was no need for using narrower slits than these. The spectra of the vapours ($p = 65$ mm of Hg) were obtained by using cell lengths of 10 cm, 2 m, and 20 m and normal gain. The effective slit widths are shown in Fig. 5. All the stronger bands, as well as other parts of the spectra of special interest, were then re-scanned with narrower slits, as described above.

From all the records taken the molar extinction coefficient, ε, was calculated, assuming ideality of the gas. For the liquid as well as for the vapour LAMBERT-BEER's law was found to be well obeyed so that all measurements, within the experimental

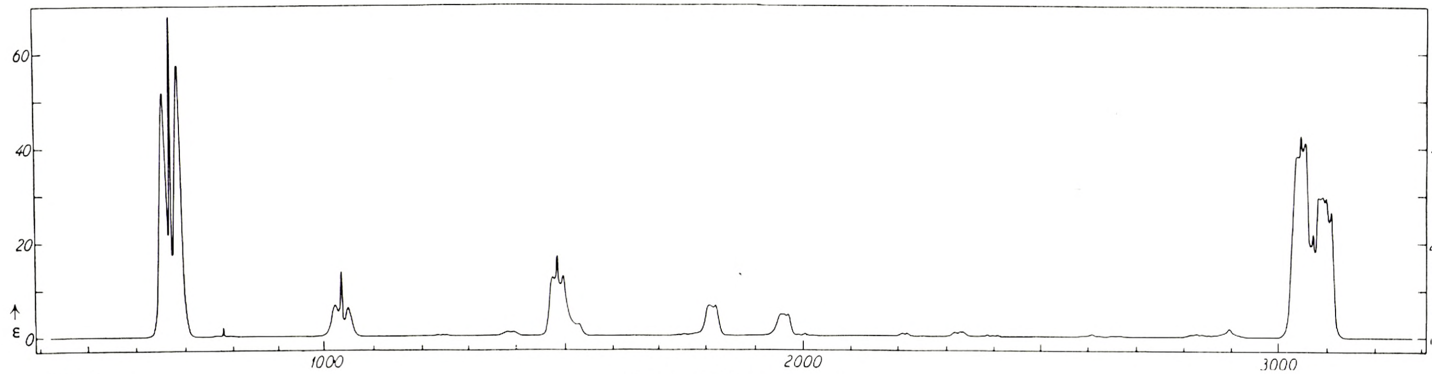

Fig. 6. C_6H_6 (vapour).

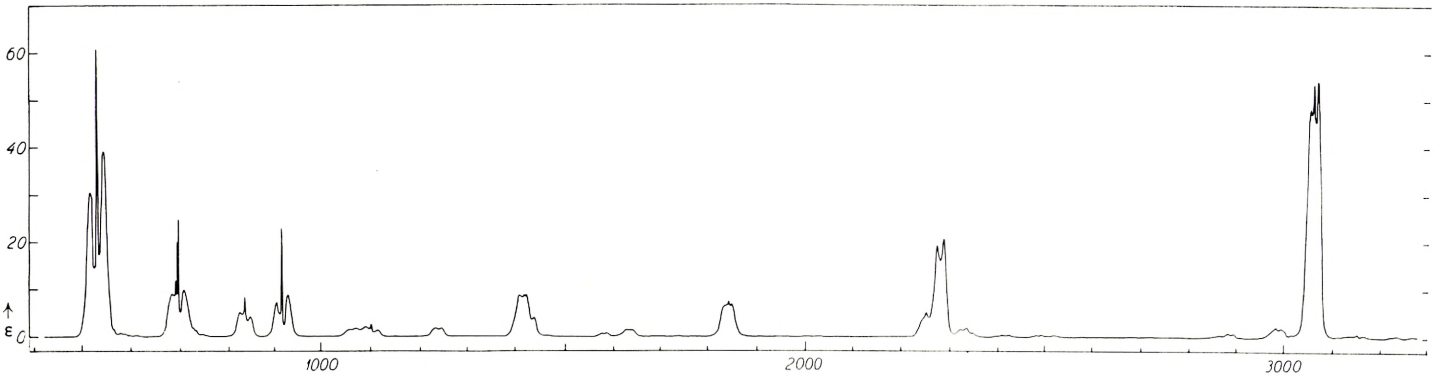

Fig. 7. sym-$C_6H_3D_3$ (vapour).

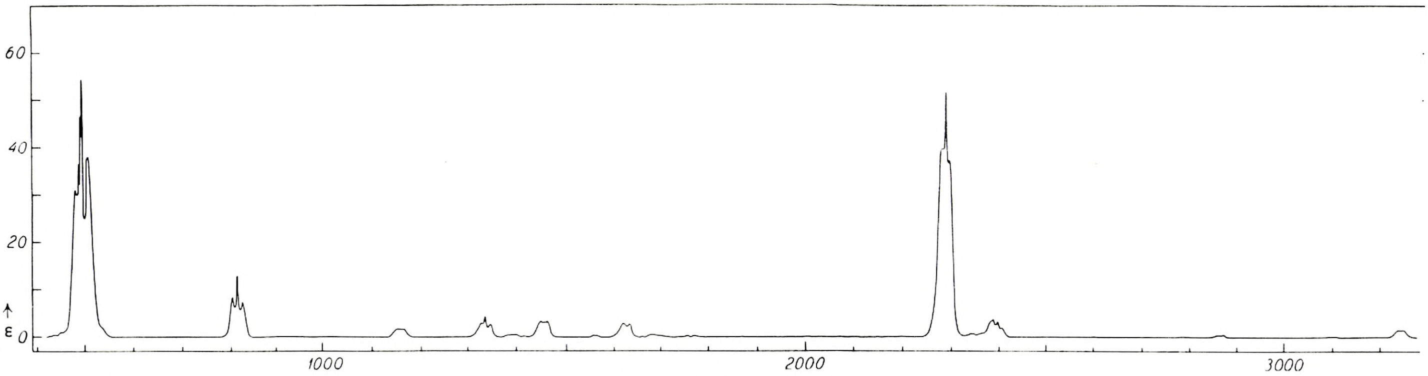

Fig. 8. C_6D_6 (vapour).

error, fitted a single extinction curve for each of the two states of the sample. For the vapour spectra, however, a few cases were observed (especially for the very strong ν_{11}) in which the gas pressure used was too low to give quite correct intensity because of insufficient pressure broadening. For ν_{11} in benzene, for instance, a slight increase in intensity, but no change in the shape of the band, was observed when the pressure in the cell was raised to 1 atm. by addition of nitrogen. As exact band intensities are of no importance for the vibrational analysis of the spectra, we refrain in this paper from giving any measurements of integrated band intensities.

Reproductions of the extinction curves obtained for the three isotopic benzenes are given on the Plate at the end of the paper. The ordinate, ε, is plotted in a logarithmic scale covering almost 5 units. This wide range in extinction is presumably about the limit obtainable in praxis because of the consequential severe demands for purity of the substance. The curves represent the measured spectra of each sample of highest isotopical purity, but are very nearly identical with the extinction curves for the pure isotopic species, obtained by extrapolation in the way mentioned above (pag. 4).

As it is rather difficult to get a correct impression of the relative band intensities from these curves we have also, as shown in Figures 6, 7, and 8 plotted the absorption curves in a linear extinction scale. From these it is clearly seen that the main part of the absorption is due to the fundamental frequencies.

All frequency measurements are given below in the Tables 4, 5, and 6, and will be commented in connection with the analysis and discussion of the spectra. All frequencies are given in cm^{-1} (vac.).

III. DISCUSSION OF THE SPECTRA

1. Theory.

The general theory of the internal vibrations of the benzene molecule has been treated thoroughly by several authors and need not be recapitulated here in any detail. For the convenience of the reader, however, a brief survey will be given in order to define the precise meaning of the terminology and the symbols used in the following discussion.

We will, without any discussion, assume it justified to consider the D_{6h} symmetry of the benzene and the benzene-d_6 molecules—and hence the D_{3h} symmetry of sym-benzene-d_3—as definitely prooved[22].

Symmetry considerations show that the normal vibrations of a D_{6h}-molecule can be allotted to 12 different symmetry classes, two to which (A_{1u} and B_{1g}) in the special case of benzene will contain no fundamentals. The D_{6h} symmetry can be defined in several ways on the basis of its inherent elements of symmetry. As seen from Table 1 we have as the group of essential symmetry elements chosen: (1) the

[22] See for instance ref. 1, 2, and 3.

Table 1.

D_{6h} (C_6H_6, C_6D_6) and **D_{3h}** (sym-$C_6H_3D_3$).

D_{6h}	D_{3h}	D_{6h}				Activity	Freq. No.
		D_{3h}					
		C_3^z	C_2^y	σ_z	i		
A_{1g}	A_1'	+	+	+	+	R, –	1, 2.
B_{1u}		+	+	+	–	–, –	12, 13.
A_{2g}	A_2'	+	–	+	+	–, –	3.
B_{2u}		+	–	+	–	–, –	14, 15.
E_g^+	E'	ε	±	+	+	R, –	6, 7, 8, 9.
E_u^-		ε	±	+	–	–, I	18, 19, 20.
B_{2g}	A_2''	+	–	–	+	–, –	4, 5.
A_{2u}		+	–	–	–	–, I	11.
E_g^-	E''	ε	±	–	+	R, –	10.
E_u^+		ε	±	–	–	–, –	16, 17.

three-fold axis perpendicular to the plane of the molecule (C_3^z), (2) the two-fold axis passing through para carbon atoms (C_2^y), (3) the plane of the molecule (σ_z), and (4) the center of symmetry (i). This is convenient for our purpose because it clearly shows the close relationship between the D_{6h} and the D_{3h} symmetries. When 3 deuterium atoms are substituted for 3 hydrogens in the 1, 3, and 5 positions the only element of symmetry destroyed is the inversion center. This causes the g- and u-classes of D_{6h} to coalesce in pairs, as shown in table 1. As the three-fold symmetry axis is preserved in D_{3h}, no splitting of the degenerate frequencies occurs. In the table are furthermore given the symbols used[23] for the various symmetry classes, and—in a self-explanatory way—the Raman and infrared selection rules.

For convenience in discussing the frequencies of benzene and its deuterium derivatives we have numbered the normal vibrations according to WILSON[24] and LANGSETH and LORD[25] as shown in Fig. 9. This set of symmetry coordinates is chosen in such a way, that each of them—besides having the correct symmetry—also represents a rough approximation to the real mode of vibration for the benzene molecule. However, as the D_{6h} symmetry is destroyed by deuterium substitution, these modes will more or less lose their identity. The actual modes of vibration in the various deuterium derivatives are to be described by means of linear combinations

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[23] We have retained the original notation of PLACZEK [Handb. d. Radiologie, Bd. VI, 2, pag. 283] for the degenerate classes in D_{6h}, according to which symmetry or antisymmetry with respect to the C_2^z axis is denoted by a +, respectively a – sign, instead of the now commonly used indices 2 resp. 1 [See G. HERZBERG, ref. 1]: f. ex. $E_g^+ = E_{2g}$, $E_u^- = E_{1u}$ etc. We find PLACZEK's notation the more logical because 1 and 2 for the non-degenerate classes refer to symmetry resp. anti-symmetry with respect to the C_2^y axis.

[24] E. BRIGHT WILSON, Jr. Phys. Rev. **45**, 106 (1934).

[25] Reference 3.

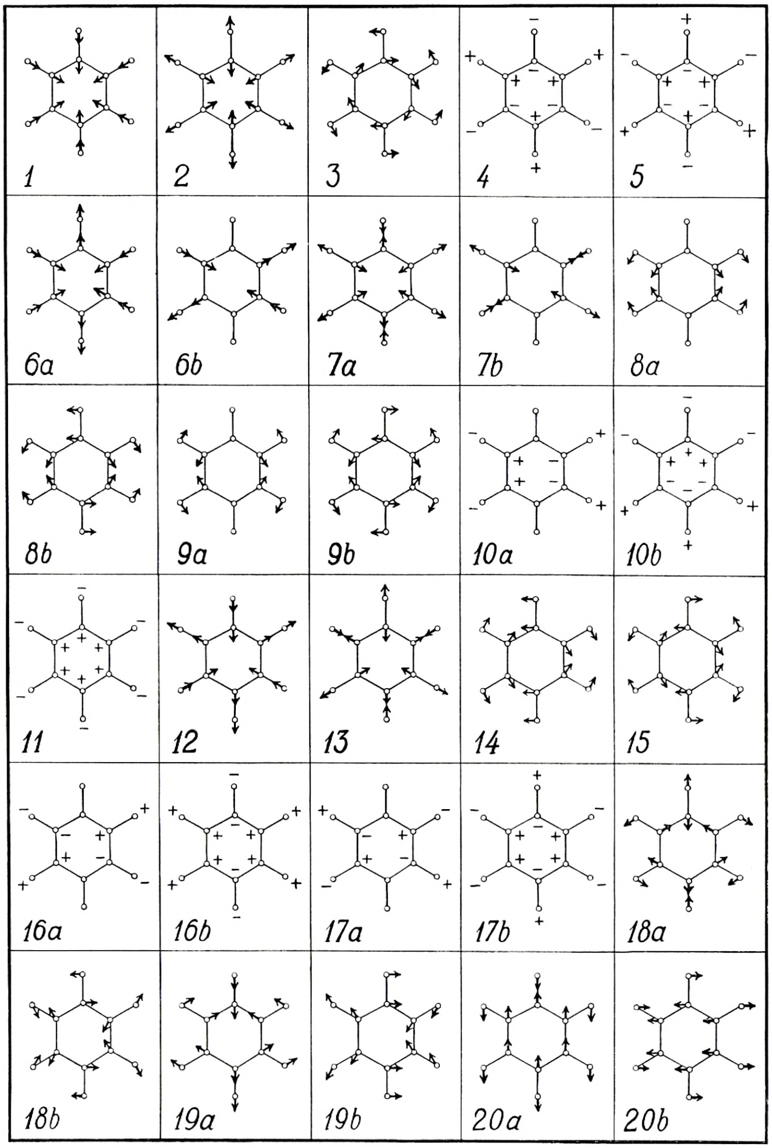

Fig. 9.

of the appropriate D_{6h} symmetry coordinates. This mixing might be expected to make the connection between one particular frequency in an intermediate deuterium derivative and one particular of the symmetry coordinates, shown in Fig. 9, quite arbitrary. However, as it is shown below it is actually possible to carry through a formal enumeration in an unambiguous way.

The only frequencies active in infrared are those of the A_{2u} (A_2'') and E_u^- (E')

species, the former giving parallel bands (P, Q, and R-branches) the latter perpendicular bands (various band forms). The observed extinction curves show that all parallel bands have a strong Q-branch. The perpendicular bands, however, show band envelopes, varying from double-maxima bands (very weak Q-branch) through unresolved single-maximum bands (medium-strong Q-branch filling up the gap between P- and R-branch) to parallel-like bands with a prominent Q-branch. The assignment of a band to one or the other of the active species on the basis of its observed contour alone is therefore often unreliable.

