The Planar Vibrations of Benzene

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(Received June 7, 1948)

A normal coordinate treatment has been carried out for the planar vibrations of benzene and its deuterium derivatives. By using the latest assignments of Ingold and co-workers, eighteen of the twenty-six harmonic force constants have been determined.

INTRODUCTION

IN an earlier paper[1] the authors have reviewed previous work on the normal vibrations of benzene, and have treated the nonplanar vibrations in some detail. It was mentioned at that time that a satisfactory normal coordinate treatment of the planar vibrations awaited more experimental data which were needed to provide a satisfactory and complete assignment. A great step in this direction has been made by Ingold and his co-workers in their 1946 series of papers.[2] We have now used their assignments in an attempt to calculate the force constants for the planar vibrations of benzene.

A number of workers have carried out such calculations before,[3] but always with assignments which were more or less incomplete. Although the assignments of Ingold *et al.* are still open to question in a few details, they represent a significant advance. Therefore, it seems worth while to bring the force constants up to date. At the same time the secular equation will be presented in the form of Wilson's **F** and **G** matrices. This will serve a twofold purpose. (i) Equations will be readily available for re-evaluating the force constants, if that should be demanded by any future change in the assignments. (ii) The secular equation for benzene or for *any* of its deuterium derivatives can be written down immediately from these matrices.

MATHEMATICAL METHODS

The general procedure is the same as that used for the non-planar vibrations. The reader is referred to our earlier paper[1] for many details which will not be repeated here.

Benzene has twenty-one fundamental planar vibrations. Of these, seven are non-degenerate and seven are doubly degenerate, giving fourteen distinct frequencies in all. Their symmetry properties and notation are shown in Table I. We have

TABLE I. Symmetry properties and notation for the planar vibrations of benzene.

D_{6h}	z C_3	z C_2	y C_2	i	No.	Ring	Notation Hyd. str.	Hyd. bend
A_{1g}	$+$	$+$	$+$	$+$	2	ν_1	ν_2	
A_{2g}	$+$	$+$	$-$	$+$	1			ν_3
B_{1u}	$+$	$-$	$+$	$-$	2	ν_{12}	ν_{13}	
B_{2u}	$+$	$-$	$-$	$-$	2	ν_{14}		ν_{15}
E_{1ga}	e	$+$	$+$	$+$	4	ν_{6a}, ν_{8a}	ν_{7a}	ν_{9a}
E_{1gb}	e	$+$	$-$	$+$	4	ν_{6b}, ν_{8b}	ν_{7b}	ν_{9b}
E_{2ua}	e	$-$	$+$	$-$	3	ν_{19a}	ν_{20a}	ν_{18a}
E_{2ub}	e	$-$	$-$	$-$	3	ν_{19b}	ν_{20b}	ν_{18b}

[1] F. A. Miller and B. L. Crawford, Jr., J. Chem. Phys. **14**, 282 (1946). In the present paper we have changed slightly our designation of the symmetry species; we now follow the usage of G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand and Company, Inc.), which has been generally accepted by molecular spectroscopists.
[2] C. K. Ingold *et al.*, J. Chem. Soc. (London), 222–333 (1946).
[3] Reference 1 reviews the earlier work.

Species	VFSC	1	2	3	4	5	6	N	VFC
A_{1g}	S_1	1	1	1	1	1	1	$6^{-1/2}$	ΔR_j
	S_2	1	1	1	1	1	1	$6^{-1/2}$	Δr_j
A_{2g}	S_3	1	1	1	1	1	1	$6^{-1/2}$	$r_0\beta_j$
B_{1u}	S_{12}	-1	1	-1	1	-1	1	$6^{-1/2}$	$R_0\alpha_j$
	S_{13}	-1	1	-1	1	-1	1	$6^{-1/2}$	Δr_j
B_{2u}	S_{14}	-1	1	-1	1	-1	1	$6^{-1/2}$	ΔR_j
	S_{15}	-1	1	-1	1	-1	1	$6^{-1/2}$	$r_0\beta_j$
E_{1ga}	S_{6a}	-2	1	1	-2	1	1	$12^{-1/2}$	$R_0\alpha_j$
	S_{7a}	-2	1	1	-2	1	1	$12^{-1/2}$	Δr_j
	S_{8a}	-1	2	-1	-1	2	-1	$12^{-1/2}$	ΔR_j
	S_{9a}	0	-1	1	0	-1	1	$1/2$	$r_0\beta_j$
E_{1gb}	S_{6b}	0	-1	1	0	-1	1	$1/2$	$R_0\alpha_j$
	S_{7b}	0	-1	1	0	-1	1	$1/2$	Δr_j
	S_{8b}	-1	0	1	-1	0	1	$1/2$	ΔR_j
	S_{9b}	2	-1	-1	2	-1	-1	$12^{-1/2}$	$r_0\beta_j$
E_{2ua}	S_{18a}	0	1	1	0	-1	-1	$1/2$	$r_0\beta_j$
	S_{19a}	-1	0	1	1	0	-1	$1/2$	ΔR_j
	S_{20a}	-2	-1	1	2	1	-1	$12^{-1/2}$	Δr_j
	S_{ra}	-2	-1	1	2	1	-1	$12^{-1/2}$	$R_0\alpha_j$
E_{2ub}	S_{18b}	2	1	-1	-2	-1	1	$12^{-1/2}$	$r_0\beta_j$
	S_{19b}	1	2	1	-1	-2	-1	$12^{-1/2}$	ΔR_j
	S_{20b}	0	1	1	0	-1	-1	$1/2$	Δr_j
	S_{rb}	0	1	1	0	-1	-1	$1/2$	$R_0\alpha_j$

