105. *Excited States of Benzene. Part XI. Comparisons between the First Ultraviolet Absorption and Fluorescence Band Systems of Isotopically Isomeric Benzenes, and Further Determinations of the Vibration Frequencies of the Upper Electronic State.*

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Consideration is given to the assignment of observed frequencies to vibrations of the upper electronic state, and also to the indirect determination of a number of upper-state vibration frequencies which have not been spectrally observed. Both subjects are discussed on the basis of comparisons between the ultraviolet spectra of the different isotopically isomeric benzenes, the central principle being that isotopic substitution cannot change the forces acting in any given electronic state. Two methods are employed, both new in the study of excited polyatomic molecules, though well known in their application to normal molecules. One is the use of the product theorem in order to provide relationships between the upper-state fundamental frequencies of vibrations of the various isotopic isomerides. The other consists in the calculation, from a limited number of upper-state frequencies, of a simplified force-system, applicable in common to all the excited molecules, and the subsequent use of this system for the approximate location of other upper-state frequencies, and thus for their eventual determination by reference back to the spectra. In these ways, assignments of many observed frequencies to upper-state vibrations are made or justified, and some unobserved vibration frequencies of the excited molecules are calculated. The determined fundamental frequencies of the upper electronic states of all the benzenes studied are correlated in tables.

Scope.—In the preceding papers we have been dealing with individual absorption and fluorescence spectra of the various isotopic isomerides of benzene. In those papers we have given a detailed interpretation of each spectrum, but have presented the supporting arguments only in so far as they could be based in each case on the internal evidence of the spectrum under consideration. An important section of the basis of the interpretation depends, however, on comparisons between the different spectra, particularly on comparisons of the absorption and fluorescence spectra of one isotopic form of benzene with those of another. These arguments of comparison we now present, thus completing the foundations of the assignments already given.

In making the comparisons, we shall introduce two methods, neither of which has before been applied to the study of electronic spectra of polyatomic molecules. The first (Section A) is the use of the product theorem of Teller and Redlich, in order to provide calculable relationships between the fundamental frequencies of isotopically isomeric molecules in their electronically excited states. Hitherto it has been implicit in all discussions of the product theorem that electronic ground states are under consideration; and all previous applications have been to ground states. But there is clearly no reason of principle why the theorem should not be applied to any electronically excited state which is sufficiently long-lived to give sharp vibrational energy levels.

The second method (Section B) consists in the calculation, from a limited number of determined frequencies, of a simplified force-system for the electronically excited state (the same system for all isotopically isomeric forms of the molecule), and the subsequent use of the system for the approximate location of other fundamental frequencies, and thus for their eventual identification by reference back to the spectra. Force systems have commonly been thus employed in the study of polyatomic molecules in their electronic ground states, but we know of no previous attempt to set up and use such a force-system for a polyatomic molecule in an excited state. Since, without these methods, our assignments of bands to vibration frequencies, and of frequencies to vibrations, could not have been nearly as extensive as they actually are, it seems that the two working tools whose employment is here introduced have some general importance for the electronic spectroscopy of polyatomic molecules.

(A) *Product Theorem applied to the Excited State.*

(1) *Theoretical Product Ratios for the* $\mathbf{B}_{2u}$ *State*.—The product theorem is, in general principle, a complete statement of the relationships which subsist between the fundamental vibration frequencies of two isotopically isomeric molecules, in an arbitrary but identical electronic state, with an arbitrary but harmonic potential system. The relationships take the form of theoretically given ratios, for pairs of isotopically isomeric molecules, of the products of complete sets of frequencies of vibrations of the same symmetry class, if the molecules have identical symmetry; or of products of the sets of frequencies of vibrations of corresponding sets of symmetry classes, if the molecules have different symmetry. The general formula, together with an explanation of the symbols, as they must be understood when the molecules have like symmetry, and when they have unlike symmetry, has been given in a former paper (*J.*, 1946, 232). In the same paper a number of theoretical product ratios were evaluated for the ground state, $\mathbf{A}_{1g}$, of benzene.