The symmetry species of combination frequencies (summation and difference bands) and overtones are easily found by means of Table 2 and 3.

D_{6h}

Table 2.

A_{1g}	A_{1u}	A_{2g}	A_{2u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	E_g^+	E_u^+	E_g^-	E_u^-	
A_{1g}	A_{1u}	A_{2g}	A_{2u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	E_g^+	E_u^+	E_g^-	E_u^-	A_{1g}
	A_{1g}	A_{2u}	A_{2g}	B_{1u}	B_{1g}	B_{2u}	B_{2g}	E_u^+	E_g^+	E_u^-	E_g^-	A_{1u}
		A_{1g}	A_{1u}	B_{2g}	B_{2u}	B_{1g}	B_{1u}	E_g^+	E_u^+	E_g^-	E_u^-	A_{2g}
			A_{1g}	B_{2u}	B_{2g}	B_{1u}	B_{1g}	E_u^+	E_g^+	E_u^-	E_g^-	A_{2u}
				A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_g^-	E_u^-	E_g^+	E_u^+	B_{1g}
					A_{1g}	A_{2u}	A_{2g}	E_u^-	E_g^-	E_u^+	E_g^+	B_{1u}
						A_{1g}	A_{1u}	E_g^-	E_u^-	E_g^+	E_u^+	B_{2g}
							A_{1g}	E_u^-	E_g^-	E_u^+	E_g^+	B_{2u}
								A_{1g} (A_{2g}) E_g^+	A_{1u} A_{2u} E_u^+	B_{1g} B_{2g} E_g^-	B_{1u} B_{2u} E_u^-	E_g^+
									A_{1g} (A_{2g}) E_g^+	B_{1u} B_{2u} E_u^-	B_{1g} B_{2g} E_g^-	E_u^+
										A_{1g} (A_{2g}) E_g^+	A_{1u} A_{2u} E_u^+	E_g^-
											A_{1g} (A_{2g}) E_g^+	E_u^-

Table 3.

D_{3h}

	E''	E'	A_2''	A_2'	A_1''	A_1'
E''	A_1' (A_2') E'					
E'	A_1'' A_2'' E''	A_1' (A_2') E'				
A_2''	E'	E''	A_1'			
A_2'	E''	E'	A_1''	A_1'		
A_1''	E'	E''	A_2'	A_2''	A_1'	
A_1'	E''	E'	A_2''	A_2'	A_1''	A_1'

( ) apply to combinations only.

2. Measurements and Assignments.

In the Tables 4, 5, and 6 are given both the observed frequencies and the assignments of the bands. Except for some extremely weak ones, all observed bands below 3300 cm^{-1} are included. Above this frequency all assigned bands as well as the more prominent of the unassigned ones are given. Furthermore we have included: (1) the inferred frequencies of all the inactive fundamentals, (2) the calculated frequencies of all infrared-active binary summation bands, (3) all the allowed binary difference bands for which the lower level has a Boltzmann factor greater than 5 $^0/_0$, and (4) a few difference bands with lower Boltzmann factor and some allowed ternary summation frequencies which for special reasons could be assigned with fair certainty.

The content of the various columns of Tables 4, 5, and 6 is as follows:

Column 1 gives the assignments of the bands, specified in accordance with our convention (Fig. 9 and Table 1). Fundamental number in brackets indicates that the frequency is a member of a Fermi-resonance multiplet. The components of a multiplet are indicated by a vertical, comb-like sign.

Column 2 gives the infrared activity: parallel band (‖), perpendicular band (⊥), or forbidden (f).

Column 3 lists the Boltzmann factors (in per cent.) for the lower levels of the difference bands.

Columns 4 and 9 give the calculated frequencies (in cm^{-1}) for vapour and liquid respectively. The fundamental frequencies used for the calculation are listed in Table 7. No correction for anharmonicity has been included. The fundamentals marked with an asterisk in Table 7, viz. 8 and 20 for benzene (both vapour and liquid) and 20 for benzene-d_6 (liquid only), appear in the spectra as Fermi multiplets only. As these states of resonance (especially those of C_6H_6) show a remarkable sturdiness in higher combinations, we have used the observed (or inferred) frequencies of the individual components of the 'fundamental multiplet' for the calculation of combination bands involving these fundamentals, rather than the assumed, unperturbed frequencies listed in Table 7. The Fermi resonance will be discussed below (see pag. 34).

Columns 5 and 10 give the frequency measurements for vapour and liquid respectively. The spectra of the liquids are the easiest to measure because the bands are rather narrow and have well-defined maxima. For the vapour spectra the band envelopes are broader and of varying shape. For complex groups of overlapping bands it was therefore often necessary to infer the contours of the individual bands before measurements of the frequencies of the assumed band centers could be made. In these cases the band forms as well as the frequencies given are tentative only.

Column 6 indicates the shape of the vapour bands. 'Q' means that a distinct Q-branch has been observed, and the frequency given in column 5 refers to its maximum. 'PR' means that a double band has been observed, and the frequency given refers then to the band minimum or to the mid-point between the two maxima. 'M' means that an intermediate structure (neither Q-branch nor double band) has been observed. In this case the mid-point of the band has been measured.

Column 7 and 11 give the molar extinction coefficient for the maximum point of the bands. These values are only very rough approximations to the true intensities, but may be of help in identifying the bands on the extinction curves on the Plate.

Column 8 and 12 give the difference, Δ (in cm^{-1}), between observed and calculated frequencies.

C_6H_6

Table 4.

Freq. No.		B %	Vapour					Liquid			
			Calc. cm^{-1}	Obs. cm^{-1}		$\varepsilon_{\max}$	Δ cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	$\varepsilon_{\max}$	Δ cm^{-1}
16	f		398	—	—	—		404	—	—	
12 — 6	$\perp$	11	404	—	—	—		404	—	—	
18 — 6	$\perp$	11	431	—	—	—		429	—	—	
10 — 16	$\perp$	29	448	ca. 448	M	0.015	0	446	446	0.1	0
15 — 6	$\perp$	11	540	539	Q	0.015	— 1	540	540	0.1	0
5 — 16	$\perp$	29	592	ca. 595	PR	0.015	ca. + 3	587	—	—	
6	f		606	—	—	—		606	—	—	
C_6H_5D			—	607	Q	0.08		—	610	1.5	
11	$\parallel$		673	673	Q	70	0	675	675	> 70	0
14 — 6	$\perp$	11	703	—	—	—		703	—	—	
4	f		707	—	—	—		707	—	—	
9 — 16	$\parallel$	29	780	779	Q	0.7	— 1	774	774	2	0
10	f		846	—	—	—		850	850	2	0
C_6H_5D			—	ca. 855	M	0.01		—	—	—	
19 — 6	$\perp$	11	876	—	—	—		873	—	—	
C_6H_5D			—	924	Q	0.006		—	—	—	
17	f		967	—	—	—		969	969	2	0
17 C^{13}			—	968	PR	0.02		—	—	—	
5	f		990	—	—	—		991	992	2	+ 1
1	f		993	—	—	—		993			— 1
6 + 16	$\parallel$		1004	1003	Q	0.5	— 1	1010	1010	4	0
12	f		1010	—	—	—		1010			0
18	$\perp$		1037	1037	Q	15	0	1035	1035	30	0
4 + 16	$\perp$		1105	1106	PR	0.01	+ 1	1111	—	—	
15	f		1146	—	—	—		1146	1147	2	+ 1
9	f		1178	—	—	—		1178	1177	4	— 1
8 — 16	$\parallel$	29	1192	1192	Q	0.07	0	1182	—	—	
(1 + 6) — 16	$\parallel$	29	1212	1212	Q	0.08	0	1200	—	—	
10 + 16	$\perp$		1244	1242	M	0.3	— 2	1254	1248	1	— 6
14	f		1309	—	—	—		1309	1309	0.6	0
14 C^{13}			—	1310	M	0.01		—	—	—	
3	f		1350	—	—	—		1346	ca. 1346	0.4	ca. 0
5 + 16	$\perp$		1388	1388	M	1	0	1395	1393	3	— 2
19	$\perp$		1482	1482	Q	20	0	1479	1479	50	0

C_6H_6

Table 4 (continued).

Freq. No.		B %	Vapour Calc. cm^{-1}	Vapour Obs. cm^{-1}		Vapour ε_{max}	Vapour Δ cm^{-1}	Liquid Calc. cm^{-1}	Liquid Obs. cm^{-1}	Liquid ε_{max}	Liquid Δ cm^{-1}
10 + 11	⊥		1519	ca. 1522	PR	3	ca. + 3	1525	1528	5	+ 3
6 + 17	∥		1573	—	—	—		1575	—	—	
9 + 16	∥		1576	—	—	—		1582	—	—	
8 C^{13}			—	ca. 1583	M	0.05		—	—	—	
8	f		1590	—	—	—		1586	1586	1	0
(1 + 6)	f		1610	—	—	—		1604	ca. 1606	1	ca. + 2
6 + 12	⊥		1616	1622	Q	0.4	+ 6	1616	1618	1.5	+ 2
6 + 18	⊥		1643	—	—	—		1641	1643	0.4	+ 2
1 + 11	∥		1666	1667	Q	0.3	+ 1	1668	1671	1	+ 3
4 + 17	⊥		1674	1673	PR	0.3	— 1	1676			— 5
4 + 12	∥		1717	1716	Q	0.1	— 1	1717	1713	0.4	— 4
6 + 15	⊥		1752	1755	Q	0.5	+ 3	1752	1756	1	+ 4
10 + 17	⊥		1813	1811	M	7	— 2	1819	1816	10	— 3
?			—	1873	PR	0.2		—	1876	0.6	
10 + 18	∥		1883	1888	Q	0.2	+ 5	1885	ca. 1885	0.5	ca. 0
6 + 14	⊥		1915	1917	PR	0.1	+ 2	1915	1917	0.5	+ 2
5 + 17	⊥		1957	1958	M	5	+ 1	1960	1961	9	+ 1
8 + 16	∥		1988	1989	Q	0.4	+ 1	1990	1988	1	— 2
(1 + 6) + 16	∥		2008	2009	Q	0.4	+ 1	2008	2005	1	— 3
?			—	2000	Q	0.2		—			
?			—	2003	Q	0.4		—			
5 + 12	∥		2000	2005	Q	0.6	+ 5	2001			+ 4
1 + 18	⊥		2030	—	—	—		2028	—	—	
20 — 1	⊥	1	2054	ca. 2050	M	0.05	ca. — 4	2043	ca. 2044	0.2	ca. + 1
(8 + 19) — 1	⊥	1	2090	—	—	—		2079	—	—	
(1 + 6 + 19) — 1	⊥	1	2107	obs.	—	—		2098	obs.		
?			—	2077	Q	0.02		—	—	—	
6 + 19	⊥		2088	obs.	—	—		2085	2083	0.1	— 2
7 — 17	∥	2	2089	2089	Q	0.04	0	2079	—	—	
?			—	2138	Q	0.03		—	—	—	
9 + 17	∥		2145	2144	Q	0.03	— 1	2147	2146	0.07	— 1
9 + 12	⊥		2188	—	—	—		2188	2185	0.1	— 3
9 + 18	⊥		2215	2214	PR	0.8	— 1	2213	2211	1.5	— 2
?			—	2254	Q	0.015		—	2250	0.1	
?			—	2280	PR	0.07		—	2283	0.2	
9 + 15	⊥		2324	2326	PR	1	+ 2	2324	2326	3	+ 2
10 + 19	∥		2328	2328	Q	1	0	2329			— 3
?			—	2364	Q	0.2		—	2363	0.2	
3 + 18	⊥		2387	2386	Q	0.4	— 1	2381	2383	0.7	+ 2
?			—	2410	Q	0.4		—	2409	0.3	
20 — 6	⊥	11	2441	2442	Q	0.05	+ 1	2430	2430	0.15	0
13 — 6	⊥	11	2451	—	—	—		2442	—	—	
?			—	ca. 2462	M	0.05		—	2453	0.15	

C_6H_6

Tabel 4 (continued).

Freq. No.		B %	Vapour					Liquid			
			Calc. cm^{-1}	Obs. cm^{-1}		$\varepsilon_{\max}$	Δ cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	$\varepsilon_{\max}$	Δ cm^{-1}
1 + 19	⊥		2475	—	—	—		2472	2470	0.15	−2
(8 + 19) − 6	⊥	11	2477	—	—	—		2466			+4
9 + 14	⊥		2487	2486	Q	0.08	−1	2487	2485	0.2	−2
(1 + 6 + 19) − 6	⊥	11	2494	—	—	—		2485			0
?			—	2520	M	0.01		—	2520	0.1	
8 + 17	∥		2557	2556	Q	0.1	−1	2555	2555	0.2	0
(1 + 6) + 17	∥		2577	2576	Q	0.1	−1	2573	2574	0.2	+1
8 + 12	⊥		2600	2611	M	0.6	(+2)	2596	2596	1	0
(1 + 6) + 12	⊥		2620					2614	2615	0.6	+1
8 + 18	⊥		2627	—	—	—		2621	—	—	
(1 + 6) + 18	⊥		2647	—	—	—		2639	—	—	
7 − 16	∥	29	2658	—	—	—		2644	—	—	
9 + 19	⊥		2660	2659	PR	0.3	−1	2657	2653	1	−4
8 + 15	⊥		2736	2751	PR	0.01	(+6)	2732	2733	0.09	+1
(1 + 6) + 15	⊥		2756					2750	2753	0.1	+3
3 + 19	⊥		2832	2827	Q	0.8	−5	2825	2820	1	−5
?			—	2853	Q	0.5		—	2853	0.5	
8 + 14	⊥		2899	2898	M	2	(−10)	2895	2888	2	−7
(1 + 6) + 14	⊥		2919					2913	2907	1	−6
20	⊥		3047	3047	Q	50	0	3036	3036	60	0
7	f		3056	—	—	—		3048	—	—	
13	f		3057	—	—	—		3048	—	—	
?			—	—	—	—		—	ca. 3058	10	
2	f		3073	—	—	—		3062	—	—	
(8 + 19)	⊥		3083	3083	Q	30	0	3072	3072	30	0
(1 + 6 + 19)	⊥		3100	3100	Q	30	0	3091	3091	40	0
?			—	3255	M	0.04		—	ca. 3250	0.2	
3 + 8 + 16	∥		3338	3328	Q	0.015	−10	3336	3326	0.07	−10
3 + (1 + 6) + 16	∥		3358	3348	Q	0.02	−10	3354	3348	0.06	−6
?			—	3408	M	0.08		—	3400	0.15	
7 + 16	∥		3454	3455	Q	0.3	+1	3452	3448	0.3	−4
?			—	3497	M	0.03		—	3488	0.15	
?			—	3523	M	0.03		—	3516	0.1	
?			—	3623	Q	0.3		—	3612	0.7	
6 + 20	⊥		3653	3654	PR	0.6	+1	3642	3643	1.5	+1
6 + 13	⊥		3663	—	—	—		3654	—	—	
6 + (8 + 19)	⊥		3689	3690	PR	0.3	+1	3678	3685	0.8	+7
6 + (1 + 6 + 19)	⊥		3706	3706	PR	0.5	0	3697	3696	1.5	−1
2 + 11	∥		3746	3743	Q	0.08	−3	3737	—	—	
4 + 13	∥		3764	—	—	—		3755	—	—	
8 + 9 + 12	⊥		3778	—	—	—		3774	3770	0.2	−4
(1 + 6) + 9 + 12	⊥		3798	—	—	—		3792	3789	0.2	−3

C_6H_6

Table 4 (continued).

