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Citation: *J. Chem. Phys.* **14**, 282 (1946); doi: 10.1063/1.1724132

View online: <http://dx.doi.org/10.1063/1.1724132>

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The only actual liquid exhibiting a peculiar second-order phase change is liquid helium. And a possible explanation of the thermal properties of this liquid assimilating it to a kind of B.E. fluid has been repeatedly suggested by London.^{1,2} The formalism necessary to describe the thermal properties of a B.E. fluid undergoing a second-order phase change in phase space would have to be somewhat similar to the formalism of the just discussed B.E. fluid model. However, as pointed out already,³ the preceding models behave rather in a normal way below their transition line. Their expansion and pressure coefficients, $(\partial V/\partial T)_p$ and $(\partial p/\partial T)_v$, are positive in contrast with those of liquid He II. It is interesting to recall in this connection that in a recent investigation London⁸ was lead to a qualitative argument accounting for this anomalous behavior of liquid He II on the very basis of a B.E. fluid model.

⁸ F. London, *J. Chem. Phys.* **11**, 203 (1943).

The difficulties inherent in the theoretical treatment of liquids are still further increased for a quantum liquid like He II. Here, the wave-length associated with the average thermal motion of the atoms may become of the same order of magnitude as the macroscopic dimensions of the vessel containing the liquid. This led Landau⁹ to build up a continuum type or hydrodynamic model for this liquid. It is as yet not clear whether the anomalous thermal properties of liquid He II in bulk are correctly accounted for by this hydrodynamic model.

We should like finally to add here that a closer analysis of phase changes of higher order observed in cooperative phenomena might disclose also the interplay of forces of opposing tendencies as those existing in the B.E. fluid models studied here. In particular, the raising or lowering of the order of a phase change might be attributed to the intervention of forces of opposing nature.

⁹ L. Landau, *J. Phys. USSR* **5**, 71 (1941).

The Non-Planar Vibrations of Benzene

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(Received January 7, 1946)

A thorough normal coordinate treatment has been carried out for the non-planar vibrations of benzene and its deuterium derivatives. The analysis has led to a critical survey of the assignments, and has furnished strong independent support for those advanced by Pitzer and Scott. It has also furnished values for all eight force constants of the complete harmonic potential function. For four of the constants two sets of values were obtained, both of which are physically reasonable and which reproduce the frequencies equally well. It was not possible to decide between them. The force constants were then used to calculate frequencies for the various deuterobenzenes. Nearly sixty such frequencies were evaluated, of which about forty could be checked against experiment. With four exceptions the errors are less than 1.5 percent. Lastly, certain valence-force constants pertaining to hydrogen vibrations have been determined.

INTRODUCTION

BENZENE has been the subject of several normal coordinate treatments.¹⁻⁹ The first

was carried out by Wilson,¹ who suggested a simplified potential function with six force con-

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¹ E. B. Wilson, Jr., *Phys. Rev.* **45**, 706 (1934).

² R. C. Lord, Jr. and D. H. Andrews, *J. Phys. Chem.* **41**, 149 (1937).

Note added in proof: R. P. Bell [*Trans. Far. Soc.* **41**, 293 (1945)] has recently shown how to improve Lord and Andrews' results for the non-planar vibrations of benzene while still using a simple valence force system with no cross terms and with only two force constants.

³ M. van den Bossche and C. Manneback, *Ann. Soc. Sci. Bruxelles* **54-B**, 230 (1934).

⁴ C. Manneback, *Ann. Soc. Sci. Bruxelles* **55-B**, 129 (1935).

⁵ C. Manneback, *Ann. Soc. Sci. Bruxelles* **55-B**, 237 (1935).

⁶ J. Duchesne and W. G. Penney, *Bull. Soc. Roy. Sci. Liege* **8**, 514 (1939).

⁷ E. Bernard, C. Manneback, and A. Verleysen, *Ann. Soc. Sci. Bruxelles* [1] **59**, 376 (1939).

⁸ E. Bernard, C. Manneback, and A. Verleysen, *Ann. Soc. Sci. Bruxelles* **60**, 45 (1940).

⁹ K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.* **65**, 803 (1943).

stants. This function was applied to the vibrations of benzene and benzene- d_6 by Lord and Andrews,² but both the function and the data with which it was used are now known to be inadequate. Meanwhile Manneback⁴ has obtained the most general potential function compatible with the simple harmonic approximation and with the D_{6h} symmetry of benzene. His equations contain twenty-six force constants for the planar vibrations and eight for the non-planar ones. The problem then became one of evaluating these various force constants by using this potential function with the correct set of vibrational assignments. In a second paper Manneback⁵ attempted this with the data then available, but because the assignments were incomplete, and in some cases incorrect, the results have little present value. Duchesne and Penney⁶ attempted a similar treatment after the assignments of Ingold and his collaborators¹⁰ had been advanced. It too must be regarded as unsatisfactory inasmuch as several force constants had to be dropped from the potential function because of insufficient data. For example only three of the eight constants for the non-planar vibrations could be evaluated. At about this same time Bernard, Manneback, and Verleysen⁷ modified Manneback's original equations to apply to the *planar* vibrations of *p*-benzene- d_2 , *sym*-benzene- d_3 , and *p*-benzene- d_4 as well as to benzene and benzene- d_6 . They were then used with Langseth and Lord's¹¹ assignments for the planar vibrations of all five substances.⁸ More recently Pitzer and Scott⁹ appear to have carried out some calculations with Manneback's equations, but no details are given.

In summary it can be said that Manneback's equations provide the complete harmonic potential function for benzene, but that the application of these equations to actual data has not been thoroughly satisfactory. In the case of the planar vibrations the assignments of at least two frequencies (numbers 14 and 15 in Wilson's terminology¹) are at best very dubious. There is also room for doubt concerning one or two other assignments. Any treatment is necessarily in-

complete until these values have been established. No attempt to use the complete potential function on the non-planar vibrations has been described.

