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THE FUNDAMENTAL FREQUENCIES OF ALL THE DEUTERATED BENZENES

APPLICATION OF THE COMPLETE ISOTOPIC RULE TO NEW EXPERIMENTAL DATA

BY

SVEND BRODERSEN AND A. LANGSETH

1742

København 1959
i kommission hos Ejnar Munksgaard

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Synopsis.

The complete isotopic rule discussed previously (Mat. Fys. Skr. Dan. Vid. Selsk. **1**, no. 5 (1958)) is used to calculate all the fundamental frequencies of the various partly deuterated benzenes from those of benzene-d_0 and benzene-d_6. The calculated frequencies are compared with new experimental values obtained in this laboratory.

All non-planar frequencies are given by strictly valid rules. In order to calculate the planar frequencies it is necessary to introduce an approximation based on the separation of high and low frequencies. No correction for anharmonicity is required. A detailed discussion is given of the setting up of the rules, especially of the approximate ones.

The agreement between calculated and observed frequencies is very satisfactory. Frequencies calculated from strictly valid rules usually agree within 0—3 cm^{-1}), those calculated from approximate rules within 0—10 cm^{-1}.

A first order approximation is proposed and shown to be of great value for surveying the changes in vibrational frequencies caused by changes in the isotopic substitution.

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Introduction.

As the initial stage to a calculation of the complete, harmonic potential function of the benzene molecule it was felt desirable to set up all isotopic rules connecting the vibrational frequencies of its various deuterated species. As the complete harmonic potential function contains 34 constants only, whereas the 13 different H-D-isotopic benzenes furnish a total number of 360 fundamental frequencies determined by these constants, it follows that there must exist quite a considerable number of interrelations between these fundamentals. By setting up these rules one gets very valuable information about which of the isotopic molecules supply new and independent data concerning the potential function.

The consideration of this problem resulted in the establishment of a "complete isotopic rule" which has previously been proposed and its validity demonstrated for one set of isotopic molecules, *viz.* C_6H_6, sym-$C_6H_3D_3$, and C_6D_6[1]. In a recent paper[2] (in the following referred to as *I*) we have discussed the theory of this rule and have considered the general conditions for its applicability also to other isotopic molecules than the benzenes. As a demonstration the rule was applied to the deuterated species of acetylene and ethylene.

The scope of the present paper is to discuss—on the basis of the theory given in *I*—the setting up of the rule and its application to the various partly deuterated benzenes. All the fundamental frequencies of these isotopic molecules have been calculated and the results are compared with new experimental values.

Finally a first-order approximation will be discussed. This is shown to be very useful for surveying the changes in vibrational frequencies caused by isotopic substitutions.

Setting Up of the Rules.

It is considered as definitely proved that the benzene molecule has D_{6h} symmetry. Hence the symmetries of the various deuterated molecules are those given in Table 1. Following Langseth and Lord[3] the two different C_{2v} symmetries, arising acording as the two-fold axis is either passing through two para carbon atoms or is oriented

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[1] Svend Brodersen and A. Langseth, Mat. Fys. Skr. Dan. Vid. Selsk. **1**, no. 1, p. 43 (1956).

[2] Id., ibid. **1**, no. 5 (1958).

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

perpendicular to this direction, are denoted C_{2v} respectively C_{2v}^{*}. In Table 1 is further given the distribution of the fundamental vibrations among the various symmetry classes. The fundamentals are numbered according to WILSON[1] and LANGSETH and LORD[2]. The component of an originally degenerate vibration which preserves a two-fold axis passing through para carbon atoms is denoted by 'a' and the other component by 'b'. The hydrogen (deuterium) stretching vibrations are indicated by use of a heavy type.

TABLE 1. Symmetries of the deuterated benzenes and of their fundamentals.

D_{6h}		D_{3h}		D_{2h}		C_{2v}		C_{2v}^{*}		C_s	
-d$_0$, -d$_6$		sym-d$_3$		p-d$_2$, p-d$_4$		-d$_1$, -d$_5$, m-d$_2$, m-d$_4$, vic-d$_3$		o-d$_2$, o-d$_4$		as-d$_3$	
A_{1g}	1, **2.**	A_1'	1, **2,** 12, **13,**	A_{1g}	1, **2,** 6 a, **7** a, 8 a, 9 a.	A_1	1, **2,** 6 a, **7** a, 8 a, 9 a, 12, **13,** 18 a, 19 a, **20** a.	A_1	1, **2,** 6 a, **7** a, 8 a, 9 a, 14, 15, 18 b, 19 b, **20** b,	A'	1, **2,** 3, 6 a, 6 b, **7** a, **7** b. 8 a, 8 b, 9 a, 9 b, 12, **13,** 14, 15, 18 a, 18 b, 19 a, 19 b, **20** a, **20** b,
B_{1u}	12, **13.**										
E_g^+	6, **7.** 8, 9.	E'	6, **7,** 8, 9, 18, 19, **20.**	B_{1u}	12, **13,** 18 a, 19 a, **20** a.						
E_u^-	18, 19, **20.**			B_{3u}	14, 15, 18 b, 19 b, **20** b.	B_1	3, 6 b, **7** b, 8 b, 9 b, 14, 15, 18 b, 19 b, **20** b.	B_1	3, 6 b, **7** b, 8 b, 9 b, 12, **13,** 18 a, 19 a, **20** a.		
B_{2u}	14, 15,	A_2'	3, 14, 15.	B_{2g}	3, 6 b, **7** b, 8 b, 9 b.						
A_{2g}	3.										
B_{2g}	4, 5,	A_2''	4, 5, 11.	B_{3g}	4, 5, 10 b.	B_2	4, 5, 10 b, 11, 16 b, 17 b,	A_2	4, 5, 10 b, 16 a, 17 a.	A''	4, 5, 10 a, 10 b. 11, 17 a, 17 b.
A_{2u}	11.			B_{2u}	11, 16 b, 17 b.						
E_u^+	16, 17.	E''	10, 16, 17.	A_{1u}	16 a, 17 a.	A_2	10 a, 16 a, 17 a.	B_2	10 a, 11, 16 b, 17 b.		
E_g^-	10.			B_{1g}	10 a.						

The starting point for the setting up of the rules is the construction of a set of external symmetry coordinates. In order to do this we place a cartesian coordinate system at each atom and oriented as shown in Fig. 1. Following the procedure described by one of the present authors[3] we get the symmetry coordinates given in Table 2. From these coordinates it is an easy matter to set up the **G** matrix of any one of the

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[1] E B WILSON, Phys. Rev. **45**, 706 (1934).
[2] A. LANGSETH and R. C. LORD, loc. cit.
[3] SVEND BRODERSEN, Mat. Fys. Skr. Dan. Vid. Selsk. **1**, no. 4 (1954).

isotopic species. For the present purpose, however, it is sufficient to know the submatrix corresponding to the H (D) coordinates. This 'isotopic **G** matrix' is given in Table 3. In the form presented here it includes the isotopic **G** matrices of all the deuterated benzenes.

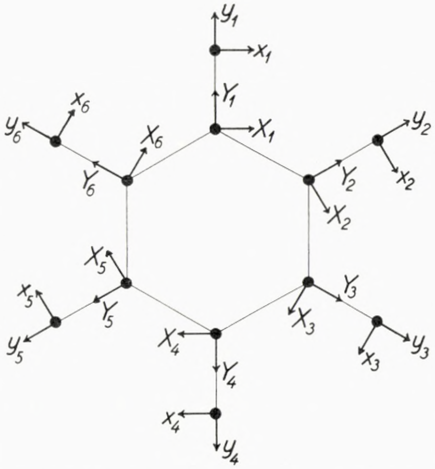

Fig. 1. Cartesian displacement coordinates.

Using the method described in *I* (pag. 10) one may now construct the coefficient-schemes of all the symmetry classes for any one of the deuterated molecules. As shown in *I* such a scheme comprises all the symmetrical minors of the isotopic **G** matrix of the class in question. But furthermore it indicates the form of the determinental equation which is an adequate expression for the complete isotopic rule determining the vibrational frequencies in the class.

In this way all the coefficient-schemes have been constructed, except that for the A' class of asym-benzene-d_3 in which case the labor involved is rather large. As shown below, however, this particular coefficient-scheme—as well as certain others—need not be known in order to set up the rule.

In Tables 4 and 5 are given a number of coefficient-schemes for the out-of-plane and for the in-plane classes respectively. From these tables the schemes of complementary species can be derived simply by interchanging H and D, as for instance that of para-benzene-d_4 from that of para-benzene-d_2. Instead of giving the total number of rows in these schemes we have collected identical rows into one row, which, therefore, is allotted an appropriate factor. No distinction has been made between 'a' and 'b' symmetry coordinates because this would be of no consequence for the calculations. For this reason the corresponding two columns have been combined and only one given for asym-benzene-d_3.

All the partly deuterated benzenes may be considered as derivatives of the D_{6h}

TABLE 2.

Class	Symmetry coordinates		Freq. no.
A_{1g}	$S_1 = 1/\sqrt{6}\,(Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6)$	C	1, 2.
	$S_2 = 1/\sqrt{6}\,(y_1 + y_2 + y_3 + y_4 + y_5 + y_6)$	H, D	
B_{1u}	$S_3 = 1/\sqrt{6}\,(Y_1 - Y_2 + Y_3 - Y_4 + Y_5 - Y_6)$	C	12, 13.
	$S_4 = 1/\sqrt{6}\,(y_1 - y_2 + y_3 - y_4 + y_5 - y_6)$	H, D	
E_{ga}^{+}	$S_{5\,\mathrm{a}} = 1/\sqrt{12}\,(2Y_1 - Y_2 - Y_3 + 2Y_4 - Y_5 - Y_6)$	C	6a, 7a,
	$S_{6\,\mathrm{a}} = 1/2\,(-X_2 + X_3 - X_5 + X_6)$	C	
	$S_{7\,\mathrm{a}} = 1/\sqrt{12}\,(2y_1 - y_2 - y_3 + 2y_4 - y_5 - y_6)$	H, D	8a, 9a.
	$S_{8\,\mathrm{a}} = 1/2\,(-x_2 + x_3 - x_5 + x_6)$	H, D	
E_{gb}^{+}	$S_{5\,\mathrm{b}} = 1/2\,(Y_2 - Y_3 + Y_5 - Y_6)$	C	6b, 7b,
	$S_{6\,\mathrm{b}} = 1/\sqrt{12}\,(2X_1 - X_2 - X_3 + 2X_4 - X_5 - X_6)$	C	
	$S_{7\,\mathrm{b}} = 1/2\,(y_2 - y_3 + y_5 - y_6)$	H, D	8b, 9b.
	$S_{8\,\mathrm{b}} = 1/\sqrt{12}\,(2x_1 - x_2 - x_3 + 2x_4 - x_5 - x_6)$	H, D	
E_{ua}^{-}	$S_{9\,\mathrm{a}} = 1/\sqrt{12}\,(2Y_1 + Y_2 - Y_3 + 2Y_4 - Y_5 + Y_6)$	C	18a, 19a,
	$S_{10\,\mathrm{a}} = 1/2\,(-X_2 - X_3 + X_5 + X_6)$	C	
	$S_{11\,\mathrm{a}} = 1/\sqrt{12}\,(2y_1 + y_2 - y_3 - 2y_4 - y_5 + y_6)$	H, D	20a, $\mathrm{T_a}$.
	$S_{12\,\mathrm{a}} = 1/2\,(-x_2 - x_3 + x_5 + x_6)$	H, D	
E_{ub}^{-}	$S_{9\,\mathrm{b}} = 1/2\,(-Y_2 - Y_3 + Y_5 + Y_6)$	C	18b, 19b,
	$S_{10\,\mathrm{b}} = 1/\sqrt{12}\,(-2X_1 - X_2 + X_3 + 2X_4 + X_5 - X_6)$	C	
	$S_{11\,\mathrm{b}} = 1/2\,(-y_2 - y_3 + y_5 + y_6)$	H, D	20b, $\mathrm{T_b}$.
	$S_{12\,\mathrm{b}} = 1/\sqrt{12}\,(-2x_1 - x_2 + x_3 + 2x_4 + x_5 - x_6)$	H, D	
B_{2u}	$S_{13} = 1/\sqrt{6}\,(X_1 - X_2 + X_3 - X_4 + X_5 - X_6)$	C	14, 15.
	$S_{14} = 1/\sqrt{6}\,(x_1 - x_2 + x_3 - x_4 + x_5 - x_6)$	H, D	
A_{2g}	$S_{15} = 1/\sqrt{6}\,(X_1 + X_2 + X_3 + X_3 + X_5 + X_6)$	C	3, $\mathrm{R_z}$.
	$S_{16} = 1/\sqrt{6}\,(x_1 + x_2 + x_3 + x_4 + x_5 + x_6)$	H, D	
B_{2g}	$S_{17} = 1/\sqrt{6}\,(Z_1 - Z_2 + Z_3 - Z_4 + Z_5 - Z_6)$	C	4, 5.
	$S_{18} = 1/\sqrt{6}\,(z_1 - z_2 + z_3 - z_4 + z_5 - z_6)$	H, D	
A_{2u}	$S_{19} = 1/\sqrt{6}\,(Z_1 + Z_2 + Z_3 + Z_4 + Z_5 + Z_6)$	C	11, $\mathrm{T_z}$.
	$S_{20} = 1/\sqrt{6}\,(z_1 + z_2 + z_3 + z_4 + z_5 + z_6)$	H, D	
E_{ua}^{+}	$S_{21\,\mathrm{a}} = 1/2\,(-Z_2 + Z_3 - Z_5 + Z_6)$	C	16a, 17a.
	$S_{22\,\mathrm{a}} = 1/2\,(-z_2 + z_3 - z_5 + z_6)$	H, D	
E_{ub}^{+}	$S_{21\,\mathrm{b}} = 1/\sqrt{12}\,(2Z_1 - Z_2 - Z_3 + 2Z_4 - Z_5 - Z_6)$	C	16b, 17b.
	$S_{22\,\mathrm{b}} = 1/\sqrt{12}\,(2z_1 - z_2 - z_3 + 2z_4 - z_5 - z_6)$	H, D	
E_{ga}^{-}	$S_{23\,\mathrm{a}} = 1/2\,(Z_2 + Z_3 - Z_5 - Z_6)$	C	10b, $\mathrm{R_a}$.
	$S_{24\,\mathrm{a}} = 1/2\,(z_2 + z_3 - z_5 - z_6)$	H, D	
E_{gb}^{-}	$S_{23\,\mathrm{b}} = 1/\sqrt{12}\,(2Z_1 + Z_2 - Z_3 - 2Z_4 - Z_5 + Z_6)$	C	10b, $\mathrm{R_b}$.
	$S_{24\,\mathrm{b}} = 1/\sqrt{12}\,(2z_1 + z_2 - z_3 - 2z_4 - z_5 + z_6)$	H, D	

TABLE 3. Isotopic **G** matrix.