Freq. No.		B %	Vapour					Liquid			
			Calc. cm^{-1}	Obs. cm^{-1}		ε_{max}	Δ cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	ε_{max}	Δ cm^{-1}
10 + 20	‖		3893	3889	Q	0.04	− 4	3886	—	—	
10 + (8 + 19)	‖		3929	—	—	—		3922	—	—	
10 + (1 + 6 + 19)	‖		3946	—	—	—		3941	—	—	
3 + 8 + 12	⊥		3950	3952	M	0.3	+ 2	3942	3935	0.6	− 7
3 + (1 + 6) + 12	⊥		3970	3972	M	0.3	+ 2	3960	3957	0.6	− 3
7 + 17	‖		4023	—	—	—		4017	—	—	
1 + 20	⊥		4040	4030	PR	0.2	− 10	4029	4027	1	− 2
5 + 13	‖		4047	—	—	—		4039	—	—	
7 + 12	⊥		4066	4070	PR	3	+ 4	4058	4057	6	1
1 + (8 + 19)	⊥		4076	—	—	—		4065	—	—	
1 + (1 + 6 + 19)	⊥		4093	—	—	—		4084	—	—	
7 + 18	⊥		4093	—	—	—		4083	4080	1.5	3
2 + 18	⊥		4110	4107	Q	0.4	− 3	4097	—	—	
7 + 15	⊥		4202	4178	PR	0.07		4194	4175	0.3	
9 + 20	⊥		4225	4198	PR	0.08		4214	4195	0.4	
9 + 13	⊥		4235	ca.4220	M	0.08		4226	4218	0.3	
9 + (8 + 19)	⊥		4261	—	—	—		4250	4243	0.2	
9 + (1 + 6 + 19)	⊥		4278	4270	M	0.05		4269	4259	0.3	
7 + 14	⊥		4365	—	—	—		4357	—	—	
3 + 20	⊥		4397	4394	PR	0.04	− 3	4382	4378	0.3	− 4
3 + (8 + 19)	⊥		4433	4424	M	0.05	− 9	4418	4413	0.15	− 5
3 + (1 + 6 + 19)	⊥		4450	—	—	—		4437	4432	0.15	− 5
7 + 19	⊥		4538	—	—	—		4527	—	—	
2 + 19	⊥		4555	4556	PR	0.1	+ 1	4541	4547	0.4	+ 6
8 + 13	⊥		4647	4600	PR	0.7		4634	4585	1	
(1 + 6) + 13	⊥		4667					4652			
8 + 20	⊥		4637	4637	PR	0.6		4622	4624	1	
(1 + 6) + 20	⊥		4658					4640			
8 + (8 + 19)	⊥		4673	4663	PR	0.06		4658	4645	1	
8 + (1 + 6 + 19)	⊥		4690					4677			
(1 + 6) + (8 + 19)	⊥		4693	4684	PR	0.6		4676	4670	1	
(1 + 6) + (1 + 6 + 19)	⊥		4710					4695			
?				5885	M	0.2		—	5880	0.3	
2 + 20	⊥		6120	5936	M	0.6	− 184	6098	5915	0.7	− 183
2 + (8 + 19)	⊥		6156	—	—	—		6134	5930	0.5	− 204
2 + (1 + 6 + 19)	⊥		6173	—	—	—		6153	5954	0.6	− 199
7 + 13	⊥		6113	6003	M	1.5	− 110	6096	5985	1	− 111
7 + 20	⊥		6103	6130	M	0.1		6084	6096	0.15	+ 12
7 + (8 + 19)	⊥		6139	6155	M	0.15		6120	6115	0.1	− 5
7 + (1 + 6 + 19)	⊥		6156					6139	6144	0.15	+ 5

sym-$C_6H_3D_3$

Table 5.

Freq. No.		B %	Vapour					Liquid			
			Calc. cm^{-1}	Obs. cm^{-1}		ε_{max}	Δ cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	ε_{max}	Δ cm^{-1}
12 − 6	⊥	12	410	—	—	—		410	—	—	
1 − 11	‖	8	425	425	Q	0.07	0	423	421	0.3	− 2
18 − 16	‖	34	465	464	Q	0.5	− 1	459	459	1.5	0
12 − 11	‖	8	473	—	—	—		471	—	—	
9 − 6	⊥	12	507	—	—	—		507	—	—	
11	‖		531	531	Q	70	0	533	533	> 70	0
5 − 16	⊥	34	549	—	—	—		544	—	—	
7 − 16	⊥	34	556	—	—	—		552	—	—	
1.3-$C_6H_4D_2$			—	566	Q	1.5		—	572	5	
6	⊥		594	594	PR	0.6	0	594	ca. 592	1.5	ca. − 2
C_6H_5D			—	608	Q	0.3		—	610	1	
?			—	611	M	0.3		—			
3 − 6	⊥	12	665	—	—	—		665	—	—	
hot bands or 4 C^{13}			—	691	Q	15		—	—	—	
			—	694	Q	20		—	—	—	
4	‖		697	697	Q	30	0	697	697	60	0
19 − 10	‖	7	706	—	—	—		700	—	—	
10	f		708	—	—	—		712	ca. 714	5	ca. + 2
14 − 6	⊥	12	727	727	Q	2	0	728	726	5	− 2
9 − 16	‖	34	733	733	Q	1.5	0	727			− 1
16 + 16	⊥		736	—	—	—		748	ca. 748	1	ca. 0
1.3-$C_6H_4D_2$			—	777	Q	0.02		—	779	0.6	
19 − 6	⊥	12	820	—	—	—		818	—	—	
18	⊥		833	833	Q	10	0	833	833	30	0
8 − 10	‖	7	872	—	—	—		863	—	—	
1.3-$C_6H_4D_2$			—	—	—	—		—	878	1	
11 + 16	⊥		899	—	—	—		907	—	—	
15	f		912	—	—	—		910	—	—	
5	‖		917	917	Q	30	0	918	918	50	0
17	f		924	—	—	—		926	—	—	
1	f		956	—	—	—		956	955	2	− 1
7 − 14	⊥	<1	961	961	Q	0.3	0	952	—	—	
6 + 16	‖		962	967	Q	0.4	+ 5	968	968	2	0
8 − 6	⊥	12	986	—	—	—		981	—	—	
12	f		1004	—	—	—		1004	1003	1	− 1
19 − 16	‖	34	1046	—	—	—		1038	1038	0.8	0
4 + 16	⊥		1065	ca. 1063	PR	2	ca. − 2	1071	1068	5	− 3
10 + 16	⊥		1076	1082	PR	2	+ 6	1086	1084	3	− 2
9	⊥		1101	1101	Q	2	0	1101	1101	7	0
1.3-$C_6H_4D_2$			—	—	—	—		—	1165	0.3	
?			—	ca. 1175	M	0.03		—	—	—	
6 + 6	⊥		1188	—	—	—		1188	—	—	

sym-$C_6H_3D_3$

Table 5 (continued).

Freq. No.		B %/0	Vapour Calc. cm⁻¹	Vapour Obs. cm⁻¹		Vapour ε_{max}	Vapour Δ cm⁻¹	Liquid Calc. cm⁻¹	Liquid Obs. cm⁻¹	Liquid ε_{max}	Liquid Δ cm⁻¹
16 + 18	∥		1201	—	—	—		1207	—	—	
8 − 16	∥	34	1212	—	—	—		1201	1199	0.4	− 2
10 + 11	⊥		1239	1241	PR	2	+ 2	1245	1245	4	0
3	f		1259	—	—	—		1259	—	—	
5 + 16	⊥		1285	1286	M	0.3	+ 1	1292	1292	1.5	0
6 + 17	⊥		1292	—	—	—		1300	—	—	
6 + 10	∥		1302	—	—	—		1306	—	—	
14	f		1321	—	—	—		1322	1322	0.7	0
4 + 10	⊥		1405	—	—	—		1409	obs.	—	
19	⊥		1414	1414	PR	10	0	1412	1412	30	0
10 + 10	⊥		1416	—	—	—		1426	—	—	
6 + 18	⊥		1427	ca. 1432	PR	4	ca. + 5	1427	1429	10	+ 2
11 + 17	⊥		1455	—	—	—		1459	—	—	
1.3-$C_6H_4D_2$			—	1465	M	0.4		—	1458	1	
9 + 16	∥		1469	—	—	—		1475	1478	0.6	+ 3
1 + 11	∥		1487	1485	Q	0.3	− 2	1489	1488	0.6	− 1
6 + 15	⊥		1506	1504	Q	0.2	− 2	1506	1502	0.4	− 4
6 + 17	∥		1518	—	—	—		1520	—	—	
11 + 12	∥		1535	—	—	—		1537	obs.	—	
10 + 18	∥		1541	—	—	—		1545	obs.	—	
1 + 6	⊥		1550	ca. 1550	M	0.06	ca. 0	1550	obs.	—	
7 − 10	∥	7	1574	—	—	—		1562	—	—	
8	⊥		1580	1580	PR	0.8	0	1575	1575	5	0
6 + 12	⊥		1598	ca. 1600	M	0.2	ca. + 2	1598	1597	0.8	− 1
4 + 17	⊥		1621	—	—	—		1623	—	—	
5 + 10	⊥		1625	—	—	—		1630	—	—	
10 + 17	⊥		1632	1635	M	1.5	+ 3	1638	1638	3	0
1 + 4	∥		1653	—	—	—		1653	—	—	
18 + 18	⊥		1666	1668	M	0.3	+ 2	1666	1666	0.7	0
7 − 6	⊥	12	1688	—	—	—		1680	—	—	
6 + 9	⊥		1695	—	—	—		1695	—	—	
13 − 6	⊥	12	1700	—	—	—		1690	—	—	
4 + 12	∥		1701	1700	Q	0.1	− 1	1701	1700	0.3	− 1
15 + 18	⊥		1745	1745	Q	0.3	0	1743	1742	0.5	− 1
17 + 18	∥		1757	—	—	—		1759	—	—	
13 − 11	⊥	8	1763	—	—	—		1751	—	—	
16 + 19	∥		1782	—	—	—		1786	—	—	
1 + 18	⊥		1789	—	—	—		1789	—	—	
9 + 10	∥		1809	—	—	—		1813	—	—	
12 + 18	⊥		1837	—	—	—		1837	—	—	
5 + 17	⊥		1841	1842	Q	6	+ 1	1844	1843	8	− 1
17 + 17	⊥		1848	—	—	—		1852	—	—	
3 + 6	⊥		1853	—	—	—		1853	—	—	
1 + 5	∥		1873	1874	Q	0.3	+ 1	1875	—	—	

sym-$C_6H_3D_3$

Table 5 (continued).

Freq. No.		B %	Vapour					Liquid			
			Calc. cm^{-1}	Obs. cm^{-1}		ε_{max}	Δ cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	ε_{max}	Δ cm^{-1}
7 − 16	∥	34	1914	—	—	—		1900	—	—	
6 + 14	⊥		1915	—	—	—		1916	—	—	
5 + 12	∥		1921	1923	Q	0.3	+ 2	1922	1922	0.6	0
9 + 18	⊥		1934	—	—	—		1934	1936	0.3	+ 2
8 + 16	∥		1948	1954	Q	0.2	+ 6	1949	1950	0.6	+ 1
6 + 19	⊥		2008	—	—	—		2006	—	—	
9 + 15	⊥		2013	2014	Q	0.2	+ 1	2011	2012	0.3	+ 1
9 + 17	∥		2025	2026	Q	0.15	+ 1	2027	2030	0.15	+ 3
1 + 9	⊥		2057	obs.	—	—		2057	—	—	
3 + 18	⊥		2092	—	—	—		2092	2094	0.08	+ 2
9 + 12	⊥		2105	obs.	—	—		2105	—	—	
?			—	2128	PR	0.04		—	2139	0.15	
10 + 19	∥		2122	—	—	—		2124	—	—	
20 − 17	∥	2	2139	2139	Q	0.06	0	2127	2127	0.15	0
14 + 18	⊥		2154	ca. 2152	PR	0.06	ca. − 2	2155	2156	0.2	+ 1
6 + 8	⊥		2174	2171	PR	0.09	− 3	2169	2168	0.4	− 1
9 + 9	⊥		2202	2205	PR	0.2	+ 3	2202	2204	0.8	+ 2
18 + 19	⊥		2247	ca. 2248	PR	5	ca. + 1	2245	2242	7	− 3
?			—	2259	PR	7		—	2259	6	
7	⊥		2282	2282	PR	20	0	2274	2274	30	0
8 + 10	∥		2288	—	—	—		2287	—	—	
13	f		2294	—	—	—		2284	—	—	
15 + 19	⊥		2326	2329	PR	2	+ 3	2322	2326	3	+ 4
17 + 19	∥		2338	2335	Q	2	− 3	2338	2339	1	+ 1
20 − 7	∥	7	2355	—	—	—		2341	—	—	
3 + 9	⊥		2360	—	—	—		2360	2361	0.4	+ 1
1 + 19	⊥		2370	—	—	—		2368	—	—	
?			—	obs.	—	—		—	2385	0.5	
?			—	2386	PR	0.2		—	2391	0.5	
8 + 18	⊥		2413	—	—	—		2408	2406	0.5	− 2
12 + 19	⊥		2418	—	—	—		2416	—	—	
9 + 14	⊥		2422	2419	PR	0.5	− 3	2423	2421	0.5	− 2
20 − 6	⊥	12	2469	—	—	—		2459	—	—	
2 − 6	⊥	12	2471	—	—	—		2461	—	—	
8 + 15	⊥		2492	2490	PR	0.6	− 2	2485	2483	0.8	− 2
8 + 17	∥		2504	—	—	—		2501	2502	0.3	+ 1
9 + 19	⊥		2515	2511	PR	0.3	− 4	2513	2513	0.5	0
2 − 11	∥	8	2534	—	—	—		2522	—	—	
1 + 8	⊥		2536	2533	PR	0.4	− 3	2531	2530	0.4	− 1
8 + 12	⊥		2584	2583	PR	0.2	− 1	2579	2575	0.5	− 4
7 + 16	∥		2650	2651	Q	0.2	+ 1	2648	2648	0.2	0
3 + 19	⊥		2673	ca. 2675	M	0.2	ca. + 2	2671	2670	0.3	− 1
8 + 9	⊥		2681	—	—	—		2676	—	—	
?			—	2690	PR	0.1		—	2688	0.2	

sym-$C_6H_3D_3$

Table 5 (continued).