It, therefore, seemed worth while to attack the problem again. A successful treatment should provide two useful results. It should furnish a set of force constants which are characteristic of the benzene ring. One may very possibly be to carry these force constants over to various derivatives of benzene in much the same manner that one already transfers force constants from one aliphatic compound to another.¹² Secondly, the analysis will serve as a severe test for the validity of the assignments in benzene and its several deuterium derivatives. If one uses observed frequencies in, say, benzene and benzene- d_6 to calculate a set of force constants, these force constants must give back correct frequencies for all the various intermediate deuterium compounds. If they do not do so, the original assignments are in error.

The obvious starting place is the non-planar vibrations, for several reasons. First, the treatment of the planar vibrations by Manneback and his co-workers^{7, 8} is quite satisfactory except for those cases where the assignments are dubious. The need here is for more experimental data. On the other hand there has been no thoroughgoing treatment of the non-planar vibrations. Second, the non-planar vibrations make the most important contributions to the various thermodynamic functions because the corresponding frequencies are relatively low. Hence it will be especially useful to have a set of force constants for these vibrations. Third, the non-planar vibrations split into relatively small

TABLE I. Symmetry properties of the non-planar vibrations of benzene (D_{6h} symmetry).

Class	C_3^2	C_2^z	C_2^y	i	No.	Notation Ring Hyd.	Sel. rules Ram IR
A_{2u}	+	+	-	-	1	ν_{11}	- +
B_{2g}	+	-	-	+	2	ν_4	- -
E_{2u}^+	e	+	+	-	2	ν_{16a}	- -
E_{2u}^-	e	+	-	-	2	ν_{16b}	- -
E_{2g}^+	e	-	+	+	1		+ -
E_{2g}^-	e	-	-	+	1	ν_{10b}	+ -

¹⁰ C. K. Ingold, *et al.*, J. Chem. Soc. 912-987 (1936).

¹¹ A. Langseth and R. C. Lord, Jr., Kgl. Danske Vid. Sels. Math. Fys. Medd 16, 6 (1938).

¹² B. L. Crawford, Jr. and S. R. Brinkley, Jr., J. Chem. Phys. 9, 69 (1941).

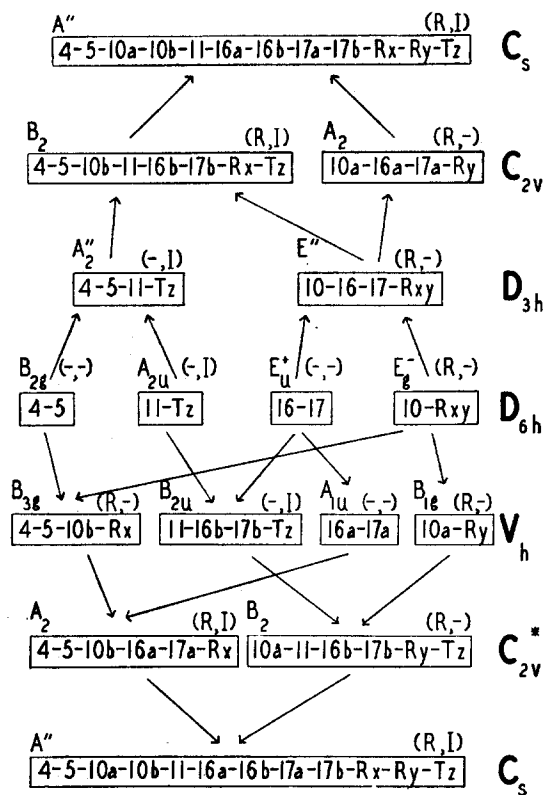


FIG. 1.

symmetry blocks, making the equations easier to handle.

We have carried out a complete normal coordinate treatment of the non-planar vibrations, evaluating all the force constants of the harmonic potential function. These constants have been used in turn to calculate a large number of frequencies for the various deuterobenzenes. The

analysis has furnished valuable support for the latest assignments, those of Pitzer and Scott.

MATHEMATICAL METHODS

There are nine non-planar vibrations in benzene, of which three pairs are doubly degenerate. Their symmetry properties are shown in Table I for D_{6h} symmetry. We have followed Wilson¹ and Langseth and Lord¹¹ in numbering the vibrations and in defining the coordinate axes. The z axis is perpendicular to the plane of the molecule; the y axis is in the plane of the molecule and passes through atoms one and four.

The thirteen possible deuterobenzenes possess in all six different symmetries. Each of the symmetry classes of the various lower symmetries is formed by a combination of the classes of D_{6h} . Fig. 1, which is taken from the paper by Langseth and Lord, shows these combinations for the non-planar vibrations.¹³ The selection rules are also indicated, R meaning Raman-active and I infrared-active. In C_{2v} symmetry the twofold axis passes through carbon atoms, as in m -benzene- d_2 . In C_{2v}^* symmetry the twofold axis bisects carbon-carbon bonds, as in o -benzene- d_2 .

To obtain the secular equation the technique of Wilson¹⁴ was used. A valence-force potential function which included all the possible second-degree interactions was first set up. Two types of non-planar valence-force coordinates (VFC) were employed. (1) The perpendicular displacement of the i th hydrogen atom out of the plane defined by the two adjacent carbon-carbon bonds was termed $r_0\gamma_i$, where r_0 is the equilibrium

Class	VFSC	VFC											
		$r_0\gamma_1$	$r_0\gamma_2$	$r_0\gamma_3$	$r_0\gamma_4$	$r_0\gamma_5$	$r_0\gamma_6$	$R_0\delta_1$	$R_0\delta_2$	$R_0\delta_3$	$R_0\delta_4$	$R_0\delta_5$	$R_0\delta_6$
A_{2u}	S_{11}	6 ⁻¹	6 ⁻¹	6 ⁻¹	6 ⁻¹	6 ⁻¹	6 ⁻¹						
B_{2g}	S_4 S_6	6 ⁻¹	-6 ⁻¹	6 ⁻¹	-6 ⁻¹	6 ⁻¹	-6 ⁻¹	6 ⁻¹	-6 ⁻¹	6 ⁻¹	-6 ⁻¹	6 ⁻¹	-6 ⁻¹
E_{ua}^+	S_{16a} S_{17a}	0	- $\frac{1}{2}$	$\frac{1}{2}$	0	- $\frac{1}{2}$	$\frac{1}{2}$	-12 ⁻¹	3 ⁻¹	-12 ⁻¹	-12 ⁻¹	3 ⁻¹	-12 ⁻¹
E_{ub}^+	S_{16b} S_{17b}	-3 ⁻¹	12 ⁻¹	12 ⁻¹	-3 ⁻¹	12 ⁻¹	12 ⁻¹	$\frac{1}{2}$	0	- $\frac{1}{2}$	$\frac{1}{2}$	0	- $\frac{1}{2}$
E_{ga}^-	S_{10a}	0	$\frac{1}{2}$	$\frac{1}{2}$	0	- $\frac{1}{2}$	- $\frac{1}{2}$						
E_{gb}^-	S_{10b}	-3 ⁻¹	-12 ⁻¹	12 ⁻¹	3 ⁻¹	12 ⁻¹	-12 ⁻¹						

FIG. 2. U matrix for transforming VFC to VFSC. $VFSC = U \times VFC$.