		A_{1g}	B_{1u}	E_{ga}^{+}		E_{gb}^{+}		E_{ua}^{-}		E_{ub}^{-}		B_{2u}	A_{2g}
		S_2	S_4	S_{7a}	S_{8a}	S_{7b}	S_{8b}	S_{11a}	S_{12a}	S_{11b}	S_{12b}	S_{14}	S_{16}
A_{1g}	S_2	a	d	g		i		h		— j			
B_{1u}	S_4	d	a	h		— j		g		i			
E_{ga}^{+}	S_{7a}	g	h	c		— k		f		l			
	S_{8a}				b		k		— e		l	j	— i
E_{gb}^{+}	S_{7b}	i	— j	— k		b		l		e			
	S_{8b}				k		c		l		— f	h	g
E_{ua}^{-}	S_{11a}	h	g	f		l		c		— k			
	S_{12a}				— e		l		b		k	i	— j
E_{ub}^{-}	S_{11b}	— j	i	l		e		— k		b			
	S_{12b}				l		— f		k		c	— g	— h
B_{2u}	S_{14}				j		h		i		— g	a	d
A_{2g}	S_{16}				— i		g		— j		— h	d	a

		B_{2g}	A_{2u}	E_{ua}^{+}	E_{ub}^{+}	E_{ga}^{-}	E_{gb}^{-}
		S_{18}	S_{20}	S_{22a}	S_{24b}	S_{24a}	S_{24b}
B_{2g}	S_{18}	a	d	j	h	— i	g
A_{2u}	S_{20}	d	a	— i	g	j	h
E_{ua}^{+}	S_{22a}	j	— i	b	k	e	— l
E_{ub}^{+}	S_{22b}	h	g	k	c	— l	f
E_{ga}^{-}	S_{24a}	— i	j	e	— l	b	k
E_{gb}^{-}	S_{24b}	g	h	— l	f	k	c

where

$a = 1/6\ (\mu_1 + \mu_2 + \mu_3 + \mu_4 + \mu_5 + \mu_6)$

$b = 1/4\ (\mu_2 + \mu_3 + \mu_5 + \mu_6)$

$c = 1/12\ (4\mu_1 + \mu_2 + \mu_3 + 4\mu_4 + \mu_5 + \mu_6)$

$d = 1/6\ (\mu_1 - \mu_2 + \mu_3 - \mu_4 + \mu_5 - \mu_6)$

$e = 1/4\ (-\mu_2 + \mu_3 + \mu_5 - \mu_6)$

$f = 1/12\ (4\mu_1 - \mu_2 + \mu_3 - 4\mu_4 + \mu_5 - \mu_6)$

$g = 2/\sqrt{12}\,(2\mu_1 - \mu_2 - \mu_3 + 2\mu_4 - \mu_5 - \mu_6)$

$h = 2/\sqrt{12}\,(2\mu_1 + \mu_2 - \mu_3 - 2\mu_4 - \mu_5 + \mu_6)$

$i = 6/\sqrt{12}\,(\mu_2 - \mu_3 + \mu_5 - \mu_6)$

$j = 6/\sqrt{12}\,(\mu_2 + \mu_3 - \mu_5 - \mu_6)$

$k = 3/\sqrt{12}\,(\mu_2 - \mu_3 + \mu_5 - \mu_6)$

$l = 3/\sqrt{12}\,(\mu_2 + \mu_3 - \mu_5 - \mu_6)$

μ_1 etc. are the reciprocal masses of the hydrogen resp. deuterium atoms.

TABLE 4. Coefficient-schemes for the non-planar classes.

			B_{2g}	A_{2u}	E_u^+	E_g^-
			S_{18}	S_{20}	S_{22}	S_{24}
sym-d_3	A_2''	1/2	*H*	*D*		
		1/2	*D*	*H*		
	E''	1/2			*H*	*D*
		1/2			*D*	*H*
p-d_2	B_{3g}	1/3	*D*			*H*
		2/3	*H*			*D*
	B_{2u}	1/3		*D*	*H*	
		2/3		*H*	*D*	
	A_{1u}	1			*H*	
	B_{1g}	1				*H*
o-d_2	A_2	1/6	*H*		*H*	*D*
		1/3	*D*		*H*	*H*
		1/2	*H*		*D*	*H*
	B_2	1/6		*H*	*D*	*H*
		1/3		*D*	*H*	*H*
		1/2		*H*	*H*	*D*
as-d_3	A''	1/18	*H*	*D*	*HH*	*DD*
		1/18	*D*	*H*	*DD*	*HH*
		1/9	*D*	*D*	*HD*	*HH*
		1/9	*D*	*D*	*HH*	*HD*
		1/9	*H*	*H*	*DD*	*HD*
		1/9	*H*	*H*	*HD*	*DD*
		2/9	*H*	*D*	*HD*	*HD*
		2/9	*D*	*H*	*HD*	*HD*

			B_{2g}	A_{2u}	E_u^+	E_g^-
			S_{18}	S_{20}	S_{22}	S_{24}
d_1	D_2	1/6	*D*	*H*	*H*	*H*
		1/6	*H*	*D*	*H*	*H*
		1/3	*H*	*H*	*D*	*H*
		1/3	*H*	*H*	*H*	*D*
	A_2	1			*H*	*H*
m-d_2	B_2	1/6	*H*	*H*	*H*	*D*
		1/6	*H*	*H*	*D*	*H*
		1/3	*H*	*D*	*H*	*H*
		1/3	*D*	*H*	*H*	*H*
	A_2	1/2			*H*	*D*
		1/2			*D*	*H*
vic-d_3	B_2	1/36	*H*	*D*	*H*	*D*
		1/36	*D*	*H*	*D*	*H*
		2/9	*H*	*H*	*D*	*D*
		2/9	*D*	*D*	*H*	*H*
		1/4	*H*	*D*	*D*	*H*
		1/4	*D*	*H*	*H*	*D*
	A_2	1/2			*H*	*D*
		1/2			*D*	*H*

species, and accordingly their fundamental frequencies may be calculated from those of the D_{6h} compounds (-d_0 and -d_6). Many of them (*viz.*: -d_1, ortho-d_2, meta-d_2, asym-d_3, ortho-d_4, meta-d_4, and -d_5) may, however, just as well be considered as D_{2h} derivatives, and their fundamental frequencies may on this basis in fact more easily be calculated from those of the D_{2h} compounds (para-d_2 and para-d_4) together with those of the D_{6h} compounds (-d_0 and -d_6), the latter being considered as having D_{2h} symmetry. Correspondingly, asym-d_3 may be treated as a C_{2v} derivative.

There are therefore several alternative combinations of partly deuterated benzenes to which the complete isotopic rule may be applied. This leaves us a certain

Table 5. Coefficient-schemes for the planar classes of sym-benzene-d$_3$, para-benzene-d$_2$, and vic-benzene-d$_3$.

			A_{1g}	B_{1u}	E_g^+		E_u^-		B_{2u}	A_{2g}
			S_2	S_4	S_7	S_8	S_{11}	S_{12}	S_{14}	S_{16}
sym-d$_3$	A_1'	1/2	*H*	*D*						
		1/2	*D*	*H*						
	E'	1/4			*H*	*H*	*D*	*D*		
		1/4			*H*	*D*	*D*	*H*		
		1/4			*D*	*H*	*H*	*D*		
		1/4			*D*	*D*	*H*	*H*		
	A_2'	1/2							*H*	*D*
		1/2							*D*	*H*
p-d$_2$	A_{1g}	1/3	*D*		*H*	*H*				
		2/3	*H*		*D*	*H*				
	B_{1u}	1/3		*D*			*H*	*H*		
		2/3		*H*			*D*	*H*		
	B_{3u}	1/3					*H*	*H*	*D*	
		2/3					*H*	*D*	*H*	
	B_{2g}	1/3			*H*	*H*				*D*
		2/3			*H*	*D*				*H*
vic-d$_3$	A_1	1/72	*D*	*H*	*H*	*H*	*D*	*D*		
		1/72	*D*	*H*	*H*	*D*	*D*	*H*		
		1/72	*H*	*D*	*D*	*H*	*H*	*D*		
		1/72	*H*	*D*	*D*	*D*	*H*	*H*		
		1/9	*D*	*D*	*H*	*D*	*H*	*H*		
		1/9	*D*	*D*	*H*	*H*	*H*	*D*		
		1/9	*H*	*H*	*D*	*D*	*D*	*H*		
		1/9	*H*	*H*	*D*	*H*	*D*	*D*		
		1/8	*H*	*D*	*H*	*H*	*D*	*D*		
		1/8	*H*	*D*	*H*	*D*	*D*	*H*		
		1/8	*D*	*H*	*D*	*H*	*H*	*D*		
		1/8	*D*	*H*	*D*	*D*	*H*	*H*		
	B_1	1/72			*H*	*H*	*D*	*D*	*H*	*D*
		1/72			*H*	*D*	*D*	*H*	*D*	*H*
		1/72			*D*	*H*	*H*	*D*	*H*	*D*
		1/72			*D*	*D*	*H*	*H*	*D*	*H*
		1/9			*H*	*H*	*D*	*H*	*D*	*D*
		1/9			*D*	*H*	*H*	*H*	*D*	*D*
		1/9			*H*	*D*	*D*	*D*	*H*	*H*
		1/9			*D*	*D*	*H*	*D*	*H*	*H*
		1/8			*H*	*H*	*D*	*D*	*D*	*H*
		1/8			*H*	*D*	*D*	*H*	*H*	*D*
		1/8			*D*	*H*	*H*	*D*	*D*	*H*
		1/8			*D*	*D*	*H*	*H*	*H*	*D*

latitude for choosing that particular combination which in practice presents the easiest way for the calculation of the fundamental frequencies of the lower-symmetrical species. In Fig. 2 is sketched how, for instance, benzene-d_1 may be considered as an 'intermediate' compound between benzene-d_0 and para-benzene-d_2. For asym-benzene-d_3 there are four different possibilities.

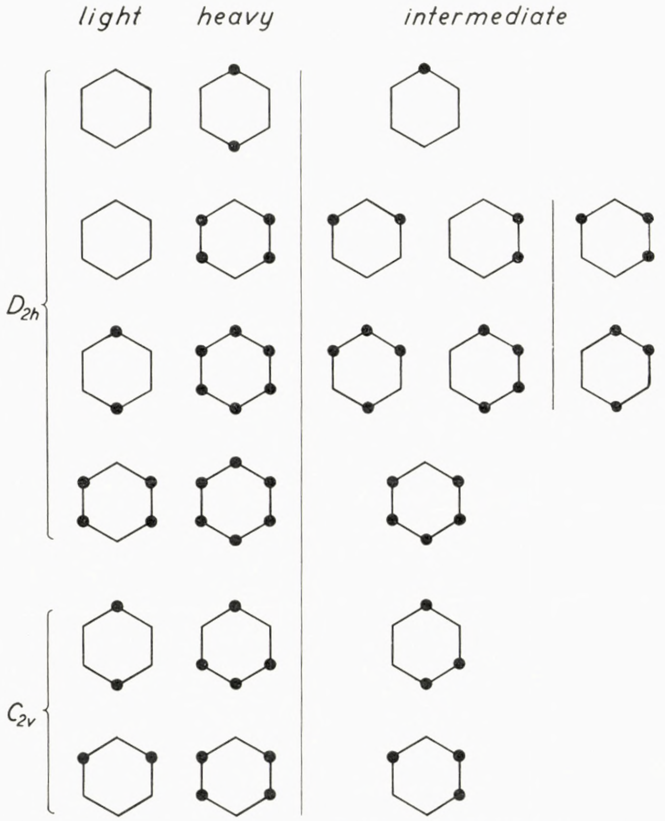

Fig. 2. Alternative possibilities for complete isotopic rules.

