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The Force Field, Vibration Frequencies, Normal Co-Ordinates, Infra-Red and Raman Intensities for Benzene

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THE FORCE FIELD, VIBRATION FREQUENCIES, NORMAL CO-ORDINATES, INFRA-RED AND RAMAN INTENSITIES FOR BENZENE

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CONTENTS

A quadratic force field with twenty-six non-zero constants is chosen for benzene and reasons are given for preferring the constants chosen when alternative values are possible. Using this field all the vibration frequencies of C_6H_6, C_6H_5D, *ortho*-, *meta*- and *para*-$C_6H_4D_2$, *sym*.- and *vic*.-$C_6H_3D_3$, *para*-$C_6H_2D_4$ and C_6D_6 are calculated and found to agree with the experimental values of Ingold and coworkers to better than 2 %. Four dipole moment derivative parameters are introduced to give satisfactory indications of the infra-red absorption intensities and ten polarizability parameters are used to give satisfactory indications of Raman shift intensities and degrees of polarization. The alternative B_{2u} class assignment of Mair & Hornig is also discussed.

INTRODUCTION

Work on the force fields of individual molecules may broadly be divided into two categories. First, there are approximate treatments, using as few force constant parameters as is feasible, which are designed to aid the interpretation of observed spectra and which act as a guide to the approximate values of any missing frequencies. Secondly, there are more exact treatments which are possible when all the frequencies are known and have been assigned to their symmetry classes. These more elaborate treatments are aimed at finding force fields which are as accurate as possible; a knowledge of such fields is important (*a*) for comparison with wave-mechanical treatments, (*b*) for comparison between molecules and suggesting trial force constants for related molecules, and (*c*) for determining the form of the normal co-ordinates, which in their turn are required for interpreting observations of infra-red and Raman effect intensities in terms of dipole moments, polarizabilities and their derivatives. The force field of benzene is discussed in this paper and the information should be of value under each of these headings inasmuch as (*a*) the treatment of the electronic structure of benzene is well developed, (*b*) substituted benzenes form a large class of compounds to which many details of the force field may be transferred, and (*c*) the ambiguities of sign, which normally arise in the interpretation of intensity measurements, may be resolved experimentally from the spectra of the various deuterated benzenes.

Previous discussions of the force field of benzene include those of Lord & Andrews (1937), Bernard, Manneback & Verleysen (1939, 1940), Pitzer & Scott (1943), Bell (1945) and Bak (1945), most of which are based on the six force constant parameters introduced by Wilson (1934). There are, however, thirty-four quadratic force constants required to describe the general force field of benzene of symmetry D_{6h}, and Miller & Crawford (1946) and Crawford & Miller (1949) have discussed this force field in algebraic form and evaluated the constants, although in some instances they do not make a final choice between alternative sets of numerical values.

Nomenclature and related matters

It is now accepted that in the equilibrium configuration benzene has a regular, planar hexagonal structure with symmetry D_{6h}. The molecule may be laid in right-hand Cartesian co-ordinates such that the z axis coincides with the C_6 axis and the y axis passes through carbon atoms 1 and 4, if the carbon atoms are numbered 1 to 6 in clockwise order as viewed from a point on the positive z axis. Two parameters R_0, the C_j—C_{j+1} distance, taken as 1·40 Å and r_0, the C_j—H_j distance,[‡] taken as 1·05 Å (H. J. M. Bowen, private communication) describe the remaining geometry of the molecule and the H or D atoms are given the same number as the carbon atom to which they are joined. Figure 1 shows this arrangement. C_3^z, C_2^z, C_2^y and σ^z form a specifying set of symmetry elements and the symmetry classes and the selection rules are given in table 1. The designations are those of Herzberg (1945) which are now normally accepted as standard. Crawford & Miller's (1949) differ from Herzberg's in that E_{1g} and E_{2g}, and also E_{1u} and E_{2u} are interchanged; the symmetry class designations in parentheses are the older designations. Also given are the transformation coefficients to obtain the symmetry co-ordinates, S, from the valency co-ordinates as given by Miller & Crawford (1946) for the non-planar classes and Crawford & Miller (1949) for the planar classes. For most purposes either the symmetry or the valency co-ordinates are suitable, but occasionally it is convenient to use local Cartesian co-ordinates, especially for depicting the form of any vibration. For this the co-ordinates for motion of the jth carbon atom from its equilibrium position in the radial, the z, and the mutually perpendicular direction

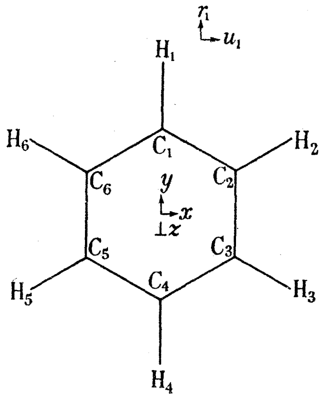

Figure 1

[‡] These distances were chosen in 1952 before several recent determinations were available; the numerical values affect the force constants through the value of ρ, and if ρ is increased by virtue of an increased C—H or decreased C—C bond length the principal modification would be to decrease Γ_1, Γ_3, Γ_4, Φ_1, Φ_2 and Φ_3.

counted positive in a clockwise sense may be taken as $\bar{R}_j$, Z_j and U_j and likewise for the H atoms $\bar{r}_j$, z_j and u_j. The valency co-ordinates are ΔR_j for the stretching of the C_j—C_{j+1} link, Δr_j for the stretching of the C_j—H_j link, β_j for bending of the C_j—H_j link relative to the bisector of the ring angle, α_j for increase of the ring angle at C_j, γ_j for out-of-plane bending of the C_j—H_j link, δ_j for twisting of the carbon skeleton about the C_j—C_{j+1} link and ϕ_j is the valency co-ordinate for twisting of both the carbon and the hydrogen atoms about C_j—C_{j+1} and is the same as $(\phi_C+\phi_H)$ as introduced by Bell (1945). The signs of β, γ, δ and ϕ are determined by their expression in terms of the right-handed systems $\bar{R}$, Z, U which are:

$$\begin{aligned}
\Delta R_j &= (2^{-1})\,(\bar{R}_j+\bar{R}_{j+1})-(3^{\frac{1}{2}}\,2^{-1})\,(U_j-U_{j+1}),\\
\Delta r_j &= \bar{r}_j-\bar{R}_j,\\
r_0\beta_j &= U_j-u_j+(3^{\frac{1}{2}}\,4^{-1}\rho)\,(\bar{R}_{j-1}-\bar{R}_{j+1})+(4^{-1}\rho)\,(U_{j-1}+2U_j+U_{j+1}),\\
R_0\alpha_j &= (3^{\frac{1}{2}}\,2^{-1})\,(\bar{R}_{j-1}-2\bar{R}_j+\bar{R}_{j+1})+(2^{-1})\,(U_{j-1}-U_{j+1}),\\
r_0\gamma_j &= z_j-Z_j+\rho(Z_{j-1}-2Z_j+Z_{j+1}),\\
R_0\delta_j &= (2\,.\,3^{-\frac{1}{2}})\,(-Z_{j-1}+2Z_j-2Z_{j+1}+Z_{j+2}),\\
R_0\phi_j &= 2R_0\delta_j+(2\,.\,3^{-\frac{1}{2}})\,R_0(\gamma_j-\gamma_{j+1}),\\
&= -(2\,.\,3^{-\frac{1}{2}})\,[Z_{j-1}-Z_j+Z_{j+1}-Z_{j+2}+\rho^{-1}(Z_j-Z_{j+1}-z_j+z_{j+1})],
\end{aligned}$$

where $\rho = r_0/R_0$.

For the planar force constants the nomenclature of Crawford & Miller (1949) has been followed, but it seemed better to extend their systematic arrangement and adopt Θ_1, Θ_2 in place of β, θ, for the C—C twisting constants, Φ_1, Φ_2, Φ_3, Φ_4, in place of ϵ, σ, ϕ, α, for the deformations of the H atoms and η_1, η_2, in place of η, ω, for the interaction constants, in the out-of-plane classes. In these symbols the potential energy V is given by:

$$\begin{aligned}
2V = {} & \Lambda_1 S_1^2+\Lambda_2 S_{14}^2+\Lambda_3(S_{8a}^2+S_{8b}^2)+2\Lambda_4(S_{19a}^2+S_{19b}^2)\\
& +\Omega_1 S_2^2+\Omega_2 S_{13}^2+\Omega_3(S_{7a}^2+S_{7b}^2)+\Omega_4(S_{20a}^2+S_{20b}^2)\\
& +\Gamma_1 S_3^2+\Gamma_2 S_{15}^2+\Gamma_3(S_{9a}^2+S_{9b}^2)+\Gamma_4(S_{18a}^2+S_{18b}^2)\\
& +\varSigma_2 S_{12}^2+\varSigma_3(S_{6a}^2+S_{6b}^2)+\Theta_1 S_4^2+\Theta_2(S_{16a}^2+S_{16b}^2)\\
& +\Phi_1 S_5^2+\Phi_2(S_{17a}^2+S_{17b}^2)+\Phi_3(S_{10a}^2+S_{10b}^2)+\Phi_4 S_{11}^2\\
& +2\xi_1 S_1 S_2+2\xi_3(S_{7a}S_{8a}+S_{7b}S_{8b})+2^{\frac{3}{2}}\xi_4(S_{19a}S_{20a}+S_{19b}S_{20b})\\
& +2\chi_3(S_{6a}S_{8a}+S_{6b}S_{8b})+2\pi_3(S_{6a}S_{9a}+S_{6b}S_{9b})\\
& +2\mu_2 S_{14}S_{15}+2\mu_3(S_{8a}S_{9a}+S_{8b}S_{9b})+2^{\frac{3}{2}}\mu_4(S_{18a}S_{19a}+S_{18b}S_{19b})\\
& +2\psi_2 S_{12}S_{13}+2\psi_3(S_{6a}S_{7a}+S_{6b}S_{7b})\\
& +2\eta_1 S_4 S_5+2\eta_2(S_{16a}S_{17a}+S_{16b}S_{17b})\\
& +2\tau_3(S_{7a}S_{9a}+S_{7b}S_{9b})+2\tau_4(S_{18a}S_{20a}+S_{18b}S_{20b}).
\end{aligned}$$

THE FORCE FIELD

A satisfactory force field should reproduce the observed vibration frequencies as closely as possible, and the aim in what follows has been to reproduce the observed frequencies of benzene and its deuterated derivatives to within 2% using a quadratic force field. The experimental observations have had a long history which will not be discussed here and reference is made to the summarizing paper of Herzfeld, Ingold & Poole (1946) which is part XXI of a series from Professor Ingold's laboratories and contains references to earlier work from this school and elsewhere. Their paper gives acceptable values for all the frequencies of benzene and hexadeuterobenzene which were accepted as the basis for the choice of force constants. It was after much of the work described here was completed that the alternative suggestions of Mair & Hornig (1946) regarding the B_{2u} frequencies came to the author's attention and discussion of this assignment is reserved to a special section.

Miller & Crawford (1946; see also Crawford & Miller 1949) have adopted the assignments of Ingold and coworkers and given numerical values for the force constants. As they state, in many of the symmetry classes an ambiguity arises in the choice of solutions of quadratic equations and two or possibly more equally satisfactory sets of force constants can be obtained. Before calculating normal co-ordinates or other quantities it is necessary to make a choice between the alternative sets.

One basis for choosing would be to calculate the frequencies of the partially deuterated benzenes with each combination of sets and compare for the best fit with experimental values. This would be tedious and it is not certain that a clear decision would result. For example, the A_2' frequencies of *sym.*-$C_6H_3D_3$ were calculated with the second preference of Crawford & Miller (1949) for the constants of the B_{2u} class. This gave 1615, 1242 and 899 cm^{-1} which are much closer to Crawford & Miller's values using their first preference, namely, 1614, 1245 and 900 cm^{-1} than to the approximate values of Herzfeld, Ingold & Poole (1946), namely, 1600, 1230 and 916 cm^{-1}. There is clearly no decision to be made between the two sets on this basis in this instance.

A second basis of choice between the two sets is that the force constants must be physically reasonable. This means that a chemist is entitled to recognize that the forces principally arise from the stretching of valency bonds and the distortion of valency angles, and that a description in these terms must give a reasonably good force field and that the interaction constants which must be added to give the exact field must be small. With this principle in mind the classes can be considered individually.