¹³ Langseth and Lord seem to have reversed the "a" and "b" designations in their Figure 2b, p. 15, for they are not consistent with the usage in the rest of the paper. We have taken the liberty of altering them in our reproduction.

¹⁴ E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

Class	VFSC	S_{11}	S_4	S_5	S_{16a}	S_{17a}	S_{16b}	S_{17b}	S_{10a}	S_{10b}
A_{2u}	S_{11}	$\frac{1}{M} + \frac{P}{6}$		$\frac{Q}{6}$		$\frac{T}{6^{1/2}}$		$\frac{Y}{2^{1/2}}$	$\frac{U}{6^{1/2}}$	$\frac{Z}{2^{1/2}}$
	S_4		$\frac{48}{M}$	$\frac{-3^{1/2}(1+4\rho)}{M}$						
B_{2g}	S_5		$\frac{-3^{1/2}(1+4\rho)}{M}$	$\frac{(1+4\rho)^2}{M} + \frac{P}{6}$		$\frac{U}{6^{1/2}}$		$\frac{Z}{2^{1/2}}$	$\frac{T}{6^{1/2}}$	$\frac{Y}{2^{1/2}}$
	S_{16a}				$\frac{16}{M}$	$\frac{4(1+3\rho)}{M}$				
E_{ua}^+	S_{17a}				$\frac{4(1+3\rho)}{M}$	$\frac{(1+3\rho)^2}{M} + \frac{S}{4}$		$\frac{T}{3^{1/2}}$	$\frac{V}{4}$	$\frac{U}{3^{1/2}}$
	S_{16b}						$\frac{16}{M}$	$\frac{4(1+3\rho)}{M}$		
E_{ub}^+	S_{17b}		(Symmetric)				$\frac{4(1+3\rho)}{M}$	$\frac{(1+3\rho)^2}{M} + \frac{W}{12}$	$\frac{U}{3^{1/2}}$	$\frac{X}{12}$
	S_{10a}								$\frac{(1+\rho)^2}{M} + \frac{S}{4}$	$\frac{T}{3^{1/2}}$
E_{gb}^-	S_{10b}									$\frac{(1+\rho)^2}{M} + \frac{W}{12}$

FIG. 3. G matrix for non-planar vibrations of the deuterobenzenes.

 M = mass of carbon. $\rho = r_0/R_0$ = C-H equilibrium distance/C-C equilibrium distance. $P = 1/m_1 + 1/m_2 + 1/m_3 + 1/m_4 + 1/m_5 + 1/m_6$. $Q = 1/m_1 - 1/m_2 + 1/m_3 - 1/m_4 + 1/m_5 - 1/m_6$. $S = 1/m_2 + 1/m_3 + 1/m_5 + 1/m_6$. $T = -1/m_2 + 1/m_3 - 1/m_5 + 1/m_6$. $U = 1/m_2 + 1/m_3 - 1/m_5 - 1/m_6$. m = mass of hydrogen (or deuterium). $V = -1/m_2 + 1/m_3 + 1/m_5 - 1/m_6$. $W = 4/m_1 + 1/m_2 + 1/m_3 + 4/m_4 + 1/m_5 + 1/m_6$. $X = 4/m_1 - 1/m_2 + 1/m_3 - 4/m_4 + 1/m_5 - 1/m_6$. $Y = -2/m_1 + 1/m_2 + 1/m_3 - 2/m_4 + 1/m_5 + 1/m_6$. $Z = -2/m_1 - 1/m_2 + 1/m_3 + 2/m_4 + 1/m_5 - 1/m_6$.

carbon-hydrogen distance and γ_i is an angle thus defined. (2) The out-of-plane ring bending vibrations were regarded as torsions around carbon-carbon bonds. Carbon atoms 1, 2, and 3 define a plane; carbon atoms 2, 3, and 4 define another. These planes intersect along the C_2-C_3 bond. The angle between the planes is designated δ_2 , and the corresponding VFC is $R_0\delta_2$, where R_0 is the equilibrium carbon-carbon distance. The corresponding coordinate for the C_1-C_2 bond is designated $R_0\delta_1$, that for the C_2-C_3 bond $R_0\delta_2$, and so on around the ring. Thus it is evident that motions of the hydrogen atoms do not affect the $R_0\delta_i$. It is important to note also that the $R_0\delta_i$ have a different symmetry with respect to our y and z axes than do the $r_0\gamma_i$. None of the former lie on the y axis, while two of the latter do. In other words the $R_0\delta_i$ have the symmetry

of the carbon-carbon bonds, while the $r_0\gamma_i$ have the symmetry of the atoms.

Symmetry factoring was obtained by using valence-force symmetry coordinates (VFSC), which are orthogonal combinations of the VFC. The matrix \mathbf{U} for the transformation $\mathbf{VFSC} = \mathbf{U} \times \mathbf{VFC}$ is given in Fig. 2. For brevity the various VFSC are designated as S_{11} , S_4 , S_5 , ... corresponding to frequencies ν_{11} , ν_4 , ν_5 , ...

The \mathbf{G} matrix for the VFSC is given in Fig. 3. It contains the atomic masses and internuclear distances. The outlined blocks indicate the way the matrix factors for D_{6h} symmetry. All the terms outside these blocks are interaction terms which depend only on the masses of the hydrogen (or deuterium) atoms. In evaluating them for the various deuterobenzenes it is important that the deuterium substituents be properly located

TABLE II. Comparison of Manneback's notation with that of this paper.