FIG. 1. Elements of the transformation **U**: **VFSC** = **U** × **VFC**. N is the normalization constant. Thus in species E_{1gb}, $S_{7b} = (1/2)(-\Delta r_2 + \Delta r_3 - \Delta r_5 + \Delta r_6)$.

Class	VFSC	S_1	S_2	S_9	S_{12}	S_{13}	S_{14}	S_{15}	S_{6a}	S_{7a}	S_{8a}	S_{9a}
A_{1g}	S_1	$1/M$	$-1/M$									
	S_2	$-1/M$	$(1/M)+A$			B				G		
A_{2g}	S_9			$[(\rho+1)^2/M]+A$			B					I
B_{1u}	S_{12}				$12/M$	$12^{1/2}/M$						
	S_{13}				$12^{1/2}/M$	$(1/M)+A$				$-H$		
B_{2u}	S_{14}						$3/M$	$-3^{1/2}/M$				
	S_{15}						$-3^{1/2}/M$	$(1/M)+A$				$-J$
$E_{ga}{}^{+}$	S_{6a}								$15/2M$	$27^{1/2}/2M$	$-27^{1/2}/2M$	$-3^{1/2}(5\rho+2)/4M$
	S_{7a}								$27^{1/2}/2M$	$(1/M)+E$	$-1/2M$	$-3\rho/4M$
	S_{8a}								$-27^{1/2}/2M$	$-1/2M$	$5/2M$	$3(\rho+2)/4M$
	S_{9a}								$-3^{1/2}(5\rho+2)/4M$	$-3\rho/4M$	$3(\rho+2)/4M$	$[(5\rho^2+4\rho+8)/8M]+C$
$E_{gb}{}^{+}$	S_{6b}											
	S_{7b}											
	S_{8b}											
	S_{9b}											
$E_{ua}{}^{-}$	S_{18a}							(Symmetric)				
	S_{19a}											
	S_{20a}											
$E_{ub}{}^{-}$	S_{18b}											
	S_{19b}											
	S_{20b}											

FIG. 2. G matrix for planar vibrations of the deuterobenzenes. M = mass of carbon in atomic weight units; m = mass of hy-
$+1/m_4+1/m_5+1/m_6]$; $B=1/6[-1/m_1+1/m_2-1/m_3+1/m_4-1/m_5+1/m_6]$; $C=1/4[1/m_2+1/m_3+1/m_5+1/m_6]$; $D=1/4\times$
$-1/m_6]$; $G=(2^{1/2}/12)[-2/m_1+1/m_2+1/m_3-2/m_4+1/m_5+1/m_6]$; $H=(2^{1/2}/12)[-2/m_1-1/m_2+1/m_3+2/m_4+1/m_5-1/m_6]$;
$L=(3^{1/2}/12)[1/m_2+1/m_3-1/m_5-1/m_6]$.

followed Wilson[4] and Langseth and Lord[5] in numbering the vibrations and in defining the coordinate axes. The z axis is taken to be perpendicular to the plane of the molecule; the y axis is in the plane of the molecule and passes through carbon atoms one and four.

Wilson's technique[6] was used to obtain the secular equation. The following four types of valence force coordinates (VFC) were employed:

1. Δr_i, the change in length of the ith C—H bond.
2. ΔR_i, the change in length of the ith C—C bond.
3. $R_0\alpha_i$, where α_i is the change in the ith C—C—C angle and R_0 is the equilibrium C—C distance.
4. $r_0\beta_i$, where β_i is the angle between the ith C—H bond and the exterior bisector of the C—C—C angle centered on the ith carbon, and r_0 is the equilibrium C—H bond distance.