A_{1g} *class*. The question here as regards the ambiguity is resolved by the condition that ξ_1 shall be small and the alternative set is rejected by Crawford & Miller (1949). However, in this case $\xi_1 = 0$ (as opposed to the more exact $-0{\cdot}420\times 10^5$ dyn/cm) gives calculated frequencies within 2 %. In view of the fact that it is necessary to assume

$$\xi_3 = \xi_4 = \psi_3 = \tau_3 = \tau_4 = 0,$$

it seemed better to put $\xi_1 = \psi_2 = 0$ also and neglect all interactions with C—H stretching co-ordinates. This puts all C—H stretching co-ordinates on the same terms when the symmetry classes become combined in the partially deuterated compounds. The errors are probably less than those caused by the neglect of anharmonicity, and a device such as that of Lord & Andrews (1937) who use different force constants for C—H and C—D stretching would profoundly modify the value of ξ_1 and show that the value $-0{\cdot}420\times 10^5$ dyn/cm had little relation to molecular reality.

A_{2g} *class*. No ambiguity arises.

B_{1u} *class*. The position is similar to the A_{1g} class, and the assumption $\psi_2 = 0$ still enabled the frequencies to be fitted with less than 2 % error.

E_{1u} *class.* Even with the assumptions $\xi_4 = \tau_4 = 0$ ambiguity arises between sets with $\Lambda_4 = 6{\cdot}14 \times 10^5$, $\mu_4 = 1{\cdot}40 \times 10^5$ and $\Lambda_4 = 3{\cdot}92 \times 10^5$, $\mu_4 = 0{\cdot}139 \times 10^5$ dyn/cm. Crawford & Miller (1949) prefer the first set, but there are two strong arguments for adopting the second: (i) the value of μ_4, the interaction constant, is ten times smaller; (ii) the value of $2\Lambda_4$ is much nearer to Λ_1 ($= 7{\cdot}62 \times 10^5$ dyn/cm). It is necessary to compare $2\Lambda_4$ with Λ_1, since the L matrix transformation (Crawford & Miller 1949) introduces a factor of 2 in front of Λ_4 and an extra factor of $2^{\frac{1}{2}}$ in front of ξ_4 and μ_4, as can be seen from an examination of the potential V. (Figures 2 and 3 of Crawford & Miller (1949) should have $2^{\frac{1}{2}}S_{19a}$ and $2^{\frac{1}{2}}S_{19b}$ as the labelling of the VFSC to be consistent with the definitions of their own figure 1.) Λ_1 and $2\Lambda_4$ are principally controlled by the C—C stretching and should be equal if interactions between the stretching of different C—C bonds are neglected. A value of $2\Lambda_4$ as high as $12{\cdot}28 \times 10^5$ dyn/cm is greater than the force constant of an ethylenic C=C which is $9{\cdot}6 \times 10^5$ dyn/cm (Herzberg 1945, p. 193) and can confidently be rejected.

B_{2u} *class* (Ingold). The choice here lies between $\Lambda_2 = 6{\cdot}72 \times 10^5$, $\mu_2 = 1{\cdot}30 \times 10^5$ and $\Lambda_2 = 4{\cdot}99 \times 10^5$, $\mu_2 = -0{\cdot}203 \times 10^5$ dyn/cm. The much lower numerical value of μ_2 is certainly in favour of the second set. Also Λ_2 is likely to be lower than Λ_1, $2\Lambda_4$ and Λ_3, since it is the B_{2u} vibration which leads to alternate long and short C—C bonds, so that in the distorted position the molecule resembles a single Kekulé structure for benzene and this is expected to have a lower energy than other arrangements with the same total degree of distortion. A Kekulé structure with C—C 1·540 Å and C=C 1·342 Å is equivalent to a distortion $S_1 = 0{\cdot}100$ Å and $S_{14} = 0{\cdot}244$ Å and all other symmetry co-ordinates zero. Such a distortion would require 34 kcal/mole with $\Lambda_1 = 7{\cdot}620 \times 10^5$, $\Lambda_2 = 6{\cdot}72 \times 10^5$ dyn/cm but only 28 kcal/mole if Λ_2 were $4{\cdot}99 \times 10^5$ dyn/cm. In the real distorted state there will remain some resonance or delocalization energy so that the value must be less than 39 kcal which Pauling (1945) gives as the resonance energy referred to a state with non-interacting double bonds. The value 5 kcal/mole which the first figures would give for the remaining delocalization energy seems rather small and the 11 kcal/mole as given by the second set is slightly preferable, especially as it is more in accord with the calculations of Coulson & Altmann (1952). Values based on the second set have for these two reasons been chosen for further calculations.

E_{2g} *class.* Even with the assumptions $\psi_3 = \xi_3 = \tau_3 = 0$, there are several sets of values for the remaining parameters which fit the observed frequencies for C_6H_6 and C_6D_6. A few trial calculations were made but no set of constants were found which had lower numerical values of the interaction constants χ_3, π_3 and μ_3 than those of Crawford & Miller (1949), and essentially their values have been adopted here. It should be emphasized that $\mu_3 = 0$ is not an assumption but the value required to give a satisfactory fit.

This completes the planar part of the force field, and the adopted values are collected in table 2. They differ slightly in exact value from those discussed above; in some cases the new values give a slightly improved fit over those of Crawford & Miller (1949), and in others are a consequence of the revised value of 1·05 Å for the C—H bond length.

Crawford & Miller (1949) have also referred to the force field in terms of valency co-ordinates and corresponding Latin force constants. This form of the field is important as being more directly related to bond properties, and it is especially in this form that the interaction constants are expected to be small. The notation of Crawford & Miller (1949) is followed, but, as they discuss, there are thirty-seven planar Latin constants whereas there are only twenty-six planar Greek constants which are sufficient for an exact description of a general quadratic force field. Four of the Latin constants, namely, l, l_p, n, n_p, are zero, since non-zero values are inconsistent with D_{6h} symmetry for the molecule. There are also three independent relationships between the valency co-ordinates by which any field can be reduced to one of twenty-six constants. These relationships are:

$$\alpha_j+\alpha_{j+1}+\alpha_{j+2}+\alpha_{j+3}+\alpha_{j+4}+\alpha_{j+5}=0,$$

$$R_0(2\alpha_j+\alpha_{j+1}-\alpha_{j+2}-2\alpha_{j+3}-\alpha_{j+4}+\alpha_{j+5})=3^{\frac{1}{2}}(-\Delta R_j+\Delta R_{j+2}+\Delta R_{j+3}-\Delta R_{j+5}),$$

$$3^{\frac{1}{2}}R_0(\alpha_{j+1}+\alpha_{j+2}-\alpha_{j+4}-\alpha_{j+5})=(-\Delta R_j-2\Delta R_{j+1}-\Delta R_{j+2}+\Delta R_{j+3}+2\Delta R_{j+4}+R_{j+5}).$$

There are many ways in which the thirty-three non-zero Latin constants may be reduced to twenty-six, but it seems best to remove explicit mention of the terms which are likely to be small, namely, those governed by f_m, f_p, i_m, i_p, n_m, k_m and k_p.

With the substitutions

$$\tilde{D}=D+2f_m-2f_p-4.3^{-\frac{1}{2}}i_m+4.3^{-\frac{1}{2}}i_p,\qquad \tilde{d}_o=d_o+f_m-f_p-2.3^{-\frac{1}{2}}i_m+2.3^{-\frac{1}{2}}i_p,$$

$$\tilde{d}_m=d_m-f_m+f_p+2.3^{-\frac{1}{2}}i_m-2.3^{-\frac{1}{2}}i_p,\qquad \tilde{d}_p=d_p-2f_m+2f_p+4.3^{-\frac{1}{2}}i_m-4.3^{-\frac{1}{2}}i_p,$$

$$\tilde{F}=F-4f_m+3f_p,\qquad \tilde{f}_o=f_o-3f_m+2f_p,$$

$$\tilde{j}_o=j_o-3^{-\frac{1}{2}}n_m,\quad \tilde{j}_m=j_m-2.3^{-\frac{1}{2}}n_m,\quad \tilde{j}_p=j_p-3^{-\frac{1}{2}}n_m,$$

$$\tilde{i}_o=i_o-2i_m+i_p,$$

$$\tilde{k}=k-4k_m+3k_p,\quad \tilde{k}_o=k_o\quad 3k_m+2k_p,$$

$$\tilde{n}_o=n_o-n_m,$$

$$\tilde{h}_o=h_o-3^{\frac{1}{2}}k_m+3^{\frac{1}{2}}k_p,\quad \tilde{h}_p=h_p+3^{\frac{1}{2}}k_m-3^{\frac{1}{2}}k_p,$$

the planar force field may be expressed as

$$\begin{aligned}2V=\;&\tilde{D}\Sigma\Delta R_j^2+2\tilde{d}_o\Sigma\Delta R_j\,\Delta R_{j+1}+2\tilde{d}_m\Sigma\Delta R_j\,\Delta R_{j+2}+2\tilde{d}_p\Sigma\Delta R_j\,\Delta R_{j+3}\\&+E\Sigma\Delta r_j^2+2e_o\Sigma\Delta r_j\,\Delta r_{j+1}+2e_m\Sigma\Delta r_j\,\Delta r_{j+2}+2e_p\Sigma\Delta r_j\,\Delta r_{j+3}\\&+Gr_0^2\Sigma\beta_j^2+2g_or_0^2\Sigma\beta_j\beta_{j+1}+2g_mr_0^2\Sigma\beta_j\beta_{j+2}+2g_pr_0^2\Sigma\beta_j\beta_{j+3}\\&+\tilde{F}R_0^2\Sigma\alpha_j^2+2\tilde{f}_oR_0^2\Sigma\alpha_j\alpha_{j+1}+2\tilde{i}_oR_0\Sigma\alpha_j(\Delta R_j+\Delta R_{j-1})\\&+2\tilde{h}_o\Sigma\Delta r_j(\Delta R_j+\Delta R_{j-1})+2h_m\Sigma\Delta r_j(\Delta R_{j+1}+\Delta R_{j-2})+2\tilde{h}_p\Sigma\Delta r_j(\Delta R_{j+2}+\Delta R_{j-3})\\&+2\tilde{j}_or_0\Sigma\beta_j(\Delta R_j-\Delta R_{j-1})+2\tilde{j}_mr_0\Sigma\beta_j(\Delta R_{j+1}-\Delta R_{j-2})+2\tilde{j}_pr_0\Sigma\beta_j(\Delta R_{j+2}-\Delta R_{j-3})\\&+2\tilde{k}R_0\Sigma\alpha_j\,\Delta r_j+2\tilde{k}_oR_0\Sigma\alpha_j(\Delta r_{j+1}+\Delta r_{j-1})+2\tilde{n}_or_0R_0\Sigma\beta_j(\alpha_{j+1}-\alpha_{j-1})\\&+2l_or_0\Sigma\beta_j(\Delta r_{j+1}-\Delta r_{j-1})+2l_mr_0\Sigma\beta_j(\Delta r_{j+2}-\Delta r_{j-2}).\end{aligned}$$

The summations are normally over the six values of j, except for cases such as $\Sigma\beta_j\beta_{j+3}$ where only three terms are involved, since values of $j>3$ would give the same quantities with the factors in reversed order.

The relationships between the Latin and Greek constants are:

$$6\tilde{D} = \Lambda_1+\Lambda_2+2\Lambda_3+4\Lambda_4+4\Sigma_2-6\Sigma_3+4\,.\,3^{\frac{1}{2}}\chi_3,$$

$$6\tilde{d}_o = \Lambda_1-\Lambda_2-\Lambda_3+2\Lambda_4+2\Sigma_2-3\Sigma_3+2\,.\,3^{\frac{1}{2}}\chi_3,$$

$$6\tilde{d}_m = \Lambda_1+\Lambda_2-\Lambda_3-2\Lambda_4-2\Sigma_2+3\Sigma_3-2\,.\,3^{\frac{1}{2}}\chi_3,$$

$$6\tilde{d}_p = \Lambda_1-\Lambda_2+2\Lambda_3-4\Lambda_4-4\Sigma_2+6\Sigma_3-4\,.\,3^{\frac{1}{2}}\chi_3,$$

$$6E = \Omega_1+\Omega_2+2\Omega_3+2\Omega_4, \quad 6e_o = \Omega_1-\Omega_2-\Omega_3+\Omega_4,$$

$$6e_m = \Omega_1+\Omega_2-\Omega_3-\Omega_4, \quad 6e_p = \Omega_1-\Omega_2+2\Omega_3-2\Omega_4,$$

$$6G = \Gamma_1+\Gamma_2+2\Gamma_3+2\Gamma_4, \quad 6g_o = \Gamma_1-\Gamma_2-\Gamma_3+\Gamma_4,$$

$$6g_m = \Gamma_1+\Gamma_2-\Gamma_3-\Gamma_4, \quad 6g_p = \Gamma_1-\Gamma_2+2\Gamma_3-2\Gamma_4,$$

$$\tilde{F} = -\Sigma_2+2\Sigma_3, \quad \tilde{f}_o = -\Sigma_2+\Sigma_3,$$

$$\tilde{\imath}_o = \chi_3,$$

$$6\tilde{h}_o = \xi_1+\xi_3+6^{\frac{1}{2}}\xi_4-2\,.\,3^{\frac{1}{2}}\psi_2+3\,.\,3^{\frac{1}{2}}\psi_3, \quad 6h_m = \xi_1-2\xi_3, \quad 6\tilde{h}_p = \xi_1+\xi_3-6^{\frac{1}{2}}\xi_4+2\,.\,3^{\frac{1}{2}}\psi_2-3\,.\,3^{\frac{1}{2}}\psi_3,$$

$$6\tilde{\jmath}_o = \mu_2-3^{\frac{1}{2}}\mu_3+2^{\frac{1}{2}}\mu_4-\pi_3, \quad 6\tilde{\jmath}_m = -\mu_2+2\,.\,2^{\frac{1}{2}}\mu_4-2\pi_3, \quad 6\tilde{\jmath}_p = \mu_2+3^{\frac{1}{2}}\mu_3+2^{\frac{1}{2}}\mu_4-\pi_3,$$

$$\tilde{k} = -\psi_2+2\psi_3, \quad \tilde{k}_o = -\psi_2+\psi_3,$$

$$\tilde{n}_o = -3^{-\frac{1}{2}}\pi_3,$$

$$6l_o = -3^{\frac{1}{2}}\tau_3+3^{\frac{1}{2}}\tau_4, \quad 6l_m = 3^{\frac{1}{2}}\tau_3+3^{\frac{1}{2}}\tau_4.$$

The numerical values are given in table 3. It can be seen that the interaction constants are all small by comparison with the principal constants; this would not be so marked with a different choice of sets of force constants and, in particular, values of η_2 or η_4 numerically greater than 1·0 × 10⁵ dyn/cm would lead to much higher numerical values of $\tilde{\jmath}_o$, $\tilde{\jmath}_m$ or $\tilde{\jmath}_p$.