Manneback ^a	This paper
m	m
M	M
c	r_0
a	R_0
k	ρ
Ω^2	λ
B^+	α
B_S	φ or σ^b
B^-	ϵ
L	488
I	$3\frac{1}{4}\eta$
B_A	σ or φ^b
N	16 θ
J	4 ω

^a Reference 4.
^b Reference 15.

with respect to the coordinate axes. The atoms in the benzene hexagon have been numbered one to six around the ring, with atoms one and four lying on the y axis. Then m_1 is the mass of the hydrogen (or deuterium) atom in position one (in atomic weight units), and so on. All these interaction terms go to zero for the two molecules of D_{6h} symmetry so that in this case the matrix factors as indicated. For lower symmetries this is no longer true. Some of these quantities will differ from zero, and the corresponding symmetry blocks of D_{6h} will be connected by these interaction terms. Thus for example class A_2'' of D_{3h} symmetry is formed by combining classes A_{2u} and B_{2g} of D_{6h} symmetry (cf. Fig. 1). The corresponding interaction term, $Q/6$, will be found unequal to zero for the deuterio-benzene having D_{3h} symmetry, i.e., *sym*-benzene- d_3 . Similarly the interaction term between E_{ua}^+ and E_{ga}^- (or between E_{ub}^+ and E_{gb}^-) will also be unequal to zero for *sym*-benzene- d_3 . All other interactions will be zero.

There are many possible combinations of this type between the classes of D_{6h} to give the classes of lower symmetries (cf. Fig. 1). It therefore seemed preferable to leave the results in the form of the **F** and **G** matrices instead of reducing them to the relatively large number of formal equations. One must refer to Wilson's first paper on the subject¹⁴ for the method of reducing the matrices to the secular equations. Wilson's method can be applied quite simply to cases where a single interaction term occurs, using an observation given in the Appendix.

The **F** matrix for the VFSC is given in Fig. 4. It contains force constants only.

A discussion of the force constants for VFC is now in order. The diagonal force constants for $r_0\gamma_i$ is termed A , while the interaction constants between the various $r_0\gamma_i$ are designated a_o , a_m , or a_p . The subscripts o , m , and p refer to the ortho-, meta-, and parapositions. Thus a_m is the constant for interaction between the out-of-plane motions of two hydrogen atoms *meta* to each other. Similarly B is the diagonal force constant for $R_0\delta_i$, and b_o , b_m , and b_p are the interaction constants between the various $R_0\delta_i$'s. The c 's are constants for interactions between the $r_0\gamma_i$'s and the $R_0\delta_i$'s. The force constants and equilibrium distances for C-H and C-D are assumed to be identical.

When the VFC have been transformed to the VFSC, the force constants become:

$$\begin{aligned}
 \alpha &= A + 2a_o + 2a_m + a_p \\
 \epsilon &= A - 2a_o + 2a_m - a_p \\
 \sigma &= A - a_o - a_m + a_p \\
 \varphi &= A + a_o - a_m - a_p \\
 \beta &= B - 2b_o + 2b_m - b_p \\
 \theta &= B - b_o - b_m + b_p \\
 \eta &= 2[-c_o + c_m - c_p] \\
 \omega &= 3\frac{1}{2}[c_o - c_p].
 \end{aligned}
 \left. \begin{array}{l} \\ \\ \\ \\ \\ \\ \\ \end{array} \right\} \begin{array}{l} \text{Hydrogen,}^{15} \\ \\ \\ \text{Ring,} \\ \\ \text{Hydrogen-ring interaction}^{16} \text{ (see Table II).} \end{array}$$

TABLE III. Frequencies used to evaluate the force constants (cm^{-1}).

No.	Benzene	<i>sym</i> -Benzene- d_3	Benzene- d_6
4		691	
5		914	
10	850	712	664
11	671	533	503
16	404 \pm 3	373	
17			

¹⁵ This does not completely agree with Manneback's results (reference 4). He would interchange our σ and φ , putting σ in class E_g^- of D_{6h} whereas we have it in E_u^+ , and *vice versa*. Inasmuch as our results were checked by two independent workers, it seems probable that Manneback's B_A and B_S are reversed in his Eqs. (44) and (44'). This will cause no error whatever unless one wishes to evaluate the valence-force constants from the Greek constants. There is one other error in the second of his Eqs. (44'). The first minus sign should be replaced by a multiplication sign.

¹⁶ It may be wondered why Manneback's notation has not been used in this paper. There are two reasons. First, four of his force constants differ from ours by a numerical factor. Our **F** or our **G** matrix would therefore have to be altered to compensate for this. Second, there is the difficulty of Manneback's force constants B_S and B_A (footnote 15). It has therefore seemed advisable to use a new terminology. Table II compares Manneback's notation with that of this paper.

It is interesting to note that the complete potential function requires only eight (Greek) force constants, but that these are expressed in terms of eleven valence-force constants. The Greek constants are the ones which are evaluated from the experimental data. Consequently we shall not always be able to calculate the valence-force constants from the Greek constants. One can do so for the hydrogen vibrations because there are four of each type. For the ring constants and the hydrogen-ring interactions it cannot be done. One must regard β , say, as being characteristic of a certain type of motion of the benzene ring as a whole. It will be impossible to say just how much B , b_o , b_m , or b_p contributes to the value of β . We shall therefore have no way of determining the relative magnitude of the ortho-, meta-, and paravalence-force interactions in this case.

The problem, then, is to evaluate the eight (Greek) force constants from the assigned vibrational frequencies. Table III lists the assignments which were used for this purpose. They are taken from the paper of Langseth and Lord,¹¹ and appear to be reasonably correct. Eight additional frequencies for the para-deutero compounds were also used,¹¹ but they have not been included in the table because they are not essential to our results.