As discussed in *I* (pag. 13) the rules for all symmetry classes of the intermediate compounds to the left in Fig. 2 are of the mean-value type. For instance, for the A_1 class of benzene-d_1 we have:

$$[(A_1)^{d_1}] = \tfrac{1}{2}\,[(A_{1g})^{d_0}\,(B_{1u})^{p\text{-}d_2}] + \tfrac{1}{2}\,[(A_{1g})^{p\text{-}d_2}\,(B_{1u})^{d_0}].$$

The coefficients of $[(A_{1g})^{d_0}]$ and $[(B_{1u})^{d_0}]$ are formed in a way analogous to that used for a hybrid class (*I*, pag. 5). The rules for asym-benzene-d_3 as a D_{2h} derivative (to the right in Fig. 2) are more complicated, involving four different hybrid classes. The frequencies of this compound are therefore more easily calculated by use of, for instance, the following rule for the in-plane fundamentals:

$$[(A_1)^{as\text{-}d_3}] = \tfrac{1}{2}[(A_1)^{p\text{-}d_2}(B_1)^{m\text{-}d_4}] + \tfrac{1}{2}[(A_1)^{m\text{-}d_4}(B_1)^{p\text{-}d_2}].$$

Here again the coefficients for para-benzene-d_2 considered as a C_{2v} compound are evaluated as for a hybrid class.

This means that all the frequencies of the following isotopic molecules: -d_1, ortho-d_2, meta-d_2, asym-d_3, ortho-d_4, meta-d_4, and -d_5, may be calculated from those of: -d_0, para-d_2, para-d_4, and -d_6. It was shown in *I* (pag. 13) that the isotopic rules are strictly valid only for the non-planar fundamentals of all the deuterated benzenes as well as for the planar fundamentals of benzene-d_1 and benzene-d_5. For the planar fundamentals of the rest of the above mentioned isotopic benzenes the rules are only approximately valid in so far as they in these cases are based on the separability of high and low frequencies.

It should be noted that sym-benzene-d_3 and vic-benzene-d_3 can not be considered as D_{2h} derivatives. This is because the two para atoms in these compounds always are different, one being a hydrogen the other a deuterium atom.

The fundamental frequencies of sym-d_3, para-d_2, para-d_4, and vic-d_3 must be calculated directly from benzene-d_0 and benzene-d_6. Two symmetry classes (E_g^+ and E_u^-) of the D_{6h} molecules contain more than one isotopic symmetry coordinate, which means that the rules are strictly valid for those symmetry classes of the intermediate compounds which do not contain these vibrations. These include all the non-planar vibrations, but of planar vibrations only the two classes A_1' and A_2' of sym-benzene-d_3. The form of the rules are immediately given by the coefficient-schemes (Tables 4 and 5) as discussed in *I* (pag. 12).

The frequencies of the remaining planar fundamentals are given only by approximate rules, the form of which is found in the following way.

We assume that the hydrogen atoms in all high-frequency vibrations move in the radial (y) direction only and in all low-frequency vibrations in the tangential (x) direction only. In other words, we assume that the movements of the hydrogen atoms in the high-frequency vibrations may be described by use of the y-symmetry coordinates only (S_2, S_4, S_{7a}, S_{7b}, S_{11a}, and S_{11b}), and in the low-frequency vibrations by use of the x-symmetry coordinates only (S_{8a}, S_{8b}, S_{12a}, S_{12b}, S_{14}, and S_{16}). Consequently, the whole problem is splitted into two, one for the high-frequency vibrations, and another for the low-frequency vibrations. In order to set up the rules the coefficient-scheme is splitted into two parts: one for the high frequencies comprising the columns labelled S_2, S_4, S_7, and S_{11}, and another for the low frequencies comprising the columns labelled S_8, S_{12}, S_{14}, and S_{16}.

As the two low frequencies **1** and **12** belong to classes containing radial symmetry coordinates only they should in this connection be taken together with the high, radial, stretching frequencies **2**, **13**, **7**, and **20**. This suggests a further splitting of the high frequency part of the coefficient-scheme into two parts: one for the frequencies

Table 6. Splitted coefficient-schemes for the planar classes of sym-benzene-d_3, para-benzene-d_2, and vic-benzene-d_3.

		Freq. No. **1** and **12**			Freq. No. **6**, **8**, **9**, **18**, **19**, **14**, **15**, and **3**					Freq. No. **2**, **13**, **7**, and **20**				
			A_{1g} S_2	B_{1u} S_4		E_g^+ S_8	E_u^- S_{12}	B_{2u} S_{14}	A_{2g} S_{16}		A_{1g} S_2	B_{1u} S_4	E_g^+ S_7	E_u^- S_{11}
sym-d_3	A_1'	1/2 1/2	*H* *D*	*D* *H*						1/2 1/2	*H* *D*	*D* *H*		
	E'				1/2 1/2	*H* *D*	*D* *H*			1/2 1/2			*H* *D*	*D* *H*
	A_2'				1/2 1/2			*H* *D*	*D* *H*					
p-d_2	A_{1g}	1/3 2/3	*D* *H*		1	*H*				1/3 2/3	*D* *H*		*H* *D*	
	B_{1u}	1/3 2/3		*D* *H*	1		*H*			1/3 2/3		*D* *H*		*H* *D*
	B_{3u}				1/3 2/3		*H* *D*	*D* *H*		1				*H*
	B_{2g}				1/3 2/3	*H* *D*			*D* *H*	1			*H*	
vic-d_3	A_1	5/18 5/18 2/9 2/9	*D* *H* *D* *H*	*H* *D* *D* *H*	1/2 1/2	*H* *D*	*D* *H*			1/36 1/36 2/9 2/9 1/4 1/4	*D* *H* *D* *H* *D* *H*	*H* *D* *D* *H* *H* *D*	*H* *D* *H* *D* *D* *H*	*D* *H* *H* *D* *H* *D*
	B_1				1/36 1/36 2/9 2/9 1/4 1/4	*D* *H* *D* *H* *D* *H*	*H* *D* *D* *H* *H* *D*	*D* *H* *H* *D* *H* *D*	*H* *D* *H* *D* *D* *H*	1/2 1/2			*H* *D*	*D* *H*

1 and **12** comprising the columns labelled S_2 and S_4, and one for the frequencies **2**, **13**, **7**, and **20** comprising all four columns labelled S_2, S_4, S_7, and S_{11}.

The coefficient-scheme splitted according to the above discussion is shown in Table 6 for sym-benzene-d_3, para-benzene-d_2, and vic-benzene-d_3. From this scheme the rules for each group of frequencies is set up in the usual way. The high frequencies **2**, **13**, **7**, and **20** may be treated as hydrogen or deuterium frequencies separately by using only the H or the D elements of the schemes as discussed in *I* (pag. 19).

To sum up, the whole calculation is splitted up into five separate parts corresponding to the following types of vibrations:

1) the non-planar vibrations (z coordinates),
2) the low-frequency planar vibrations from classes containing hydrogen tangential (x) coordinates,
3) the low-frequency vibrations from classes containing radial (y) coordinates only,
4) the deuterium stretching vibrations (y coordinates), and
5) the hydrogen stretching vibrations (y coordinates).

The validity of this procedure is based on the assumption that the high and the low frequencies respectively correspond to pure radial and pure tangential vibrations as far as the hydrogen (deuterium) atoms are concerned. This is doubtless correct to a sufficient approximation for the high frequencies. For the low frequencies of the E_g^+ and E_u^- classes, however, it can not be strictly true, although it is obvious that most of these frequencies correspond to tangential vibrations. A further discussion of this point will be given in connection with the comparison between calculated and observed frequencies (pag. 34).

Observed Frequencies.

The normal frequencies of the benzene-d_0 and benzene-d_6 molecules, which are used as the basis for the present calculations, are given in Table 7. Except for minor corrections made on the basis of new Raman data the assigned frequencies are the result of the detailed investigation and analysis of the spectra of benzene-d_0, sym-benzene-d_3, and benzene-d_6 reported on previously[1].

The frequencies of the partly deuterated benzenes are all from measurements carried out in this laboratory[2]. The samples used for the present investigation were all except one (para-benzene-d_2) the same as those used previously to obtain the Raman spectra[3]. The preparations have been described by LANGSETH and KLIT[4].

The Raman spectra of all the deuterated benzenes in the liquid state have been reinvestigated using photographic technique. The spectra were excited with as well filtered ($NaNO_2$) as with unfiltered mercury radiation. The Raman frequencies were measured both from photographic enlargements (by interpolations between lines of the iron arc) and from microphotometer curves.

The infrared spectra of both gas and liquid state have been recorded on a Beckman IR 3 spectrometer using the technique previously described[1].

All the samples investigated (except that of sym-benzene-d_3) contained an appreciable amount of lower deuterated compounds. But as the spectra of all the dif-

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[1] SVEND BRODERSEN and A. LANGSETH, Mat. Fys. Skr. Dan. Vid. Selsk. **1**, no. 1 (1956).
[2] SVEND BRODERSEN, N. GROVING, A. LANGSETH, and E. MADSEN, unpublished work.
[3] A. LANGSETH and R. C. LORD, Mat. Fys. Medd. Dan. Vid. Selsk. **16**, no. 6 (1938).
[4] A. LANGSETH and A. KLIT, ibid. **15**, no. 13 (1938).

ferent isotopic species were available, it was in most cases possible to subtract the bands orriginating from the lower deuterated compounds. In no case bands due to other impurities have been detected.

TABLE 7. Fundamental frequencies of benzene-d_0 and benzene-d_6.

Class	Freq. No.	Vapour		Liquid	
		$-d_0$	$-d_6$	$-d_0$	$-d_6$
A_{1g}	1	992.8	945.5	992.5	945.1
	2	3073.5	2303.2	3062	2294
B_{1u}	12	1010	970	1010	970
	13	3057	2285	3048	2275
E_g^+	6	607	579	607	579
	7	3055	2275	3047	2267
	8	1600*	1558	1595*	1553
	9	1177	868	1177	868
E_u^-	18	1037	814	1035	812
	19	1482	1333	1479	1330
	20	3068*	2288	3057*	2276*
B_{2u}	14	1309	1282	1309	1282
	15	1146	824	1146	823
A_{2g}	3	1350	1059	1346	1055
B_{2g}	4	707	599	707	599
	5	990	829	991	830
A_{2u}	11	673	496	675	497
E_u^+	16	398	345	404	351
	17	967	787	969	789
E_g^-	10	845	659	849	663

* Assumed, unperturbed frequency.

Because of the enormous number of bands measured in all these spectra we shall not attempt to give a complete list of observed frequencies or even to bring graphical reproductions of the spectra. In Tables 8–18 are given the frequencies interpreted as fundamentals. Normally they correspond to the more prominent bands of the spectra. Only the bands assigned to inactive fundamentals, observed in the liquid state, are weak.

Numerical Calculations.

Although the proof of the complete isotopic rule is based on the harmonic approximation we have not found it necessary to make any attempt to adjust the observed frequencies for benzene-d_0 and benzene-d_6 to fit this approximation. Because the calculations based on the isotopic rule really are a kind of interpolation between the frequencies of the 'light' and the 'heavy' compound the anharmonicity tends to cancel. The calculations were consequently carried out directly from the frequencies given in Table 7. As the fundamental frequencies assigned for the vapour and the liquid state differ a little we have carried through two series of calculations, one for each state.

Even if this is a tedious task, most of the calculations may be carried out on an electric desk calculator (digit capacity: 10–10–20). In one case, however, we have to solve an equation of 13. degree (class A' of asym-benzene-d_3), which can not be done with this kind of machine. In order to solve this problem and at the same time to increase the speed and the accuracy of the calculations, it was decided to use an electronic computor.

A code has been worked out for the danish electronic computor DASK. The code was made so that it should be of universal use for all calculations based on the complete isotopic rule.

For each special problem a set of operational orders must be set up. For benzene these orders are identical for the non-planar and the low planar frequencies (**6**, **8**, **9**, **18**, **19**, **14**, **15**, and **3**). This convenience is caused by the formal conformity of the x and z symmetry coordinates (Table 2).

The results of the calculations are given in Tables 8–18 (pag. 25–33). The hydrogen stretching frequencies have not been calculated because we know that the resulting frequencies all will fall inside the original interval, which is only 18 cm^{-1} for the vapour and 15 cm^{-1} for the liquid (see Table 7). Furthermore, it seems rather futile to make these calculations in view of: a) the uncertainty of the basic frequencies, b) the errors arrising from the introduced approximations, c) the experimental errors, and d) the great probability in this region for resonance because of accidental degeneracy.

First-Order Approximation.

It may be difficult to survey the changes in frequencies calculated from the rule for the various isotopic species. For this reason we have found it convenient to introduce the following first-order approximation: The squares of the frequencies are calculated from those of the full-symmetry compounds by linear interpolation following the rule given by the appropriate column in the coefficient-scheme.

This approximation has the following advantages:

1. The first-order frequencies have a certain physical significance. They account for the pure isotopic effect on a single vibration neglecting the interaction with all other vibrations.
2. The sum of the squares of the first-order frequencies equals that of the correctly calculated (the highest degree coefficient in the secular equation is correct).
3. The first-order frequencies are easily calculated (see below).