A_{2u} and E_{1g} classes. Each of these out-of-plane classes contains only one frequency and no ambiguity arises.

B_{2g} class. Miller & Crawford (1946) give the choice between

$$\Theta_1 = 0{\cdot}203\times10^5,\ \eta_1 = 0{\cdot}258\times10^5 \quad \text{and} \quad \Theta_1 = 0{\cdot}339\times10^5,\ \eta_1 = 0{\cdot}373\times10^5\ \text{dyn/cm}.$$

Though the smaller value of η_1 in the first set seems preferable the choice is not clear, especially as a choice of the ratio η_1/Θ_1 as low as possible would give preference to the second set.

E_{2u} class. The choice here is between

$$\Theta_2 = 0{\cdot}157\times10^5,\ \eta_2 = -0{\cdot}154\times10^5 \quad \text{and} \quad \Theta_2 = 0{\cdot}757\times10^5,\ \eta_2 = -0{\cdot}515\times10^5\ \text{dyn/cm},$$

and again a reason for choosing the first set as giving the smallest numerical value of η_2 is not convincing. Indeed, Ferguson (1953) prefers the second set for this class.

The calculations of Crawford & Parr (1949) can be read as predicting the ratio $\Theta_1/\Theta_2 = 1{\cdot}25$ which is most nearly fulfilled if the first preference is taken in each class. Some additional support can be obtained if the force field is converted directly into Latin constants as for the planar classes, since the choice of the first set in the B_{2g} and E_{2u} classes gives the lowest interaction constants.

But a far more conclusive argument in favour of this choice can be obtained by recognizing that the difficulty in these classes is related to the fact that the twisting described by the δ are not really those with which the valency forces are concerned, as has been pointed out by

Bell (1945). Rather, the force opposing twisting arises from the incomplete sideways overlap of the p_z atomic orbitals on adjacent C atoms; the directions of these orbitals are determined by the positions of the H atoms as well as of the C atoms, although the value of δ is given by the positions of the C atoms only. Following Bell (1945) it is possible to replace δ by a truer twisting function ϕ which is defined above. New symmetry co-ordinates S_4^* and S_{16}^*, which are the same function of ϕ as S_4 and S_{16} are of δ, can be introduced and the non-planar force field written

$$2V_{\text{non-planar}} = \Phi_1^* S_5^2 + \Phi_2^*(S_{17a}^2 + S_{17b}^2) + \Phi_3(S_{10a}^2 + S_{10b}^2) + \Phi_4 S_{11}^2$$
$$+ \Theta_1^* S_4^2 + \Theta_2^*(S_{16a}^{*2} + S_{16b}^{*2}) + 2\eta_1^* S_4^* S_5 + 2\eta_2^*(S_{16a}^* S_{17a} + S_{16b}^* S_{17b}).$$

The relationships between the two sets of Greek constants are:

$$\Phi_1^* = \Phi_1 + 4.3^{-1}\rho^{-2}\Theta_1 - 4.3^{-\frac{1}{2}}\rho^{-1}\eta_1, \quad \Phi_2^* = \Phi_2 + \rho^{-2}\Theta_2 + 2\rho^{-1}\eta_2,$$
$$\Theta_1^* = 4^{-1}\Theta_1, \quad \Theta_2^* = 4^{-1}\Theta_2,$$
$$\eta_1^* = 2^{-1}\eta_1 - 3^{-\frac{1}{2}}\rho^{-1}\Theta_1, \quad \eta_2^* = 2^{-1}\eta_2 + 2^{-1}\rho^{-1}\Theta_2.$$

Latin force constants P, p_o, p_m, p_p; Q, q_o, q_m, q_p; and t_o, t_m, t_p, can now be introduced referring to the $\gamma\gamma$, $\phi\phi$ and $\gamma\phi$ terms in the force field. The general field with eleven constants is capable of reduction to one of eight by means of the internal relationships between the ϕ and γ. These relationships are

$$\phi_j + \phi_{j+1} + \phi_{j+2} + \phi_{j+3} + \phi_{j+4} + \phi_{j+5} = 0,$$
$$\phi_j + 2\phi_{j+1} + \phi_{j+2} - \phi_{j+3} - 2\phi_{j+4} - \phi_{j+5} = 2.3^{-\frac{1}{2}}(2\gamma_j + \gamma_{j+1} - \gamma_{j+2} - 2\gamma_{j+3} - \gamma_{j+4} + \gamma_{j+5}),$$
$$\phi_j - \phi_{j+2} - \phi_{j+3} + \phi_{j+5} = 2.3^{-\frac{1}{2}}(-\gamma_{j+1} - \gamma_{j+2} + \gamma_{j+4} + \gamma_{j+5}).$$

Removing explicit reference to the q_m, q_p and t_p type terms the force field with only eight Latin constants can be written

$$2V = \tilde{P} r_0^2 \Sigma\gamma_j^2 + 2\tilde{p}_o r_0^2 \Sigma\gamma_j\gamma_{j+1} + 2\tilde{p}_m r_0^2 \Sigma\gamma_j\gamma_{j+2} + 2\tilde{p}_p r_0^2 \Sigma\gamma_j\gamma_{j+3}$$
$$\tilde{Q} R_0^2 \Sigma\phi_j^2 + 2\tilde{q}_o R_0^2 \Sigma\phi_j\phi_{j+1} + 2\tilde{t}_o R_0 r_0 \Sigma\gamma_j(\phi_{j-1} - \phi_j) + 2\tilde{t}_m R_0 r_0 \Sigma\gamma_j(\phi_{j-2} - \phi_{j+1}),$$

in which

$$\tilde{P} = P + 8.3^{-1}\rho^{-2}(q_m - q_p) - 8.3^{-\frac{1}{2}}\rho^{-1}t_p, \quad \tilde{p}_o = p_o + 4.3^{-1}\rho^{-2}(q_m - q_p) - 4.3^{-\frac{1}{2}}\rho^{-1}t_p,$$
$$\tilde{p}_m = p_m - 4.3^{-1}\rho^{-2}(q_m - q_p) + 4.3^{-\frac{1}{2}}\rho^{-1}t_p, \quad \tilde{p}_p = p_p - 8.3^{-1}\rho^{-2}(q_m - q_p) + 8.3^{-\frac{1}{2}}\rho^{-1}t_p,$$
$$\tilde{Q} = Q - 4q_m + 3q_p, \quad \tilde{q}_o = q_o - 3q_m + 2q_p,$$
$$\tilde{t}_o = t_o - t_p, \quad \tilde{t}_m = t_m - 2t_p.$$

The Latin force constants are given in terms of the Greek constants by

$$6\tilde{P} = \Phi_1^* + 2\Phi_2^* + 2\Phi_3^\dagger + \Phi_4, \quad 6\tilde{p}_o = -\Phi_1^* - \Phi_2^* + \Phi_3^\dagger + \Phi_4,$$
$$6\tilde{p}_m = \Phi_1^* - \Phi_2^* - \Phi_3^\dagger + \Phi_4, \quad 6\tilde{p}_p = -\Phi_1^* + 2\Phi_2^* - 2\Phi_3^\dagger + \Phi_4,$$
$$\tilde{Q} = -\Theta_1^* + 2\Theta_2^*, \quad \tilde{q}_o = -\Theta_1^* + \Theta_2^*,$$
$$\tilde{t}_o = 3^{-\frac{1}{2}}\eta_2^*, \quad \tilde{t}_m = 2^{-1}\eta_1^* + 3^{-\frac{1}{2}}\eta_2^*,$$

in which $\Phi_3^\dagger$ stands for

$$\Phi_3 + 4.3^{-\frac{1}{2}}\rho^{-1}\eta_1^* + 8.3^{-1}\rho^{-2}\Theta_1^* + 4\rho^{-1}\eta_2^* - 4\rho^{-2}\Phi_2^*.$$

Greatest interest is attached to the numerical value of $\tilde{Q}$, and with the four permutations between the sets of force constants the possible values are

$$0{\cdot}028\times10^5,\quad 0{\cdot}328\times10^5,\quad -0{\cdot}006\times10^5\quad\text{and}\quad 0{\cdot}294\times10^5\,\text{dyn/cm}.$$

$\tilde{Q}$ should be related to the force constant used by Bell (1945) who ignored all interactions, i.e. it should approximate to k'/R_0^2, where k' is defined in Bell's paper and given the value $7{\cdot}7\times10^{-13}$ dyn/cm/rad which leads to an expected value of $\tilde{Q}$ near $0{\cdot}039\times10^5$ dyn/cm. It is only the first of the above values, which was obtained by taking the first preference in the B_{2g} and E_{2u} classes, that lies within a factor of 7 of this value, so that a conclusive reason has been found for taking these sets. The numerical agreement is even closer with the revised value of Cole & Thompson (1950) whose value of $Q = 0{\cdot}40\times10^4$ dyn/cm is equivalent to an expectation of $\tilde{Q}$ of $0{\cdot}030\times10^5$ dyn/cm, since there is a factor of 3/4 difference in the definitions. $\tilde{Q}$ accepted here is $0{\cdot}0290\times10^5$ dyn/cm. The adopted values of the Greek constants are given in table 2 and of the Latin constants which correspond in table 3. The smaller values of η_1^*, η_2^* compared to η_1, η_2 and the smaller range of Φ values using the Bell-type field show that the ϕ-type of twisting represents intrinsic valency forces in contrast to the δ-type twisting.

The frequencies

Having chosen the force field from the observed frequencies, the procedure was reversed and the frequencies were calculated back from the constants chosen with the results shown for C_6H_6 and C_6D_6 in tables 4 to 13. The observed frequencies are taken from the papers of Ingold and coworkers (Herzfeld, Ingold & Poole 1946; Angus, Ingold & Leckie 1936; Poole 1946; Bailey, Hale, Ingold & Thompson 1936; Bailey, Carson & Ingold 1946). Since the Raman frequencies are for the liquid state, the infra-red frequencies for the liquid are quoted where possible, and in cases for which only the infra-red frequency for the vapour is known it is followed by the letter *v*. Values preceded by *ca* are those for which direct observation is impossible, and approximate frequencies have been derived from overtones, etc. The calculated frequencies were obtained in the usual way from the latent roots of the GF product matrix and the normal co-ordinates were obtained at the same time from the latent vectors corresponding to these roots. These are indicated in tables 4 to 13 by the S' which are the amplitudes of the symmetry co-ordinates for a classical vibration in the normal co-ordinate with energy $\frac{1}{2}h\nu$, that is, $S' = \partial S/\partial Q$, where Q is the normal co-ordinate involved for the vibration frequency in the same column of the table. Also given are the amplitudes of vibration of the local Cartesian co-ordinates, that is, $\bar{R}' = \partial\bar{R}/\partial Q$, etc., with the same normalization to the energy $\frac{1}{2}h\nu$. Only a representative value of each of these co-ordinates is given in the tables, since the remainder are simple multiples thereof as indicated for each symmetry class at the foot of the tables for the carbon motions, while the identities in which the capital letters are replaced by the corresponding small letters hold for the hydrogen motions.