The calculated value of any given force constant will vary slightly from one deuterobenzene to another. There are at least two reasons for this. First, the vibrations are not purely harmonic as assumed. The anharmonicity decreases as more deuterium atoms are introduced into the molecule because the average amplitude of vibration becomes smaller. Consequently, diagonal force constants will increase with increasing deuterium substitution. Whenever possible we have used values midway between those for the two extremes of light and heavy benzene. A second reason for inconstancy is the fact that some of the experimental frequencies were measured on the liquid and some on the vapor. It is well known that a vibrational frequency is usually somewhat higher in the gaseous than in the liquid state. Neither effect is very marked, however.

The following numerical values were employed 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 = 1.08 Å.

R_0 = C-C equilibrium distance = 1.39 Å.

$\rho = r_0/R_0 = 0.777$.

ν = frequency in wave numbers = $\text{const.} \times \lambda^4$, 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 FORCE CONSTANTS

α and ϕ

The evaluation of α and ϕ scarcely needs comment. Frequency 11, which goes with α , is the only member of class A_{2u} in D_{6h} symmetry. Taking the frequency to be 671 cm^{-1} in benzene and 503 cm^{-1} in benzene- d_6 , one calculates values of 0.2467 and 0.2573, respectively. These values differ by 4 percent, which is probably somewhat too much to attribute to change in anharmonicity alone and may indicate some slight experimental error. The average value of α is 0.252.

Four values of ϕ may be obtained with equal ease from ν_{10} in benzene and benzene- d_6 and from ν_{10a} in p -benzene- d_2 and p -benzene- d_4 . The following results are obtained:

benzene	$\nu_{10} = 849.7$	$\phi = 0.3389$
p -benzene- d_2	$\nu_{10a} = 850.0$	$\phi = 0.3391$
p -benzene- d_4	$\nu_{10a} = 662.3$	$\phi = 0.3405$
benzene- d_6	$\nu_{10} = 663.5$	$\phi = 0.3417$
		$\phi(\text{average}) = 0.340$

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

β , η , and ϵ

Now that α and ϕ are known, the evaluation of β , η , and ϵ can be readily carried out in either of two ways. One method is to use the equations for class A_2'' or D_{3h} . This class contains frequencies 4, 5, and 11 and force constants α , β , η , and ϵ . (Figs. 1 and 4.) The value of α is now known, so that the three frequencies will suffice to determine the three unknown force constants. The assignment of 691, 914, and 533 cm^{-1} to the three vibrations is reasonably certain. On carrying out the calculation one finds an interesting result; two sets of values are obtained for the

Class	VFSC	S_{11}	S_4	S_5	S_{16a}	S_{17a}	S_{16b}	S_{17b}	S_{10a}	S_{10b}
A_{2u}	S_{11}	α								
B_{2g}	S_4		β	η						
	S_5		η	ϵ						
E_{ua}^+	S_{16a}				θ	ω				
	S_{17a}				ω	σ				
E_{ub}^+	S_{16b}						θ	ω		
	S_{17b}						ω	σ		
E_{ga}^-	S_{10a}								φ	
E_{gb}^-	S_{10b}									φ

FIG. 4. F matrix for non-planar vibrations of the deuterobenzenes.

force constants (Table IV). The value for ϵ , which is the constant for the hydrogen vibration, is unique, but there is no obvious means of choosing between the two sets of values for β and η . The difficulty arises because β (or η) is obtained from a quadratic equation, and both roots of the quadratic are physically reasonable.

One can also evaluate β , η , and ϵ from class B_{3g} of V_h symmetry, which contains frequencies 4, 5, and 10b and force constants φ , β , η , and ϵ . Using Langseth and Lord's assignments of 634, 966, and 738 cm^{-1} for *p*-benzene- d_2 and of 605, 927, and 765.3 for *p*-benzene- d_4 , and using the known value of φ , one gets again two sets of solutions as indicated in Table IV.

It is apparent that sets 1 and 3 are comparable, and sets 2 and 4. The differences between comparable values are large, and may be due to any of the following reasons: (a) an error in φ or, more probably, in α (incidentally the average values of these constants were used); (b) a small error in the assignments for the three compounds; (c) the fact that the frequencies for *sym*-benzene- d_3 are vapor-phase frequencies, while those for the *para* derivatives are liquid-phase frequencies. (This, however, probably should make the diagonal force constants ϵ and β higher for the former than for the latter, since

frequencies are usually higher in the vapor state. The converse is found.) It should be mentioned that sets 1 and 2 give identical results when used to calculate frequencies, and so do sets 3 and 4. One must then decide which particular set to use, or whether to take the average of, say, sets 1 and 3. We arbitrarily chose to use set 1 in later calculations, as it seemed to give somewhat better agreement with observed results than did either set 3 or the average of sets 1 and 3.

One is now in a position to calculate ν_4 and ν_5 in benzene. These frequencies have never been assigned with certainty. Pitzer and Scott selected the weak Raman line at 685 cm^{-1} for ν_4 , and then used the product rule to calculate ν_5 as 1016 cm^{-1} . We have calculated ν_4 and ν_5 from our values for ϵ , β , and η , using both sets 1 and 3. The results are:

	Set 1	Set 3
ν_4	693	669
ν_5	993	1041

It will be observed that the calculated values for ν_4 bracket the weak line at 685 cm^{-1} . This offers strong support for the choice of Pitzer and Scott, and makes an otherwise weak assignment very probable. We then follow these authors in taking ν_5 to be about 1015 cm^{-1} .

θ , σ , and ω

The obvious place from which to calculate these force constants is class E'' of D_{3h} symmetry, which contains frequencies 10, 16, and 17 and force constants φ , θ , σ , and ω . The value of φ has already been found, so that one has three frequencies with which to evaluate three unknown force constants. Langseth and Lord assigned the values 711.7, 373, and 815 cm^{-1} to ν_{10} , ν_{16} , and ν_{17} , respectively, in *sym*-benzene- d_3 . Unfortunately these authors are uncertain about the assignment for ν_{17} , and we shall see later that it must be revised upward by about 100 cm^{-1} . But using their values for the moment, one can

TABLE IV. Values for ϵ , β , and η .

	From D_{3h}		From V_h	
	1	2	3	4
ϵ	0.532	0.532	0.585	0.585
β	0.203	0.339	0.205	0.367
η	0.258	0.373	0.279	0.415

TABLE V. Location of ν_{17} .