The only point of difference which has to be taken into account in calculating theoretical ratios for the excited state, $\mathbf{B}_{2u}$, of benzene arises from the slightly different dimensions of the excited molecule. We know that both the normal and the excited molecules possess the same symmetry, $\mathbf{D}_{6h}$. However, the excited molecule is somewhat larger than the other, as is shown by the degradation of the rotational structure of bands towards the red in both absorption and fluorescence spectra. From a semi-quantitative estimate of the variation of band intensity along the main totally symmetrical progressions, in particular, from the result that the second members of such progressions are the strongest members, whilst the first and third possess about equal intensity, it is possible independently to estimate the increase of size accompanying the electronic excitation. Using both methods, Sponer, Nordheim, Sklar, and Teller have estimated that the C–C bond-length increases by 1·2—1·5% (*J. Chem. Physics*, 1939, **7**, 207). From our analysis of the spectra, we shall conclude (Part XII) that the C–C bond-length increases by 2·5%, whilst the C–H bond-length decreases by 1·0%, as a result of the electronic excitation. We take these values in calculating upper-state product ratios.

Some theoretical product ratios for the electronically excited state are given in Table I. They are called harmonic values, because of the neglect of the anharmonicity of the vibrations. Just as for the ground state (*J.*, 1946, 233), so also for the excited state, the general effect of anharmonicity should be to cause the ratios of the products of observed frequencies to fall slightly below the theoretical ratios here given. This is borne out by our experience. The effect of anharmonicity on the observed product ratios of the excited state is very similar in magnitude to the previously found effect on the product ratios of the ground state; and therefore, in calculating frequencies of the excited state from the product ratios, we make an allowance for anharmonicity according to the same scale as that adopted in the former calculations relating to the ground state (*loc. cit.*).

TABLE I.

Theoretical (Harmonic) Values of the Frequency Product Ratios for Some Pairs of the Excited Molecules C_6H_6, C_6H_5D, 1 : 4-$C_6H_4D_2$, 1 : 3 : 5-$C_6H_3D_3$, 1 : 2 : 4 : 5-$C_6H_2D_4$, *and* C_6D_6.

(a) *Greatest common symmetry* D_{6h}.

Symmetry class.	$\frac{C_6H_6}{C_6D_6}$.	Symmetry class.	$\frac{C_6H_6}{C_6D_6}$.	Symmetry class.	$\frac{C_6H_6}{C_6D_6}$.
A_{1g}	1·414	B_{1u}	1·414	E_g^+	1·978
A_{2g}	1·291	B_{2g}	1·414	E_u^+	1·414
A_{2u}	1·362	B_{2u}	1·414	E_g^-	1·291
				E_u^-	1·925

(b) *Greatest common symmetry* D_{3h}.

D_{6h} Classes.	D_{3h} Class.	$\frac{C_6H_6}{C_6H_3D_3}$.	$\frac{C_6H_3D_3}{C_6D_6}$.	D_{6h} Classes.	D_{3h} Class.	$\frac{C_6H_6}{C_6H_3D_3}$.	$\frac{C_6H_3D_3}{C_6D_6}$.
A_{1g}, B_{1u}	A_1'	1·414	1·414	E_g^+, E_u^-	E'	1·960	1·962
A_{2g}, B_{2u}	A_2'	1·346	1·352	E_u^+, E_g^-	E''	1·346	1·352
A_{2u}, B_{2g}	A_2''	1·387	1·388				

(c) *Greatest common symmetry* V_h.

D_{6h} Classes.	V_h class.	$\frac{C_6H_6}{C_6H_4D_2}$.	$\frac{C_6H_6}{C_6H_2D_4}$.	$\frac{C_6H_4D_2}{C_6H_2D_4}$.	$\frac{C_6H_4D_2}{C_6D_6}$	$\frac{C_6H_2D_4}{C_6D_6}$.
A_{1g}, E_g^+	A_g	1·414	1·998	1·414	1·998	1·414
A_{1u}, E_u^+	A_u	1·000	1·414	1·414	1·414	1·000
A_{2g} E_g^+	B_{1g}	1·368	1·877	1·371	1·884	1·373
A_{2u}, E_u^+	B_{1u}	1·396	1·380	0·988	1·380	1·396
B_{1g}, E_g^-	B_{2g}	1·000	1·291	1·291	1·291	1·000
B_{1u}, E_u^-	B_{2u}	1·396	1·948	1·396	1·948	1·396
B_{2g}, E_g^-	B_{3g}	1·326	1·369	1·031	1·374	1·331
B_{2u}, E_u^-	B_{3u}	1·396	1·948	1·396	1·948	1·396

(d) *Greatest common symmetry* C_{2v}.