In order to demonstrate how the first-order frequencies are calculated we may take some examples from the planar frequencies of para-benzene-d_2.

For the frequencies **1** and **12** we use the two columns in the coefficient-scheme labelled A_{1g} and B_{1u} respectively (see Table 6). In both cases we get

$$\lambda = \tfrac{1}{3}\,\lambda_D + \tfrac{2}{3}\,\lambda_H$$

where λ_D and λ_H are the squares of the frequencies in benzene-d_6 and benzene-d_0 respectively.

For the low frequencies of the B_{3u} class we get for **18**b and **19**b (originally in the E_u^- class)

$$\lambda = \tfrac{2}{3}\,\lambda_D + \tfrac{1}{3}\,\lambda_H$$

whereas for **14** and **15** we get

$$\lambda = \tfrac{1}{3}\,\lambda_D + \tfrac{2}{3}\,\lambda_H .$$

Instead of using a column of the coefficient-scheme we may equally well take the corresponding diagonal element of the isotopic **G**-matrix (see *I* pag. 10). Let us denote this element $(1-\alpha)\,\mu_H + \alpha\mu_D$. The first-order frequencies in the class are then given by

$$\lambda = (1-\alpha)\,\lambda_H + \alpha\lambda_D .$$

The value of α is easily calculated as the sum of the squares of the coefficients for the deuterium atoms in the corresponding symmetry coordinates. From Table 2 and the above given rules for the splitting of the coefficient-scheme we get the following values for α:

	$-d_1$	$p-d_2$	$o-d_2$ $m-d_2$	vic-d_3 sym-d_3	as-d_3	$o-d_4$ $m-d_4$	$p-d_4$	$-d_5$
non-degenerate vibrations	1/6	2/6	2/6	3/6	3/6	4/6	4/6	5/6
a-components of low-frequency vibrations b-components of high-frequency vibrations	0	0	3/6	3/6	1/4	3/6	1	1
b-components of low-frequency vibrations a-components of high-frequency vibrations	2/6	4/6	1/6	3/6	3/4	5/6	2/6	4/6

Note, that the mean-value for α for the two components of a degenerate vibration equals that for a non-degenerate vibration.

The first-order approximation is indicated in Fig. 3–11 by use of a thin line. The abcissa in these diagrams is linear in square of frequency. The first-order approximation is consequently represented by a straight line for a non-degenerate vibration, but by a broken line for a degenerate vibration.

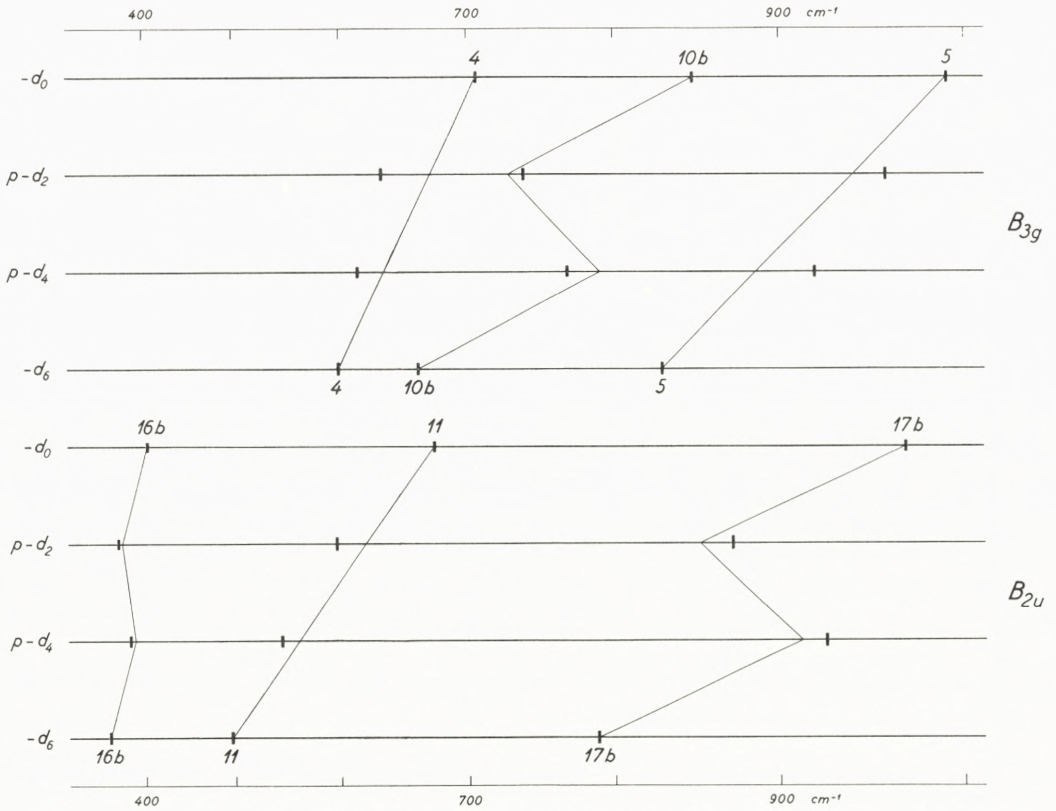

Fig. 3. Non-planar classes of the D_{2h} compounds.

If we next pass on to the frequencies calculated from the complete isotopic rule (indicated in the diagrams by heavy marks) we take the interaction of the vibrations into account. This interaction causes a mixing of the vibrations. The effect on the frequencies is a splitting, following the above given rule that the sum of the squares of the frequencies is maintained.

The magnitude of this splitting is very different in the various cases. Isolated frequencies maintain the first-order approximation value within the experimental error. This is demonstrated by the fundamentals **1** and **12**, in o-d$_2$, p-d$_2$, 0-d$_4$, and p-d$_4$, which in our approximation do not interact with other frequencies.

The frequencies of distinct carbon vibrations, which have nearly the same frequency in benzene-d_0 and benzene-d_6, shift very little from the first order approximation values. This is demonstrated by the fundamentals **6**a, **6**b, **8**a, **8**b, **14**, **16**a, and **16**b. Exceptions are cases where the first-order approximation value happens to be close to that of another vibration of the same symmetry. This is very clearly demonstrated by the fundamentals **1** and **12** in benzene-d_1, meta-d_2, vic-d_3, sym-d_3, asym-d_3, meta-d_4, and benzene-d_5, as well as by **14** in benzene-d_1 and meta-d_2.

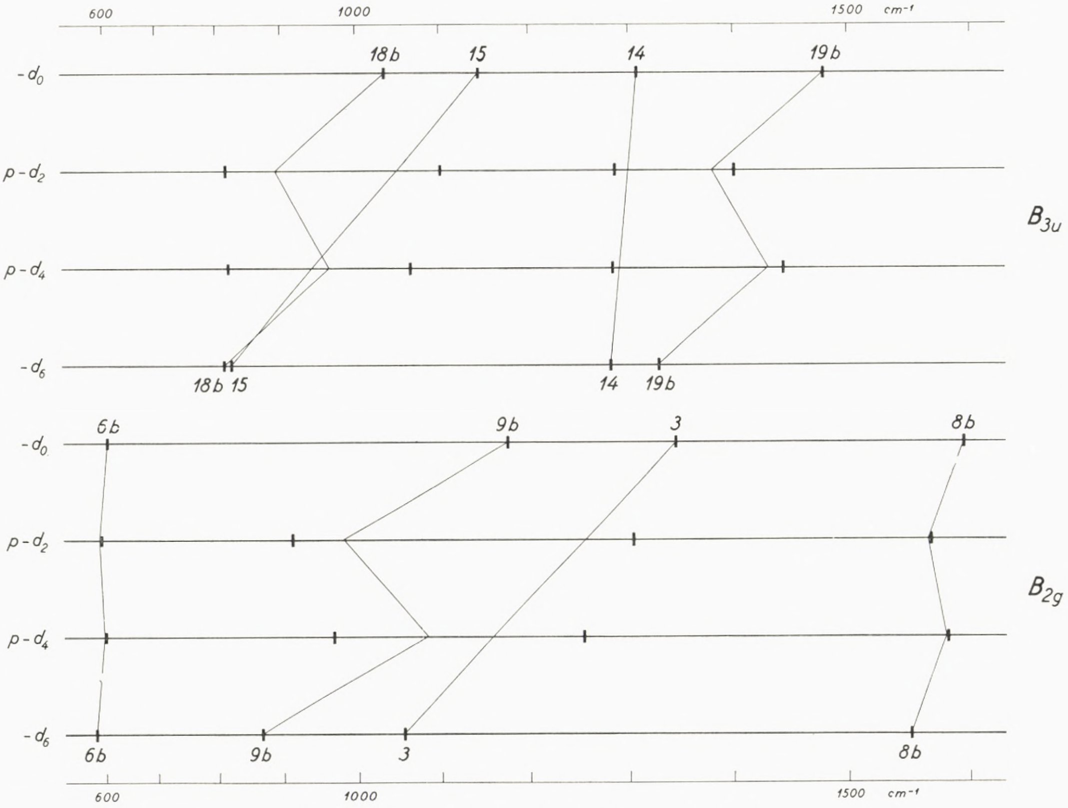

Fig. 4. Planar classes of the D_{2h} compounds.

The frequencies of distinct hydrogen (deuterium) vibrations, having very different frequencies in benzene-d_0 and benzene-d_6, are liable to shift very far from the first-order approximation values. This is especially the case for the stretching vibrations, where the mixing is so complete that almost pure hydrogen and deuterium frequencies result. In these cases the first-order approximation is of no value, and the corresponding diagrams are therefore not given.

In a more complicated manner the hydrogen (deuterium) bending vibrations mix with each other as well as with bending vibrations being partly hydrogen (deuterium) partly carbon vibrations. Especially the fundamentals **18**, **15**, and **9** are often mixed very completely resulting in a large splitting of the frequencies.

The physical reason for the splitting of the first-order approximation frequencies is the following. In the full-symmetry compounds the atoms are oscillating according to the restrictions given by the symmetry of the class to which the frequency in question belongs. In the first-order approximation these restrictions are maintained for the partly deuterated compounds in spite of their lower symmetries. But when the approximation is abandoned these restrictions vanish and certain interactions arise. In the simplest case of two interacting vibrations we get the well-known splitting into two new vibrations, one in which primarily the hydrogen atoms and the corresponding carbon atoms oscillate, and another in which primarily the deuterium atoms and the corresponding carbon atoms oscillate. The first one will have a higher, the latter a lower frequency than both of the first-order approximation frequencies. In the limit

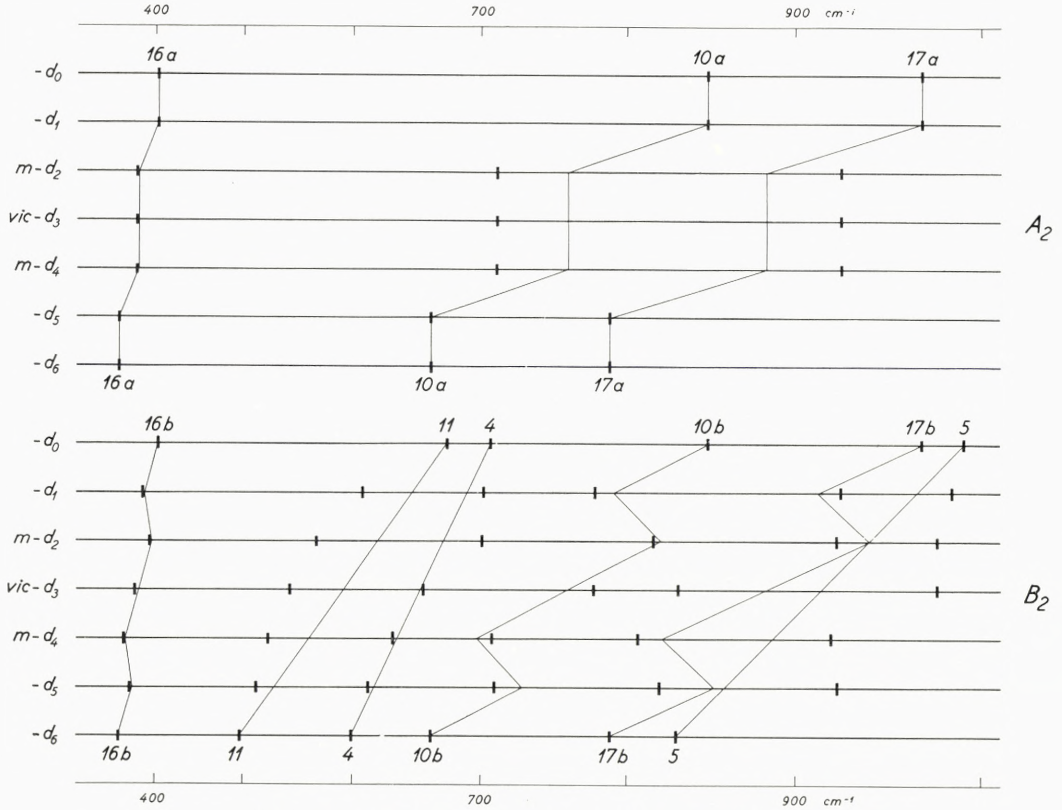

Fig. 5. Non-planar classes of the C_{2v} compounds.

this splitting may result in a pure hydrogen vibration and a pure deuterium vibration with frequencies being some sort of mean values of the two frequencies in benzene-d_0, respectively benzene-d_6. This is the case for the hydrogen (deuterium) stretching frequencies. The result of the mixing of more than two vibrations is in principle the same, which is evident from the diagrams.