The calculations have been extended to partly deuterated benzenes and the results are compared with the experimental values for C_6H_5D (Bailey, Gordon, Hale, Herzfeld, Ingold & Poole 1946), *ortho*-, *meta*- (Langseth & Lord 1938) and *para*- (Herzfeld, Hobden, Ingold & Poole 1946; Bailey, Carson, Gordon & Ingold 1946) $C_6H_4D_2$, *vic*.- (Langseth &

Lord 1938) and *sym.*- (Bailey, Hale, Herzfeld, Ingold, Leckie & Poole 1946) $C_6H_3D_3$ and *para*-$C_6H_2D_4$ (Herzfeld, Hobden, Ingold & Poole 1946; Bailey, Carson, Gordon & Ingold 1946) in tables 14 to 20. The provisional assignments of Langseth & Lord (1938) have been freely altered to give improved agreement, but the assignments of Ingold and coworkers are confirmed with the possible exception of the B_{2u}-like frequencies discussed below and the three minor points marked ! in the tables. These changes are made since (i) calculation indicates that of the two frequencies near 1580 cm^{-1} for *para*-$C_6H_4D_2$ the B_{1g} frequency should be slightly higher than the A_g and also, unexpectedly, should be more intense in the Raman effect if the polarizability gradient tensor discussed below is reliable. Similarly for the frequencies near 600 cm^{-1}, the calculations indicate that the A_g vibration should be slightly higher and there is therefore slight evidence that the 600·9 cm^{-1} shift belongs to the A_g class and that of 596·6 cm^{-1} to the B_{1g} class. The effect of the reversals is to leave the frequency product in each class virtually unchanged and agreement with the Redlich–Teller product rule is unaffected. (ii) There is a similar problem in *para*-$C_6H_2D_4$ for which the calculated A_g frequency at 583·7 cm^{-1} lies below that for the B_{1g} class, indicating again a reversal of the original assignment. However, in this case there is no reason to alter the assignment of shifts near 1570 cm^{-1}, and the switch of the lower frequencies slightly worsens the agreement with the product rule and its necessity remains in some doubt. (iii) Calculations of the B_{2u} frequency near 815 cm^{-1} in *para*-$C_6H_2D_4$ suggest that it should be lower than the neighbouring frequency of the B_{3u} class and show over twice the intensity in the infra-red spectrum. On both grounds a reversal of the original assignment is indicated.

It is of some interest to assess the degree to which the symmetry co-ordinates approximate to the normal co-ordinates. To this end the percentage of the potential energy stored in each term of the force field is indicated in tables 4 to 13. For the planar classes the principal term is usually over 70 % and the corresponding symmetry co-ordinate is a useful qualitative description of the vibrational mode, and expressions such as 'C—H stretching vibration' and 'C—H deformation vibration' are valid. For the E_{1u} class, table 13 shows that the C—H deformation, S_{18}, and the C—C stretching, S_{19}, co-ordinates are largely excited together, and that whereas the description of the 1332 cm^{-1} frequency in C_6D_6 as a C—C stretching and 811 cm^{-1} as C—D deformation can broadly be upheld, for C_6H_6 the description of 1033 cm^{-1} as the C—C stretching and 1480 cm^{-1} as the C—H deformation frequency has considerable justification. For the out-of-plane classes B_{2g} and E_{2u} of tables 6 and 12 the interaction terms are so large as to make the description suspect. If, however, transformation is made to the alternative symmetry co-ordinates S_4^* and S_{16}^*, the interaction terms are much smaller and the vibrations are essentially C—H deformation and C—C ϕ-type twisting except in the B_{2g} class of C_6H_6, where there is considerable mixing.

INFRA-RED INTENSITIES

No accurate measurements of infra-red band areas are available for benzene, and the use of the normal co-ordinates to determine accurate dipole moment gradients must await further experimental work. Nevertheless, it is feasible to make a start on this problem and at least to predict the relative order of band strengths. For this it is necessary, at present, to work in arbitrary units of intensity, and so the experimental values quoted in the tables are 10 times the reciprocal of the pressure in cm Hg required to give 50 % absorption at the P and R maxima in a cell 45 cm long. This unit is taken as it is of a convenient magnitude and may be obtained directly from the curves of Ingold and coworkers. The shape of all perpendicular bands should be nearly the same, and the values should approximate to the relative band areas. Likewise amongst the parallel bands, although the relative intensities between the two types will be in error.

In the out-of-plane classes, S_{11} is the only co-ordinate in the same symmetry class as μ_z in benzene itself and a knowledge of the value of S'_{11} for the normal co-ordinate is sufficient to determine the intensity in all cases since this is proportional to $\nu\left(\frac{\partial\mu_z}{\partial S_{11}}S'_{11}\right)^2$, where, as above, $S' = \partial S/\partial Q$. In the arbitrary intensity units employed agreement with experiment is obtained with

$$\text{intensity} = (\nu/1000)\,(25S'_{11})^2,$$

with S'_{11} in ångströms and a normal co-ordinate normalized to energy $\frac{1}{2}h\nu$. This expression gives the calculated intensities of tables 9 and 14 to 20. Although agreement with experiment is not all that could be desired, the bands are all of the predicted order of magnitude, and it would be premature to expect much better agreement considering the neglect of such factors as band area, resolving power, pressure broadening, amplifier linearity, solubility of benzene in grease, condensation on cell windows, incipient Fermi degeneracy, anharmonicity, etc.

For the planar vibrations, μ_x, μ_y are in the E_{1u} class and the intensity should be proportional to

$$\left(\frac{\partial\mu_y}{\partial S_{18a}}S'_{18a}+\frac{\partial\mu_y}{\partial S_{19a}}S'_{19a}+\frac{\partial\mu_y}{\partial S_{20a}}S'_{20a}\right)^2+\left(\frac{\partial\mu_x}{\partial S_{18b}}S'_{18b}+\frac{\partial\mu_x}{\partial S_{19b}}S'_{19b}+\frac{\partial\mu_x}{\partial S_{20b}}S'_{20b}\right)^2,$$

with
$$\frac{\partial\mu_y}{\partial S_a} = -\frac{\partial\mu_x}{\partial S_b}.$$

Comparison with the three E_{1u} vibration intensities of benzene gives the three dipole moment gradients provided it is clear whether to take the positive or negative square root of the intensity in each case. It is not easy to predict by inspection which sign should be taken, and it is better to take all possible combinations of sign, predict the intensities of the deuterated benzenes with the dipole gradients obtained and choose the set which gives the best fit. In the present case it is found that the fact that the 1332 cm^{-1} absorption of C_6D_6 is so much weaker than the 1480 cm^{-1} absorption of C_6H_6 means that only solutions in which $\partial\mu/\partial S_{18}$ and $\partial\mu/\partial S_{19}$ are of the same sign can be accepted. The relative sign of $\partial\mu/\partial S_{20}$ is not given with certainty with the present experimental accuracy, but the best fit was obtained with the expression

$$\text{intensity} = (\nu/1000)\,(17S'_{18}+14S'_{19}+16S'_{20})^2.$$

This intensity is naturally doubled when the a and b vibrations retain their degeneracy. There is no direct clue to the absolute signs of the dipole gradients. However, for the out-of-plane vibrations it is known (Bell, Thompson & Vago 1948) that the H atom is at the positive end of the moving link dipole, and it seems likely that this would be so for the S_{18} co-ordinate also. In both cases the sp^2 hybridized carbon atomic orbital is not easily able to follow the H atom in direction, and as a consequence the electrons are liable to remain nearer their positions in the equilibrium configuration, so that the centre of the negative charges does not move as far as the centre of positive charges. If these signs are adopted, figure 2 shows the direction of the dipole for the phase crudely indicated, the point of the arrow being the negative end of the dipole.

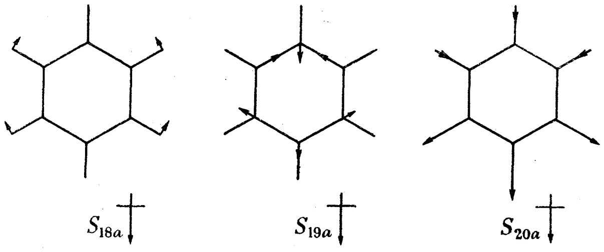

FIGURE 2

RAMAN INTENSITIES AND DEPOLARIZATION FACTORS

Although Angus *et al.* (1936) provide integrated intensities for the Raman shifts of C_6H_6 and C_6D_6, they are not of the accuracy which could be obtained with modern spectrometers using photo-electric detection, and again only approximate calculations are feasible. Before inclusion in tables 4, 7, 8 and 14 to 20, the experimental values of relative intensity have been multiplied by

$$(1-e^{-h\nu/kT})\,(1-\nu/\nu_0)^{-4}$$

to correct to 0° K and a standard observational frequency ν_0 assumed to be 24 700 cm^{-1} corresponding to the 4047 Å line of Hg (see Woodward & Long 1949). This factor is fairly significant and increases the intensity of a shift of 3000 cm^{-1} by over 50 % relative to a shift of 1000 cm^{-1}. For C_6H_6 and C_6D_6 the relative strengths between the compounds is known from an experiment with the mixed liquids and only one scale factor is involved. For the other compounds only peak intensities are known, and in each case a factor has been included so that observed and calculated intensities agree for the strongest line of each compound and its observed intensity is given in brackets in tables 14 to 20. The depolarization factors, ϱ, are quoted unchanged; $\varrho = 0{\cdot}86 = \frac{6}{7}$ indicates full depolarization. In the tables *i*, for included, means that the observations refer to two vibrations and that the vibration in question accounts for only part of the intensity.

The Raman intensities are best discussed in terms of the symmetric polarizability derivative, $\bar{\alpha}'$, and the anisotropic polarizability derivative, γ'. These symbols are in general use (Long 1953) for these quantities and have been used here since confusion with the ring C—C—C deformation and the out of plane C—H deformation angles is slight. The Raman intensity referred to a fixed observational frequency and 0° K is proportional to

$$45\bar{\alpha}'^2+13\gamma'^2$$

for the Stokes lines and the depolarization factor is given by

$$\varrho = 6\gamma'^2/(45\bar{\alpha}'^2+7\gamma'^2).$$

The non-zero components of $\bar{\alpha}'$ belong exclusively to the A_{1g} class and are given by

$$9\bar{\alpha}'^2 = \left[\left(\frac{2\partial\alpha_{xx}}{\partial S_1}+\frac{\partial\alpha_{zz}}{\partial S_1}\right)S_1'+\left(\frac{2\partial\alpha_{xx}}{\partial S_2}+\frac{\partial\alpha_{zz}}{\partial S_2}\right)S_2'\right]^2,$$

remembering the identity $\partial\alpha_{xx}/\partial S = \partial\alpha_{yy}/\partial S$ which holds for this class. For the in-plane vibrations γ'^2 has three non-zero components:

$$\gamma'^2 = \left[\left(\frac{\partial\alpha_{zz}}{\partial S_1}-\frac{\partial\alpha_{xx}}{\partial S_1}\right)S_1'+\left(\frac{\partial\alpha_{zz}}{\partial S_2'}-\frac{\partial\alpha_{xx}}{\partial S_2}\right)S_2'\right]^2$$

for the A_{1g} class, as can be obtained from the more general formula (Herzberg 1945) by the use of the same identity:

$$\gamma'^2 = 3\left(\frac{\partial\alpha_{xx}}{\partial S_{6a}}S_{6a}'+\frac{\partial\alpha_{xx}}{\partial S_{7a}}S_{7a}'+\frac{\partial\alpha_{xx}}{\partial S_{8a}}S_{8a}'+\frac{\partial\alpha_{xx}}{\partial S_{9a}}S_{9a}'\right)^2,$$

which is obtained by use of the identity $\partial\alpha_{xx}/\partial S = -\partial\alpha_{yy}/\partial S$ which holds for the E_{2ga} vibrations:

$$\gamma'^2 = 3\left(\frac{\partial\alpha_{xy}}{\partial S_{6b}}S_{6b}'+\frac{\partial\alpha_{xy}}{\partial S_{7b}}S_{7b}'+\frac{\partial\alpha_{xy}}{\partial S_{8b}}S_{8b}'+\frac{\partial\alpha_{xy}}{\partial S_{9b}}S_{9b}'\right)^2$$

for the E_{2gb} vibrations and there is the further identity

$$\frac{\partial\alpha_{xx}}{\partial S_a} = -\frac{\partial\alpha_{xy}}{\partial S_b}$$

for this decomposition of the degenerate E_{2g} class. The total value of γ'^2 is the sum of the separate γ'^2 for the classes involved. R_z is in the inactive A_{2g} class, and so rotations do not affect the intensities of the Raman lines of the planar vibrations.