[4] E. Bright Wilson, Jr., Phys. Rev. 45, 706 (1934).
[5] A. Langseth and R. C. Lord, Jr., Kgl. Danske Vid. Sels. Math.-Fys. Medd. 16, 6 (1938).
[6] E. Bright Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

It is important to note that the ΔR_i have a different symmetry with respect to the x and y axes than do the other three types of VFC. The ΔR_i have the symmetry of the carbon-carbon bonds, whereas the remaining VFC have the symmetry of the atoms.

Symmetry factoring was obtained by using valence force symmetry coordinates ($VFSC$), which are orthonormal combinations of the VFC. The matrix $\mathbf{U}$ for the transformation $\mathbf{VFSC}=\mathbf{U}\times\mathbf{VFC}$ is given in a condensed form in Fig. 1. The various $VFSC$ are designated as S_1, S_2, $\cdots$ corresponding to normal vibrations ν_1, ν_2, $\cdots$. Three redundant coordinates appear among the $VFSC$ as a consequence of the fact that benzene is a ring molecule. The necessity of ring closure imposes three restrictions on the various possible normal vibrations. The redundant coordinate in A_{1g} was easily eliminated at the start. The remaining two were kept in the $\mathbf{U}$ matrix. They are designated S_{ra} and S_{rb} of species E_{2ua} and E_{2ub}. These two coordinates were carried through to the G matrix and were then

S_{6b}	S_{7b}	S_{8b}	S_{9b}	S_{18a}	S_{19a}	S_{20a}	S_{18b}	S_{19b}	S_{20b}
	I					H			J
			$-G$	J			$-H$		
$-J$						$-G$			$-I$
			H	$-.$			G		
	K					F			L
			$-K$	D			$-L$		
$15/2M$	$27^{1/2}/2M$	$-27^{1/2}/2M$	$-3^{1/2}(5\rho+2)/4M$	$\bullet$					
$27^{1/2}/2M$	$(1/M)+C$	$-1/2M$	$-3\rho/4M$			L			D
$-27^{1/2}/2M$	$-1/2M$	$5/2M$	$3(\rho+2)/4M$						
$-3^{1/2}(5\rho+2)/4M$	$-3\rho/4M$	$3(\rho+2)/4M$	$[(5\rho^2+4\rho+8)/8M]+E$	$-L$			F		
				$[(9\rho^2+12\rho+8)/8M]+C$	$-6^{1/2}(3\rho+2)/4M$	$3\rho/4M$	$-K$		
				$[-6^{1/2}(3\rho+2)/4M]$	$3/M$	$-6^{1/2}/2M$			K
				$3\rho/4M$	$-6^{1/2}/2M$	$(1/M)+E$			
							$[(9\rho^2+12\rho+8)/8M]+E$	$-6^{1/2}(3\rho+2)/4M$	$3\rho/4M$
							$-6^{1/2}(3\rho+2)/4M$	$3/M$	$-6^{1/2}/2M$
							$3\rho/4M$	$-6^{1/2}/2M$	$(1/M)+C$

drogen in atomic weight units; $\rho=r_0/R_0=$C—H equilibrium distance/C—C equilibrium distance; $A=1/6[1/m_1+1/m_2+1/m_3$ $[-1/m_2+1/m_3+1/m_5-1/m_6]$; $E=1/12[4/m_1+1/m_2+1/m_3+4/m_4+1/m_5+1/m_6]$; $F=1/12[4/m_1-1/m_2+1/m_3-4/m_4+1/m_5$ $I=(6^{1/2}/12)[-1/m_2+1/m_3-1/m_5+1/m_6]$; $J=(6^{1/2}/12)[1/m_2+1/m_3-1/m_5-1/m_6]$; $K=(3^{1/2}/12)[-1/m_2+1/m_3-1/m_5+1/m_6]$;

removed by applying the transformations

$$\tilde{L} \times G'(E_{2ua}) \times L = G(E_{2ua})$$

and

$$\tilde{L} \times G'(E_{2ub}) \times L = G(E_{2ub})$$

where L is the matrix:

L	S_{18}	S_{19}	S_{20}	S_r
S_{18}	1	0	0	0
S_{19}	0	$2^{-1/2}$	0	$2^{-1/2}$
S_{20}	0	0	1	0
S_r	0	$-2^{-1/2}$	0	$2^{-1/2}$

$\tilde{L}$ is the transpose of L, $G'(E_{2ua})$ is the G matrix for symmetry block E_{2ua} containing the redundant coordinate, and $G(E_{2ua})$ is the G matrix for block E_{2ua} with the redundant coordinate removed.

The final G matrix is given in Fig. 2. The outlined blocks indicate the way the matrix factors for D_{6h} symmetry. Terms outside these blocks are interaction terms which are zero for benzene and benzene-d_6, but which may be different from zero in the intermediate deuterium derivatives of lower symmetry. By leaving the results in this form, the secular equation for any deuterium derivative of benzene can be obtained with very little trouble.[1] The reader is referred to Wilson's first paper on the subject[6] for the method of reducing the matrices to the explicit equations.