Freq. No.		B %	Vapour					Liquid			
			Calc. cm^{-1}	Obs. cm^{-1}		ε_{max}	Δ cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	ε_{max}	Δ cm^{-1}
20 − 16	∥	34	2695	—	—	—		2679	—	—	
14 + 19	⊥		2735	2732	PR	0.15	−3	2734	2732	0.2	−2
?			—	2751	PR	0.15		—	2751	0.1	
11 + 13	∥		2825	2818	Q	0.09	−7	2817	obs.	—	
19 + 19	⊥		2828	—	—	—		2824	—	—	
3 + 8	⊥		2839	obs.	—	—		2834	2834	0.3	0
?			—	obs.	—	—		—	2860	0.8	
6 + 7	⊥		2876	2874	PR	1	−2	2868	2868	1	0
6 + 13	⊥		2888	—	—	—		2878	—	—	
8 + 14	⊥		2901	2894	PR	1	−7	2897	2890	1.5	−7
7 + 10	∥		2990	2991	Q	3	+1	2986	2979	3	−7
4 + 13	∥		2991				0	2981			−2
8 + 19	⊥		2994	2996	PR	2	+2	2987			−8
20	⊥		3063	3063	Q	40	0	3053	3053	40	0
2	f		3065	—	—	—		3055	—	—	
7 + 18	⊥		3115	3118	PR	0.4	+3	3107	3104	1	−3
13 + 18	⊥		3127	—	—	—		3117	3119	1	+2
8 + 8	⊥		3160	3160	Q	1	0	3150	3148	1.5	−2
7 + 15	⊥		3194	—	—	—		3184	—	—	
7 + 17	∥		3206	—	—	—		3200	3196	0.5	−4
5 + 13	∥		3211	—	—	—		3202	—	—	
1 + 7	⊥		3238	3237	PR	0.6	−1	3230	3230	1.5	0
7 + 12	⊥		3286	3286	PR	0.5	0	3278	3278	1	0
?			—	3338	M	0.08		—	3330	0.2	
7 + 9	⊥		3383	—	—	—		3375	—	—	
9 + 13	⊥		3395	3392	Q	0.05	−3	3385	3386	0.15	+1
16 + 20	∥		3431	3434	Q	0.15	+3	3427	3428	0.2	+1
3 + 7	⊥		3541	—	—	—		3533	3533	0.1	0
?			—	ca. 3580	M	0.06		—	3568	0.2	
2 + 11	∥		3596	3594	Q	0.06	−2	3588	3592	0.2	+4
7 + 14	⊥		3603	—	—	—		3596			−4
6 + 20	⊥		3657	3657	PR	0.6	0	3647	3647	1	0
6 + 2	⊥		3659				−2	3649			−2
7 + 19	⊥		3696	—	—	—		3686	—	—	
13 + 19	⊥		3708	—	—	—		3696	ca. 3695	0.2	ca. −1
?			—	ca. 3748	M	0.07		—	3735	0.2	
2 + 4	∥		3762	—	—	—		3752	—	—	
10 + 20	∥		3771	3773	Q	0.05		3765	ca. 3766	0.15	ca. +1
?			—	3828	PR	0.1		—	3806	0.2	
7 + 8	⊥		3862	3864	PR	0.4	+2	3849	3852	0.8	+3
8 + 13	⊥		3874				−10	3859			−7
18 + 20	⊥		3896	3894	M	0.15	−2	3886	3888	0.3	+2
2 + 18	⊥		3898				−4	3888			0
15 + 20	⊥		3975	3979	PR	0.1	+4	3963	3962	0.2	−1

sym-$C_6H_3D_3$

Table 5 (continued).

Freq. No.		B %	Vapour Calc. cm^{-1}	Vapour Obs. cm^{-1}		ε_{max}	Δ cm^{-1}	Liquid Calc. cm^{-1}	Liquid Obs. cm^{-1}	ε_{max}	Δ cm^{-1}
2 + 5	‖		3982	—	—	—		3973	—	—	
17 + 20	‖		3987	—	—	—		3979	3980	0.4	+ 1
1 + 20	⊥		4019	4019	PR	0.1	0	4009	4010	0.3	+ 1
12 + 20	⊥		4067	4066	M	1.5	− 1	4057	4057	3	0
9 + 20	⊥		4164	4157	Q	0.2	− 7	4154	4150	0.5	− 4
2 + 9	⊥		4166				− 9	4156			− 6
?			—	4256	M	0.03		—	4246	0.15	
3 + 20	⊥		4322	—	—	—		4312	4312	0.1	0
14 + 20	⊥		4384	4390	M	0.05	+ 6	4375	4380	0.2	+ 5
19 + 20	⊥		4477	4495	M	1	+ 18	4465	4480	0.9	+ 15
2 + 19	⊥		4479				+ 16	4467			+ 13
7 + 7	⊥		4564	4434	M	0.15	− 130	4548	4430	0.2	− 118
7 + 13	⊥		4576				− 142	4558			− 128
8 + 20	⊥		4643	4642	M	0.8	− 1	4628	4630	1	+ 2
2 + 8	⊥		4645				− 3	4630			0
7 + 20	⊥		5345	5346	M	0.4	+ 1	5327	5332	0.4	+ 5
2 + 7	⊥		5347				− 1	5329			+ 3
13 + 20	⊥		5357				− 11	5337			− 5
?			—	5908	M	0.2		—	5882	0.2	
?			—	5945	M	0.3	—	—	5935	0.3	
20 + 20	⊥		6126	6000	M	0.8	− 126	6106	5980	0.5	− 126
2 + 20	⊥		6128				− 128	6108			− 128
?			—	6070	M	0.1		—	6053	0.1	

C_6D_6

Table 6.

Freq. No.		B %	Vapour Calc. cm^{-1}	Vapour Obs. cm^{-1}		ε_{max}	Δ cm^{-1}	Liquid Calc. cm^{-1}	Liquid Obs. cm^{-1}	ε_{max}	Δ cm^{-1}
1 − 11	‖	9	449	449	Q	1	0	448	ca. 445	1.5	ca. − 3
5 − 16	⊥	37	484	—	—	—		479	—	—	
hot bands or 11 C^{13}	‖		—	489	Q	40		—	—	—	
	‖		—	493	Q	50		—	—	—	
11	‖		496	496	Q	60	0	497	497	> 70	0
9 − 16	‖	37	524					518	517	20	− 1
9 − 16 R-branch				ca. 535	M	3					
6	f		579	—	—	—		579	580	1	+ 1
4	f		599	—	—	—		599	obs.		
C_6HD_5			—	612	Q	0.01		—	—	—	

C_6D_6

Table 6 (continued).

Freq. No.		B %	Vapour					Liquid			
			Calc. cm^{-1}	Obs. cm^{-1}		$\varepsilon_{\max}$	Δ cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	$\varepsilon_{\max}$	Δ cm^{-1}
10	f		660	—	—	—		664	664	1.5	0
19 − 10	∥	8	673	673	Q	0.03	0	666			−2
14 − 6	⊥	12	703	—	—	—		703	—	—	
C_6HD_5			—	708	Q	0.02		—	711	0.4	
19 − 6	⊥	12	754	755	PR	0.03	+ 1	751	753	0.6	+ 2
17	f		787	—	—	—		789	—	—	
18	⊥		814	814	Q	15	0	812	812	40	0
15	f		824	—	—	—		823	—	—	
5	f		829	—	—	—		830	—	—	
9	f		869	—	—	—		869	868	2	− 1
C_6HD_5			—	922	Q	0.2		—	—	—	
6 + 16	∥		924	928	Q	0.2	+ 4	930	930	1	0
4 + 16	⊥		944	944	PR	0.2	0	950	950	1	0
1	f		945	—	—	—		945	945	1	0
12	f		970	—	—	—		970	970	0.6	0
10 + 16	⊥		1005	1008	M	0.2	+ 3	1015	1012	0.7	− 3
3	f		1059	—	—	—		1055	1055	0.15	0
?			—	1086	PR	0.01		—	—	—	
10 + 11	⊥		1156	1155	M	2	− 1	1161	1162	3	+ 1
5 + 16	⊥		1174	1178	PR	0.3	+ 4	1181	ca. 1183	0.6	ca. + 2
3 + 18 − 10	∥	8	1213	1209	Q	0.06	− 4	1203	1202	0.3	− 1
8 − 16	∥	37	1213	1214	Q	0.06	+ 1	1202			0
9 + 16	∥		1214	1217	Q	0.06	+ 3	1220	1222	0.1	+ 2
14 + 16 − 16 or 14 C^{13}	⊥	37	—	ca. 1277	PR	0.05		—	—	—	
14	f		1282	—	—	—		1282	ca. 1283	0.5	ca. + 1
19	⊥		1333	1333	Q	5	0	1330	1330	20	0
6 + 17	∥		1366	—	—	—		1368	—	—	
4 + 17	⊥		1386	1391	M	0.6	+ 5	1388	1392	1.5	+ 4
6 + 18	⊥		1393				− 2	1391			− 1
6 + 15	⊥		1403	ca. 1407	PR	0.3	ca. + 4	1402	—	—	
1 + 11	∥		1441	—	—	—		1442	—	—	
10 + 17	⊥		1447	1450	M	4	+ 3	1453	1453	7	0
10 + 18	∥		1474	—	—	—		1476	ca. 1477	0.5	ca. + 1
2 − 18	⊥	4	1489	ca. 1485	PR	0.2	ca. − 4	1481	—	—	
6 + 12	⊥		1549	—	—	—		1549	—	—	
8 C^{13}?			—	1555	Q	0.5		—	1551	1.5	
8	f		1558	—	—	—		1553			− 2
?			—	ca. 1567	PR	0.5		—	1570	0.8	
4 + 12	∥		1569	—	—	—		1569			+ 1
(1 + 19) − 10	∥	8	—	—	—	—		1606	—	—	
20 − 10	∥	8	1628	—	—	—		1616	—	—	
5 + 17	⊥		1616	1620	PR	3	+ 4	1619	1618	7	− 1
9 + 17	∥		1656	1654	Q	0.4	− 2	1658	1656	0.5	− 2
9 + 18	⊥		1683	1681	PR	0.6	− 2	1681	1680	0.9	− 1

C_6D_6

Table 6 (continued).

Freq. No.		B %	Vapour					Liquid			
			Calc. cm^{-1}	Obs. cm^{-1}		ε_{max}	Δ cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	ε_{max}	Δ cm^{-1}
13 − 4	∥	6	1686	—	—	—		1676	—	—	
9 + 15	⊥		1693	ca. 1700	PR	0.5	ca. + 7	1692	1691	0.6	− 1
13 − 6	⊥	12	1706	—	—	—		1696	—	—	
(1 + 19) − 6	⊥	12	—	—	—	—		1691	—	—	
20 − 6	⊥	12	1709	—	—	—		1701	—	—	
?			—	—	—	—		—	ca. 1720	0.1	
1 + 18	⊥		1759	ca. 1765	PR	0.02	+ 6	1757	1768	0.05	+ 11
5 + 12	∥		1799	1800	Q	0.09	+ 1	1800	1798	0.3	− 2
?			—	1803	Q	0.1		—	—	—	
2 − 11	∥	9	1807	—	—	—		1796	—	—	
10 + 10 + 11	∥		1816	1817	Q	0.06	+ 1	1825	—	—	
9 + 12	⊥		1839	—	—	—		1839	—	—	
6 + 14	⊥		1861	1865	PR	0.4	+ 4	1861	1863	0.8	+ 2
3 + 18	⊥		1873	1878	PR	0.3	+ 5	1867	1868	0.8	+ 1
8 + 16	∥		1903	1903	Q	0.1	0	1904	1904	0.4	0
?			—	1907	Q	0.15		—	—	—	
6 + 19	⊥		1912	1915	Q	0.1	+ 3	1909	—	—	
7 − 16	∥	37	1929	—	—	—		1915	—	—	
?			—	—	—	—		—	1954	0.05	
10 + 19	∥		1993	1998	Q	0.08	+ 5	1994	1994	0.2	0
?			—	2037	PR	0.015		—	2032	0.04	
?			—	—	—	—		—	2055	0.03	
?			—	2114	PR	0.02		—	ca. 2110	0.1	
9 + 14	⊥		2151	2149	Q	0.1	− 2	2151	2152	0.4	+ 1
9 + 19	⊥		2202	2201	PR	0.15	− 1	2199	2198	0.8	− 1
7	f		2274	—	—	—		2266	—	—	
13	f		2285	—	—	—		2275	—	—	
1 + 19	⊥		2278	—	—	—					
(1 + 19)	⊥							2270	2270	30	0
20	⊥		2288	2288	Q	50	0	2280	2280	50	0
2	f		2303	—	—	—		2293	—	—	
?			—	2341	Q	0.8		—	2335	1.5	
8 + 17	∥		2345	2345	Q	0.8	0	2342	2343	1	+ 1
8 + 18	⊥		2372	2365	PR	1	− 7	2365	2363	2	− 2
8 + 15	⊥		2382	2383	PR	4	+ 1	2376	2376	3	0
3 + 19	⊥		2392	2397	Q	4	+ 5	2385	2389	5	+ 4
?			—	2456	Q	0.08		—	2447	0.15	
8 + 12	⊥		2528	2529	PR	0.1	+ 1	2523	2522	0.3	− 1
?			—	ca. 2570	M	0.03		—	2573	0.07	
7 + 16	∥		2619	2619	Q	0.2	0	2617	2614	0.3	− 3
?			—	—	—	—		—	2653	0.06	
?			—	2771	M	0.07		—	2772	0.2	
?			—	2795	Q	0.07		—	—	—	
2 + 11	∥		2799	2798	Q	0.07	− 1	2790	2792	0.1	+ 2

C_6D_6

Table 6 (continued).