Trial	Freq. No.	Bz(calc.)	<i>s</i> -Bz- <i>d</i> ₃ (assumed)	Bz- <i>d</i> ₆ (calc.)
1	10	—	711.7	—
	16	398	373	350
	17	1002	950	805
2	10	—	711.7	—
	16	403	373	346
	17	958	920	789
3	10	—	711.7	—
	16	409	373	342
	17	912	890	772

calculate some tentative force constants. Once again two sets of results are obtained. Both sets reproduce Langseth and Lord's assignments in *m*-benzene-*d*₂, *sym*-benzene-*d*₃, *vic*-benzene-*d*₃, and *m*-benzene-*d*₄, but they do *not* give back the observed frequencies of benzene and benzene-*d*₁ nor of benzene-*d*₅ and benzene-*d*₆. Thus for example instead of getting 404 cm⁻¹ for ν_{16} in benzene, one calculates 433 cm⁻¹. It must be concluded that Langseth and Lord's assignments are not internally consistent through this series of isotopic molecules.

Zeigler and Andrews¹⁷ were led by a study of the heat capacity of solid benzene-*d*₆ to suggest that Langseth and Lord's value for ν_{17} was too low. Pitzer and Scott⁹ have discussed the assignment at some length. They say that 815 cm⁻¹ for ν_{17} in *sym*-benzene-*d*₃ leads to an unreasonable potential function, and also that it leads to a calculated heat capacity for benzene which is too high. By a consideration of weak bands they assign 985 cm⁻¹ in benzene and 790 cm⁻¹ in benzene-*d*₆. From these values they find ν_{17} to be 950 cm⁻¹ in *sym*-benzene-*d*₃.

We arrive at essentially the same results, but by a different procedure. There are three relevant cases where one can be fairly certain that ν_{10} and ν_{16} are correctly assigned, namely 712 and 373 cm⁻¹ in *sym*-benzene-*d*₃ and 404 cm⁻¹ in benzene. The correct set of force constants *must* reproduce these three values. Only two of these frequencies belong to *sym*-benzene-*d*₃, however. Our procedure was to estimate a value for the third frequency in *sym*-benzene-*d*₃ (ν_{17}), and then to use these three frequencies to calculate a trial

set of values for θ , σ , and ω . These in turn were then used to calculate ν_{16} and ν_{17} in benzene, with the hope that they would give 404 cm⁻¹ for ν_{16} . It soon became apparent that in order to obtain 404 cm⁻¹, one has to choose ν_{17} for *sym*-benzene-*d*₃ within the range 890–950 cm⁻¹. The results for three such trials are indicated in Table V. Obviously ν_{17} is confined within the following ranges: (a) 890–950 cm⁻¹ in *sym*-benzene-*d*₃; (b) 910–1000 cm⁻¹ in benzene; (c) 770–805 cm⁻¹ in benzene-*d*₆. One cannot locate ν_{17} more precisely in this way because the calculated value of ν_{16} in benzene is rather insensitive to changes of ν_{17} in *sym*-benzene-*d*₃. Furthermore the numerical value of ν_{16} in benzene has an uncertainty of about 3 cm⁻¹.¹⁸

The next step is to look in these regions of the spectra for weak bands that may be attributed to ν_{17} . It may be noted that ν_{10a} , ν_{16a} , and ν_{17a} will have the same numerical values in the following groups of compounds because the corresponding portions of the **G** matrices are identical: (a) benzene, benzene-*d*₁, and *p*-benzene-*d*₂; (b) *m*-benzene-*d*₂, *sym*-benzene-*d*₃, *vic*-benzene-*d*₃, *m*-benzene-*d*₄; (c) *p*-benzene-*d*₄, benzene-*d*₅, benzene-*d*₆. Thus the search may be extended to the spectra of these additional compounds.

Starting with benzene, one finds a very weak infra-red band in the vapor at 962 cm⁻¹, and in the liquid at 985 cm⁻¹. Inasmuch as ν_{17} is forbidden to appear in benzene, and as selection rules are rigorous in the vapor phase, the first of these cannot be accepted. The second would be a possibility if it really belonged to a vibration different from the 962 cm⁻¹ one, and if liquid forces were breaking down the selection rules. This 985 cm⁻¹ band appears as a shoulder on the strong 1033-cm⁻¹ absorption, so that it is difficult to estimate the frequency and intensity accurately. One concludes that the spectrum of benzene offers little help. In benzene-*d*₆ a very weak line is observed at 790 cm⁻¹ in the Raman spectrum of the liquid. If this is ν_{17} , it appears in violation of the selection rules. Pitzer and Scott were the first to assign 985 and 790 to ν_{17} . Going now to the intermediate isotopic derivatives, we find a possibility in the weak Raman

¹⁷ W. Zeigler and D. H. Andrews, J. Am. Chem. Soc. **64**, 2482 (1942).

¹⁸ See p. 928 of reference 10.

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

	1	2
α	0.252	—
φ	0.340	—
ϵ	0.532	— ^a
β	0.203	0.339 ^a
η	0.258	0.373 ^a
σ	0.402	—
θ	0.157	0.757
ω	-0.154	-0.515

* Set 1 was used in most of the calculations.

^a See also Table IV.

line at 920 cm^{-1} in *vic*-benzene- d_3 , observed by Langseth and Lord. They had assigned it to ν_{9b} , but questioned their choice. There are no other observed frequencies in these ranges than these three (with the exception of the very intense breathing frequency ν_1 , which cannot be mistaken). We therefore take ν_{17} to be 920 cm^{-1} in *sym*-benzene- d_3 , and 790 cm^{-1} in benzene- d_6 . In benzene it will be somewhere near 985 cm^{-1} , the uncertainty being due to its appearance as a shoulder on another strong band.

The justification for this assignment will be found in its results. Using 711.7, 373, and 920 cm^{-1} for ν_{10} , ν_{16} , and ν_{17} in *sym*-benzene- d_3 , and taking $\varphi=0.340$, one calculates the following two sets of values for the force constants.