We now turn to the potential function. The F matrix for the VFSC is given in Fig. 3. One will note that it includes all the possible interaction constants for the planar vibrations that are compatible with the symmetry of benzene—twenty-six in all. The scheme of notation for these force constants (hereafter termed "Greek" constants) is outlined in Table IIA.

The force constants for the VFSC can be expressed in terms of the constants for the VFC (hereafter termed "Latin" constants). The notation for the latter is indicated in Table IIB. For example, the diagonal force constant for $\Delta r_i \times \Delta r_i$ is termed E, while the interaction constants for the various $\Delta r_i \times \Delta r_j (i \neq j)$ are termed e_o, e_m, and e_p.
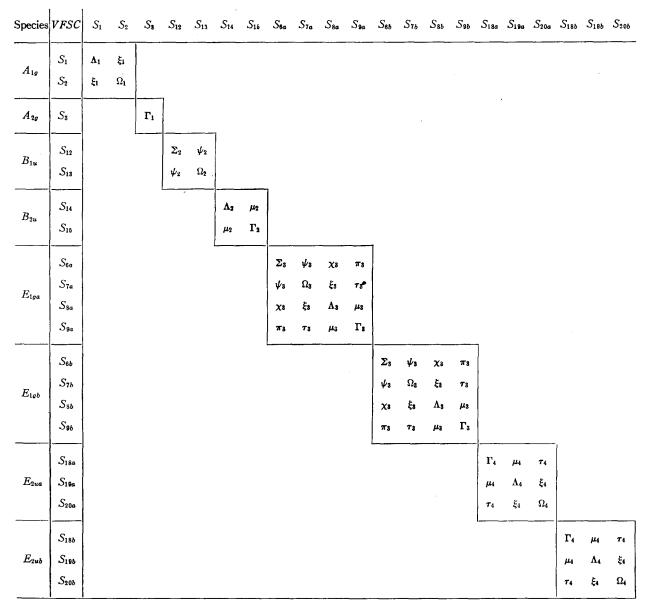
Species	VFSC	S_1	S_2	S_3	S_{12}	S_{13}	S_{14}	S_{15}	S_{6a}	S_{7a}	S_{8a}	S_{9a}	S_{6b}	S_{7b}	S_{8b}	S_{9b}	S_{18a}	S_{19a}	S_{20a}	S_{18b}	S_{19b}	S_{20b}
A_{1g}	S_1	Λ_1	ξ_1																			
	S_2	ξ_1	Ω_1																			
A_{2g}	S_3			Γ_1																		
B_{1u}	S_{12}				Σ_2	ψ_2																
	S_{13}				ψ_2	Ω_2																
B_{2u}	S_{14}						Λ_2	μ_2														
	S_{15}						μ_2	Γ_2														
E_{1ga}	S_{6a}								Σ_3	ψ_3	χ_3	π_3										
	S_{7a}								ψ_3	Ω_3	ξ_3	τ_3										
	S_{8a}								χ_3	ξ_3	Λ_3	μ_3										
	S_{9a}								π_3	τ_3	μ_3	Γ_3										
E_{1gb}	S_{6b}												Σ_3	ψ_3	χ_3	π_3						
	S_{7b}												ψ_3	Ω_3	ξ_3	τ_3						
	S_{8b}												χ_3	ξ_3	Λ_3	μ_3						
	S_{9b}												π_3	τ_3	μ_3	Γ_3						
E_{2ua}	S_{18a}																Γ_4	μ_4	τ_4			
	S_{19a}																μ_4	Λ_4	ξ_4			
	S_{20a}																τ_4	ξ_4	Ω_4			
E_{2ub}	S_{18b}																			Γ_4	μ_4	τ_4
	S_{19b}																			μ_4	Λ_4	ξ_4
	S_{20b}																			τ_4	ξ_4	Ω_4

Fig. 3. **F** matrix for planar vibrations of the deuterobenzenes.

The subscripts o, m, and p refer to the ortho, meta, and para positions. Thus e_o is the constant for interaction between the stretching of two C−H bonds which are ortho to each other. Similarly, the various l's are interaction constants between hydrogen stretchings and hydrogen bendings. Interaction constants bearing no subscripts refer to immediately adjacent positions. For example, l itself is the constant for interaction between the stretching of a given C−H bond and the bending of that same bond—for $\Delta r_1 \times r_0 \beta_1$, $\Delta r_2 \times r_0 \beta_2$, etc.