To calculate the polarizability gradients from the observed integrated intensities involves the selection between alternative roots of quadratic equations in such a way as to give the best fit for the isotopic molecules. This seemed to be obtained with the expressions

$$\bar{\alpha}'^2 = (9{\cdot}6S_1'-2{\cdot}7S_2')^2,$$

$$\gamma'^2 = (8{\cdot}9S_1'-7{\cdot}8S_2')^2 \qquad \text{for the } A_{1g} \text{ class,}$$

$$\gamma'^2 = (3{\cdot}8S_6'+4{\cdot}1S_7'-3{\cdot}2S_8'+0{\cdot}8S_9')^2 \qquad \text{for the } E_{2g} \text{ class,}$$

but other expressions led to intensities and depolarizations not wholly outside the experimental uncertainty. In view of this, further discussion of the relative signs in terms of intuitive expectations of the polarizability derivatives or bond polarizabilities would be premature, except to point out that many of the signs are unexpected, e.g. the opposite signs of the coefficients of S_1 and S_2 in $\bar{\alpha}'$. This has already been noticed by Lord & Teller (1937) who undertook a similar treatment for the A_{1g} class, although their numerical values are somewhat different as they did not include the $(1-\nu/\nu_0)^{-4}$ term in the intensities.

These authors also discussed the E_{1g} class which is more troublesome, since it also contains the rotations R_x, R_y. Their treatment relates the intensity of hexadeuterobenzene to that of benzene itself and is cumbersome for the partly deuterated molecules. It is easier to adapt their treatment to give functions of the symmetry co-ordinates and two parameters, one of which relates to the polarizability of the whole molecule and the other to the change of polarizability occurring during the S_{10} vibration. The forms of the E_{1g}-like vibrations are not exclusively determined by the internal motions which must be supplemented by the condition of no rotation; this determines the ratio z_j/Z_j for the E_{1g} class of the molecules with D_{6h} symmetry, and this ratio will depend on the moment of inertia and the masses m_j. If, however, the median plane of the carbon atoms is taken as a reference x^*y^* plane for a co-ordinate system $x^*y^*z^*$, coincident with xyz at equilibrium, there is no ambiguity about $\partial\alpha_{x^*y^*}/\partial S_{10a}$ which is independent of the masses. If, further, the angles of rotation of the carbon plane with respect to the xy, space-fixed, plane of the inertia ellipsoid are taken as ω_x and ω_y for rotation about x and y respectively, then

$$\gamma'^2 = 3\left(\frac{\partial\alpha_{x^*z^*}}{\partial S_{10a}} S'_{10a} + (\alpha_{zz} - \alpha_{xx})\,\omega_y\right)^2 \quad \text{for } E_{1ga} \text{ vibrations},$$

$$\gamma'^2 = 3\left(\frac{\partial\alpha_{y^*z^*}}{\partial S_{10b}} S'_{10b} + (\alpha_{yy} - \alpha_{zz})\,\omega_x\right)^2 \quad \text{for } E_{1gb} \text{ vibrations},$$

for which ω_x and ω_y are assumed small and there are the identities $\partial\alpha_{x^*z^*}/\partial S_{10a} = -\partial\alpha_{y^*z^*}/\partial S_{10b}$ and $\alpha_{xx} = \alpha_{yy}$, and the α are the elements of the polarizability tensor of the whole molecule. The above expressions hold also for the deuterated benzenes except for 1:2:4-trideuterobenzene in which the E_{1ga} and E_{1gb} vibrations are merged into the same class A''. Expressions for ω_x and ω_y in terms of S_{10} for D_{6h} symmetry are

$$\omega_y I_y = 3^{\frac{1}{2}} R_0 (1+\rho)\, m S_{10a},$$
$$\omega_x I_x = 3^{\frac{1}{2}} R_0 (1+\rho)\, m S_{10b},$$

in which the I are the moments of inertia and m is the mass of the H or D atom. When S_{10} has its amplitude S'_{10} the ω are the librational amplitudes for a vibration of energy $\frac{1}{2}h\nu$ which are required for substitution in the intensity expressions. For lower symmetry the values of ω depend on the other S' of the same symmetry class but they are still expressed in terms only of the S', I and the masses of the peripheral atoms.

Best numerical fit was obtained with

$$\gamma'^2 = (0{\cdot}41 S'_{10} + 10{\cdot}2\omega)^2,$$

where ω is the librational amplitude in radians. The molecular polarizabilities have been given as

$$\alpha_{xx} = \alpha_{yy} = 123{\cdot}1 \times 10^{-25} > \alpha_{zz} = 63{\cdot}5 \times 10^{-25}\,\text{cm}^3$$

by Stuart & Volkmann (1933), and so it seems that $\partial\alpha_{x^*z^*}/S_{10a}$ must be negative, which is the reverse of that to be expected for a crude picture for which it would be said that the C—H bond is likely to have a higher polarizability along its length than in the perpendicular directions. This rather surprising result suggests that the assumptions, expectations and validity of an isolated bond picture of the polarizability requires closer investigation, although it is possible that the assumption of the space-fixed orientation of the inertia ellipsoid is too naïve to apply to the liquid state. An unusually large polarizability perpendicular to the C—H bonds might be accompanied by a large numerical value of $\partial\alpha_{zz}/\partial S_2$ which would help to explain the relative signs of the polarizability derivatives in the A_{1g} class. More accurate measurements, if possible in the gas phase, should establish the relative signs with greater certainty. The Raman shift intensities calculated for the Stokes lines corrected to a fixed frequency ν_0 are given in tables 4, 7, 8 and 14 to 20 in the arbitrary units required for agreement with the C_6H_6 lines and are seen to be satisfactorily in agreement with experiment, as are the depolarization factors, when the approximate nature of the measurements are considered. Classes which are not derived from the A_{1g} class of benzene all have theoretical depolarization factors of $\frac{6}{7}$ for all lines.

Alternative B_{2u} assignment

Although the figures given above show that the assignments of Ingold and coworkers are reasonably acceptable, there remains considerable doubt concerning the B_{2u} carbon frequency of C_6H_6 and the related modes of the other molecules. A suggestion has been made by Mair & Hornig (1949) that this frequency lies at 1311 cm^{-1} and not at 1648 cm^{-1}, and that the hydrogen deformation of this class is at 1147 cm^{-1}. To fit these frequencies and the C_6D_6 frequencies at 1285 and 825 cm^{-1}, the required force constants are

$$\Lambda_2 = 3{\cdot}940\times10^5,\quad \Gamma_2 = 0{\cdot}822\times10^5 \quad\text{and}\quad \mu_2 = 0{\cdot}30\times10^5\,\text{dyn/cm},$$

if the alternative set (Hornig 1950) with

$$\Lambda_2 = 4{\cdot}361\times10^5,\quad \mu_2 = 0{\cdot}667\times10^5\,\text{dyn/cm}$$

are excluded on the grounds of the large value of μ_2 and consequently of the $\tilde{J}$ which would be more than doubled. The force constants for the Mair & Hornig assignment have been included in tables 2 and 3 as alternatives and the calculated quantities in tables 11, 17, 19 and 20. From the latter it can be seen that the new assignment is equally acceptable for these partially deuterated compounds. Apart from the B_{2u}-like carbon frequencies the changes are small, and this is likely to be true for the remaining compounds, so that a recalculation of the B_1 classes of C_6H_5D, *meta*-$C_6H_4D_2$, *vic.*-$C_6H_3D_3$ or the A_1 class of *ortho*-$C_6H_4D_2$ was not attempted in view of the labour involved and the fact that there is no conclusive evidence for the Mair & Hornig assignment.

Two comments in favour of the new assignment can be made. (i) A B_{3u} frequency of *para*-$C_6H_4D_2$ is observed at *1106* cm^{-1}. Initial calculations with a force field for the Ingold assignment which gave the closely related B_{2u} frequency of C_6H_6 at 1112 cm^{-1} (observed *ca.* *1110* cm^{-1}) predicted 1082 cm^{-1} for the *para*-$C_6H_4D_2$ frequency which is more than 2 % from the observed. A small adjustment of the constants raised the C_6H_6 frequency to 1122 cm^{-1} and the *para*-$C_6H_4D_2$ frequency to 1088 cm^{-1} as given in tables 11 and 17; both of these are within 2 % of the required values, although it is unexpected to find that one should be too high and the related frequency too low. Admittedly, the frequency *1110* cm^{-1} of Ingold *et al.* may be too low, but the position is in contrast to the Mair & Hornig case for which the calculated B_{3u} frequency of *para*-$C_6H_4D_2$ is 1103 cm^{-1} which is within 0·3 % without any need for adjustment or compromise. (ii) The predicted infra-red intensities of the B_{2u}-like carbon vibrations of the B_{3u} class of *para*-$C_6H_4D_2$ and $C_6H_2D_4$ are low but yet not zero and are of a magnitude that should be clearly visible on the curves of Bailey, Carson, Gordon & Ingold (1936), and the observed bands at *1603* and *1585* cm^{-1} respectively must be due to these vibrations. These are 14 cm^{-1} lower than the calculated values in each case, whereas the related C_6H_6 frequency inferred at *1648* cm^{-1} is 18 cm^{-1} higher than the calculated. Again the force constants are in the nature of a compromise. For the Mair & Hornig assignment there is agreement to within 3 cm^{-1} with half the presumed overtone frequency for the corresponding vibrations at 1292 and 1287 cm^{-1} in each case. Admittedly, there is no sign of absorption at these frequencies in the infra-red spectra where they are permitted to appear by the selection rules, but the expected intensity is extremely slight as indicated in tables 17 and 20 and bands of these intensities would not be visible on the experimental curves.

The majority of the calculations were performed with either a Friden ultramatic electric desk calculator or the matrix calculator described by Dr Robb (1954), whom I wish to thank for the loan of it. The larger classes with 10 or 11 frequencies were computed by the Mathematics Division of the National Physical Laboratory for which I should like to thank Dr Wilkinson. Also, sincere thanks are due to the National Coal Board for sponsoring the program on the infra-red spectra of aromatic compounds and to Professor H. W. Melville, F.R.S., for his interest.

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TABLE 1. SYMMETRY CLASSES, SELECTION RULES AND DEFINITION OF SYMMETRY CO-ORDINATES

$_{6h}$ class	C_3^z	C_2^z	C_2^y	σ^z	Raman	infra-red		coefficient for $j=$ 1	2	3	4	5	6	times	
$_{g}$	+	+	+	+	$\alpha_{xx}=\alpha_{yy}$, α_{zz}	*ia*	S_1	1	1	1	1	1	1	$6^{-\frac{1}{2}}$	ΔR_j
							S_2	1	1	1	1	1	1	$6^{-\frac{1}{2}}$	Δr_j
$_{g}$	+	+	−	+	*ia*	*ia*	S_3	1	1	1	1	1	1	$6^{-\frac{1}{2}}$	$r_0\beta_j$
$_{g}$	+	−	−	−	*ia*	*ia*	S_4	1	−1	1	−1	1	−1	$6^{-\frac{1}{2}}$	$R_0\delta_j$
							S_5	1	−1	1	−1	1	−1	$6^{-\frac{1}{2}}$	$r_0\gamma_j$
							S_4^*	1	−1	1	−1	1	−1	$6^{-\frac{1}{2}}$	$R_0\phi_j$
$_{ga}(E_{ga}^{+})$	*e*	+	+	+	$\alpha_{xx}=-\alpha_{yy}$	*ia*	S_{6a}	−2	1	1	−2	1	1	$12^{-\frac{1}{2}}$	$R_0\alpha_j$
							S_{7a}	−2	1	1	−2	1	1	$12^{-\frac{1}{2}}$	Δr_j
							S_{8a}	−1	2	−1	−1	2	−1	$12^{-\frac{1}{2}}$	ΔR_j
							S_{9a}	0	−1	1	0	−1	1	2^{-1}	$r_0\beta_j$
$_{gb}(E_{gb}^{+})$	*e*	+	−	+	α_{xy}	*ia*	S_{6b}	0	−1	1	0	−1	1	2^{-1}	$R_0\alpha_j$
							S_{7b}	0	−1	1	0	−1	1	2^{-1}	Δr_j
							S_{8b}	−1	0	1	−1	0	1	2^{-1}	ΔR_j
							S_{9b}	2	−1	−1	2	−1	−1	$12^{-\frac{1}{2}}$	$r_0\beta_j$
$_{ga}(E_{ga}^{-})$	*e*	−	+	−	α_{xz}	*ia*	S_{10a}	0	1	1	0	−1	−1	2^{-1}	$r_0\gamma_j$
$_{gb}(E_{gb}^{-})$	*e*	−	−	−	α_{yz}	*ia*	S_{10b}	−2	−1	1	2	1	−1	$12^{-\frac{1}{2}}$	$r_0\gamma_j$
$_{u}$	+	+	−	−	*ia*	μ_z	S_{11}	1	1	1	1	1	1	$6^{-\frac{1}{2}}$	$r_0\gamma_j$
$_{u}$	+	−	+	+	*ia*	*ia*	S_{12}	−1	1	−1	1	−1	1	$6^{-\frac{1}{2}}$	$R_0\alpha_j$
							S_{13}	−1	1	−1	1	−1	1	$6^{-\frac{1}{2}}$	Δr_j
$_{u}$	+	−	−	+	*ia*	*ia*	S_{14}	−1	1	−1	1	−1	1	$6^{-\frac{1}{2}}$	ΔR_j
							S_{15}	−1	1	−1	1	−1	1	$6^{-\frac{1}{2}}$	$r_0\beta_j$
$_{ua}(E_{ua}^{+})$	*e*	+	+	−	*ia*	*ia*	S_{16a}	−1	2	−1	−1	2	−1	$12^{-\frac{1}{2}}$	$R_0\delta_j$
							S_{17a}	0	−1	1	0	−1	1	2^{-1}	$r_0\gamma_j$
							S_{16a}^*	−1	2	−1	−1	2	−1	$12^{-\frac{1}{2}}$	$R_0\phi_j$
$_{ub}(E_{ub}^{+})$	*e*	+	−	−	*ia*	*ia*	S_{16b}	1	0	−1	1	0	−1	2^{-1}	$R_0\delta_j$
							S_{17b}	−2	1	1	−2	1	1	$12^{-\frac{1}{2}}$	$r_0\gamma_j$
							S_{16b}^*	1	0	−1	1	0	−1	2^{-1}	$R_0\phi_j$
$_{ua}(E_{ua}^{-})$	*e*	−	+	+	*ia*	μ_y	S_{18a}	0	1	1	0	−1	−1	2^{-1}	$r_0\beta_j$
							S_{19a}	−1	0	1	1	0	−1	2^{-1}	ΔR_j
							S_{20a}	−2	−1	1	2	1	−1	$12^{-\frac{1}{2}}$	Δr_j
$_{ub}(E_{ub}^{-})$	*e*	−	−	+	*ia*	μ_x	S_{18b}	2	1	−1	−2	−1	1	$12^{-\frac{1}{2}}$	$r_0\beta_j$
							S_{19b}	1	2	1	−1	−2	−1	$12^{-\frac{1}{2}}$	ΔR_j
							S_{20b}	0	1	1	0	−1	−1	2^{-1}	Δr_j