Freq. No		B %	Vapour					Liquid			
			Calc. cm^{-1}	Obs. cm^{-1}		ε_{max}	Δ cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	ε_{max}	Δ cm^{-1}
8 + 14	$\perp$		2840	2838	Q	0.3	− 2	2835	2830	0.6	− 5
6 + 13	$\perp$		2864	—	—	—		2858	—	—	
6 + (1 + 19)	$\perp$							2849	2845	0.6	− 4
6 + 20	$\perp$		2867	2867	PR	0.8	0	2859	2858	1.5	− 1
4 + 13	$\parallel$		2884	—	—	—		2874	—	—	
8 + 19	$\perp$		2891	ca. 2890	M	0.1	ca. − 1	2883	ca. 2878	0.2	− 5
?			—	2926	PR	0.04		—	2919	0.15	
10 + (1 + 19)	$\parallel$							2934	ca. 2942	0.15	(ca. + 2)
10 + 20	$\parallel$		2948	2947	Q	0.05	− 1	2944			
?			—	—	—	—		—	2953	0.15	
?			—	2973	PR	0.05		—	2965	0.2	
?			—	3005	M	0.07		—	3000	0.2	
7 + 17	$\parallel$		3061	3064	Q	0.05	+ 3	3055	—	—	
C_6HD_5			—	3065	PR	0.15		—	3051	0.2	
7 + 18	$\perp$		3088	ca. 3085	PR	0.15	− 3	3078	3076	0.6	− 2
7 + 15	$\perp$		3098	—	—	—		3089	—	—	
5 + 13	$\parallel$		3114	3115	Q	0.2	+ 1	3105	3110	0.4	+ 5
2 + 18	$\perp$		3117				− 2	3105			+ 5
9 + 13	$\perp$		3154	—	—	—		3144	—	—	
9 + (1 + 19)	$\perp$							3139	3135	0.3	− 4
9 + 20	$\perp$		3157	3155	PR	0.1	− 2	3149	3147	0.3	− 2
1 + (1 + 19)	$\perp$							3215	—	—	
1 + 20	$\perp$		3233	—	—	—		3225	—	—	
7 + 12	$\perp$		3244	3244	M	2	0	3236	3234	4	− 2
?			—	3280	M	0.3		—	3272	0.5	
3 + (1 + 19)	$\perp$							3325	3323	0.3	(− 7)
3 + 20	$\perp$		3347	3335	Q	0.06	− 12	3335			
7 + 14	$\perp$		3556	—	—	—		3548	3547	0.07	− 1
7 + 19	$\perp$		3607	ca. 3575	PR	0.05	ca. − 32	3596	3576	0.15	− 20
2 + 19	$\perp$		3636	3636	Q	0.15	0	3623	3622	0.4	− 1
8 + 13	$\perp$		3843	3817	PR	0.6	− 26	3828	3802	1	− 26
8 + (1 + 19)	$\perp$							3823	3828	0.6	(− 1)
8 + 20	$\perp$		3846	3843	Q	0.3	− 3	3833			
?			—	4413	Q	0.2		—	4392	0.2	
?			—	4438	PR	0.3		—	4404	0.2	
7 + 13	$\perp$		4559	4460	M	0.6	− 101	4541	4453	0.9	− 88
7 + (1 + 19)	$\perp$							4536	ca. 4538	0.1	ca. + 2
7 + 20	$\perp$		4562	4550	M	0.7	− 12	4546	4555	0.08	+ 9
2 + (1 + 19)	$\perp$							4563	4483	2	(− 86)
2 + 20	$\perp$		4591	4500	M	2	− 91	4573			
?			—	4614	M	0.07		—	4602	0.1	
?			—	4641	M	0.04		—	4626	0.06	

Table 7.

Assigned Fundamental Frequencies.

Symmetry		Freq. No.	C_6H_6		sym-$C_6H_3D_3$		C_6D_6	
D_{6h}	D_{3h}		gas	liquid	gas	liquid	gas	liquid
A_{1g}	A_1'	1	993	993	956	956	945	945
		2	3073	3062	3065	3055	2303	2293
B_{1u}		12	1010	1010	1004	1004	970	970
		13	3057	3048	2294	2284	2285	2275
A_{2g}	B_2'	3	1350	1346	1259	1259	1059	1055
B_{2u}		14	1309	1309	1321	1322	1282	1282
		15	1146	1146	912	910	824	823
E_g^+	E'	6	606	606	594	594	579	579
		7	3056	3048	2282	2274	2274	2266
		8	1599*	1594*	1580	1575	1558	1553
		9	1178	1178	1101	1101	869	869
E_u^-		18	1037	1035	833	833	814	812
		19	1482	1479	1414	1412	1333	1330
		20	3064*	3053*	3063	3053	2288	2276*
B_{2g}	A_2''	4	707	707	697	697	599	599
		5	990	991	917	918	829	830
A_{2u}		11	673	675	531	533	496	497
E_g^-	E''	10	846	850	708	712	660	664
E_u^+		16	398	404	368	374	345	351
		17	967	969	924	926	787	789

* Assumed, unperturbed frequency.

3. Procedure of Assignment.

As a matter of principle all the spectroscopically inactive fundamentals must be inferred from the observed frequencies of their active combination bands. On the other hand, the assignment of these must be accomplished on the basis of a set of assumed fundamentals frequencies. Consequently, the problem can only be solved by trial and error.

First a preliminary set of fundamental frequencies was chosen based on the observed infrared-active fundamentals and the most plausible values for the remaining frequencies taken from earlier workers[26]. Then all binary combinations active in infrared were calculated and preliminary assignments made by comparison with the observed spectrum.

Subsequently the frequencies of the inactive fundamentals were adjusted to give minimum deviation between calculated and observed frequencies of summation bands, and, especially, of difference bands. The justification of this procedure will be discussed below in connection with anharmonicity (pag. 34).

For sym-benzene-d_3 the analysis along this line was fairly simple because of the larger number of observed fundamentals and combination bands.

For benzene and benzene-d_6 the following procedure was used: from combination bands with the observed fundamentals (A_{2u} and E_u^-) the frequencies of 16, 17 (E_u^+) were determined, then 4 and 5 (B_{2g}) from combinations with these, and finally 3 (A_{2g}), 14 and 15 (B_{2u}) and 12 (B_{1u}) from combinations with the now established frequencies. For 13 (B_{1u}) see pag. 37.

By consideration of those fundamentals, which are observed both in the vapour and in the liquid state, it is seen that the difference between vapour and liquid frequencies is almost constant for the three substances. We have therefore adopted this as a general principle for other fundamentals also.

Next a revised list of calculated combination frequencies was made and compared with the observed frequencies, and so on until finally a set of fundamental frequencies was obtained which allowed the best possible reproduction of the observed spectrum. These fundamental frequencies are given in Table 7, and commented further below (pag. 36).

4. Intensities.

a. *Fundamentals.* As already mentioned the intensities given in Table 4, 5, and 6 are peak intensities only. These afford a fairly correct measure for the relative

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[26] A. Langseth and R. C. Lord, Jr., Reference 3.
N. Herzfeld, C. K. Ingold, and H. G. Poole, J. Chem. Soc. **1946**, 316.
R. D. Mair and D. F. Hornig, Reference 7.
Foil A. Miller, Reference 10.
K. S. Pitzer and D. W. Scott, J. Amer. Chem. Soc. **65**, 803 (1943).
F. A. Miller and B. L. Crawford, Jr., Reference 1.

intensities of the stronger bands. However, for the weak bands, which generally are strongly overlapped by others of similar or higher intensities, quite appreciable deviations from the true intensity ratios may often occur.

We have measured the integrated intensities of the strongest bands in the spectra and found the isotope intensity rules[27] to be fulfilled satisfactorily. There seems, however, to be deviations outside the experimental error, which indicate a perceptible electrical—rather than mechanical—anharmonicity of the vibrations. However, as our intensity measurements are not sufficiently accurate for elucidating these finer details, we will in the following confine ourselves to a more qualitative discussion of the general intensity relations in the observed spectra.

As expected the allowed fundamentals appear as the most intense bands in the spectra of C_6H_6 and C_6D_6. The lowering of the symmetry from D_{6h} to D_{3h} for sym-$C_6H_3D_3$ brings, according to the selection rules, the fundamental frequencies 4 and 5 (B_{2g}) and 6, 7, 8, and 9 (E_g^+) into formal, infrared activity. It is to be expected, however, that the effective change in certain of the vibrational modes, especially of the destinct carbon-ring vibrations, will be very slight. In fact, the fundamentals 6, 8, and 9 appear in the vapour spectrum of sym-$C_6H_3D_3$ as weak bands only, the intensities being of the same order of magnitude as for allowed, binary combinations. The frequencies 4 and 5, on the other hand, are both observed with band intensities, which clearly indicates them as fundamentals. This is obviously caused by the proximity of the very intense fundamental 11 which has the same symmetry as 4 and 5 (A_2'').

None of the fundamentals (or, for that matter, none of the combinations) forbidden in infrared have been observed in the vapour spectra.

In the spectra of the liquids the relative band intensities are very similar to those in the vapour. For the liquid state the selection rules are no longer strictly obeyed, causing several of the forbidden fundamentals to appear with intensities like allowed, binary combinations.

b. *C^{13}-isotopic benzenes.* The natural C^{13}-abundance being 1.1 $^0/_0$ means that all samples contain ca. 7 $^0/_0$ of mono-C^{13}-benzenes. As these isotopic derivatives have C_{2v} symmetry, 27 out of the 30 fundamentals will be infrared active. These might be expected to give rise to several spurious bands, which would be difficult to assign unambigously. As will be seen from Tables 4, 5, and 6, only a few tentative assignments to C^{13}-species have been made.

Because of the small percentage change in mass, the effect of the replacement of one of the C^{12}-atoms with C^{13} can be regarded as a perturbation only of the vibrational system[28]. As the resulting isotopic effect is caused by the change in kinetic energy, only vibrations in which the C^{13}-atom is participating strongly will show a perceptible

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[27] B. L. CRAWFORD, Jr., J. Chem. Phys. **20**, 977 (1952).
J. C. DECIUS, J. Chem. Phys. **20**, 1039 (1952).

[28] E. TELLER, Hand- u. Jahrb. d. chem. Phys. **9**, II, p. 141.

shift in frequency, and even then only 5—10 cm^{-1} at the very outside. This means that the change in the different modes must be small and, therefore, that the infrared activities must be very nearly the same as for the corresponding fundamentals of the pure C^{12}-molecule. Bands due to C^{13}-species should, consequently, mainly be expected to appear in the spectra very close to the intense bands, where they will be rather difficult to observe, being overlapped by the ca. 15 times stronger C^{12}-bands. Except for some of the distinct carbonring frequencies all transitions forbidden in the pure C^{12}-molecule will have so low intensities (further diminished by the 7 per cent. abundance of the C^{13}-species) that they presumably will be unobservable.

c. *Binary summation bands.* These are as expected mostly much weaker than the fundamental frequencies. Even if the individual intensities vary considerably, the mean intensity of the binary summation bands seems roughly to be a 100 times lower than that of allowed fundamentals. About 70 °/₀ of all allowed combinations have been observed and assigned, the remaining being unobserved either because they apparently have too low intensity, or often because they are obscured by stronger bands.

From the present experimental material it seems impossible empirically to find a principle which would allow to predict the intensities of the different combinations. There exists, however, an obvious parallelism between the activities of the individual combination bands in the three spectra. One interesting thing is that the allowed combinations between out-of-plane H(D)-vibrations, viz. $5+17$, $10+17$, and $10+11$, appear with exceptionally high intensities in all three spectra.

d. *Binary difference bands.* The intensity of a difference band is generally expected to be approximately the intensity of the corresponding summation band multiplied by the Boltzmann factor for the lower level. This holds in some cases, but often it does not. The most striking instance, already discussed by Mair and Hornig[29], is $9-16$ which in the spectrum of C_6H_6 appears as a rather prominent band, whereas $9+16$ is unobserved and must be weaker than the difference.

e. *Ternary summation bands.* The average intensity of ternary combinations seems to be about a factor 10—20 lower than that of the binary. Several (and in certain regions all) of the weak bands observed are due to ternary or higher combinations. A good deal of these have been calculated, but we refraim from making any assignments, the number of allowed combinations being too large. Mostly there will be an allowed ternary combination for at least every 10 cm^{-1}.

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[29] Reference 7.

5. Anharmonicity.

A striking feature of the analysis given in Tables 5, 6, and 7 is the surprisingly small anharmonicity observed. It is true that most of the fundamental frequencies are not directly observed, but have been inferred from combination frequencies, assuming the anharmonicity to be as small as possible. This assumption is primarily justified by those cases in which summation frequencies of accurately known fundamentals have been observed. Furthermore it is seen from Tables 5, 6, and 7, columns 8 and 12 that it is in fact possible to carry through an analysis giving anharmonicities differing no more than a few cm^{-1} from zero. It is interesting to note that there seems to be no distinct preference for a negative rather than a positive anharmonicity.

In a few cases, however, a large negative anharmonicity has been observed for combinations of two hydrogen-(deuterium)-stretching frequencies. For $2+20$, for instance, the anharmonicities found are: ca. $-200\ \mathrm{cm}^{-1}$ for C_6H_6, ca. $-130\ \mathrm{cm}^{-1}$ for sym-$C_6H_3D_3$, and ca. $-90\ \mathrm{cm}^{-1}$ for C_6D_6, i. e. values in the approximate ratios 2 to $\sqrt{2}$ to 1. It should be emphasized, however, that on account of the large anharmonicities the assignment of these high-frequency bands to this specific combination is more or less tentative.

6. Fermi Resonance.

Because of the relatively large number of fundamental frequencies of the benzene molecule or its deuterium derivatives the spectra might be expected to display rather complicated vibrational structures in consequence of the inherent high probability for accidental degeneracies.

The well-known strong doublet at about $1600\ \mathrm{cm}^{-1}$ observed in the Raman spectrum of benzene was first explained by WILSON[30] as due to Fermi resonance between 8 and $1+16$. Similarly, HERZBERG[31] explained the three strong infrared bands observed in benzene in the $3000\ \mathrm{cm}^{-1}$-region—where only one active fundamental, 20, should be expected—as a Fermi triplet due to an accidental degeneracy of 20, $8+19$, and $1+6+19$.

It is surprising that nearly all cases of Fermi resonance observed in the complete C_6H_6 spectrum originate in these coincidence. Further, that no strong Fermi resonance at all is found in sym-$C_6H_3D_3$, and that only one coincidence—viz. of 20 and $1+19$—causes a resonance of medium strength in the spectrum of liquid C_6D_6. In practically all cases, where different bands of the same symmetry species are nearly-coinciding, no or very little perturbation is observed. In a few cases only, especially at high frequencies, new and unquestionable Fermi resonances are observed. In these cases detailed assignments have not been attempted.

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[30] E. B. WILSON, Jr., Phys. Rev. **46**, 146 (1934).

[31] G. HERZBERG, Reference 1, pag. 362.

Tabel 8.