	1	2
σ	0.402	0.402
θ	0.157	0.757
ω	-0.154	-0.515

Again there is no obvious reason for preferring one set over the other. We arbitrarily chose set 1 for later calculations.

Using these force constants, one calculates ν_{17} to be 789 cm^{-1} in benzene- d_6 , in good agreement with the observed 790 cm^{-1} . For benzene, one calculates 958 cm^{-1} in place of the (rather indefinite) 985 cm^{-1} . Pitzer and Scott have already pointed out that this assignment explains the rather strong infra-red bands in benzene at 1810 and 1965 cm^{-1} , which appear in both gas and liquid, as the allowed combination tones $\nu_{10}+\nu_{17}$ and $\nu_5+\nu_{17}$. A value of about 955 cm^{-1} is indicated for ν_{17} from these considerations.

This assignment of ν_{17} is further strengthened by some results for *p*-benzene- d_2 . Frequencies 16*b* and 17*b* become infra-red active in this

derivative. Their values were calculated from the force constants σ , θ , and ω to be 360 and 868 cm^{-1} , respectively. A sample of *p*-benzene- d_2 was prepared and the infra-red spectrum of the vapor obtained.¹⁹ A strong band was observed at 872 cm^{-1} , which may very well be ν_{17} . This offers valuable support for the assignments and for the values of the force constants.

Thus we have arrived at virtually the same conclusions concerning ν_{17} as did Pitzer and Scott, but by quite a different method. Indeed, our assignments for all the out-of-plane vibrations are essentially the same as theirs.

This completes the determination of the force constants. For convenience they have been gathered together in Table VI. Where two or more sets of values were obtained, the first set was the one which was used in our calculations.

FURTHER RESULTS

Once all the force constants are at hand, one can proceed to calculate many of the non-planar frequencies for the various deuterium derivatives. This has been done for those cases where the symmetry blocks are not too large to make the labor prohibitive. Table VII gives the results. Thirty-nine of the fifty-nine calculated frequencies may be checked against experiment. The maximum error is 4.3 percent or 16 cm^{-1} . With but four exceptions, calculated and observed values agree within 1.5 percent. The results may, therefore, be considered satisfactory.

One is also now able to evaluate the valence-force constants which are associated with the hydrogen vibrations—i.e., A , a_o , a_m , and a_p . Introducing the numerical values of α , ϵ , σ , and φ , one calculates $A=0.378$, $a_o=-0.057$, $a_m=0.007$, and $a_p=-0.026$. It is interesting to note that the force constant connecting the out-of-plane displacements of two hydrogen atoms para to each other is about half of that for the case where they are ortho. From the signs of these force constants it is evident that the potential energy required for a "dishing" of the hydrogens (i.e., all the hydrogens above the carbon ring) is less than that for a "puckering" of the hydrogens (hydrogen atoms alternately

¹⁹ Detailed results of this investigation will be published separately.

TABLE VII. Calculated *vs.* observed frequencies.

Freq. No.	Benzene			Benzene- <i>d</i> ₁			<i>o</i> -benzene- <i>d</i> ₂			<i>m</i> -benzene- <i>d</i> ₂			<i>p</i> -benzene- <i>d</i> ₂			<i>sym</i> -benzene- <i>d</i> ₃		
	Calc.	Obs.	Diff. (%)	Calc.	Obs.	Diff.	Calc.	Obs.	Diff.	Calc.	Obs.	Diff.	Calc.	Obs.	Diff.	Calc.	Obs.	Diff.
4	693	685 ^a	+1.2										633	634	-0.2	691	(691)	—
5	993	v.											959	966	-0.7	914	(914)	—
11	678	(671)	+1.0				579	582	-0.5				600	594 ^a	+1.0	533	(533)	—
10a				851	852	-0.1	783	782	+0.1	712	711	+0.1	851	850	+0.1	712	(712)	—
10b													729	738	-1.2			
16a	403	(404) ^a	-0.7	403	403	0.0				373	374	-0.3	403	400 ^b	+0.8	373	(373)	—
16b							391	384	+1.8				360	i.r.				
17a										920	—		958	v.				
17b	958	~985 ^a	?	958	—		945	—					868	872 ^c		920	d.	

Freq. No.	<i>vic</i> -benzene- <i>d</i> ₃			<i>o</i> -benzene- <i>d</i> ₄			<i>m</i> -benzene- <i>d</i> ₄			<i>p</i> -benzene- <i>d</i> ₄			Benzene- <i>d</i> ₅			Benzene- <i>d</i> ₆		
	Calc.	Obs.	Diff.	Calc.	Obs.	Diff.	Calc.	Obs.	Diff.	Calc.	Obs.	Diff.	Calc.	Obs.	Diff.	Calc.	Obs.	Diff.
4										615	605	+1.7				600	v.	
5										918	927	-1.0				812	v. ^e	
11				534	—					549	i.r.					498	(503)	-1.0
10a	712	712	0.0	737	739	-0.3	712	711	+0.1	662	662	0.0	662	664	-0.3	662	(664)	-0.3
10b										759	765	0.8						
16a	373	374	-0.3				373	375	+0.5	346	v.		346	—		346	337 ^a	+2.7
16b				353	369	-4.3				377	i.r.							
17a	920	920	0.0				920			789	v.		789	—		789	790 ^a	-0.1
17b				863	—					918	i.r.							

Observed values taken from references 10 and 11.
 ()—Used to evaluate force constants.
 Italic numbers indicate values which appear in violation of selection rules
 v.—Forbidden in both Raman and infra-red.
 i.r.—Allowed in infra-red only; hasn't been studied.

^a Reference 10.
^b Reference 11, p. 21, p. 67 (footnote).
^c Footnote 19.
^d Would be hidden by strong i.r. band at 914.
^e Would be hidden by strong i.r. band at 811.

above and below the carbon ring). This is borne out by the frequencies of the corresponding vibrations. The "dishing" frequency (ν_{11}) is 671 cm^{-1} ; the "puckering" frequency (ν_5) is about 1015 cm^{-1} (calculated).²⁰

One might deduce from this that attractive forces prevail between the hydrogen atoms, making it energetically cheaper to displace two hydrogen atoms in the same direction out of the equilibrium plane than in opposite directions. And indeed this is compatible with the geometry of the molecule. The van der Waals radius of hydrogen is $1.2 \pm 0.1 \text{ \AA}$,²¹ while the closest hydrogen atoms in benzene are approximately 2.47 \AA apart. Thus they may well be far enough removed so that repulsive forces no longer predominate. However, it must be admitted that according to this concept a_m cannot be more positive than both a_o and a_p —although actually

it is. One must, therefore, conclude that this simple hypothesis is untenable. We have no adequate explanation to suggest.