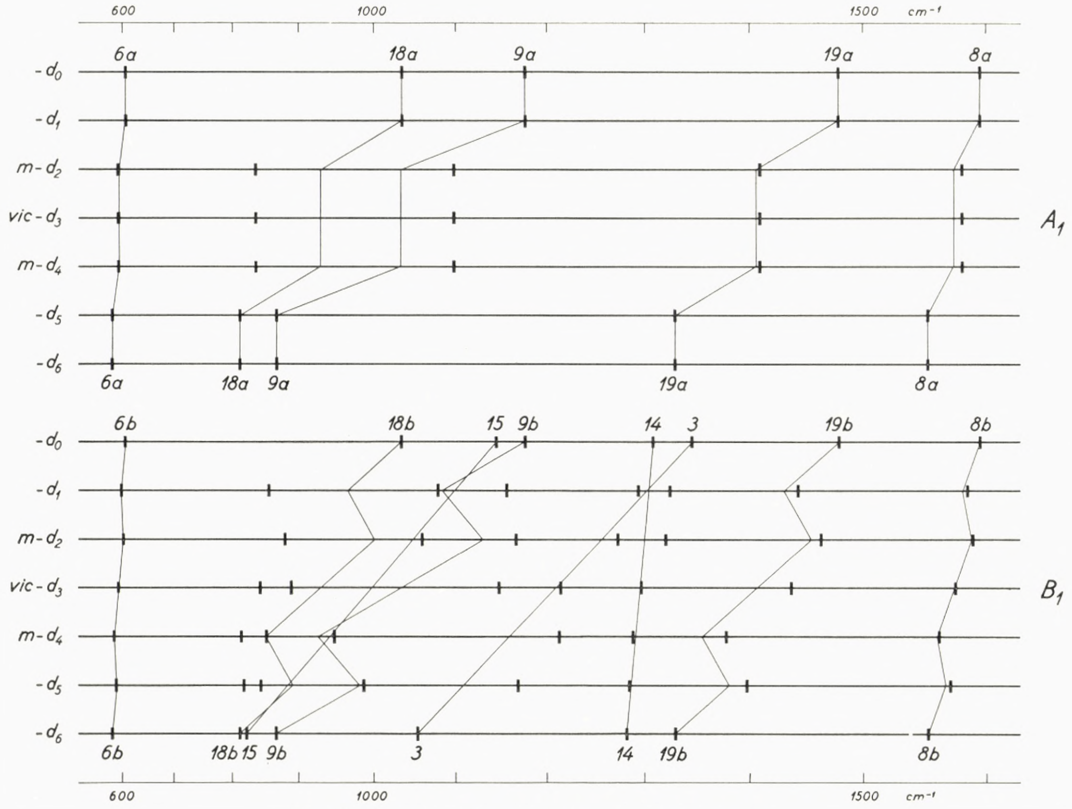

Fig. 6. Planar classes of the C_{2v} compounds.

As a consequence of this point of view, the highest frequency of an intermediate compound can never exceed the highest frequency in the corresponding symmetry class of benzene-d_0, and analogously, the lowest frequency of an intermediate compound can never be lower than the lowest one in the corresponding symmetry class of benzene-d_6. Also this general rule is distinctly demonstrated by the diagrams.

The degree of mixing of the vibrations, and the consequent splitting of the frequencies, depends largely on the closeness of the first-order frequencies as well as on the carbon or hydrogen character of the vibrational modes. These factors are, however, not the only ones responsible for the magnitude of the effect. This is evident from the behaviour of the frequencies **1** and **12** shown in Fig. 11 (pag. 23).

The strongly varying splittings may be explained in the following way. The common three-fold symmetry of the D_{6h} classes A_{1g} and B_{1u} divides both the carbon atoms and the hydrogen atoms into two sets, inside each of which the atoms are restricted to oscillate identically. In the first-order approximation these two sets move alike, in-phase and out-of-phase respectively. If the two sets are loaded equally —as in ortho-d$_2$, para-d$_2$, ortho-d$_4$, and para-d$_4$—we get no mixing and, hence, no splitting. If there is one deuterium atom more in one set than in the other—as in benzene-d$_1$, vic-d$_3$, asym-d$_3$, and -d$_5$—we get a slight mixing, resulting in a slight splitting of the frequencies **1** and **12**. If the disparity between the loading of the two sets is two deuterium atoms—as in meta-d$_2$ and meta-d$_4$—we get a moderate mixing and a moderate splitting. Finally—in sym-d$_3$—we have a disparity of three deuterium atoms, and therefore a large mixing and a large splitting. Mathematically this is expressed by the different values of the **G** matrix element $G_{2,4}$, or by the corresponding coefficient-scheme.

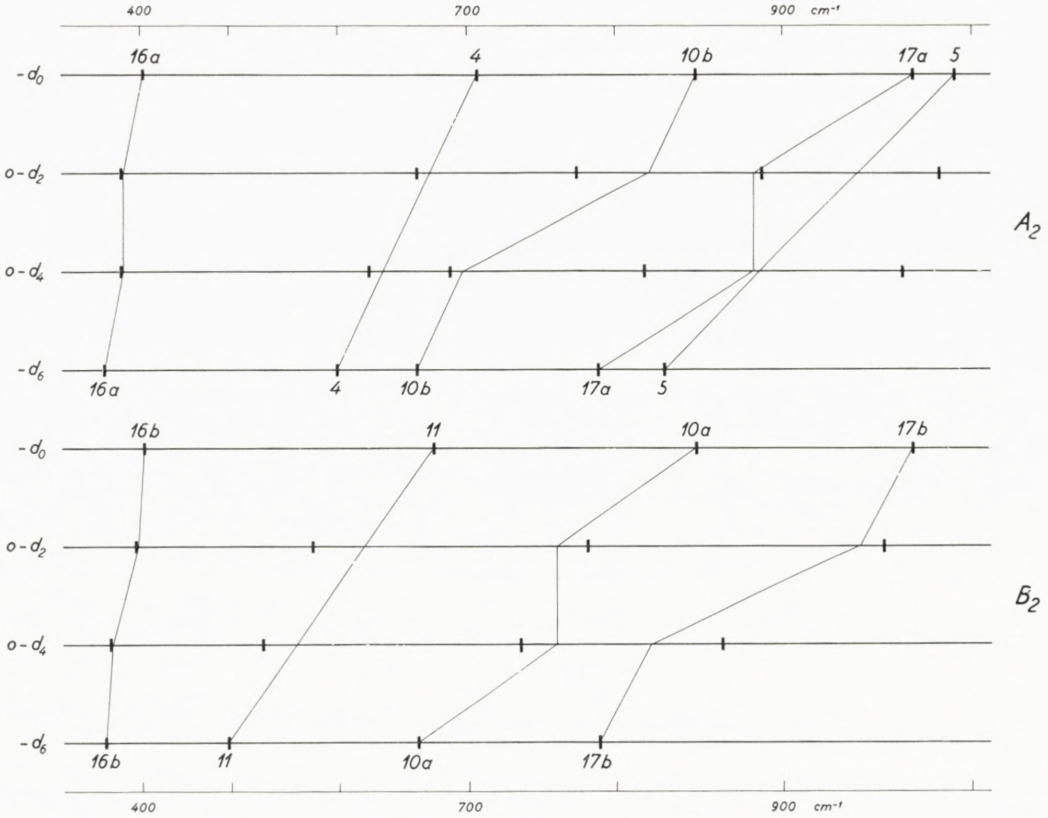

Fig. 7. Non-planar classes of the C_{2v}^{*} compounds.

As a result of the mixing the vibrational modes may undergo a considerable change from their original form. Consequently, the numbering of the fundamentals in the intermediate compounds will be more or less arbitrary. In order to have a fixed convention, we have numbered all fundamentals in a definite class of a definite compound in accordance with the order of the first-order approximation frequencies. In this way we probably succeed in labelling each fundamental with the number of its main component.

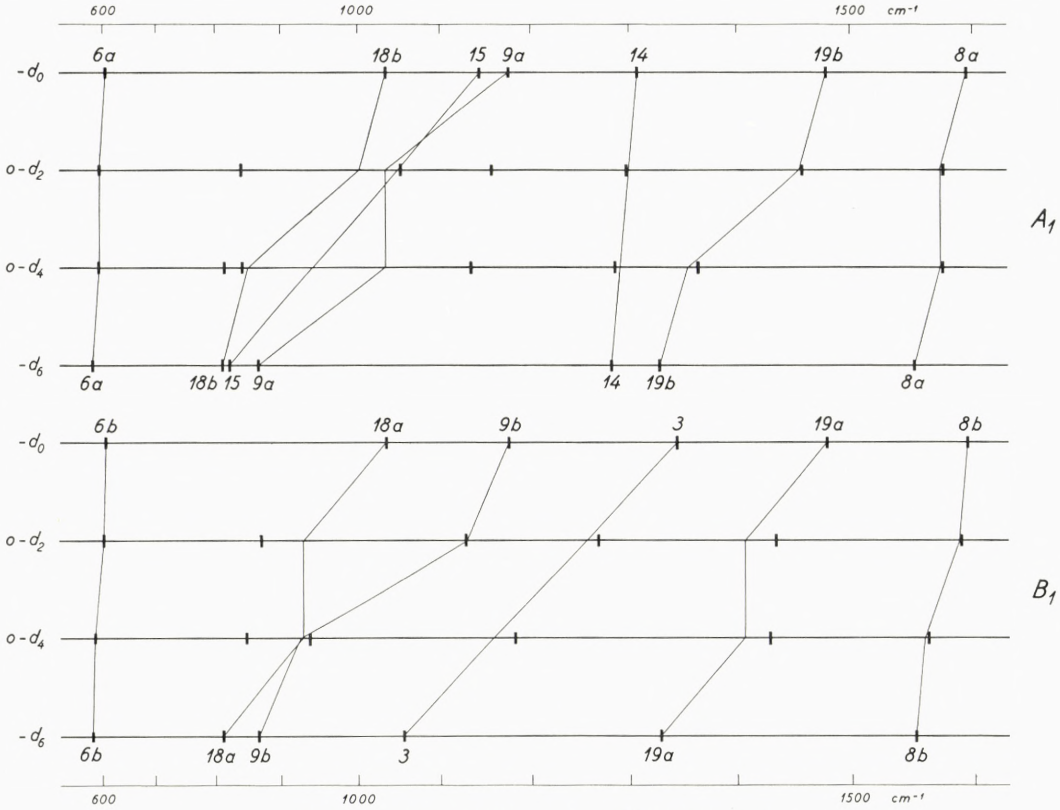

Fig. 8. Planar classes of the C^{*}_{2v} compounds.

One of the most important properties of a fundamental vibration is its spectral activity (Raman and infrared). As a consequence of the mixing of active and inactive vibrations, the activity is distributed among all the vibrations in accordance with the mixing proportions. On the basis of the above given comments on the relation between mixing and observed shift from the first-order frequencies, it is therefore possible to give a rough estimate of the intensities of the fundamental bands in the spectrum of an intermediate compound. Such estimates, performed simply by inspection of the diagrams, have proved to be a very important help in assigning the observed frequencies.

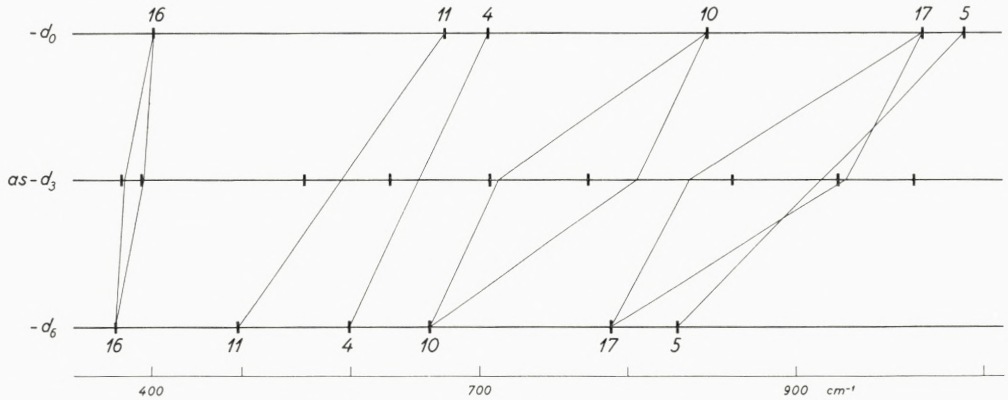

Fig. 9. Non-planar class of the C_8 compound.