	Interacting levels.	Vapour		Liquid	
		Unpert. freq.	Obs.	Unpert. freq.	Obs.
C_6H_6	8	1599	1590	1594	1586
	1 + 6	1601	1610	1596	1604
	20	3064	3047	3053	3036
	8 + 19	3082	3083	3072	3072
	11 + 6 + 19	3084	3100	3074	3091
C_6D_6	1 + 19	2278	—	2274	2270
	20	2288	2288	2276	2280

The feeble tendency for Fermi resonance probably means that the anharmonic terms in the potential function of the benzene molecule generally are small. This is in agreement with the above-mentioned observation that the anharmonicities as a rule are very small for low-frequency combinations, but may be of appreciable magnitude for some of the H-stretching combinations at higher frequencies.

On the other hand, the Fermi resonances: (8) ~ (1 + 6) and (20) ~ (8 + 19) ~ (1 + 6 + 19) in benzene and—to a lesser extent, (20) ~ (1 + 19) in liquid benzene, are remarkably persistent in combinations with other fundamentals. Especially the (8) ~ (1 + 6) doublet, which has a rather characteristic appearance, making it easily recognizable at several places in the benzene spectrum, has been a help rather than a complication for the analysis. For this reason we have used the observed frequencies of these 'fundamental multiplets' instead of the assumed frequencies for the unperturbed fundamentals given in Table 7, for calculating the combination frequencies[32].

This is, of course, the correct method for calculating difference bands, whereas rather large deviations from the observed positions of the summation bands might be expected. However, in most cases as well the splitting as the relative intensities of the 'fundamental multiplets' are maintained in the summation band. Only in a few cases the resonance breaks completely down and one band only is observed. In these cases the Δ, given in brackets in the tables, is calculated by means of the unperturbed fundamental frequencies.

An interesting case is the resonance (20) ~ (1 + 19) in C_6D_6, observed in the liquid, but not in the vapour. Seven summation bands, but unfortunately no difference bands, involving the fundamental 20, were observed. None of these bands show any sign of resonance in the vapour, whereas in the liquid four of them did, but three did not. The explanation seems to be that the anharmonic terms responsible

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[32] If this procedure is consistently followed it may happen that one particular combination can be calculated in two different way; for instance, the (1 + 6 + 8 + 19) combination in benzene as (8) + (1 + 6 + 19) = 690 cm^{-1} or as (1 + 6) + (8 + 19) = 4693 cm^{-1}. Both values are given in Table 4.

for this interaction are comparatively small. The resonance is therefore rather sensitive to the closeness of the coincidence of the unperturbed levels, 20 and 1 + 19.

Table 8 shows the assumed frequencies of the unperturbed levels (see pag. 38) and the observed frequencies of the 'fundamental multiplets' in C_6H_6 and C_6D_6.

It is seen that for C_6H_6 the coincidence of 1 + 6 and 8 is almost exact, whereas for the triplet there is a gap of ca. 20 cm^{-1} between the fundamental, 20, and the two combinations. For C_6D_6 the coincidence of 20 and 1 + 19 is almost exact in the liquid; but nevertheless the resulting resonance is weak, as it is often broken in combinations. In the vapour the 10 cm^{-1} gap between the unperturbed levels is sufficient to prevent a measureable interaction.

IV. FUNDAMENTAL FREQUENCIES

In principle the assignment given in Table 7 does not differ from that given by INGOLD et al[33] as modified by MAIR and HORNIG[34]. However, owing to the higher resolving power of the instrument we consider our fundamental frequencies to be more accurate. We have, furthermore, assigned frequencies for the gaseous and the liquid state separately.

In the following a discussion is given—when necessary—of the assignment of the individual fundamentals. Each section, comprising fundamentals within a D_{3h} symmetry class, is accompanied by a graphical representation of the frequencies in question. The abscissa is linear in square of the frequency and the ordinate linear in mass of the isotopic molecules. A diagram of this kind may be regarded as a graphical representation of the sum rule for isotopic frequencies, according to which the sum of the square of the fundamental frequencies in sym-$C_6H_3D_3$ is equal to the mean value of the corresponding sums for C_6H_6 and C_6D_6[35]. If the conversion of C_6H_6 into C_6D_6 hypothetically were effected by a continuous and equal increase in mass of the hydrogen atoms (i. e. without destroying the D_{6h} symmetry), the frequency-squares would to a first approximation follow the straight lines indicated between the fundamentals of C_6H_6 and C_6D_6. If, however, the mass of the hypothetical molecule midway between these two is redistributed so as to produce the real sym-$C_6H_3D_3$ molecule, the symmetry is lowered from D_{6h} to D_{3h}. But as the fundamentals from two different symmetry classes of C_6H_6 and C_6D_6 are combined in one class of sym-$C_6H_3D_3$ a mixing of the vibrational modes occur, resulting in a tendency for each frequency to avoid its neighbours. This splitting of interacting frequencies is very nicely illustrated in the diagrams. It is seen that the shifts are symmetrical in such a way that the ful-

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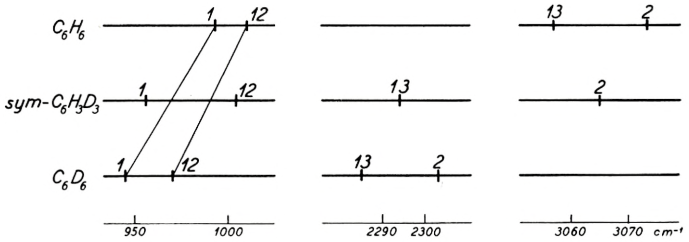
[33] Reference 26.
[34] Reference 7.
[35] See further pag. 42.

filment of the sum rule is preserved. For the H- and D-stretching vibrations the splitting is so strong that very nearly pure H- or D-frequencies result.

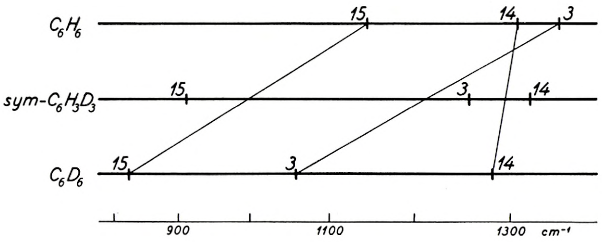
The enumeration of the fundamental frequencies of sym-$C_6H_3D_3$ has been determined by consideration of these diagrams.

1. A_1' (A_{1g} and B_{1u}) Fundamentals.



The totally symmetrical frequencies 1 and 2 in C_6H_6 and C_6D_6 have been measured in the Raman spectra of the gaseous state by STOICHEFF[36]; we have adopted his values. The frequencies of 13 for C_6H_6 and C_6D_6 could not be determined satisfactorily from the infrared spectra in the usual way. Instead, they were inferred on the basis of the following consideration. The H-stretching fundamental 2 in sym-$C_6H_3D_3$ in reality originates equally in 2 and 13 in C_6H_6, and the square of its frequency should therefore be expected to be equal to the mean of the square of the two C_6H_6-frequencies. Correspondingly, 13 in sym.-$C_6H_3D_3$ must originate equally in 2 and 13 in C_6D_6. These assumptions are sufficient for the calculation of 13 in both C_6H_6 and C_6D_6[37].

2. A_2' (A_{2g} and B_{2u}) Fundamentals.



These fundamentals have long evaded a definite establishment. The present assignment confirm decisively those first proposed by MAIR and HORNIG.

These fundamentals are all inactive in both Raman and infrared spectra; but

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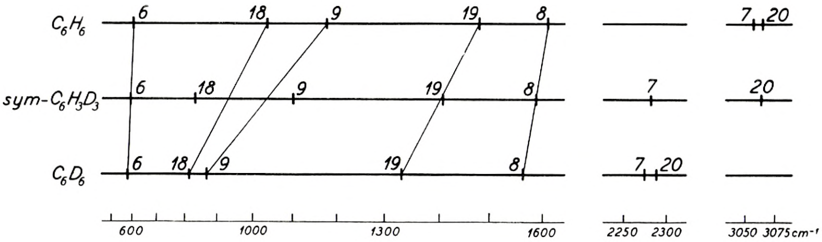
[36] B. P. STOICHEFF, Canad. Journ. Phys. **32**, 339 (1954).

[37] A justification of this argumentation will be discussed below in connection with the sum rule, pag. 45.

3, 14 and 15 in C_6H_6, 14 in sym-$C_6H_3D_3$, and 3 and 14 in C_6D_6 appear in the infrared spectra of the liquids as forbidden transitions, although 3 in C_6H_6 and 14 in C_6D_6 are very weak. Several of the summation bands, however, are rather strong so that especially 15 in C_6H_6 and in sym-$C_6H_3D_3$ are well established. The remaining fundamentals have been determined in the usual way.

3. E′ (E_g^+ and E_u^-) Fundamentals.



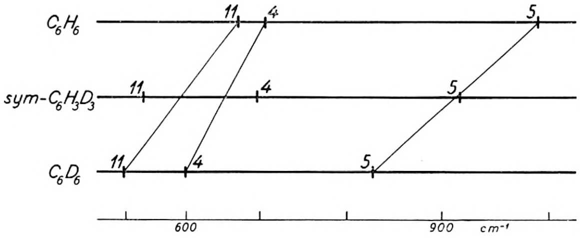
A special problem arises for the fundamentals 8 and 20 in C_6H_6 (both vapour and liquid) and for 20 in C_6D_6 (liquid), which have been observed as Fermi multiplets only. In order to be able to apply the product rule and the sum rule it is necessary to estimate the frequencies of the hypothetic, unperturbed fundamentals.

The assumed, unperturbed frequencies as well as the frequencies of the components in the observed resonance groups are given in Table 8. In the Raman spectrum of liquid C_6H_6 the low-frequency components of the (8) ~ (1 + 6) doublet is definitely the stronger and must therefore contain more of the fundamental than the high-frequency component. We have assumed the unperturbed 8 in liquid benzene to be 1954 cm^{-1}, i. e. 1 cm^{-1} lower than the observed mean value. Similarly, we have adopted 1599 cm^{-1} for 8 in the vapour. This gives the same shift (5 cm^{-1}) in the frequency of this fundamental from liquid to vapour as observed in both sym-$C_6H_3D_3$ and C_6D_6 (Cp. Table 7).

For the (1 + 19) ~ (20) doublet in liquid C_6D_6 it is the high frequency component which is the stronger of the two. The unperturbed 20 (liquid) is assumed to be 2276 cm^{-1}, i. e. 1 cm^{-1} higher than the mean value.

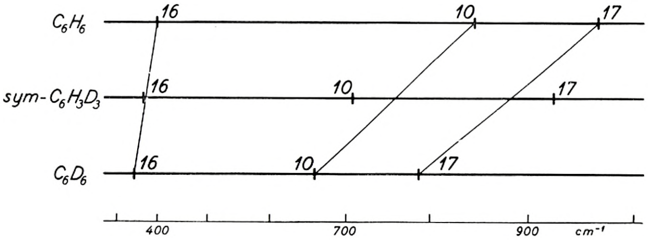
The 'fundamental triplet', (20) ~ (8 + 19) ~ (1 + 6 + 19), shows, within experimental error, the same splittings and about the same relative intensities of its components in both gaseous and liquid C_6H_6. Therefore, the state of resonance must be very nearly identical, the only difference being a shift in frequency of the triplet as a whole from one spectrum to the other. This shift (11 cm^{-1}) is assumed to be the same for the unperturbed fundamental. If we presume the sum of the squares of the three unperturbed frequencies to be equal to that of the three observed components, and furthermore assume the frequencies of the unperturbed summation bands to be close to the calculated values, we get the following frequencies for the unperturbed 20: 3064 cm^{-1} (vapour) and 3053 cm^{-1} (liquid). The shifts in frequency of 20, liquid to vapour, are 10 and 12 cm^{-1} for sym-$C_6H_3D_3$ and C_6D_6 respectively.

4. A_2'' (B_{2g} and A_{2u}) Fundamentals.



The frequencies of the inactive 4 and 5 fundamentals were inferred in the usual way without any complication.

5. E″ (E_g^+ and E_u^-) Fundamentals.



The fundamental 17 in sym-$C_6H_3D_3$ is placed at 924 cm^{-1} (vapour) and at 926 cm^{-1} (liquid). These values are based on several summation frequencies and confirmed by the product and the sum rule (see pag. 40). Ingold et al.[38] have placed 17 at 947 cm^{-1} on the basis of a Raman line of this frequency observed in liquid sym-$C_6H_3D_3$. We prefer, however, to assign this line to the fundamental 1 in one of the two different $C_5^{12}C^{13}H_3D_3$ species present, as we disagree with their arguments against this assignment. We consider 17 as unobserved in Raman effect.

It is interesting to note (cp. Table 7) that all fundamentals corresponding to out-of-plane vibrations (i. e. the A_2'' and E″ D_{3h}-classes) have higher frequencies in the liquid than in the gaseous phase, whereas the reverse situation is the normal one for all planar vibrations.

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[38] Reference 8.

V. APPLICATION OF PRODUCT RULE AND SUM RULES

1. Product Rule.

The Teller-Redlich product rule may in the present case be applied to the fundamental frequencies of C_6H_6 and C_6D_6 within each of the symmetry classes. For sym-$C_6H_3D_3$ each of the 5 symmetry classes may be combined with the appropriate frequencies of C_6H_6 or C_6D_6. This gives in total 20 relations, of which, however, only 15 are independent.

In Table 9 are listed the results obtained by applying the product rule to the fundamental frequencies, given in Table 7, for the gaseous as well as the liquid state. The theoretical ratios (in Table 9 printed in italics) are calculated by using the following atomic masses: H = 1.0081, D = 2.0147, and C = 12.0038. For the moments of inertia the experimental values given by Stoicheff[39] have been used.

The deviations of the experimental ratios from the theoretical values are given both in per cent, δ, and as the random error, μ (in cm^{-1}), to be assumed for everyone of the frequencies involved, in order to explain the deviation.

As the product rule is strictly valid for harmonic vibrations only, the observed deviations may be regarded as measures of the anharmonicity of the frequencies involved. However, experimental errors will of course be included as well. For this reason we consider it premature to discuss the anharmonicities of the various fundamentals in any details, the more so because we hope shortly to be able to extent the experimental material to several of the remaining, isotopic benzenes.

There are, however, certain general conclusions which can be drawn from the figures in Table 9. First and foremost, the observed agreement between theoretical and experimental ratios is very satisfactory and can be considered as strong circumstantial evidence for the correctness of the assignment.

Considering the experiences up till now in applying the product rule to hydrogen-deuterium isotopic molecules, the observed deviations are remarkably low except for those cases, in which H-(D)-stretching vibrations are involved: A' (A_{1g} and B_{1u}), and E' (E_g^+ and E_u^-). The comparatively high anharmonicity for the B_{1u} class and, especially, the positive anharmonicity for the B_{2u} class possibly indicated by the deviations found for these classes, may be due to the special nature of the potential function caused by the delocalized π-electrons of the benzene ring.