Just as for the non-planar vibrations, there are fewer Greek constants (26) than Latin constants

(37).[7] The Greek constants are the ones which are evaluated from the experimental frequencies. Even if they could all be determined (which is not the case at present), it would be impossible to evaluate the harmonic *valence force* potential function completely. However, the terms for hydrogen stretching and hydrogen bending motions can be determined, since there are four Greek constants and four Latin constants in each case. The relations are:

[7] Several of these thirty-seven Latin constants may be shown to be equal to zero by symmetry. Examples are $n = n_o = 0$. Nevertheless, there are still fewer Greek than Latin constants because of the redundancy relations among the *VFC* mentioned above.

Hydrogen stretching:

$$\Omega_1 = E + 2e_o + 2e_m + e_p.$$
$$\Omega_2 = E - 2e_o + 2e_m - e_p.$$
$$\Omega_3 = E - e_o - e_m + e_p.$$
$$\Omega_4 = E + e_o - e_m - e_p.$$

Hydrogen bending:

$$\Gamma_1 = G + 2g_o + 2g_m + g_p.$$
$$\Gamma_2 = G - 2g_o + 2g_m - g_p.$$
$$\Gamma_3 = G - g_o - g_m + g_p.$$
$$\Gamma_4 = G + g_o - g_m - g_p.$$

The problem, then, is to evaluate the twenty-six Greek force constants from the assigned frequencies of light and heavy benzene (and intermediate deuterium derivatives if necessary). For this purpose the assignments of Ingold and co-workers[8] were employed. They are given later in Table V.

The following numerical values were used in the calculations:

m = mass of hydrogen (or deuterium) = 1.008 (or 2.016) atomic weight units.

M = mass of carbon = 12.01 atomic weight units.

r_0 = C−H and C−D equilibrium distance = 1.08A.

R_0 = C−C equilibrium distance = 1.39A.

$\rho = r_0/R_0 = 0.777$.

ν = frequency in wave numbers = const. $\times \lambda^{\frac{1}{2}}$, where λ is a root of the secular equation. When masses are in atomic weight units and force constants are 10^{-5} times their value in dynes/cm, the constant is 1302.9.

EVALUATION OF THE FORCE CONSTANTS

Species $A_{1g}(\nu_1, \nu_2)$

The two vibrations in this species are the totally symmetrical C−H and C−C stretching modes (the "breathing" frequencies). It is often assumed that the interactions between C−H stretching vibrations and other modes are negligible. If we assume this by putting the interaction constant ξ_1 equal to zero, we can evaluate the two constants Λ_1 and Ω_1 from the two frequencies of benzene or from those of benzene-d_6. The results will not quite agree because of differing degrees of anharmonicity in the two molecules. We find:

	Benzene	Benzene-d_6	Average
Λ_1	7.617	7.623	6.620
Ω_1	5.085	5.154	5.119
ξ_1	(0)	(0)	(0)

[8] Reference 2, p. 332.

TABLE II.

A. Notation for force constants for *VFSC*.

	Ring stretch	Hyd. stretch	Ring bend	Hyd. bend
Ring stretch	Λ	ξ	χ	μ
Hydrogen stretch		Ω	ψ	τ
Ring bend			Σ	π
Hydrogen bend				Γ

B. Notation for force constants for *VFC*.

	Ring stretch ΔR_i	Hyd. stretch Δr_i	Ring bend $R_0 \alpha_i$	Hyd. bend $r_0 \beta_i$
Ring stretch ΔR_i	D, d_o, d_m, d_p	$h_o\ h_m\ h_p$	$i_o\ i_m\ i_p$	$j_o\ j_m\ j_p$
Hyd. stretch Δr_i		$E\ e_o\ e_m\ e_p$	$k\ k_o\ k_m\ k_p$	$l\ l_o\ l_m\ l_p$
Ring bend $R_0\alpha_i$			$F\ f_o\ f_m\ f_p$	$n\ n_o\ m_m\ m_p$
Hyd. bend $r_0\beta_i$				$G\ g_o\ g_m\ g_p$

It is to be remembered that the force constants must be multiplied by 10^5 to convert to dynes/cm.

A more exact procedure is to use the two frequencies of benzene and the two for benzene-d_6 to provide three independent equations from which Λ_1, Ω_1, and ξ_1 may be evaluated. It is noteworthy that one gets only three, rather than four, independent equations from these four frequencies. The equation of highest degree for each of the two molecules has the form $f(k's) = \lambda_1 \cdot \lambda_2 \times f(\text{masses})$. When one substitutes the known values for the λ's and for the masses of benzene and benzene-d_6, the equations become identical (except for anharmonic effects). This is a general result for any symmetry species.[9] Hence, if a species has n genuine normal vibrations, the frequencies of the original molecule and its completely substituted isotopic derivative give only $2n - 1$ independent equations for evaluating the force constants.