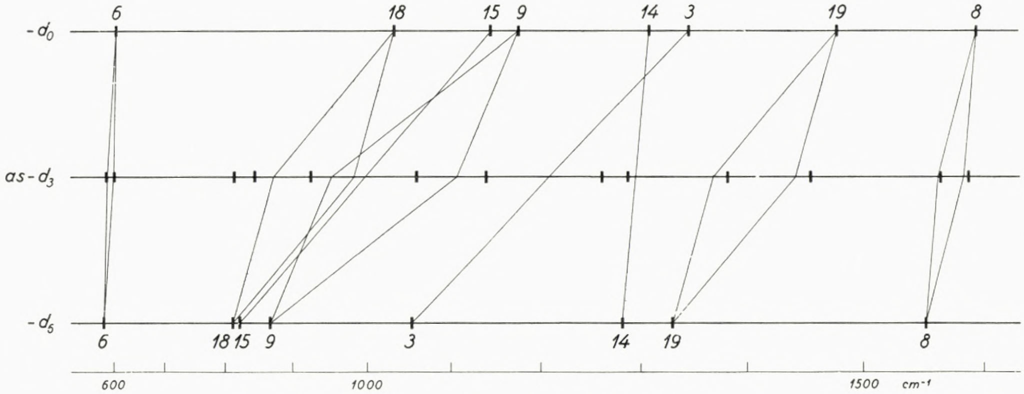

Fig. 10. Planar class of the C_8 compound.

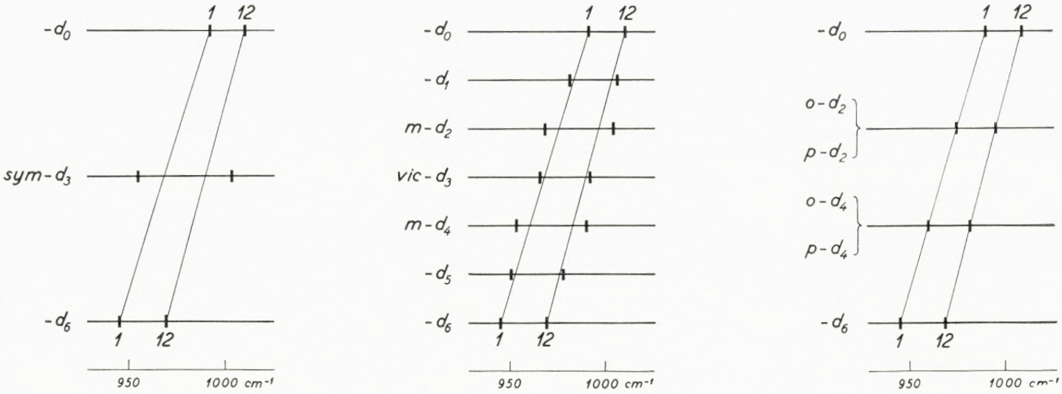

Fig. 11. Frequencies **1** and **12**.

Results.

The results obtained are collected in the Tables 8–18 giving the calculated and observed fundamental frequencies together with their estimated spectral activities. Each table contains the results for one of the partly deuterated benzenes separately, arranged in the order of increasing frequencies. As already mentioned, only frequencies of observed bands interpreted as fundamentals are included in the tables. The various columns contain the following information:

The *frequency number* assigned in accordance with the convention discussed above (pag. 22).

The *symmetry class* of the fundamental frequency (cf. Table 1).

The *estimated activities* (see pag. 22), for Raman and infrared separately, by use of the following scale:

f = forbidden by selection rules,
0 = inactive in D_{6h}, formally active in the lower-symmetrical intermediate compound, but unperturbed (not shifted from its first-order position),
1 = ditto, but slightly perturbed,
2 = ditto, but strongly perturbed, or fundamental originally active in D_{6h}.

The first two groups (*f* and 0) are expected to be inactive; the latter two (1 and 2) should show an increasing activity in the given order. The distinction between activity 1 and 2 is of course rather vague.

As the main object of the experimental investigation was to obtain as accurate measurements of the vibrational frequencies as possible, we have found it difficult on the basis of this experimental material to find a reliable measure for the intensities, especially for the Raman lines. Furthermore it is impossible to assign an intensity to each single component of the complicated groups of overlapping bands in the infrared vapour spectra. We have therefore decided not to include any quantitative statements of observed intensities in the tables, but are referring to the discussion of the spectral activity given below (pag. 34).

The *calculated frequencies* (cf. pag. 15) for as well the gaseous as the liquid state. They are given in cm^{-1} without a decimal because several of the basic frequencies are not known with greater accuracy.

The *observed frequencies* (cf. pag. 13) for the gaseous state from the infrared spectra, and for the liquid state from both infrared spectra (I) and Raman spectra (R). If a band observed in the spectrum of the vapour has a Q-branch, the frequency given refers to the maximum of this and is in the table marked ‘Q’. These frequencies are fairly reliable. All other frequencies measured in the spectra of the vapour refer to the estimated midpoints of the bands, and are consequently less accurate. The frequencies for the liquid state (peak frequencies) are normally accurate to $\pm 1\ \text{cm}^{-1}$, but for the weak and broad Raman bands the error may increase to $\pm 5\ \text{cm}^{-1}$. If two such bands are lying close together (as is, for instance, the case with **6** a and **6** b) they are often not resolved. In such cases the frequency given will be a mean value of the supposed doublet.

The *differences* between calculated and observed frequencies. These are in the tables given for the three cases separately: vapour (I), liquid (I), and liquid (R).

Benzene-d_1 TABLE 8.

Freq. no.	Sym. class	Estimated activity		Frequencies in cm^{-1}							
				Vapour			Liquid				
				Calc.	Obs.	Diff.	Calc.	Obs.		Diff.	
		I	R		I	I		I	R	I	R
16b	B_2	1	1	377			383		381		+2
16a	A_2	f	0	398			404		403*		+1
6b	B_1	1	2	598	..		598	..	602		−4
6a	A_1	0	2	607	..		607	..			+5
11	B_2	2	2	606	607 Q	−1	608	608		0	+6
4	B_2	2	2	701	698 Q	+3	702	699	..	+3	
10b	B_2	2	2	776	777 Q	−1	780	779	779	0	+1
10a	A_2	f	2	845	..		849	..	850		−1
18b	B_1	2	2	858	857 Q	+1	857	858	857	+1	0
17b	B_2	2	2	923	924 Q	−1	925	926	925	+1	0
17a	A_2	f	0	967	..		969	..	969*		0
1	A_1	0	2	983	..		982	978	980	+4	+2
5	B_2	2	2	984	..		985		..	+7	
12	A_1	0	2	1006	..		1006	1007	1007	−1	−1
18a	A_1	2	0	1037	1034 Q	+3	1035	1033	1032	+2	+3
9b	B_1	2	2	1080	1077	+3	1079	1077	1076	+2	+3
15	B_1	2	2	1157	..		1157	ca. 1159	1158	ca. −2	−1
9a	A_1	0	2	1177	..		1177	ca. 1174	1177	ca. +3	0
3	B_1	1	1	1295	..		1294	..	1291		+3
14	B_1	1	1	1327	..		1325	..	..		
19b	B_1	2	1	1446	1440 to		1443	1448	..	−5	
19a	A_1	2	0	1482	1490		1479	1473	..	+6	
8b	B_1	1	2	1590	..		1585	..	1576		+9
8a	A_1	0	2	1600	..		1595	..	1593		+2
7a	A_1	2	2	2286	2277 Q	+9	2276	2269	2270	+7	+6
7b	B_1	0	2					3012			
13	A_1	2	2	3055	3032		3047	3020	3042		
20a	A_1	2	2	to	3045		to	3030	3057		
20b	B_1	2	0	3074	3082		3062	3061	3066		
2	A_1	2	2		..			3076			

* Extremely weak lines.

o-Benzene-d_2

TABLE 9.

Freq. no.	Sym. class	Estimated activity		Frequencies in cm^{-1}							
				Vapour			Liquid				
				Calc.	Obs.	Diff.	Calc.	Obs.		Diff.	
		I	R		I	I		I	R	I	R
16a	A_2	f	1	368			374		ca. 385		ca. — 9
16b	B_2	1	1	387			393				ca. + 8
11	B_2	2	2	575	575 Q	0	577	579	582	— 2	— 5
6a	A_1	1	2	592	. .		592	. .	597		— 5
6b	B_1	1	2	603	. .		603	. .			+ 6
4	A_2	f	2	663	. .		663	. .	661		+ 2
10b	A_2	f	2	772	. .		775	. .	779		— 4
10a	B_2	2	2	778	780 Q	— 2	782	781		+ 1	+ 3
18b	A_1	2	2	843	843 Q	0	842	840	840	+ 2	+ 2
18a	B_1	2	2	872	871Q	+ 1	871	872	. .	— 1	
17a	A_2	f	2	886	. .		888	. .	. .		
17b	B_2	2	2	952	952 Q	0	954	954	. .	0	
1	A_1	0	2	977	. .		977	. .	974		+ 3
5	A_2	f	2	981	. .		983	. .	. .		
12	B_1	0	0	997	. .		997	. .	. .		
9a	A_1	2	2	1055	1055 Q	0	1053	1055	1054	— 2	— 1
9b	B_1	2	2	1130	ca. 1130	ca. 0	1129	1128	1128	+ 1	+ 1
15	A_1	2	2	1159	. .		1159	ca. 1160	1158		+ 1
3	B_1	2	2	1271	. .		1268	. .	. .		
14	A_1	1	1	1299	. .		1298	. .	. .		
19a	B_1	2	2	1437	1448	— 11	1434	1438	. .	— 4	
19b	A_1	2	1	1461	1457 Q	+ 4	1458	1451	. .	+ 7	
8a	A_1	1	2	1582	. .		1577	. .	1566		+ 11
8b	B_1	1	2	1595	. .		1590	ca. 1587	1587	ca. + 3	+ 3
7b	B_1	2	2	2281	2282 Q	— 1	2271	2270	2275	+ 1	— 4
7a	A_1	2	2	2291	2288 Q	+ 3	2281	2276		+ 5	+ 6
13	B_1	2	2	3055 to 3074			3047 to 3062				
20a	B_1	2	2		3074 Q			3060	3030		
20b	A_1	2	2		3081			3070	3058		
2	A_1	2	2		. .			. .	. .		

m-Benzene-d_2

TABLE 10.

16a	A_2	f	1	370			376		375		+ 1
16b	B_2	1	1	386			392		ca. 390		ca. + 2
11	B_2	2	2	566	566 Q	0	568	569	. .	— 1	
6a	A_1	1	2	593	. .		592	. .	598		— 6
6b	B_1	1	2	603	. .		603	. .			+ 5
4	B_2	2	2	701	697 Q	+ 4	701	699	. .	+ 2	
10a	A_2	f	2	707	. .		711	ca. 715	712	ca. — 4	— 1
10b	B_2	2	2	812	813 Q	— 1	816	816	819	0	— 3

m-Benzene-d_2

TABLE 10 (continued).

Freq. no.	Sym. class	Estimated activity		Frequencies in cm^{-1}							
				Vapour			Liquid				
				Calc.	Obs.	Diff.	Calc.	Obs.		Diff.	
		I	R		I	I		I	R	I	R
18a	A_1	2	2	838	ca. 834	ca. + 4	837	836	838	+ 1	— 1
18b	B_1	2	2	882	879 Q	+ 3	881	877	880	+ 4	+ 1
5	B_2	2	2	921	922 Q	— 1	923	923	. .	0	
17a	A_2	f	2	924	. .		926	. .	. .		
1	A_1	0	2	970	. .		969	. .	970		— 1
17b	B_2	2	2	976	977 Q	— 1	977	ca. 977	. .	ca. 0	
12	A_1	0	2	1004	. .		1004	. .	1006		— 2
9b	B_1	2	2	1061	1052 Q	+ 9	1060	1051	1052	+ 9	+ 8
9a	A_1	2	2	1099	1104 Q	— 5	1098	1107	1109	— 9	— 11
15	B_1	2	2	1167	. .		1167	ca. 1170	1167	ca. — 3	0
3	B_1	1	2	1274	1277	— 3	1273	1280	. .	— 7	
14	B_1	1	2	1323	. .		1321	. .	. .		
19a	A_1	2	1	1413	1425	— 12	1410	1420	1418	— 10	— 8
19b	B_1	2	1	1467	1461	+ 6	1464	1457	. .	+ 7	
8a	A_1	1	2	1586	. .		1581	1582	1584	— 1	— 3
8b	B_1	1	2	1594	. .		1589			+ 7	+ 5
7b	B_1	2	2	2282	2270 Q	+ 12	2272	2263	2270	+ 9	+ 2
7a	A_1	2	2	2290	2290	0	2280	2281	2282	— 1	— 2
13	A_1	2	2	3055 to 3074	3076		3047 to 3062				
20a	A_1	2	2					3057	3048		
20b	B_1	2	2					3071	3059		
2	A_1	2	2					. .	. .		

p-Benzene-d_2

TABLE 11.

Freq. no.	Sym. class	Estimated activity I	Estimated activity R	Vapour Calc.	Vapour Obs. I	Vapour Diff. I	Liquid Calc.	Liquid Obs. I	Liquid Obs. R	Liquid Diff. I	Liquid Diff. R
16b	B_{2u}	1	f	358			364		. .		
16a	A_{1u}	f	f	398			404		. .		
6b	B_{2g}	f	2	591	. .		591	. .	595		— 4
11	B_{2u}	2	f	595	596 Q	— 1	597	597	. .	0	
6a	A_{1g}	f	2	607	. .		607	. .	599		+ 8
4	B_{3g}	f	2	633	. .		635	. .	633		+ 2
10b	B_{3g}	f	2	739	. .		741	. .	736		+ 5
18b	B_{3u}	2	f	817	818 Q	— 1	815	820	. .	— 5	
10a	B_{1g}	f	2	845	. .		849	. .	849		0
17b	B_{2u}	2	f	871	873 Q	— 2	873	873	. .	0	
9b	B_{2g}	f	2	913	. .		913	908	909	+ 5	+ 4
5	B_{3g}	f	2	957	. .		958	957	. .	+ 1	
17a	A_{1u}	f	f	967	. .		969	. .	. .		
1	A_{1g}	f	2	977	. .		977	. .	978		— 1
12	B_{1u}	0	f	997	. .		997	. .	. .		
18a	B_{1u}	2	f	1037	1032 Q	+ 5	1035	1030	. .	+ 5	

p-Benzene-d_2

TABLE 11 (continued).