Another striking feature is the very low anharmonicities observed for all non-planar vibrations: A_2'' (A_{2u} and B_{2g}) and E'' (E_g^- and E_u^+).

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[39] Reference 36, (C_6H_6 and C_6D_6); A. Langseth and B. P. Stoicheff, Canad. Journ. Phys. **34**, 350 (1956), (sym-$C_6H_3D_3$).

Table 9.

Symmetry		Freq. No.	C_6H_6 / C_6D_6			C_6H_6 / s-$C_6H_3D_3$			s-$C_6H_3D_3 / C_6D_6$		
D_{6h}	D_{3h}		*Teor.* Obs. {Vap. Liq.	δ %	μ cm^{-1}	*Teor.* Obs. {Vap. Liq.	δ %	μ cm^{-1}	*Teor.* Obs. {Vap. Liq.	δ %	μ cm^{-1}
			1.4137								
A_{1g}		1, 2	1.4021	−0.8	2.9						
			1.4032	−0.7	2.6	*1.4137*			*1.4137*		
	A'					1.3961	−1.2	2.3	1.3990	−1.0	1.8
			1.4137			1.3976	−1.1	2.1	1.4006	−0.9	1.6
B_{1u}		12, 13	1.3930	−1.5	5.3						
			1.3950	−1.3	4.8						
			1.2856								
A_{2g}		3	1.2748	−0.8	5.0						
			1.2758	−0.8	4.6	*1.3449*			*1.3513*		
	A_2'					1.3352	−0.7	1.4	1.3559	+0.3	0.6
			1.4137			1.3331	−0.9	1.8	1.3607	+0.7	1.2
B_{2u}		14, 15	1.4201	+0.5	1.2						
			1.4218	+0.6	1.6						
		6, 7	*1.9985*								
E_g^+			1.9569	−2.1	2.8						
		8, 9	1.9588	−2.0	2.7	*1.9609*			*1.9623*		
	E'					1.9308	−1.5	1.4	1.9223	−2.0	1.7
		18, 19	*1.9254*			1.9271	−1.7	1.5	1.9326	−1.5	1.2
E_u^-			1.9967	−1.5	3.4						
		20	1.9013	−1.2	2.9						
			1.4137								
B_{2g}		4, 5	1.4095	−0.3	0.6						
			1.4093	−0.3	0.6	*1.3871*			*1.3881*		
	A_2''					1.3879	+0.1	0.1	1.3780	−0.7	0.8
			1.3620			1.3867	0.0	0.0	1.3802	−0.6	0.6
A_{2u}		11	1.3569	−0.4	1.1						
			1.3581	−0.3	0.8						
			1.2856								
E_g^-		10	1.2818	−0.3	1.1						
			1.2801	−0.4	1.6	*1.3449*			*1.3513*		
	E''					1.3525	+0.6	0.6	1.3434	−0.6	0.5
			1.4137			1.3495	+0.3	0.3	1.3409	−0.8	0.7
E_u^+		16, 17	1.4175	+0.3	0.3						
			1.4136	0.0	0.0						

2. First-order Sum Rule.

As already mentioned there excist, besides the product rule, certain sum rules, which additionally relate the frequencies of isotopic molecules. For the present case the first-order sum rule, as formulated by Decius and Wilson[40], states that for the fundamentals within each of the five symmetry classes of the common D_{3h} symmetry, the sum of the squares of the frequencies in C_6H_6 and C_6D_6 is equal to twice the corresponding sum for sym-$C_6H_3D_3$, according to the superposition condition:

$$C_6H_6 + C_6D_6 = 2C_6H_3D_3\,.$$

Table 10 contains the sums of the squares of the fundamental frequencies for each of the isotopic molecules (vapour as well as liquid), and the difference:

$$\varDelta = \sum \lambda\,(C_6H_6) + \sum \lambda\,(C_6D_6) - 2\sum \lambda\,(C_6H_3D_3).$$

The theoretical value of $\varDelta$ is zero. As for the product rule the observed deviations are given both in per cent. (of $2\sum$ sym.), δ, and as the random error, μ (in cm^{-1}), to be assumed for all frequencies involved, in order to explain the deviation.

It is seen from Table 10 that the agreement is excellent. Obviously the sum rule is obeyed to a higher approximation than the product rule, as was to be expected. From the arithmetic of the sum rule it is easily seen that this has a greater tendency for cancelling anharmonicity, when applied to observed frequencies, than the product rule, which is explicitely related to harmonic vibrations.

Besides emphazing the independent confirmation of the correctness of the assignments offered by the sum rule, we will for the present refrain from any further discussion of Table 10.

Table 10.

	C_6H_6 $\left\{\begin{array}{l}\text{Vap.}\\ \text{Liq.}\end{array}\right.$	s-$C_6H_3D_3$ $\left\{\begin{array}{l}\text{Vap.}\\ \text{Liq.}\end{array}\right.$	C_6D_6 $\left\{\begin{array}{l}\text{Vap.}\\ \text{Liq.}\end{array}\right.$	$\varDelta$	δ %	μ cm^{-1}
A_1'	20 794 727	16 578 613	12 358 959	− 3540	− 0.01	0.2
	20 672 297	16 471 633	12 267 399	− 3570	− 0.01	0.2
A_2'	4 849 297	4 161 866	3 443 981	− 30454	− 0.04	3.0
	4 838 513	4 160 865	3 433 878	− 49339	− 0.06	4.9
E'	26 310 646	21 344 215	16 363 271	− 14513	− 0.03	0.6
	26 165 535	21 225 180	16 245 387	− 39438	− 0.09	1.7
A_2''	1 932 878	1 608 659	1 292 058	+ 7618	+ 0.24	1.2
	1 937 555	1 612 622	1 294 710	+ 7021	+ 0.22	1.1
E''	1 809 209	1 490 464	1 173 994	+ 2275	+ 0.08	0.4
	1 824 677	1 504 296	1 186 618	+ 2703	+ 0.09	0.5

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[40] J. C. Decius and E. B. Wilson, Jr., J. Chem. Phys. **19**, 1409 (1951). cp. L. M. Sverdlow, Doklady Akad. Nauk. S.S.S.R. **78**, 1115 (1951).

3. Higher-order sum rules.

In their above-mentioned paper on the sum rule Decius and Wilson give a hint of the possible existence of higher order rules, such as for the sum of the products of frequency squares by pairs, but they do not consider these rules any further.

For the present isotopic molecules the higher order sum rules are very useful. Including the ordinary sum rule they may all be derived simultaneously from a relation, which for this case can be formulated as:

$$\mathsf{D}^{\mathrm{h}}_{\mathrm{I}} \times \mathsf{D}^{\mathrm{d}}_{\mathrm{II}} + \mathsf{D}^{\mathrm{d}}_{\mathrm{I}} \times \mathsf{D}^{\mathrm{h}}_{\mathrm{II}} = 2\,\mathsf{D}^{\mathrm{s}}_{\mathrm{III}}. \tag{1}$$

Here D stands for the secular determinant of a single symmetry class, normalized to unity coefficient of the unknown in its highest power. I and II refer to two symmetry classes of C_6H_6 and C_6D_6 which combine into one class, III of sym-$C_6H_3D_3$. The indices h, d, and s refer to C_6H_6, C_6D_6, and sym-$C_6H_3D_3$ respectively.

It can be shown that this relation, in the ordinary, harmonic approximation, is strictly valid for all the common D_{3h} symmetry classes except for the E' $(E^{+}_{g} + E_{u})$ class, in which case the rule is only approximately valid, although to a surprisingly good approximation[41].

With the symmetry class A'_2 $(A_{2g} + B_{2u})$ as an example (1) is equivalent to:

$$\left.\begin{aligned}&[x - \lambda^{\mathrm{h}}_{3}]\,[x^2 - (\lambda^{\mathrm{d}}_{14} + \lambda^{\mathrm{d}}_{15})\,x + \lambda^{\mathrm{d}}_{14}\lambda^{\mathrm{d}}_{15}] + [x - \lambda^{\mathrm{d}}_{3}]\,[x^2 - (\lambda^{\mathrm{h}}_{14} + \lambda^{\mathrm{h}}_{15})\,x + \lambda^{\mathrm{h}}_{14}\lambda^{\mathrm{h}}_{15}] = \\ &\qquad 2\,[x^3 - (\lambda^{\mathrm{s}}_{3} + \lambda^{\mathrm{s}}_{14} + \lambda^{\mathrm{s}}_{15})\,x^2 + (\lambda^{\mathrm{s}}_{3}\lambda^{\mathrm{s}}_{14} + \lambda^{\mathrm{s}}_{3}\lambda^{\mathrm{s}}_{15} + \lambda^{\mathrm{s}}_{14}\lambda^{\mathrm{s}}_{15})\,x - \lambda^{\mathrm{s}}_{3}\lambda^{\mathrm{s}}_{14}\lambda^{\mathrm{s}}_{15}]\end{aligned}\right\} \tag{2}$$

where λ is the square of the fundamental frequency. Equation (2) splits into the following relations:

$$\lambda^{\mathrm{h}}_{3} + \lambda^{\mathrm{d}}_{14} + \lambda^{\mathrm{d}}_{15} + \lambda^{\mathrm{d}}_{3} + \lambda^{\mathrm{h}}_{14} + \lambda^{\mathrm{h}}_{15} = 2\,(\lambda^{\mathrm{s}}_{3} + \lambda^{\mathrm{s}}_{14} + \lambda^{\mathrm{s}}_{15}) \tag{3}$$

$$\lambda^{\mathrm{h}}_{3}\,(\lambda^{\mathrm{d}}_{14} + \lambda^{\mathrm{d}}_{15}) + \lambda^{\mathrm{d}}_{3}\,(\lambda^{\mathrm{h}}_{14} + \lambda^{\mathrm{h}}_{15}) = 2\,(\lambda^{\mathrm{s}}_{3}\lambda^{\mathrm{s}}_{14} + \lambda^{\mathrm{s}}_{3}\lambda^{\mathrm{s}}_{15} + \lambda^{\mathrm{s}}_{14}\lambda^{\mathrm{s}}_{15}) \tag{4}$$

$$\lambda^{\mathrm{h}}_{3}\lambda^{\mathrm{d}}_{14}\lambda^{\mathrm{d}}_{15} + \lambda^{\mathrm{d}}_{3}\lambda^{\mathrm{h}}_{14}\lambda^{\mathrm{h}}_{15} = 2\,\lambda^{\mathrm{s}}_{3}\lambda^{\mathrm{s}}_{14}\lambda^{\mathrm{s}}_{15} \tag{5}$$

of which (3) is the ordinary sum rule, (4) and (5) expressions for second-order and third-order sum rules respectively. The last one (5) may be written as:

$$\frac{\lambda^{\mathrm{h}}_{3}}{\lambda^{\mathrm{d}}_{3}} + \frac{\lambda^{\mathrm{h}}_{14}\lambda^{\mathrm{h}}_{15}}{\lambda^{\mathrm{d}}_{14}\lambda^{\mathrm{d}}_{15}} = 2\,\frac{\lambda^{\mathrm{s}}_{3}\lambda^{\mathrm{s}}_{14}\lambda^{\mathrm{s}}_{15}}{\lambda^{\mathrm{d}}_{3}\lambda^{\mathrm{d}}_{14}\lambda^{\mathrm{d}}_{15}} \tag{6}$$

or

$$\frac{\lambda^{\mathrm{d}}_{3}}{\lambda^{\mathrm{h}}_{3}} + \frac{\lambda^{\mathrm{d}}_{14}\lambda^{\mathrm{d}}_{15}}{\lambda^{\mathrm{h}}_{14}\lambda^{\mathrm{h}}_{15}} = 2\,\frac{\lambda^{\mathrm{s}}_{3}\lambda^{\mathrm{s}}_{14}\lambda^{\mathrm{s}}_{15}}{\lambda^{\mathrm{h}}_{3}\lambda^{\mathrm{h}}_{14}\lambda^{\mathrm{h}}_{15}} \tag{7}$$

These equations, (6) and (7), constitute two relations between the four ratios of the product rule for these symmetry classes.

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[41] A discussion of higher order sum rules will be given elsewhere.

Table 11.

Symmetry	Freq. No.	Vapour		Liquid	
		Calc.	Obs.	Calc.	Obs.
A_1'	1	955	956	955	956
	2	3065	3065	3055	3055
	12	1004	1004	1004	1004
	13	2294	2294	2284	2284
A_2'	3	1253	1259	1251	1259
	14	1321	1321	1319	1322
	15	912	912	911	910
E'	6	592	594	592	594
	7	2281	2282	2271	2271
	8	1585	1580	1580	1575
	9	1099	1101	1098	1101
	18	838	833	837	833
	19	1413	1414	1410	1412
	20	3060	3063	3051	3053
A_2''	4	701	697	701	697
	5	916	917	918	918
	11	530	531	531	533
E''	10	708	708	711	712
	16	370	368	376	374
	17	924	924	926	926

The total number of sum rules analogous with (3), (4), and (5) is equal to the number of fundamentals in the D_{3h} symmetry class. Consequently, it is possible to calculate the fundamental frequencies of one of the isotopic molecules from those of the two others.

Table 11 gives the result of such a calculation of the frequencies of sym-$C_6H_3D_3$ from those of C_6H_6 and C_6D_6 (listed in Table 7). It is seen that the agreement between the calculated and the assigned fundamental frequencies is excellent for the symmetry classes A_1', A_2', A_2'', and E'', for which the higher-order sum rules are strictly valid. Even for the E' class, for which the rules are only approximately valid, the agreement is remarkably good. As pointed out above for the first order sum rule, also the higher-order sum rules must be valid to a higher approximation than the harmonic one because of an inherent tendency to cancellation of the anharmonicity. For this reason the agreement obtained here is much better than that normally achieved by calculations based on harmonic force constants.

4. Approximate Splitting of the Sum Rules.

It has been showed by CRAWFORD and EDSALL[41] and by WILSON[42] that it is possible to separate the hydrogen stretching frequencies from the other fundamen-

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[41] B. L. CRAWFORD, Jr., and J. T. EDSALL, J. Chem. Phys. **7**, 223 (1939).

[42] E. B. WILSON, Jr., J. Chem. Phys. **7**, 1047 (1939); **9**, 76 (1941).

tals, which generally have much lower frequencies and in this way obtain a secular determinant of lower degree which still reproduces the low-frequency fundamentals to a good approximation. Correspondingly, one may split the sum rules into three sets, approximately valid for each of the following groups: (1) the hydrogen stretching frequencies (about 3100 cm^{-1}), (2) the deuterium stretching frequencies (about 2300 cm^{-1}), and (3) the remaining fundamental frequencies (below ca. 1600^{-1}). This can be done simply by applying the rules, in accordance with the scheme given above, separately to each of these groups of fundamentals within the symmetry classes in question.