For species A_{1g} of benzene this procedure furnishes two sets of roots, but only the following set is physically reasonable.

Λ_1	7.832	(Ring stretch)
Ω_1	5.003	(Hyd. stretch)
ξ_1	−0.4198	(Interaction)

It is clear that the usual neglect of interactions between C−H stretching and other vibrations is not justified in terms of accurate values of force constants. However, the frequency values (as well as the diagonal force-constant values) are relatively insensitive to these particular interaction constants, so that for the purpose of calculating frequencies they may be neglected—particularly in view of uncertainties due to anharmonicity. This is exemplified by the results in Table III.

[9] Use is made of it in the derivation of the Teller-Redlich product rule. O. Redlich, Zeits. f. physik. Chemie 28B, 371 (1935).

TABLE III. Calculated values for the A_{1g} frequencies.

		Observed	Calc. ($\xi_1 = 0$)*	Calc. ($\xi_1 \neq 0$)
Benzene	ν_1	992	992	996
	ν_2	3062	3072	3061
Benzene-d_6	ν_1	943	943	939
	ν_2	2293	2285	2294

* The average values of Λ_1 and Ω_1 were used.

Species $A_{2g}(\nu_3)$

There is only one frequency and one force constant in this species. One finds:

	Benzene	Benzene-d_6	Average
Γ_1	0.8253	0.8347	0.8300

Species $B_{1u}(\nu_{12}, \nu_{13})$

This species contains a hydrogen stretching and a ring bending vibration. Again we calculate two sets of values by first omitting the interaction constant and then including it.

	Benzene	Benzene-d_6	Average
Ω_2	5.076	5.131	5.104
Σ_2	0.6587	0.6636	0.6612
ψ_2	(0)	(0)	(0)

If one includes ψ_2, one finds two sets of roots.

	Set 1	Set 2	
Ω_2	5.002	5.002	(Hyd. stretch)
Σ_2	0.6768	2.467	(Ring bend)
ψ_2	0.1064	−2.994	(Interaction)

Both sets are physically possible, but set 1 is more plausible because it contains an interaction constant which is smaller in magnitude than the diagonal constant Σ_2, and because the absolute value of Σ_2 is more reasonable.

Species $B_{2u}(\nu_{14}, \nu_{15})$

The assignment of ν_{14} is still in considerable doubt. We shall use Ingold's values of 1648 cm^{-1} in benzene and 1571 cm^{-1} in benzene-d_6 to calculate provisional values for the force constants. Neither ν_{14} nor ν_{15} is a C$-$H stretching mode, so the interaction constant is important and we do not attempt to set it equal to zero. Again two sets of roots are obtained.

	Set 1	Set 2	
Γ_2	0.94993	0.9493	(Hyd. bend)
Λ_2	6.724	4.989	(Ring stretch)
μ_2	1.299	−0.2030	(Interaction)

It is hard to choose a preferred set in this case, and we make no attempt to do so, because the assign-

ments may well be incorrect. It seems more useful to give the explicit equations for this species so that any different assignment can be readily used to obtain the corresponding force constants. The equations are

$$\lambda_1 + \lambda_2 = (1/M)[3\Lambda_2 + \Gamma_2 - 12^{\frac{1}{2}}\mu_2] + \Gamma_2/m.$$
$$\lambda_1 \cdot \lambda_2 = (3/mM)[\Lambda_2\Gamma_2 - \mu_2{}^2].$$

Species $E_{2u}(\nu_{18}, \nu_{19}, \nu_{20})$

The spectra of light and heavy benzene furnish a total of six frequencies in E_{2u}, but as pointed out earlier there are only five independent equations for solving for the force constants. The complete potential function contains six force constants. Obviously, a complete solution is impossible. Two possible alternatives suggest themselves. (i) One can assume that the value of the C$-$H stretching constant, Ω_4, is the same as in species A_{1g} and B_{1u} (5.003 and 5.002, respectively). This can be inserted in the equations, giving five equations in five unknown force constants. The assumption is probably good, but the solution promises to be formidable. (ii) One can assume some of the interaction constants are zero. The logical choices are τ_4 and ξ_4, the interactions between C$-$H stretching and the other two forms of motion involved. One then has five equations in four unknowns. Since, in practice, the most important use of force constants is in calculating frequencies, the most desirable procedure is one in which as few constants as possible are used consistent with results of the requisite accuracy. This suggests that the dropping of the two interaction constants is not only easier but also more practical. Consequently this method was used. Again one obtains two sets of roots.