ia = inactive; the α are the elements of the polarizability tensor and the μ are the dipole moment components; *e* = degenerate.

TABLE 2. ADOPTED FORCE CONSTANTS (10^5 DYN/CM)

planar		non-planar	
Ω_1	5·120	Φ_1	0·525
Ω_2	5·100	Φ_2	0·430
Ω_3	5·020	Φ_3	0·342
Ω_4	5·150	Φ_4	0·248
Γ_1	0·833	Θ_1	0·196
Γ_2	0·910 (or 0·822)	Θ_2	0·156
Γ_3	0·851	η_1	0·245
Γ_4	0·914	η_2	−0·160
Λ_1	7·620	equivalent to	
Λ_2	5·160 (or 3·940)	Φ_1^*	0·235
Λ_3	5·380	Φ_2^*	0·280
$2\Lambda_4$	7·340	Φ_3	0·342
Σ_2	0·661	Φ_4	0·248
Σ_3	0·846	Θ_1^*	0·0490
χ_3	−0·18	Θ_2^*	0·0390
μ_2	−0·13 (or 0·30)	η_1^*	−0·028
μ_3	0·00	η_2^*	0·024
$2^{\frac{1}{2}}\mu_4$	0·18		
π_3	0·22		
all others	0 (assumed)		

Alternatives in brackets refer to Mair & Hornig's assignment.

TABLE 3. VALUES OF THE LATIN FORCE CONSTANTS (10^5 DYN/CM)

	planar		non-planar
$\tilde{D}$	5·757 (or 5·553)	$\tilde{P}$	0·286
$\tilde{d}_o$	0·430 (or 0·633)	$\tilde{p}_o$	0·012
$\tilde{d}_m$	0·317 (or 0·113)	$\tilde{p}_m$	−0·022
$\tilde{d}_p$	0·370 (or 0·573)	$\tilde{p}_p$	−0·017
$\tilde{E}$	5·093	$\tilde{Q}$	0·0290
e_o	0·025	$\tilde{q}_o$	−0·0100
e_m	0·008	$\tilde{t}_o$	0·014
e_p	−0·040	$\tilde{t}_m$	0·000
$\tilde{G}$	0·879 (or 0·864)		
g_o	−0·002 (or 0·012)		
g_m	−0·003 (or −0·018)		
g_p	−0·034 (or −0·019)		
$\tilde{F}$	1·031		
$\tilde{f}_o$	0·185		
$\tilde{i}_o$	−0·180		
$\tilde{j}_o$	−0·028 (or 0·043)		
$\tilde{j}_m$	0·008 (or −0·063)		
$\tilde{j}_p$	−0·028 (or 0·043)		
$\tilde{n}_o$	−0·127		
all others	0		

Alternatives in brackets refer to Mair & Hornig's assignment.

TABLE 4. RESULTS FOR THE A_{1g} CLASS OF C_6H_6 AND C_6D_6

A_{1g} class	C_6H_6		C_6D_6	
$\nu_{\text{calc.}}$ (cm^{-1})	992·4	3073·0	943·4	2286·4
$\nu_{\text{obs.}}$	*991·6*	*3061·9*	*943·2*	*2292·6*
S_1' (Å)	0·0506	−0·0094	0·0485	−0·0161
S_2'	0·0065	0·1086	0·0126	0·0921
$\Lambda_1 S_1'^2$ (%)	98·9	1·1	95·7	4·3
$\Omega_1 S_2'^2$	1·1	98·9	4·3	95·7
$\bar{R}_1'$ (Å)	0·0206	−0·0038	0·0198	−0·0066
$\bar{r}_1'$	0·0233	0·0405	0·0249	0·0310
Raman int.:				
calc.	12·0	17·8	9·8	17·9
obs.	*11·7*	*18·0*	*11·4*	*15·2*
$\varrho_{\text{calc.}}$	0·09	0·41	0·07	0·35
$\varrho_{\text{obs.}}$	*0·09*	*0·4*	*0·08*	*0·35*

$$\bar{R}_1' = \bar{R}_2' = \bar{R}_3' = \bar{R}_4' = \bar{R}_5' = \bar{R}_6'.$$

TABLE 5. RESULTS FOR THE A_{2g} CLASS OF C_6H_6 AND C_6D_6

A_{2g} class	C_6H_6	C_6D_6
$\nu_{\text{calc.}}$ (cm^{-1})	1328·3	1031·1
$\nu_{\text{obs.}}$	*ca. 1326*	*ca. 1037*
S_3' (Å)	0·1779	0·1568
$\Gamma_1 S_3'^2$ (%)	100·0	100·0
U_1' (Å)	0·0085	0·0124
u_1'	−0·0578	−0·0423

$$U_1' = U_2' = U_3' = U_4' = U_5' = U_6'.$$

TABLE 6. RESULTS FOR THE B_{2g} CLASS OF C_6H_6 AND C_6D_6

B_{2g} class	C_6H_6		C_6D_6	
$\nu_{\text{calc.}}$ (cm^{-1})	705·9	992·2	600·9	824·5
$\nu_{\text{obs.}}$	*ca. 705*	*985*	*ca. 601*	*ca. 827*
S'_4 (Å)	0·3895	−0·1672	0·2395	−0·3489
S'_5	−0·1262	0·2602	0·0057	0·2735
$S^{*\prime}_4$	0·3906	0·4667	0·4966	0·1443
$\Theta_1 S'^2_4$ (%)	212·2	27·8	94·2	145·7
$\Phi_1 S'^2_5$	59·6	180·4	0·2	239·9
$2\eta_1 S_4 S_5$	−171·8	−108·2	5·6	−285·6
$\Theta^*_1 S^{*\prime 2}_4$	53·3	54·2	101·3	6·2
$\Phi^*_1 S'^2_5$	26·8	80·8	0·1	107·5
$2\eta^*_1 S^{*\prime}_4 S'_5$	19·9	−35·0	−1·4	−13·7
Z'_1 (Å)	0·0230	−0·0099	0·0141	−0·0206
z'_1	0·0403	0·0668	0·0588	0·0294

$$Z'_1 = -Z'_2 = Z'_3 = -Z'_4 = Z'_5 = -Z'_6.$$

TABLE 7. RESULTS FOR THE E_{2g} CLASS OF C_6H_6 AND C_6D_6

E_{2g}	C_6H_6				C_6D_6			
$\nu_{\text{calc.}}$ (cm^{-1})	610·0	3044·0	1599·3	1179·5	574·4	2274·8	1545·0	868·3
$\nu_{\text{obs.}}$	*605·6*	*3046·8*	*ca. 1595*	*1178·0*	*577·4*	*2264·9*	*1551·5*	*867·3*
S'_6 (Å)	0·1097	0·0257	−0·0758	0·0463	0·1018	0·0474	−0·0704	0·0520
S'_7	−0·0025	0·1090	0·0075	−0·0031	−0·0042	0·0913	0·0191	−0·0046
S'_8	0·0252	−0·0066	0·0619	−0·0177	0·0243	−0·0155	0·0629	−0·0044
S'_9	−0·0422	−0·0068	0·0932	0·1402	−0·0580	−0·0155	0·0669	0·1185
$\Sigma_3 S'^2_6$ (%)	84·1	0·9	15·3	7·7	76·9	4·2	13·7	13·3
$\Omega_3 S'^2_7$	0·2	98·6	0·9	0·2	0·8	92·6	6·0	0·6
$\Lambda_3 S'^2_8$	28·2	0·4	65·0	7·2	27·8	2·9	69·5	0·6
$\Gamma_3 S'^2_9$	12·5	0·1	23·3	71·4	25·1	0·4	12·4	69·3
$2\chi_3 S'_6 S'_8$	−8·2	0·1	5·3	1·3	−7·8	0·6	5·2	0·5
$2\pi_3 S'_6 S'_9$	−16·8	−0·1	−9·8	12·2	−22·8	−0·7	−6·8	15·7
$\overline{R}'_{1a}$ (Å)	0·0311	0·0055	−0·0100	0·0090	0·0290	0·0096	−0·0085	0·0124
$\bar{r}'_{1a}$	0·0325	−0·0574	−0·0143	0·0108	0·0314	−0·0431	−0·0196	0·0150
U'_{2a}	−0·0174	0·0006	−0·0178	0·0033	−0·0165	0·0024	−0·0185	−0·0021
u'_{2a}	−0·0266	0·0000	0·0206	0·0784	−0·0344	−0·0002	0·0073	0·0628
Raman int.:								
calc.	2·2	8·2	3·8	2·9	1·6	9·1	3·0	2·2
obs.	*2·2*	*8·1*	*ca. 4·5*	*2·7*	*1·3*	*9·2*	*2·6*	*2·6*

$$\overline{R}'_{1a} = -2\overline{R}'_{2a} = -2\overline{R}'_{3a} = \overline{R}'_{4a} = -2\overline{R}'_{5a} = -2\overline{R}'_{6a} = 2.3^{-\frac{1}{2}}\overline{R}'_{2b} = -2.3^{-\frac{1}{2}}\overline{R}'_{3b} = 2.3^{-\frac{1}{2}}\overline{R}'_{5b} = -2.3^{-\frac{1}{2}}\overline{R}'_{6b},$$
$$U'_{2a} = -U'_{3a} = U'_{5a} = -U'_{6a} = -2^{-1}3^{\frac{1}{2}}U'_{1b} = 3^{\frac{1}{2}}U'_{2b} = 3^{\frac{1}{2}}U'_{3b} = -2^{-1}3^{\frac{1}{2}}U'_{4b} = 3^{\frac{1}{2}}U'_{5b} = 3^{\frac{1}{2}}U'_{6b},$$
$$\overline{R}'_{1b} = \overline{R}'_{4b} = U'_{1a} = U'_{4a} = 0.$$

TABLE 8. RESULTS FOR THE E_{1g} CLASS OF C_6H_6 AND C_6D_6

E_{1g} class	C_6H_6	C_6D_6
$\nu_{\text{calc.}}$ (cm^{-1})	851·1	660·7
$\nu_{\text{obs.}}$	*848·9*	*661·7*
S'_{10} (Å)	0·2223	0·1959
$\Phi_3 S'^2_{10}$ (%)	100·0	100·0
Z'_{2a} (Å)	−0·0130	−0·0190
z'_{2a}	0·0884	0·0647
ω (rad.)	0·01072	0·01567
Raman int.:		
calc.	1·04	1·50
obs.	*1·0*	*1·5*

$$Z'_{2a} = Z'_{3a} = -Z'_{5a} = -Z'_{6a} = -2^{-1}3^{\frac{1}{2}}Z'_{1b} = -3^{\frac{1}{2}}Z'_{2b} = 3^{\frac{1}{2}}Z'_{3b} = 2^{-1}3^{\frac{1}{2}}Z'_{4b} = 3^{\frac{1}{2}}Z'_{5b} = -3^{\frac{1}{2}}Z'_{6b}, \quad Z'_{1a} = Z'_{4a} = 0.$$