D_{6h} classes.	C_{2v} class.	$\frac{C_6H_6}{C_6H_5D}$.	$\frac{C_6H_5D}{C_6H_4D_2}$.	$\frac{C_6H_5D}{C_6H_3D_3}$.	$\frac{C_6H_5D}{C_6H_2D_4}$.	$\frac{C_6H_5D}{C_6D_6}$.
A_{1g}, B_{1u}, E_g^+, E_u^-	A_1	1·405	1·405	1·973	2·773	5·474
A_{2g}, B_{2u}, E_g^+, E_u^-	B_1	1·382	1·383	1·910	2·649	5·072
A_{1u}, B_{1g}, E_u^+, E_g^-	A_2	1·000	1·000	1·346	1·821	1·823
A_{2u}, B_{2g}, E_u^+, E_g^-	B_2	1·359	1·362	1·375	1·387	2·583

(2) *Excited* C_6H_6 *and* C_6D_6 : *The* A_{1g} *Vibrations* (cf. Part II, Sections 2 and 7; and Part IV, Sections 2 and 7).—The fundamental frequencies of the ring-swelling vibration, A_{1g}(C), are well established: they are 923 cm.$^{-1}$ for excited benzene and 879 cm.$^{-1}$ for excited hexadeuterobenzene. The fundamental frequency of the hexagonal hydrogen-stretching vibration, A_{1g}(H), of benzene,

3130 cm.$^{-1}$, also appears clearly from the analysis of the absorption spectrum of benzene (Part II, Section 7).

On the other hand, the frequency of the totally symmetrical hydrogen-stretching vibration of hexadeuterobenzene does not unambiguously emerge from our analysis of the absorption spectrum of that substance. We have suggested that the relevant band is that at 40146 cm.$^{-1}$, in which case the vibration frequency would be 2357 cm.$^{-1}$ (*Nature*, 1946, **158**, 163). But the band has another conceivable explanation (Part IV, Table I), and there may be overlapping bands in this region. Therefore we have calculated this fundamental frequency, from those mentioned in the preceding paragraph, with the help of the product rule. We find :

$$\text{For } C_6D_6 :\!-A_{1g}(\text{H})_{\text{excited}} = 2340 \text{ cm.}^{-1}$$

Just as for benzene, this frequency of excited hexadeuterobenzene is a little above the corresponding frequency for the normal state of that substance, 2292·6 cm.$^{-1}$, as given by the Raman spectrum of liquid hexadeuterobenzene (Poole, *J.*, 1946, 245), or 2286 cm.$^{-1}$, as given by the fluorescence spectrum of hexadeuterobenzene vapour (Part IV, Section 6).

(3) *Excited* C_6H_6 *and* C_6D_6 : *The* B_{1u} *Vibrations.*—These vibrations do not appear to leave any record of their frequencies in the ultraviolet spectra of benzene and hexadeuterobenzene. On the other hand, the two A_{1g} and two B_{1u} vibrations of each of these compounds are collectively related through the product theorem to the four A_1' vibrations of 1 : 3 : 5-trideuterobenzene, and we know the frequencies of all four of these vibrations of excited 1 : 3 : 5-trideuterobenzene from our analysis of the appropriate absorption spectrum (Part VI, Sections 2 and 8). It is therefore possible to calculate the product of the two B_{1u} frequencies for excited benzene, and for excited hexadeuterobenzene.

On account of the weak coupling of hydrogen-stretching vibrations, the frequency of the trigonal hydrogen-stretching vibration, B_{1u}(H), either for excited benzene or for excited hexadeuterobenzene, must be very nearly identical with that of the corresponding hexagonal hydrogen-stretching vibration, A_{1g}(H). By assuming exact equivalence, we can use the calculated frequency products to compute, with very little error, the frequencies of the trigonal carbon-bending vibrations, B_{1u}(C), of excited benzene and hexadeuterobenzene. We thus obtain the following data :

$$\text{For } C_6H_6 :\!-B_{1u}(\text{C})_{\text{excited}} = 985 \text{ cm.}^{-1}; \quad B_{1u}(\text{H})_{\text{excited}} = 3130 \text{ cm.}^{-1}$$
$$\text{For } C_6D_6 :\!-B_{1u}(\text{C})_{\text{excited}} = 940 \text{ cm.}^{-1}; \quad B_{1u}(\text{H})_{\text{excited}} = 2340 \text{ cm.}^{-1}$$