The low-frequency fundamentals of the A_1' ($A_{1g} + B_{1u}$) and E' ($E_g^+ + E_u^-$) classes calculated in this way agree within 0.4 cm^{-1} with the frequencies calculated above (Table 11). It is quite remarkable that the error introduced by a splitting of the sum rules to all appearance is insignificant.

For the hydrogen and deuterium stretching frequencies this approximation predicts the square of the frequencies in sym-$C_6H_6D_3$ simply to be the mean value of those in C_6H_6 or C_6D_6. For the A_1' ($A_{1g} + B_{1u}$) classes this is just what was assumed in order to calculate the fundamental 13 in C_6H_6 and C_6D_6 (cp. pag. 37). For the E' ($E_g^+ + E_u^-$) classes the agreement is less accurate. This may of course be due to the approximate nature of the splitting of the sum rule. It is, however, more likely that the assumed frequency of the unperturbed fundamental 20 in C_6H_6 is estimated about 6 cm^{-1} too low.

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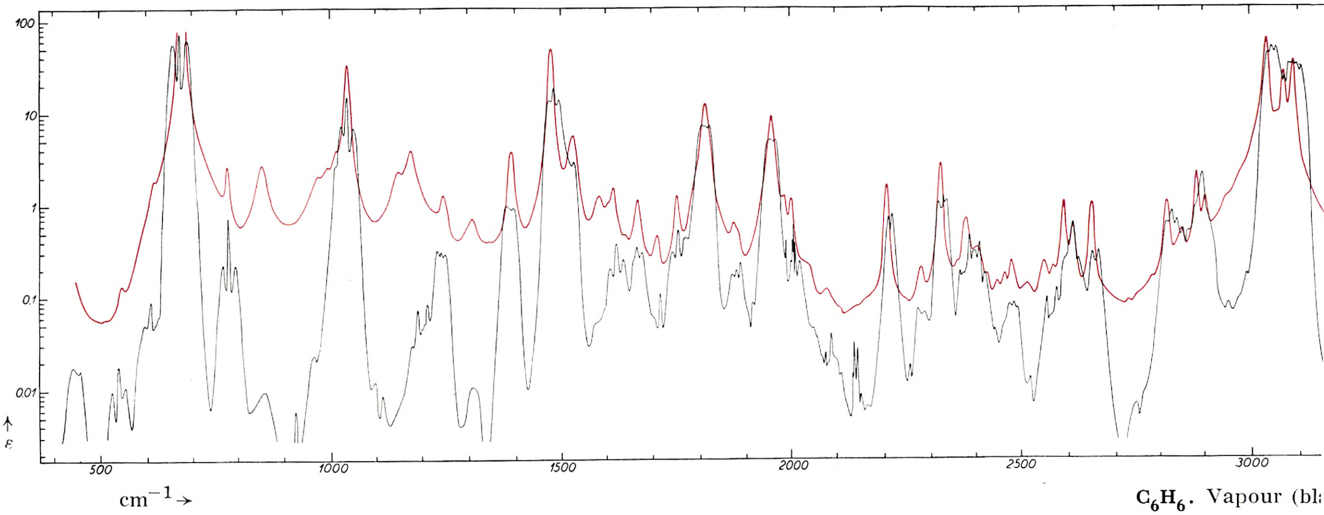
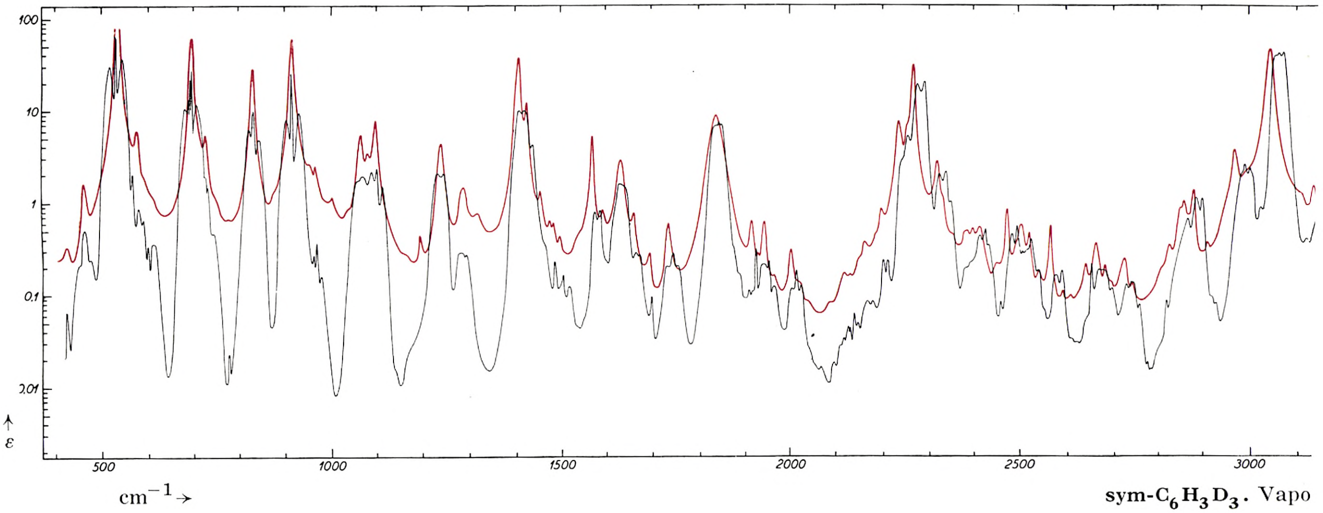
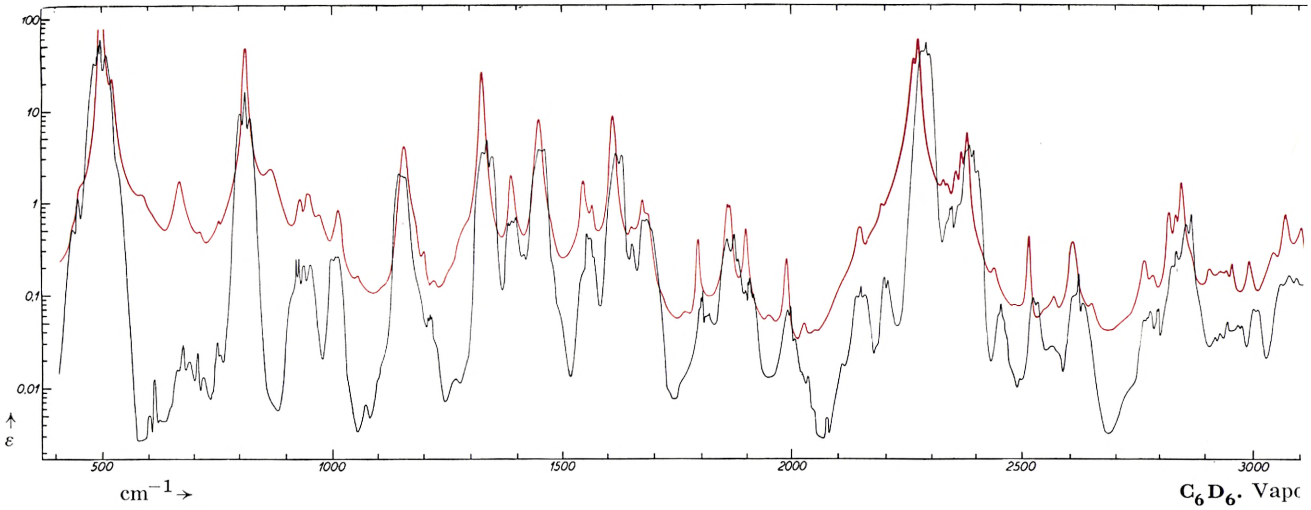


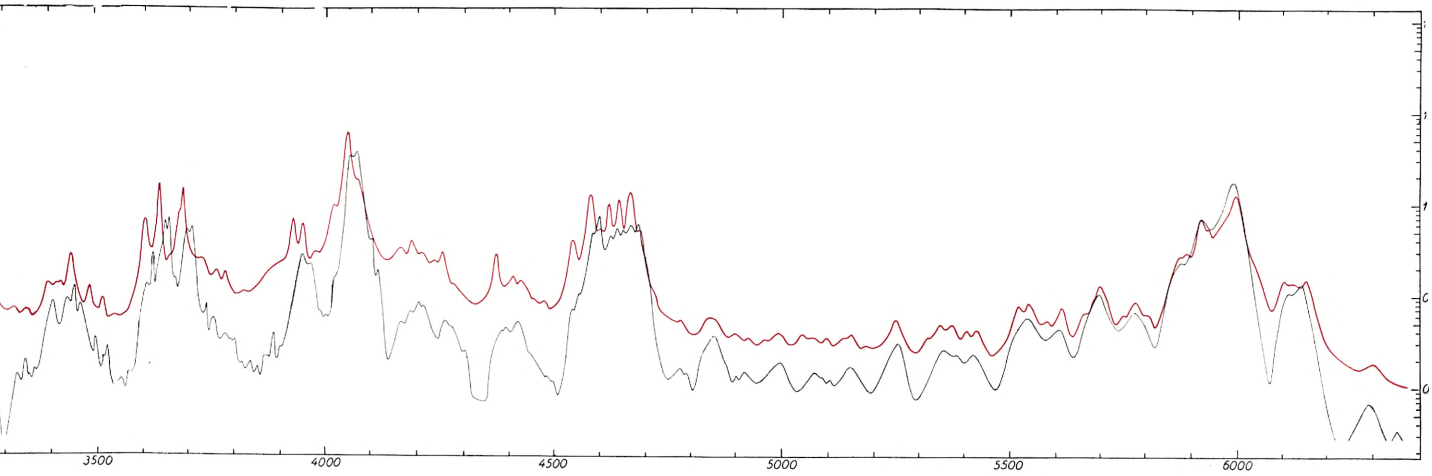
C_6H_6. Vapour (bl



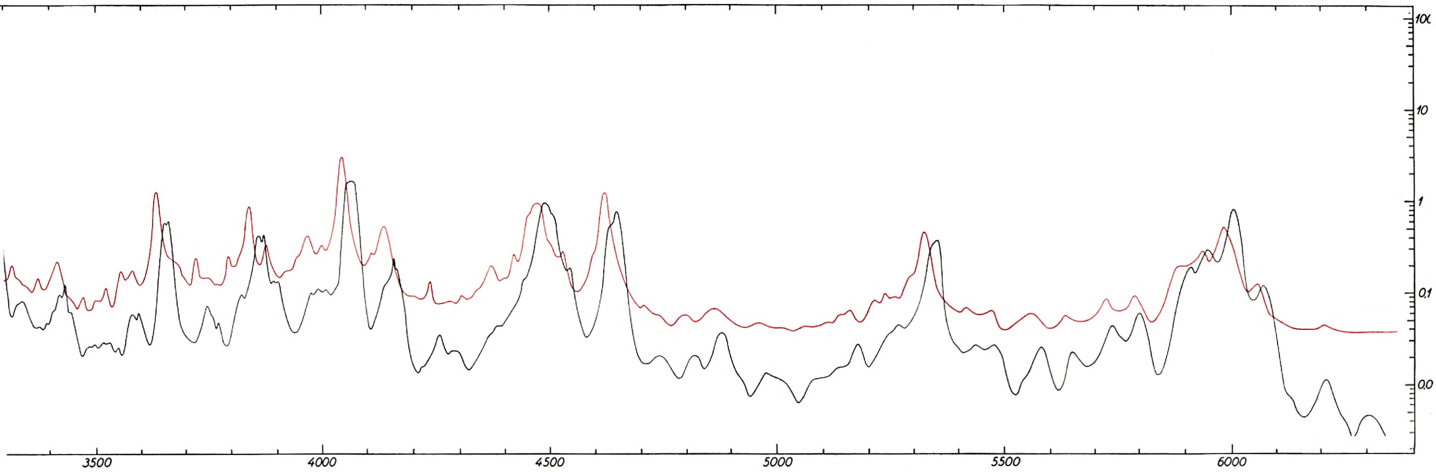
sym-$C_6H_3D_3$. Vapo



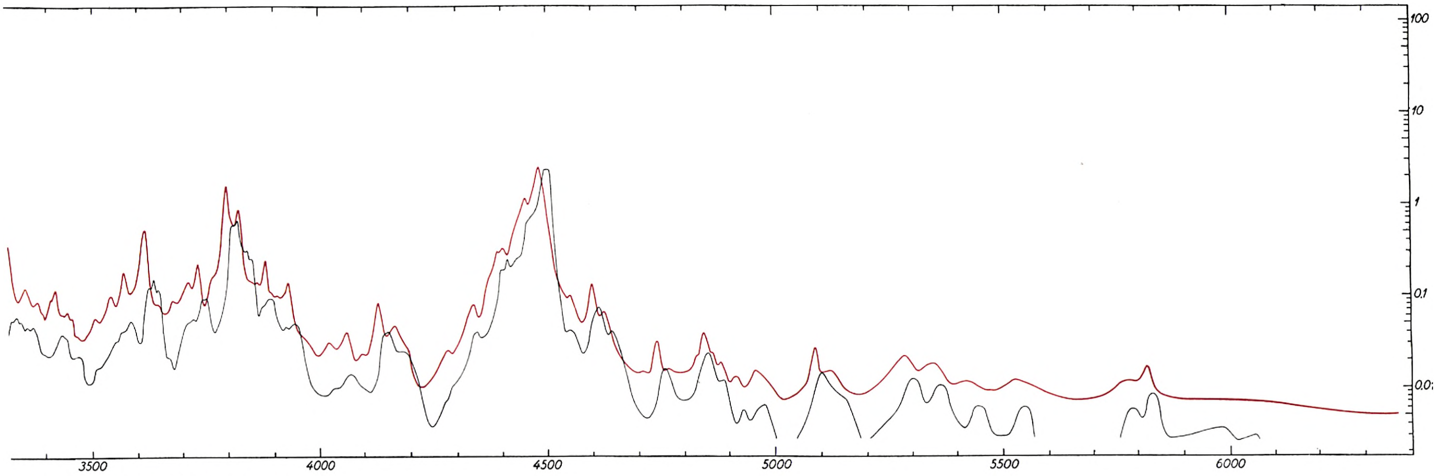
C_6D_6. Vapo



rve) and liquid (red curve).



x curve) and liquid (red curve).



curve) and liquid (red curve).

Det Kongelige Danske Videnskabernes Selskab

Matematisk-fysiske Skrifter

Mat. Fys. Skr. Dan. Vid. Selsk.

Bind **1**

(uafsluttet / en cours de publication)

	kr. ø.
1. Brodersen, Svend, and Langseth, A.: The Infrared Spectra of Benzene, sym-Benzene-d_3, and Benzene-d_6. 1956	14.00

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