Table 9. Results for the A_{2u} class of C_6H_6 and C_6D_6

A_{2u} class	C_6H_6	C_6D_6
$\nu_{\text{calc.}}$ (cm^{-1})	673·0	494·1
$\nu_{\text{obs.}}$	*671*	*496·5v*
S'_{11} (Å)	0·2321	0·1989
$\Phi_4 S'^2_{11}$ (%)	100·0	100·0
Z'_1 (Å)	−0·0073	−0·0117
z'_1	0·0874	0·0695
i.r. int.:		
calc.	22	12
obs.	*18*	*14*

$$Z'_1 = Z'_2 = Z'_3 = Z'_4 = Z'_5 = Z'_6.$$

Table 10. Results for the B_{1u} class of C_6H_6 and C_6D_6

B_{1u} class	C_6H_6		C_6D_6	
$\nu_{\text{calc.}}$ (cm^{-1})	1012·2	3067·8	961·5	2284·4
$\nu_{\text{obs.}}$	*ca. 1010*	*ca. 3062*	*ca. 963*	*ca. 2290*
S'_{12} (Å)	0·1734	0·0328	0·1660	0·0562
S'_{13}	−0·0068	0·1087	−0·0131	0·0921
$\Sigma_2 S'^2_{12}$ (%)	98·8	1·2	95·4	4·6
$\Omega_2 S'^2_{13}$	1·2	98·8	4·6	95·4
$\bar{R}'_1$ (Å)	0·0204	0·0039	0·0196	0·0066
$\bar{r}'_1$	0·0232	−0·0405	0·0249	−0·0310

$$\bar{R}'_1 = -\bar{R}'_2 = \bar{R}'_3 = -\bar{R}'_4 = \bar{R}'_5 = -\bar{R}'_6.$$

Table 11. Results for the B_{2u} class of C_6H_6 and C_6D_6

B_{2u} class	Ingold C_6H_6		Ingold C_6D_6		Mair & Hornig C_6H_6		Mair & Hornig C_6D_6	
$\nu_{\text{calc.}}$ (cm^{-1})	1629·8	1122·3	1572·5	822·8	1307·2	1147·8	1285·7	825·6
$\nu_{\text{obs.}}$	*ca. 1648*	*ca. 1110*	*ca. 1571*	*ca. 825*	*1310*	*1150*	*ca. 1285*	*ca. 825*
S'_{14} (Å)	0·0645	0·0383	0·0713	0·0227	0·0731	0·0355	0·0805	0·0109
S'_{15}	−0·1006	0·1327	−0·0643	0·1259	−0·1085	0·1349	−0·0588	0·1353
$\Lambda_2 S'^2_{14}$ (%)	66·3	34·0	84·1	16·2	81·0	21·8	100·0	2·9
$\Gamma_2 S'^2_{15}$	28·5	71·9	12·1	88·3	37·3	65·6	11·1	91·7
$2\mu_2 S'_{14} S'_{15}$	5·2	−5·9	3·8	−4·5	−18·3	12·6	−11·1	5·4
U'_1 (Å)	0·0152	0·0090	0·0168	0·0053	0·0172	0·0084	0·0190	0·0026
u'_1	−0·0259	0·0632	−0·0094	0·0568	−0·0271	0·0634	−0·0050	0·0578

$$U'_1 = -U'_2 = U'_3 = -U'_4 = U'_5 = -U'_6.$$

Table 12. Results for the E_{2u} class of C_6H_6 and C_6D_6

E_{2u} class	C_6H_6		C_6D_6	
$\nu_{\text{calc.}}$	404·2	984·0	349·7	804·6
$\nu_{\text{obs.}}$	*405*	*ca. 970*	*ca. 352*	*ca. 793*
S_{16} (Å)	0·2784	0·1176	0·2425	0·1741
S_{17}	0·0679	0·2495	0·0359	0·2390
S^*_{16}	0·3758	−0·4301	0·3894	−0·2892
$\Theta_2 S^2_{16}$ (%)	150·7	11·1	132·1	29·6
$\Phi_2 S^2_{17}$	24·7	137·0	8·0	153·7
$2\eta_2 S_{16} S_{17}$	−75·4	−48·1	−40·1	−83·3
$\Theta^*_2 S^{*2}_{16}$	68·7	37·0	85·2	20·5
$\Phi^*_2 S^2_{17}$	16·1	89·4	5·2	100·3
$2\eta^*_2 S^*_{16} S_{17}$	15·2	−26·4	9·6	−20·8
Z_{2a} (Å)	0·0348	0·0147	0·0303	0·0218
z_{2a}	0·0792	−0·0770	0·0806	−0·0488

$$Z'_{2a} = -Z'_{3a} = Z'_{5a} = -Z'_{6a} = 2^{-1}3^{\frac{1}{2}}Z'_{1b} = -3^{\frac{1}{2}}Z'_{2b} = -3^{\frac{1}{2}}Z'_{3b} = 2^{-1}3^{\frac{1}{2}}Z'_{4b} = -3^{\frac{1}{2}}Z'_{5b} = -3^{\frac{1}{2}}Z'_{6b},\ Z'_{1a} = Z'_{4a} = 0.$$

TABLE 13. RESULTS FOR THE E_{1u} CLASS OF C_6H_6 AND C_6D_6

E_{1u} class	C_6H_6			C_6D_6		
$\nu_{\text{calc.}}$	1033·4	1489·2	3079·0	807·9	1331·2	2288·4
$\nu_{\text{obs.}}$	*1033*	*1480*	*ca. 3080*	*811*	*1332*	*2283*
S'_{18} (Å)	0·0813	0·1515	0·0076	0·1025	0·1077	0·0157
S'_{19}	0·0424	−0·0378	−0·0088	0·0270	−0·0476	−0·0164
S'_{20}	0·0040	−0·0057	0·1084	0·0042	−0·0144	0·0917
$\Gamma_4 S'^2_{18}$ (%)	29·4	71·0	0·1	59·9	40·1	0·5
$2\Lambda_4 S'^2_{19}$	64·2	35·4	0·9	33·3	62·8	4·3
$\Omega_4 S'^2_{20}$	0·4	0·6	99·0	0·6	4·1	95·4
$2^{\frac{3}{2}}\mu_4 S'_{18} S'_{19}$	6·0	−7·0	0·0	6·2	−7·0	−0·2
$\overline{R}'_{1a}$ (Å)	−0·0165	−0·0096	0·0053	−0·0138	−0·0121	0·0090
$\bar{r}'_{1a}$	−0·0188	−0·0129	−0·0573	−0·0162	−0·0204	−0·0439
U'_{2a}	−0·0102	−0·0135	0·0005	−0·0036	−0·0170	0·0016
u'_{2a}	−0·0646	0·0500	−0·0005	−0·0637	0·0214	−0·0009
i.r. int.:						
calc.	8·8	11·2	19	7·1	2·3	10
obs.	*7·9*	*9·2*	*ca. 17*	*ca. 10*	*2·5*	*16*

$$\overline{R}'_{1a} = 2\overline{R}'_{2a} = -2\overline{R}'_{3a} = -\overline{R}'_{4a} = -2\overline{R}'_{5a} = 2\overline{R}'_{6a} = -2.3^{-\frac{1}{2}}\overline{R}'_{2b} = -2.3^{-\frac{1}{2}}\overline{R}'_{3b} = 2.3^{-\frac{1}{2}}\overline{R}'_{5b} = 2.3^{-\frac{1}{2}}\overline{R}'_{6b},$$
$$\overline{R}'_{1b} = R'_{4b} = 0,$$
$$U'_{2a} = U'_{3a} = -U'_{5a} = -U'_{6a} = 2^{-1}3^{\frac{1}{2}}U'_{1b} = 3^{\frac{1}{2}}U'_{2b} = -3^{\frac{1}{2}}U'_{3b} = -2^{-1}3^{\frac{1}{2}}U'_{4b} = -3^{\frac{1}{2}}U'_{5b} = 3^{\frac{1}{2}}U'_{6b}, \quad U'_{1a} = U'_{4a} = 0.$$

TABLE 14. RESULTS FOR MONODEUTEROBENZENE (C_{2v})

ν (cm^{-1})		Raman int.		ϱ		i.r. int.	
calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
A_1 class		*a*		*p*		*a*	
3075·5	*3066 v*	8·0	*i. 24*	0·41	*i. 0·43*	4·6	*ca. 2*
3069·9	*3060*	4·2	*i. 24*	0·69	*i. 0·43*	1·0	*ca. 1*
3069·9	*3054·8*	5·4	*i. 24*	0·41	*i. 0·43*	0·7	*ca. 1*
2282·9	*2269·0*	4·3	*2·4*	0·51	*0·61*	1·7	*2·3*
1589·9	*1591·1*	1·6	*2·6*	0·85	*0·8*	0·05	—
1482·2	*1479*	0·02	*mw*	0·38	—	5·2	*ca. 4*
1177·7	*1175·6*	1·4	*1·8*	0·84	*0·8*	0·01	—
1029·9	*1031·0*	0·16	*0·4*	0·09	—	4·0	*2·1*
1006·0	*1006·8*	2·0	*2·4*	0·09	*0·40*	0·11	—
979·1	*980·0*	9·3	*(9·3)*	0·08	*0·28*	0·14	—
603·5	*i. 601·8*	1·1	*i. 2·1*	0·86	*i. 0·81*	0·00	—
A_2 class		*a*		*dp*		*ia*	
984·0	*ca. 970*	0·00	—	—	—	—	—
851·1	*849·9*	0·52	*i. 1·2*	—	—	—	—
404·2	*ca. 405*	0·00	—	—	—	—	—
B_1 class (Ingold)		*a*		*dp*		*a*	
3078·9	*3077*	0·00	*i. 24*	—	—	9·4	*ca. 3*
3044·0	*3044*	4·1	*i. 24*	—	—	0·00	—
1623·8	*ca. 1620*	0·1	—	—	—	0·08	—
1592·6	*1574·3*	1·8	*1·8*	—	—	0·2	—
1455·0	*1449*	0·1	*mw*	—	—	4·0	*ca. 4*
1300·7	*1292*	0·2	*0·3*	—	—	0·00	*0·1*
1145·1	*1158·2*	0·7	*1·0*	—	—	0·07	*0·1*
1074·7	*1075*	0·2	*0·3*	—	—	2·0	*1·4*
857·4	*857·1*	0·3	*i. 1·2*	—	—	2·1	*1·6*
603·0	*i. 601·8*	1·0	*i. 2·1*	—	—	0·01	—
B_2 class		*a*		*dp*		*a*	
989·4	*995*	0·00	*w*	—	—	0·0	*0·2*
934·3	*922*	0·08	*w*	—	—	0·4	*1·2*
780·4	*778·7*	0·32	*0·5*	—	—	4·0	*11*
700·7	*698 v*	0·01	—	—	—	3·2	*5·5*
607·0	*608 v*	0·08	—	—	—	13	*24*
382·4	*380*	0·03	*mw*	—	—	0·1	*0·3*

TABLE 15. RESULTS FOR *ortho*-DIDEUTEROBENZENE (C_{2v})

ν (cm^{-1})		Raman int.			
calc.	obs.	calc.	obs.	ϱ calc.	i.r. int. calc.
A_1 class (Ingold)		*a*		*p*	*a*
3075·4	*i. 3064*	10·4	*i. 14*	0·42	4·0
3049·5	*3035·3*	5·0	*5*	0·69	0·8
2285·7	*2280·8*	6·4	*7*	0·40	2·7
1617·8	—	0·2	—	0·86	0·04
1582·3	*i. 1588·0*	1·8	*i. 4*	0·85	0·4
1455·5	—	0·3	—	0·35	4·3
1146·9	*1160*	0·7	*2*	0·86	0·03
1046·0	*1055·4*	0·4	*1*	0·23	3·0
974·7	*976·0*	10·8	*(11)*	0·08	0·03
842·4	*841·6*	0·5	*1*	0·70	1·0
596·4	*i. 598·3*	0·9	*i. 5*	0·86	0·01
A_2 class		*a*		*dp*	*ia*
988·7	—	0·00	—	—	—
894·5	—	0·23	—	—	—
775·9	*773·8*	0·27	*0*	—	—
665·9	*658*	0·06	*0*	—	—
373·2	*i. 384*	0·02	*i. 0*	—	—
B_1 class		*a*		*dp*	*a*
3076·0	*i. 3064*	0·0	*i. 14*	—	7·2
3057·1	*3053*	1·9	*14*	—	0·5
2280·1	*2270·5*	2·4	*4*	—	0·8
1583·6	*i. 1588*	1·5	*i. 4*	—	0·2
1440·8	—	0·0	—	—	3·4
1258·4	*1248*	0·3	*0*	—	0·00
1130·8	*1130·7*	0·9	*2*	—	0·8
995·3	*992·8*	0·0	*3*	—	0·01
864·5	*856*	0·1	*0*	—	3·2
598·2	*i. 598·3*	1·0	*i. 5*	—	0·01
B_2 class		*a*		*dp*	*a*
968·2	—	0·02	—	—	0·2
782·6	*782·1*	0·45	*1*	—	5·7
575·2	*581·6*	0·15	*0*	—	13
392·6	*i. 384*	0·03	*0*	—	0·1