In conclusion it may be pointed out that the numerical values for these force constants should be applicable to derivatives of benzene. Crawford and Brinkley¹² have already outlined methods for such a transfer of force constants between aliphatic compounds

ACKNOWLEDGMENT

One of us (FAM) wishes to express his appreciation to the National Research Council for the grant of a fellowship.

APPENDIX

In most of the isotopic molecules of lower symmetry, two blocks of the D_{6h} \mathbf{G} matrix (Fig. 3) were connected by only one interaction term, so that the complete block of the \mathbf{G} matrix for the isotopic case could be written

$$\begin{bmatrix} g_1^1 & \cdots & g_m^1 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ g_1^m & \cdots & g_m^m & d & \cdots & 0 \\ \hline 0 & \cdots & d & g_{m+1}^{m+1} & \cdots & g_{m+n}^{m+1} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 0 & g_{m+1}^{m+n} & \cdots & g_{m+n}^{m+n} \end{bmatrix}, \quad (\text{A1})$$

²⁰ The frequencies depend also on the reduced masses and on interaction with other vibrations which may be in the same symmetry class, but these effects alone could hardly produce the large difference of 340 cm^{-1} which is observed.

²¹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1940), second edition, p. 189.

with d representing the interaction. If we denote the secular equations for the separate blocks (setting $d=0$) by

$$0 = A(\lambda) = \sum_{i=0}^m a_i \lambda^{m-i}, \quad (\text{A2})$$

$$0 = B(\lambda) = \sum_{j=0}^n b_j \lambda^{n-j}, \quad (\text{A3})$$

and their product by

$$0 = C(\lambda) = A(\lambda) \cdot B(\lambda) = \sum_{k=0}^{m+n} c_k \lambda^{m+n-k}, \quad (\text{A4})$$

$$c_k = \sum_{i=0}^k a_i b_{k-i},$$

then the secular equation with $d \neq 0$ is simply obtained from $C(\lambda)$: wherever the product $g_m^m g_{m+1}^{m+1}$ appears, one has only to substitute therefor $(g_m^m g_{m+1}^{m+1} - d^2)$.

This is easily seen. For, of all possible minors of the \mathbf{G} matrix (A1) containing d , those which do not obviously vanish will be of the same form as (A1)—i.e., will have d 's "bridging" the principal diagonal—or will be of the form

$$\left[\begin{array}{cccc|c} g_1^1 & \cdots & g_k^1 & g_m^1 & \\ \cdots & \cdots & \cdots & \cdots & \\ g_1^k & \cdots & g_k^k & g_m^k & X \\ \hline 0 & \cdots & 0 & d & \\ \hline & & & 0 & X \end{array} \right], \quad (\text{A5})$$

or of the form

$$\left[\begin{array}{ccc|c} g_k^k & \cdots & g_m^k & \\ \cdots & \cdots & \cdots & 0 \\ g_k^m & \cdots & g_m^m & \\ \hline 0 & \cdots & d & \\ \cdots & \cdots & \cdots & X \\ 0 & \cdots & 0 & \end{array} \right]. \quad (\text{A6})$$

The determinants of the form (A6) will clearly not contain d , while determinants of the form (A5) will correspond to vanishing minors of the \mathbf{F} matrix; hence no contribution from d will arise in either of these cases. So we need consider only minors of the form (A1). Such a determinant may be expanded, by Laplace's development, in the second minors of second-order determinants based on the m th and $(m+1)$ th columns. To be non-vanishing, these second minors must be obtained by striking out one of the first m rows and one of the last n ; this restricts the second-order determinants which will actually contribute to those of the types

$$\begin{vmatrix} X & 0 \\ 0 & X \end{vmatrix}, \quad \begin{vmatrix} X & 0 \\ d & X \end{vmatrix}, \quad \begin{vmatrix} X & d \\ d & X \end{vmatrix}.$$

There is but one of this last type, and it will contribute the term $(g_m^m g_{m+1}^{m+1} - d^2)$ —the only way in which d can appear in the final secular equation.

Similar considerations can be applied if more than one interaction couples two blocks, but the increased complexity makes it scarcely worth while.

The Infra-Red Spectra of *p*-Benzene- d_2 and *p*-Benzene- d_4

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INTRODUCTION

IN a paper by the authors which appears in this issue¹ reference is made to some experimental work on the infra-red spectrum of *p*-benzene- d_2 . The purpose of this note is to present the data on this compound, together with that on *p*-benzene- d_4 , in detail sufficient for the above-mentioned paper. The work was originally undertaken for the purpose of locating ν_{14} and ν_{15} and for completing the analysis of the vibrational spectrum of benzene. This aspect will be discussed in a later report.

PREPARATION OF SAMPLES

The deuterium compounds were prepared by

¹ F. A. Miller and B. L. Crawford, Jr., *J. Chem. Phys.* **14**, 282 (1946).

the method of Langseth and Klit,² which involves the continuous formation of a Grignard reagent and its decomposition with deuterium chloride. The last step is the separation of the deuterio-benzene from the great excess of diethyl ether solvent by distillation. In the case of the *p*-benzene- d_4 an unknown intermediate fraction boiling at 70–75° was obtained in addition to the desired *p*-benzene- d_4 fraction at 76.3–77.0°.³ On exposure to air this intermediate fraction

² A. Langseth and A. Klit, *Kgl. Danske Vid. Sels. Math. fys. Medd.* **15**, No. 13 (1938).

³ Because these temperatures are uncorrected for atmospheric pressure (745 mm) and for errors in calibration of the thermometer (at least 1.2°), they have only relative significance. The boiling point of benzene was observed to be 77.0° under the same conditions, although the correct value is 80.1°.