	Set 1	Set 2
Ω_4	5.147	5.147
Γ_4	0.8698	0.8698
Λ_4	6.143	3.917
μ_4	1.399	0.1393
ξ_4	(0)	(0)
τ_4	(0)	(0)

It was found that the calculated force constants varied rather appreciably, depending upon just how the equations were solved for them. There are several reasons for this. First, anharmonicities are different for benzene and benzene-d_6, and this is ignored in the process of solution. Second, the method of solution sometimes involves taking small differences between large numbers. Consequently, we do not claim that the values of the above constants express accurate physical reality. They will, however, give moderately good calculated values for the frequencies (Table V).

The reader may have noticed that in every symmetry class the values of the diagonal constants for C−H stretching and C−H bending are determined uniquely. Only for the ring stretching and bending constants, and for the interaction constants, are two sets of roots obtained. This is because constants of the first type are readily evaluated by comparing the equations for benzene with those of benzene-d_6. For the evaluation of the remaining force constants, however, it was found that it was not as helpful to have two sets of equations as we had expected. This is due to the fact that the potential function is anharmonic, and the anharmonicity has a larger effect on the experimental frequencies of benzene than on those of benzene-d_6. Hence the two sets of equations are not actually satisfied by a common set of values for the force constants. For the same reason it is not helpful to introduce the equations for deuterium derivatives of lower symmetry. Therefore, after first evaluating the diagonal C−H stretching and bending constants, we confined ourselves wherever possible to the equations for one isotopic molecule.

Species $E_{1g}(v_6, v_7, v_8, v_9)$

In this species benzene and benzene-d_6 furnish eight frequencies, or seven independent equations, from which to evaluate ten force constants. Obviously, the values of at least three constants must be assumed. A reasonable procedure is to set the constants for interaction with C−H stretching equal to zero: $\psi_3 = \xi_2 = \tau_3 = 0$. One can then evaluate Ω_3 and Γ_3 without much trouble by comparing the resulting equations for benzene and those of benzene-d_6. One finds $\Omega_3 = 5.044$, $\Gamma_3 = 0.8491$. With these values introduced, the relation between force constants and the sum of the frequency parameters is identically the same for benzene and benzene-d_6; thus one has six equations to determine the five remaining constants. To do this, we first assumed the three interaction constants π_3, μ_3, and χ_3 to be small, and neglected second-order terms; we could then solve for the diagonal constants, and found $\Lambda_3 = 5.66$ and $\Sigma_3 = 0.741$. (There was also a second pair of roots, not physically reasonable.) Using these values, we adjusted the interaction constants by a least-squares procedure, and found $\pi_3 = 0.241$, $\chi_3 = -0.181$, with μ_3 negligible. These values gave frequencies in good agreement with the observed, except for v_6; to improve this, we readjusted Σ_3 by a least-squares procedure, and found $\Sigma_3 = 0.810$. With the set of constants so obtained, we calculated the frequencies shown in Table V, in satisfactory agreement with the observed values.

This completes the determination of the force constants. For convenience the results have been gathered together in Table IV, where the various sets are arranged in order of decreasing preference.

FURTHER RESULTS

One can now use the force constants to calculate the vibrational frequencies. Table V gives the results. The preferred set of force constants has been used in each case. For benzene and benzene-d_6, we have merely calculated back the frequencies used in evaluating the force constants, but a few independent checks can be obtained from sym-benzene-d_3 as shown. In principle all the planar frequencies for the various deutero-benzenes should be calculable, but the symmetry blocks are so large that the labor is prohibitive. It may be noted that the calculated and observed values agree within 1.0 percent in all but six cases, with a maximum error of 2.2 percent.

It is now also possible to evaluate the valence force potential constants for the hydrogen stretching and bending motions. One finds, by use of Eqs. (1) and (2):

$$
\begin{array}{ll}
E = 5.065 & G = 0.8695 \\
e_o = 0.017 & g_o = -0.0164 \\
e_m = -0.031 & g_m = +0.0101 \\
e_p = -0.034 & g_p = -0.0268
\end{array}
$$

We do not attach much significance to these results because the hydrogen vibrations are especially subject to anharmonicity, and hence so are the

TABLE IV. Values of the force constants ($k \times 10^{-5}$ dyne/cm).

Species	Force constant	1st preference	2nd preference
A_{1g}	Λ_1	7.83	7.62
	Ω_1	5.00	5.12
	ξ_1	−0.420	0*
A_{2g}	Γ_1	0.830	
B_{1u}	Ω_2	5.00	5.10
	Σ_2	0.677	0.661
	ψ_2	0.106	0*
B_{2u}	Γ_2	0.949	0.949
	Λ_2	6.72	4.99
	μ_2	1.30	−0.203
E_{2u}	Ω_4	5.15	5.15
	Γ_4	0.870	0.870
	Λ_4	6.14	3.92
	μ_4	1.40	0.139
	ξ_4	0*	0*
	τ_4	0*	0*
E_{1g}	Ω_3	5.04	
	Γ_3	0.849	
	Σ_3	0.810	
	Λ_3	5.66	
	ψ_3	0*	
	χ_3	0.181	
	π_3	0.241	
	ξ_3	0*	
	τ_3	0*	
	μ_3	0	

* Assumed to be zero.