Freq. no.	Sym. class	Estimated activity		Frequencies in cm^{-1}							
				Vapour			Liquid				
				Calc.	Obs.	Diff.	Calc.	Obs.		Diff.	
		I	R		I	I		I	R	I	R
15	B_{3u}	2	f	1101	1104	— 3	1101	1104	. .	— 3	
9a	A_{1g}	f	2	1177	. .		1177	1173	1173	+ 4	+ 4
14	B_{3u}	2	f	1288	. .		1287	1291	. .	— 4	
3	B_{2g}	f	2	1307	. .		1304	. .	1311		— 7
19b	B_{3u}	2	f	1404	1413	— 9	1401	1409	. .	— 8	
19a	B_{1u}	2	f	1482	1473 Q	+ 9	1479	1468	. .	+ 11	
8b	B_{2g}	f	2	1575	. .		1570	. .	1570		0
8a	A_{1g}	f	2	1600	. .		1595	. .	1587		+ 8
7a	A_{1g}	f	2	2284	. .		2276	. .	2279		— 3
13	B_{1u}	2	f	2287	2279	+ 8	2276	2270	. .	+ 6	
20a	B_{2g}	2	f	3055 to 3074	3056		3047 to 3062	3048	. .		
20b	B_{1u}	2	f		3084			3075	. .		
7b	B_{3u}	f	2		. .			. .	3040		
2	A_{1g}	f	2		. .			. .	3055		

sym-Benzene-d_3

TABLE 12.

16	E''	f	1	370	||||||||		376	||||||||	375		+ 1
11	A_2''	2	f	530	531 Q	— 1	531	533	. .	— 2	
6	E'	1	2	593	594	— 1	592	ca. 592	594	ca. 0	— 2
4	A_2''	2	f	701	697 Q	+ 4	701	697	. .	+ 4	
10	E''	f	2	707	. .		711	ca. 714	711	ca. — 3	0
18	E'	2	2	838	833 Q	+ 5	837	833	834	+ 4	+ 3
15	A_2'	f	f	912	. .		911	. .	. .		
5	A_2''	1	f	916	917 Q	— 1	918	918	. .	0	
17	E''	f	2	924	. .		926	. .	. .		
1	A_1'	f	2	956	. .		955	955	956	0	— 1
12	A_1'	f	2	1004	. .		1004	1003	1004	+ 1	0
9	E'	2	2	1099	1101 Q	— 2	1098	1101	1102	— 3	— 4
3	A_2'	f	f	1253	. .		1252	. .	. .		
14	A_2'	f	f	1321	. .		1319	1322	. .	— 3	
19	E'	2	1	1413	1414	— 1	1410	1412	1417	— 2	— 7
8	E'	1	2	1586	1580	+ 6	1581	1575	1575	+ 6	+ 6
7	E'	2	2	2282	2282	0	2272	2274	2264	— 2	
13	A_1'	f	2	2294	. .		2285	. .	2282		
20	E'	2	2	3055	3063 Q		3047	3053	3054		
2	A_1'	f	2	3074	. .		3062	. .			

vic-Benzene-d_3

TABLE 13.

Freq. no.	Sym. class	Estimated activity		Frequencies in cm^{-1}							
				Vapour			Liquid				
				Calc.	Obs.	Diff.	Calc.	Obs.		Diff.	
		I	R		I	I		I	R	I	R
16b	B_2	1	1	367			373		375		— 2
16a	A_2	f	1	370			376				+ 1
11	B_2	2	2	543	543 Q	0	545	546	544	— 1	+ 1
6b	B_1	1	2	592	. .		592	. .	593		— 1
6a	A_1	1	2	593	. .		592	. .			— 1
4	B_2	2	2	656	656 Q	0	657	656	655	+ 1	+ 2
10a	A_2	f	2	707	. .		711	. .	712	. .	— 1
10b	B_2	2	2	776	776 Q	0	779	780	779	— 1	0
17b	B_2	2	2	829	830 Q	— 1	831	831	838	0	— 7
18a	A_1	2	2	838	842 Q	— 4	837	ca. 840		ca. — 3	— 1
18b	B_1	2	2	845		+ 3	844			ca. + 4	+ 6
15	B_1	2	2	892	890	+ 2	890	888	. .	+ 2	
17a	A_2	f	2	924	. .		926	924	. .	+ 2	
1	A_1	0	2	967	. .		967	967	965	0	+ 2
5	B_2	2	2	976	976 Q	0	977	977	. .	0	
12	A_1	0	2	993	. .		992	ca. 995	993	ca. — 3	— 1
9a	A_1	2	2	1099	ca. 1098	c. + 1	1098	1097	1096	+ 1	+ 2
9b	B_1	2	2	1150	ca. 1140	c. + 10	1149	1148	1150	+ 1	— 1
3	B_1	1	1	1217	. .		1214	. .	. .		
14	B_1	1	1	1297	. .		1297	. .	. .		
19a	A_1	2	1	1413	c. 1400 to c. 1450		1410	1412	. .	— 2	
19b	B_1	2	1	1440			1437	1437	. .	0	
8b	B_1	1	2	1580	. .		1575	1580	1578	— 5	— 3
8a	A_1	1	2	1586	. .		1581		1585	+ 1	— 4
7a	A_1	2	2	2280	c. 2260 to c. 3010		2271	2268	2261	+ 3	
7b	B_1	2	2	2282			2272		2281	+ 4	
13	A_1	2	2	2296			2285	2288	2288	— 3	
20a	A_1	2	2	3055 to 3074	3070		3047 to 3062	3060	3059		
20b	B_1	2	2								
2	A_1	2	2								

as-Benzene-d_3

TABLE 14.

16a	A''	1	1	354			360		. .		
16b	A''	1	1	383			389		388		+ 1
11	A''	2	2	558	558 Q	0	560	560	577	0	+ 3
6a	A'	1	2	585	. .		585	. .	592		— 7
6b	A'	1	2	602	. .		602	. .			+ 10
4	A''	2	2	632	632 Q	0	633	633	633	0	0
10a	A''	?	2	705	706 Q	— 1	708	707	706	+ 1	+ 2

as-Benzene-d_3

TABLE 14 (continued).

Freq. no.	Sym. class	Estimated activity		Frequencies in cm^{-1}							
				Vapour			Liquid				
				Calc.	Obs.	Diff.	Calc.	Obs.		Diff.	
		I	R		I	I		I	R	I	R
10b	A''	2	2	772	773 Q	— 1	775	c. 773	774	c. + 2	+ 1
18a	A'	2	2	817	814 Q	+ 3	815	818	820	— 3	— 5
9a	A'	2	2	847	845 Q	+ 2	846	842	842	+ 4	+ 4
17a	A''	2	2	861	863 Q	— 2	864	864	864	0	0
5	A''	2	2	921	921 Q	0	923	922	c. 921	+ 1	+ 2
18b	A'	2	2	927		+ 6	926			+ 4	+ 5
17b	A''	2	2	962	963 Q	— 1	964	965	. .	— 1	
1	A'	0	2	967	. .		967		966	+ 2	+ 1
12	A'	0	2	993	. .		992	985	986*	+ 7	+ 6
15	A'	2	2	1062	1052 Q	+ 10	1061	1051	1054	+ 10	+ 7
9b	A'	2	2	1140	1136	+ 4	1140	1140	1140	0	0
3	A'	2	2	1266	1262	+ 4	1263	1269	1268	— 6	— 5
14	A'	1	1	1288	. .		1288	1294	. .	— 6	
19a	A'	2	2	1384	1396	— 12	1382	1392	1389	— 10	— 7
19b	A'	2	2	1459	1451	+ 8	1456	1447	. .	+ 9	
8a	A'	1	2	1570	. .		1565	. .	1556		+ 9
8b	A'	1	2	1593	. .		1588	. .	1579		+ 9
7a	A'	2	2	2278	2279 Q		2270	2271	2270		
7b	A'	2	2	2287			2276		2281		
13	A'	2	2	2292			2282		2295		
20a	A'	2	2	3055 to 3074	3078		3047 to 3062	3056 3068	3054		
20b	A'	2	2								
2	A'	2	2								

* Probably in resonance with (16a + 4), calc. = 993, obs. = 1004, unobs. in infrared. The Raman line at 995 may be assigned to (16b + 6b).

o-Benzene-d_4

TABLE 15.

16b	B_2	1	1	352			358		. .		
16a	A_2	f	1	368			374		373		+ 1
11	B_2	2	2	530	530 Q	0	531	531	535	0	— 4
6b	B_1	1	2	584	. .		584	. .	588		— 4
6a	A_1	1	2	592	. .		592	. .			+ 4
4	A_2	f	2	625	. .		626	. .	627		— 1
10b	A_2	f	2	685	. .		688	. .	688		0
10a	B_2	2	2	734	737 Q	— 3	737	738	739	— 1	— 2
18b	A_1	2	2	817	. .		815	817	c. 816	— 2	c. — 1
17a	A_2	f	2	816	. .		818	. .			c. + 2
15	A_1	2	2	844	846 Q	— 2	844	843	842	+ 1	+ 2
9b	B_1	2	2	849		+ 3	848			+ 5	+ 6
17b	B_2	2	2	862	864 Q	— 2	865	865	862	0	+ 3

o-Benzene-d_4

TABLE 15 (continued).

Freq. no.	Sym. class	Estimated activity I	Estimated activity R	Vapour Calc.	Vapour Obs. I	Vapour Diff. I	Liquid Calc.	Liquid Obs. I	Liquid Obs. R	Liquid Diff. I	Liquid Diff. R
18a	B_1	2	2	939	934 Q	+ 5	938	932	932	+ 6	+ 6
1	A_1	0	2	962	. .		961	962	961		0
5	A_2	f	2	962	. .		964	. .	. .		
12	B_1	0	0	984	. .		984	. .	. .		
9a	A_1	2	2	1137	. .		1136	1135	1137	+ 1	− 1
3	B_1	2	2	1187	. .		1183	. .	. .		
14	A_1	1	1	1286	. .		1286	. .	. .		
19b	A_1	2	1	1368	1378	− 10	1366	1373	1376	− 7	− 10
19a	B_1	2	2	1431	1426	+ 5	1428	1424	. .	+ 4	
8b	B_1	1	2	1569	. .		1564	. .	1571		− 7
8a	A_1	1	2	1581	. .		1576	. .			+ 5
7a	A_1	2	2	2278			2269				
7b	B_1	2	2	2280	2285 Q		2271	2271	2272		
13	B_1	2	2	2287	2300 Q		2276	2289	2290		
20b	A_1	2	2	2298			2288				
20a	B_1	2	2	3055 to 3074	3068		3047 to 3062	3056	3058		
2	A_1	2	2								

m-Benzene-d_4

TABLE 16.

Freq. no.	Sym. class	Estimated activity I	Estimated activity R	Vapour Calc.	Vapour Obs. I	Vapour Diff. I	Liquid Calc.	Liquid Obs. I	Liquid Obs. R	Liquid Diff. I	Liquid Diff. R
16b	B_2	1	1	352	‖‖‖‖		358	‖‖‖‖	. .		
16a	A_2	f	1	370			376		376		0
11	B_2	2	2	523	524 Q	− 1	524	524	. .	0	
6b	B_1	1	2	584	. .		584	. .	588		− 4
6a	A_1	1	2	593	. .		592	. .			+ 4
4	B_2	2	2	631	630 Q	+ 1	633	633	633	0	0
10b	B_2	2	2	705	705 Q	0	708	706	710	+ 2	− 2
10a	A_2	f	2	707	. .		711	. .			+ 1
17b	B_2	2	2	805	806 Q	− 1	807	806	. .	+ 1	
15	B_1	2	2	817	818 Q	− 1	815	817	. .	− 2	
18a	A_1	2	2	838	833 Q	+ 5	837	831	834	+ 6	+ 3
18b	B_1	2	2	854	. .		854	. .	848		+ 6
5	B_2	2	2	918	919 Q	− 1	920	920	. .	0	
17a	A_2	f	2	924	. .		926	. .	. .		
9b	B_1	2	2	950	. .		948	946	. .	+ 2	
1	A_1	0	2	954	. .		954	. .	954		0
12	A_1	0	2	991	. .		991	. .	993*		− 2
9a	A_1	2	2	1099	1097 Q	+ 2	1098	1096	1097	+ 2	+ 1
3	B_1	1	2	1216	. .		1213	. .	c. 1206		c. + 7
14	B_1	1	1	1288	. .		1288	. .	. .		

* In resonance with (16b + 4), calc. = 991, obs. = 987.

m-Benzene-d$_4$

TABLE 16 (continued).