TABLE 16. RESULTS FOR *meta*-DIDEUTEROBENZENE (C_{2v})

ν (cm^{-1})		Raman int.			
calc.	obs.	calc.	obs.	ϱ calc.	i.r. int. calc.
A_1 class		*a*		*p*	*a*
3077·4	*i. 3058·8*	3·0	*i. 9*	0·41	7·4
3070·2	*i. 3058·8*	7·9	*i. 9*	0·41	0·2
3048·6	*3047*	4·4	*4*	0·72	0·2
2284·2	*2284·4*	6·3	*4*	0·41	0·9
1585·7	*1583·1*	1·9	*3*	0·84	0·2
1430·9	*1418·8*	0·3	*0*	0·85	3·4
1097·5	*1107·7*	0·8	*1*	0·77	1·4
1004·7	*1006·1*	3·3	*4*	0·09	0·00
965·3	*970·5*	7·9	*(8)*	0·08	0·01
841·2	*838·1*	0·5	*1*	0·86	2·8
595·8	*i. 598·4*	0·9	*i. 3*	0·86	0·03
A_2 class		*a*		*dp*	*ia*
938·6	—	0·22	—	—	—
713·5	*710·5*	0·51	*2*	—	—
375·4	*374*	0·04	*0*	—	—
B_1 class (Ingold)		*a*		*dp*	*a*
3061·7	*i. 3058·8*	2·1	*i. 9*	—	4·8
2281·7	*2272·1*	2·4	*2*	—	2·6
1616·2	—	0·1	—	—	0·05
1579·0	*1563·0*	2·0	*1*	—	0·00
1464·1	—	0·03	—	—	4·7
1276·1	—	0·2	—	—	0·00
1157·3	*1168·4*	0·8	*2*	—	0·00
1045·8	*1051*	0·05	*0*	—	2·8
876·2	*855*	0·2	*0*	—	1·4
597·8	*i. 598·4*	1·0	*i. 3*	—	0·01
B_2 class		*a*		*dp*	*a*
986·7	—	0·00	—	—	0·00
927·8	—	0·07	—	—	1·0
816·7	*818*	0·43	*0·5*	—	2·7
700·5	—	0·00	—	—	3·4
566·6	—	0·05	—	—	12·0
391·5	—	0·01	—	—	0·1

ν (cm^{-1})		Raman int.		ϱ		i.r. int.	
calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
A_g class		a		p		ia	
3063·5	3055·0	13·4	i. 17	0·60	i. 0·50	—	—
2278·6	2280·0	8·5	6·6	0·51	0·62	—	—
1579·7	1569·3!	1·4	1·9	0·79	0·8	—	—
1174·6	1173·4	1·4	2·5	0·81	0·87	—	—
975·6	978·0	11·1	(11·1)	0·08	0·41	—	—
597·9	600·9!	1·1	i. 1·6	0·86	i. 0·85	—	—
A_u class		ia				ia	
984·0	ca. 970	—	—	—	—	—	
404·2	ca. 405	—	—	—	—	—	—
B_{1g} class		a		dp		ia	
3044·0	3042	4·1	i. 17	—	—	—	—
1586·3	1587·0!	2·2	3·9	—	—	—	—
1290·9	1309·0	0·4	0·2	—	—	—	—
913·6	908·5	1·0	1·0	—	—	—	—
597·4	596·6	0·9	i. 1·6	—	—	—	—
B_{1u} class		ia				a	
886·7	876v	—	—	—	—	3·2	9
596·7	597v	—	—	—	—	15	16
362·4	367v	—	—	—	—	0·3	1·4
B_{2g} class		a		dp			
851·1	849·5	0·52	0·5	—	—	—	—
B_{2u} class		ia				a	
3071·5	ca. 3040v	—	—	—	—	3·1	i. 1·6
2287·5	2275v	—	—	—	—	3·6	3·9
1476·4	1469v	—	—	—	—	5·4	5·0
1027·8	1033v	—	—	—	—	3·6	5·3
988·7	992v	—	—	—	—	0·6	0·6
B_{3g} class		a		dp		ia	
959·2	967	0·06	ms	—	—	—	—
738·2	736	0·26	0·3	—	—	—	—
634·7	634·1	0·36	0·5	—	—	—	—
B_{3u} class (Ingold)		ia				a	
3078·9	ca. 3079v	—	—	—	—	9·2	i. 4·5
1616·9	ca. 1613	—	—	—	—	0·4	—
1402·6	1413v	—	—	—	—	2·4	4·0
1087·8	1106v	—	—	—	—	1·2	1·2
817·4	814v	—	—	—	—	2·8	4·8
(Mair & Hornig)							
3078·9	ca. 3079v	—	—	—	—	9·2	i. 4·5
1419·0	1413v	—	—	—	—	2·9	4·0
1291·8	ca. 1291	—	—	—	—	0·00	—
1103·1	1106	—	—	—	—	1·1	1·2
818·1	814v	—	—	—	—	2·9	4·8

ν (cm^{-1})		Raman int.		ϱ	i.r. int.
calc.	obs.	calc.	obs.	calc.	calc.
A_1 class		a		p	a
3075·5	3058·7	8·8	10	0·41	4·4
3056·4	i. 3050·6	2·1	i. 7	0·84	0·3
2287·5	2288·1	8·4	9	0·38	2·5
2279·6	i. 2280·8	2·4	i. 5	0·85	0·2
1578·1	1582·2	1·7	3	0·86	0·4
1418·8	—	0·3	1	0·81	3·1
1097·0	1095·5	0·9	2	0·82	1·4
990·1	992·3	1·6	4	0·09	0·01
963·5	965·3	9·1	(9)	0·08	0·01
835·2	i. 838·7	0·6	i. 3	0·81	3·3
591·0	i. 592	0·8	i. 4	0·86	0·02
A_2 class		a		dp	ia
938·6	920	0·22	0	—	—
713·5	712	0·51	2	—	—
375·4	i. 374	0·04	i. 1	—	—
B_1 class (Ingold)					
3061·7	i. 3050·6	2·0	i. 7	—	4·8
2281·5	i. 2280·8	2·4	i. 5	—	2·5
1610·5	—	0·2	—	—	0·02
1567·7	1575·3	1·5	4	—	0·2
1435·4	—	0·02	—	—	3·4
1201·1	—	0·04	—	—	0·1
1142·4	1150·4	0·7	2	—	0·3
881·6	863·4	0·04	0	—	2·8
843·1	i. 838·7	0·5	i. 3	—	0·7
591·0	i. 592	0·9	i. 4	—	0·00
B_2 class		a		dp	a
984·9	—	0·00	—	—	0·1
834·0	i. 838·7	0·10	i. 3	—	1·6
779·9	779·3	0·32	1	—	3·2
659·5	657	0·02	0	—	0·2
542·1	—	0·20	—	—	12
372·4	i. 374	0·01	i. 1	—	0·00

TABLE 19. RESULTS FOR *sym.*-TRIDEUTEROBENZENE (D_{3h})

ν (cm^{-1})		Raman int.		ϱ		i.r. int.	
calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
A_1' class		*a*		*p*		*ia*	
3070·4	*3052·7*	8·7	(*8·7*)	0·41	*0·45*	—	—
2285·5	*2281·9*	8·4	*5*	0·36	*0·45*	—	—
1004·0	*1003·6*	4·0	*3·5*	0·09	*0·15*	—	—
950·7	*956·2*	6·9	*8*	0·08	*0·15*	—	—
A_2' class (Ingold)		*ia*				*ia*	
1605·0	*ca. 1600*	—	—	—	—	—	—
1249·3	*ca. 1230*	—	—	—	—	—	—
899·8	*ca. 916*	—	—	—	—	—	—
(Mair & Hornig)							
1311·7	—	—	—	—	—	—	—
1246·9	—	—	—	—	—	—	—
905·0	—	—	—	—	—	—	—
A_2'' class		*ia*				*a*	
916·1	*915v*	—	—	—	—	2·9	*4·3*
700·5	*691v*	—	—	—	—	3·4	*ca. 5*
529·5	*533v*	—	—	—	—	11	*6·7*
E' class		*a*		*dp*		*a*	
3061·7	*3082*	3·9	—	—	—	9·5	*5·1*
2281·6	*2292*	4·8	—	—	—	5·1	*5·5*
1573·6	*1573·1*	3·4	*1·5*	—	—	0·2	*0·4*
1427·0	*1408*	0·5	—	—	—	6·7	*4·4*
1087·1	*1101·8*	1·3	*0·7*	—	—	2·8	*1·5*
841·2	*833·5*	1·0	*0·6*	—	—	5·1	*4·2*
590·1	*593·0*	1·8	*0·7*	—	—	0·07	*0·3*
E'' class		*a*		*dp*		*ia*	
938·6	*947*	0·43	*m*	—	—	—	—
713·5	*710·2*	1·02	*0·6*	—	—	—	—
375·4	*372·7*	0·08	*mw*	—	—	—	—

TABLE 20. RESULTS FOR 2:3:5:6-TETRADEUTEROBENZENE (V_h)

ν (cm^{-1})		Raman int.		ϱ		i.r. int.	
calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
A_g class		*a*		*p*		*ia*	
3053·8	*3045·0*	8·9	*8*	0·52	*0·72*	—	—
2282·5	*2285·0*	12·6	*i. 11*	0·41	*i. 0·53*	—	—
1567·5	*1572·0*	2·2	*i. 5*	0·80	*i. 0·87*	—	—
960·6	*960·9*	10·4	(*10·4*)	0·08	*0·39*	—	—
872·5	*862·2*	1·3	*1·6*	0·77	*0·87*	—	—
583·7	*585·8!*	0·8	*i. 1·3*	0·86	*i. 0·84*	—	—
A_u class		*ia*				*ia*	
804·6	*ca. 793*	—	—	—	—	—	—
349·7	*ca. 352*	—	—	—	—	—	—
B_{1g} class		*a*		*dp*		*ia*	
2274·8	*2272*	4·6	*i. 11*	—	—	—	—
1562·7	*1564·0*	1·2	*i. 5*	—	—	—	—
1242·0	*1255·3*	0·6	*0·5*	—	—	—	—
956·7	*954*	0·6	*mw*	—	—	—	—
587·5	*589·0!*	1·0	*i. 1·3*	—	—	—	—
B_{1u} class		*ia*				*a*	
940·2	*925v*	—	—	—	—	2·0	*3·7*
545·2	*548v*	—	—	—	—	13	*14*
378·8	*383v*	—	—	—	—	0·5	*1·0*
B_{2g} class		*a*		*dp*		*ia*	
660·7	*663·6*	0·75	*0·9*	—	—	—	—
B_{2u} class		*ia*				*a*	
3075·2	*3078v*	—	—	—	—	6·2	*5·9*
2285·7	*i. 2280v*	—	—	—	—	1·7	*i. 6·8*
1351·7	*1353v*	—	—	—	—	1·3	*1·3*
978·1	*977v*	—	—	—	—	0·01	*0·2*
812·4	*812v!*	—	—	—	—	3·9	*i. 4·2*
B_{3g} class		*a*		*dp*		*ia*	
919·9	*929·7*	0·15	*0·3*	—	—	—	—
768·0	*767·1*	0·28	*0·4*	—	—	—	—
616·8	*615·1*	0·15	*0·3*	—	—	—	—
B_{3u} class (Ingold)		*ia*				*a*	
2288·8	*i. 2280v*	—	—	—	—	5·5	*i. 6·8*
1599·1	*ca. 1585*	—	—	—	—	0·6	—
1422·0	*1439v*	—	—	—	—	3·5	*4·3*
1046·0	*1057v*	—	—	—	—	2·5	*1·9*
816·9	*819v!*	—	—	—	—	1·6	*ca. 2*
(Mair & Hornig)							
2288·8	*i. 2280v*	—	—	—	—	5·5	*i. 6·8*
1437·5	*1439v*	—	—	—	—	4·0	*4·3*
1287·0	*ca. 1290*	—	—	—	—	0·01	—
1052·9	*1057v*	—	—	—	—	2·3	*1·9*