TABLE V. Calculated *vs.* assigned frequencies (cm^{-1}).

Spe-cies	Freq. no.	Benzene Calc.	Benzene Assigned	Benzene % Diff.	sym-benzene-d_3 Calc.	sym-benzene-d_3 Assigned	sym-benzene-d_3 % Diff.	Benzene-d_6 Calc.	Benzene-d_6 Assigned	Benzene-d_6 % Diff.
A_{1g}	1	996	992	+0.4	948	956	−0.8	939	943	−0.4
	2	3061	3062	0.0	3065	3053	+0.4	2294	2293	0.0
A_{2g}	3	1323	1326	−0.2	1245	1230±2%	—	1034	1037	+0.3
B_{1u}	12	1017	1010	+0.7	1006	1004	+0.2	960	963	−0.3
	13	3058	3060	0.0	2289	2282	+0.3	2291	2290	0.0
B_{2u}	14	1647	1648	0.0	1614	1600	+0.9	1572	1571	+0.1
	15	1112	1110	+0.2	900	920	−2.2	824	825	−0.1
E_{2u}	18	1053	1037	+1.3				815	813	+0.2
	19	1469	1485	−1.1				1320	1333	−1.0
	20	3082	3080	+0.1				2301	2294	+0.3
E_{1g}	6	599	606	−1.2				568	577	−1.6
	7	3050	3047	+0.1				2280	2265	+0.7
	8	1617	1596	+1.3				1561	1552	+0.6
	9	1180	1178	+0.2				869	867	+0.2

Greek constants from which these values are calculated.

Internal Rotation I

A Product Rule for *Cis*- and *Trans*-Isomers

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(Received July 12, 1948)

The assumption of equal force constants in the potential functions of *cis*- and *trans*-forms leads to a product rule for the planar vibrations of rotational isomers.
The rotational isomers of symmetrical dichloro- and dibromoethane are *trans*- and "gauche."

IF the potential energy of a molecule is expressed as the most general quadratic function of the displacements from the equilibrium configuration, it has been shown[1] that the product of the frequencies of the normal modes of vibration belonging to the same symmetry class can be expressed as the product of two functions. One of these is a function of the force constants only, and the other a function of the masses of the atoms and internuclear distances in the molecule. If some of the atoms of a molecule are replaced by their isotopes the potential energy of the isotopic molecule involves the same force constants as that for the original molecule since isotopic substitution does not change the internal field. Consequently the ratio of the product of the frequencies of a molecule to the product of the frequencies belonging to the same symmetry class of the isotopic molecule is the ratio of the two functions involving masses and internuclear distances only. The Teller-Redlich[2] product rule expresses this ratio in terms of molecular weights and moments of inertia.

To obtain a product rule for rotational isomers it is necessary as a first approximation to assume that the force constants appearing in the potential function of the two isomers are the same.[3] This will be true to a very good approximation for all planar force constants[4] but need not be true for out-of-plane constants where in general the rotational isomers have different activation energies and thus different curvatures of the potential function at their respective minima. Even for the in-plane vibrations the interaction constants between groups or atoms on neighboring atoms will in general be quite different for *cis*- and *trans*-configurations. However, to a good first approximation, the interaction constants between atoms whose internuclear distance is independent of azimuthal angle will not be very

TABLE I.

Type	Cis-C_{2v} No. of vib'ns	Cis-C_{2v} Non-genuine vib'ns	Type	Trans-C_{2h} No. of vib'ns	Trans-C_{2h} Non-genuine vib'ns
A_1	5	T_y	A_g	5	R_z
B_1	4	$T_x R_z$	B_u	4	$T_x T_y$
A_2	2	R_y	A_u	2	T_z
B_2	1	$T_z R_x$	B_g	1	$R_x R_y$

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

[2] E. Teller, quoted in W. R. Angus *et al.*, J. Chem. Soc. (1936), p. 971; O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).

[3] E. L. Pace, J. Chem. Phys. **15**, 528 (1947), has obtained a product rule for the E_g and E_u vibrations of an X_2Y_6 molecule by assuming the force constants to be the same and that the interaction constants of the XY_3 groups may be neglected.

[4] J. A. A. Ketelaar, Rec. Trav. Chim. **58**, 266 (1939); J. Sherman and J. A. A. Ketelaar, Physica **6**, 572 (1939). Both valence bond and molecular orbital treatments of *cis*- and *trans*-dichloroethylenes gave the same C−Cl bond length. This means that the bond constants are the same.