Freq. no.	Sym. class	Esti-mated activity		Frequencies in cm^{-1}							
				Vapour			Liquid				
				Calc.	Obs.	Diff.	Calc.	Obs.		Diff.	
		I	R		I	I		I	R	I	R
19b	B_1	2	1	1381	1370 to 1430		1378	1384	c. 1376	— 6	c. + 2
19a	A_1	2	1	1413			1410	1402	1414	+ 8	— 4
8b	B_1	1	2	1567	. .		1562	1570	1568	— 8	— 6
8a	A_1	1	2	1586	. .		1581		1574	+ 11	+ 7
7a	A_1	2	2	2277	2281 Q	— 4	2269	2275	2273	— 6	— 4
7b	B_1	2	2	2282		+ 1	2272			— 3	— 1
13	A_1	2	2	2287		+ 6	2276			+ 1	+ 3
20a	A_1	2	2	2297	2295 Q	+ 2	2287	2287	2288	0	— 1
20b	B_1	2	2	3055 to 3074	3060		3047 to 3062	3052	3052		
2	A_1	2	2								

p-Benzene-d$_4$

TABLE 17.

16a	A_{1u}	f	f	345			351		. .		
16b	B_{2u}	1	f	374			380		. .		
11	B_{2u}	2	f	545	545 Q	0	546	546	. .	0	
6a	A_{1g}	f	2	579	. .		579	. .	588		— 9
6b	B_{2g}	f	2	600	. .		600	. .			+ 12
4	B_{3g}	f	2	615	. .		616	617	617	— 1	— 1
10a	B_{1g}	f	2	659	. .		663	664	663	— 1	0
10b	B_{3g}	f	2	769	. .		771	. .	768		+ 3
17a	A_{1u}	f	f	787	. .		789	. .	. .		
18a	B_{1u}	2	f	814	811	+ 3	812	817	. .	— 5	
15	B_{3u}	2	f	820	820 Q	0	819		. .	+ 2	
9a	A_{1g}	f	2	868	. .		868	. .	862		+ 6
5	B_{3g}	f	2	918	. .		920	. .	928		— 8
17b	B_{2u}	2	f	924	924 Q	0	926	926		0	— 2
1	A_{1g}	f	2	962	. .		961	965	961	— 4	0
9b	B_{2g}	f	2	970	. .		969		. .	+ 4	
12	B_{1u}	0	f	984	. .		984	984	. .	0	
18b	B_{3u}	2	f	1067	1057 Q	+ 10	1065	1056	. .	+ 9	
3	B_{2g}	f	2	1257	. .		1254	. .	1255		— 1
14	B_{3u}	1	f	1284	. .		1284	. .	. .		
19a	B_{1u}	2	f	1333	1354	— 21	1330	1350	. .	— 20	
19b	B_{3u}	2	f	1447	1435 Q	+ 12	1444	1432	. .	+ 12	
8a	A_{1g}	f	2	1558	. .		1553	. .	c. 1565		c. — 12
8b	B_{2g}	f	2	1588	. .		1583	. .	1574		+ 9
7b	B_{2g}	f	2	2275	. .		2267	. .	2272		— 5
13	B_{1u}	2	f	2286	2285 Q	+ 1	2275	2273	. .	+ 2	
20b	B_{3u}	2	f	2288		+ 3	2276		. .	+ 3	
7a	A_{1g}	f	2	2294	. .		2285	. .	2285		0
20a	B_{1u}	2	f	3055 to 3074	3075		3047 to 3062	3065	. .		
2	A_{1g}	f	2		. .			. .	3047		

Benzene-d_5

TABLE 18.

Freq. no.	Sym. class	Estimated activity		Frequencies in cm^{-1}							
				Vapour			Liquid				
				Calc.	Obs.	Diff.	Calc.	Obs.		Diff.	
		I	R		I	I		I	R	I	R
16a	A_2	f	0	345	‖‖‖‖		351	‖‖‖‖	. .		
16b	B_2	1	1	360	‖‖‖‖		366	‖‖‖‖	367		— 1
11	B_2	2	2	512	512 Q	0	513	514	. .	— 1	
6a	A_1	0	2	579	. .		579	. .	. .		— 5
6b	B_1	1	2	589	. .		588	. .	584		+ 4
4	B_2	2	2	613	613 Q	0	613	614	613	— 1	0
10a	A_2	f	2	659	. .		663	. .	664		— 1
10b	B_2	2	2	706	706 Q	0	710	709	711	+ 1	— 1
17a	A_2	f	0	787	. .		789	. .	. .		
18a	A_1	2	0	814	818 Q	— 4	812	814	. .	— 2	
15	B_1	2	2	820		+ 2	818		815	+ 4	+ 3
17b	B_2	2	2	818		0	820			+ 6	+ 5
18b	B_1	2	2	846	. .		845	838	840	+ 7	+ 5
9a	A_1	0	2	868	. .		868	. .	859		+ 9
5	B_2	2	2	921	922 Q	— 1	923	923	928	0	— 5
1	A_1	0	2	951	. .		951	. .	950		+ 1
12	A_1	0	2	979	. .		979	. .	980		— 1
9b	B_1	2	2	989	986 Q	+ 3	987	984	. .	+ 3	
3	B_1	1	2	1172	. .		1169	. .	1175		— 6
14	B_1	1	1	1284	. .		1284	1289*	. .	— 5	
19a	A_1	2	0	1333	1344	— 11	1330	1341	. .	— 11	
19b	B_1	2	1	1400	1392	+ 8	1397	1388	. .	+ 9	
8a	A_1	0	2	1558	. .		1553	. .	1564		— 11
8b	B_1	1	2	1576	. .		1571	. .			+ 7
7b	B_1	0	2	2275	. .		2267	. .	2271		— 4
7a	A_1	2	2	2280	2283	— 3	2271	2275		— 4	0
13	A_1	2	2	2286		+ 3	2275			0	+ 4
20b	B_1	2	0	2288		+ 5	2276		. .	+ 1	
20a	A_1	2	2	2300	c. 2302	c. — 2	2291	2291	2289	0	+ 2
2	A_1	2	2	3055 to 3074	3046		3047 to 3062	3050	3053		

* May equally well be assigned to (16b + 5), calc. = 1289.

Discussion.

The agreement between calculated and observed frequencies can not be expected to be equally good for all the fundamental vibrations. For the non-planar vibrations, where the rules are strictly valid, the agreement is excellent, practically within the experimental error. Especially the fine agreement with the very reliable Q-branch frequencies measured for the gaseous state should be pointed out. Here the mean deviation is 1 cm^{-1} only.

For the planar vibrations we have, in addition to the usual neglect of anharmonicity, introduced the approximation of separating the high and the low frequencies. We should therefore expect a poorer agreement between calculated and observed values. Nevertheless, many frequencies are calculated correctly within a few cm^{-1}. All the greater deviations may be accounted for in one of the following two ways:

1. Accidental resonance with over—or combination-tones may perturb the fundamentals. As the probability for this phenomenon is rapidly increasing with increasing frequency, the assigned frequencies for the high fundamental frequencies are only to be considered as tentative.

2. The low frequencies, **6**, **8**, **9**, **18**, and **19**, may correspond to vibrations, which involve a considerable portion of radial motion of the hydrogen (deuterium) atoms (cf. pag. 13). To a first approximation this tends to permute the calculated frequencies of the a and b components. No such tendency is, however, observed for **9** and **18**, and the fundamentals mixed strongly with these are also calculated correctly. This means that the vibrations **9** and **18** practically are pure deformations. The frequencies **6**, **8**, and **19**, however, are in most cases observed within the interval between the frequencies calculated for the two components, a and b. This indicates that these vibrations are not pure deformations. We estimate their 'content' of stretching mode to be about 50, 20, and 10 per cent. for **6**, **8**, and **19** respectively. We must, therefore, emphasize that the assignments given for the observed frequencies to one or the other of the two components are to be considered as more or less tentative. This is especially the case for **6**, and to some extent also for **8**. For **19**, however, a permutation of the given assignments would probably require too large changes to be made for other frequencies to be compatible with the observed spectra.

The very satisfactory general agreement obtained for all the frequencies of all the deuterated benzenes gives, in our opinion, the final proof of the correctness of the fundamental frequencies of benzene-d_0 and benzene-d_6 used as the basis for the calculations.

As already mentioned we do not consider our present experimental material to be suitable for quantitative statements of the intensities of the observed fundamentals. We shall, therefore, confine ourselves to the following general discussion.

Qualitatively the observed intensities agree very well with the estimated ones given in the Tables 8–18 (cp. pag. 24). Thus it is seen that the frequencies in inactive classes (f), as well as the frequencies unperturbed by active fundamentals (0), are in fact unobserved in the spectra. Only in a few cases are such frequencies—activated by intermolecular perturbations—observed in the infrared spectra of the liquid phase, and then always as very weak bands only.

Furthermore, it is evident that fundamentals which are only slightly perturbed (1), in most cases escape observation. For the typical carbon vibration **14** this means, that infrared activity is only to be expected in the few instances where a component of the infrared active **19** is relatively nearby in the first-order approximation. Raman activity is never to be expected, as there is no Raman active frequency in the vicinity in any of the partly deuterated benzenes. Any resonance that may arise with the nearby **3** is of no importance in this connection as **3** is both infrared and Raman inactive. This is undoubtedly the reason why the B_{1u} fundamental **14** so long has eluded the correct assignment.

The rough estimate of the activity, based on a fundamental's observed deviation from its first-order position, may be of valuable help in the interpretation of the spectra. It must, however, be emphazised that the intensity by no means is proportional to the difference between observed and first-order frequency. If more than two frequencies are strongly involved in the interaction, which very often is the case, the situation may be rather complicated. A limiting case would be a fundamental appearing in the spectrum at its first-order frequency in spite of strong, simultaneous interactions with other fundamentals if these interactions cancel by accident. In this case the fundamental may possibly show an appreciable intensity even if it—as far as the frequency is concerned—is unperturbed. A certain caution must, therefore, be exercised in the application of this intensity estimate.

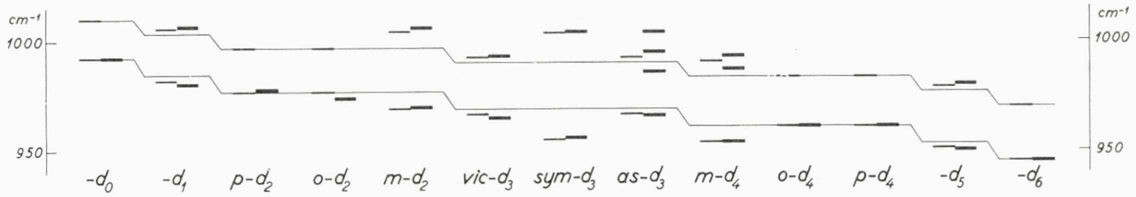

Fig. 12. Frequencies **1** and **12**.
First-order approximation: thin lines, calculated: medium lines, and observed: heavy lines.

In Fig. 12 are shown both the first-order approximation, the calculated, and the observed frequencies for **1** and **12**. This special diagram may be compared with the analogous one given in 1938 by Langseth and Lord[1]. It nicely demonstrates how **12** is only active as a consequence of resonance with **1**, in which case the calculated frequencies deviate from the first-order approximation values. In two cases **12** further is in resonance with combination vibrations as indicated in the tables.

Conclusion.

From the material presented in this paper, as well as from the examples discussed in *I*, it is seen that the complete isotopic rule is able to predict the fundamental frequencies of intermediate isotopic species with a remarcable accuracy.

The main application of the rule will probably be as a help to the interpretation of vibrational spectra. For all cases in which the complete rule is valid, strictly or approximately, the calculation of the frequencies of one or more intermediate compounds will give a check on the correctness of the assignment which has hitherto been

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[1] A. Langseth and R. C. Lord, Jr., loc. cit., Fig. 3, pag. 27.

lacking. Even in cases where the complete rule can not be applied, a useful knowledge the behavior of the fundamentals by varying isotopic substitution may be gained from the use of the rule to similar molecules. In this connection the survey obtained by use of the first-order approximation and the diagrams may be pointed out.

In the view of the approximations introduced as a basis for the approximate rule—harmonicity and separation of low and high frequencies—the accuracy of the rule is surprising. As already mentioned, this is—at least as far as the harmonicity in concerned—to some extent accounted for by the nature of the rule, being in reality a kind of interpolation between two sets of observed frequencies. If only the effect of the anharmonicity varies 'linearly' within the interval in question, the errors will tend to cancel. Therefore, no conclusions with regard to the real magnitude of the introduced approximation can safely be drawn.

These circumstances have an important bearing on the problem of calculating the potential function from the observed frequencies. It is obvious that an intermediate compound, the frequencies of which are given by strictly valid rules from the frequencies of the full-symmetry compounds, do not contribute any new information concerning the potential function. But also in those cases where an approximate rule is valid, the frequencies of the intermediate compound are of problematic value for such calculations. In both cases, however, the rule may be used to calculate the unperturbed frequencies of fundamentals which are involved in Fermi resonance with other frequencies.

The existence of the complete isotopic rule reveals a general complementarity principle with regard to the fundamental frequencies of the various isotopic species: to the same extent as the importance of these frequencies for the calculation of the potential function may be decreasing, to the same extent their importance for assignment purposes will be increasing.

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