The corresponding fundamental frequencies for the ground state of benzene are B_{1u}(C) = 1010 cm.$^{-1}$ and B_{1u}(H) = 3060 cm.$^{-1}$, and for the ground state of hexadeuterobenzene, B_{1u}(C) = 963 cm.$^{-1}$ and B_{1u}(H) = 2290 cm.$^{-1}$. These figures, given by Herzfeld, Ingold, and Poole, are based largely on Raman and infra-red combination tones (*J.*, 1946, 316). Thus the carbon-bending frequencies are a little reduced, and the hydrogen-stretching frequencies are a little raised, by the electronic excitation.

It is useful to check the four frequencies of the excited state against the product theorem, since the B_{1u} product ratio is not determined by the ratios employed in the calculation of the frequency products. We find :

$$\frac{\Pi B_{1u}(C_6H_6{}^*)}{\Pi B_{1u}(C_6D_6{}^*)} = \frac{985 \times 3130}{940 \times 2340} = 1{\cdot}403 \text{ (Harmonic value } 1{\cdot}414) \dagger$$

(4) *Excited States of* C_6H_6 *and* C_6D_6. *The* E_g^+ *Vibrations* (cf. Part II, Sections 2, 3, and 7; and Part IV, Sections 2, 3, 7, and 11).—Three of the four fundamental frequencies of this symmetry class are definitely known for both excited benzene and excited hexadeuterobenzene. The carbon-bending vibrations of benzene and hexadeuterobenzene have the frequencies 521 cm.$^{-1}$ and 499 cm.$^{-1}$, the carbon-stretching vibrations the frequencies 1470 cm.$^{-1}$ and 1403 cm.$^{-1}$, and the hydrogen-stretching vibrations the frequencies 3080 cm.$^{-1}$ and 2320 cm.$^{-1}$, respectively. The difficulty has been with the hydrogen-bending vibration. The absorption spectrum of benzene gives no clear indication of the frequency of this vibration in the upper electronic state. The absorption spectrum of hexadeuterobenzene indicates, but does not firmly establish, the value 830 cm.$^{-1}$. However, indirect support for a value in this close neighbourhood is obtained in the absorption spectrum of 1 : 3 : 5-trideuterobenzene (Part VI, Section 3); and we have two independent theoretical reasons for expecting a value only slightly lower than the

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† In this and similar formulæ the excited (**B$_{2u}$**) state is distinguished by an asterisk.

ground-state value 867 cm.$^{-1}$ (Part XII). Therefore we adopt the value 830 cm.$^{-1}$ as probably correct, and calculate the corresponding benzene frequency with the aid of the product rule :

$$\text{For } C_6H_6 :\text{—}E_g^+(\text{H } 2)_{\text{excited}} = 1130 \text{ cm.}^{-1}$$

A band of moderate or low intensity displaced by this amount above the electronic origin would be difficult to distinguish in the absorption spectrum of benzene, because it would fall (Part II, Table I) amongst the peaks of a rather strong and complex band (Part II, Sections 2 and 4) of the main series (band A^2_1). The calculated frequency may be somewhat inexact, because the product ratio contains the above-mentioned carbon-stretching frequencies, and these themselves, as we have remarked in the papers cited, may have been rendered inexact by resonance displacement of the relevant bands. The hydrogen-bending frequency for the ground state of benzene is 1178 cm.$^{-1}$ (cf. *J.*, 1946, 332).

(5) *Excited States of* C_6H_6 *and* C_6D_6. *The* E_g^- *Vibration* (cf. Part II, Section 5; Part III, Section 4; Part IV, Section 6; and Part V, Section 5).—Amongst the most prominent of the sequence frequencies appearing in the absorption and fluorescence spectra of benzene and hexadeuterobenzene are those which have the values 265 cm.$^{-1}$ for benzene and 208 cm.$^{-1}$ for hexadeuterobenzene. They obviously correspond to each other, and represent differences between the lower- and the upper-state fundamental frequencies of the same vibration. The intensities with which the bands appear suggest Boltzmann factors belonging to frequencies around the region 500—800 cm.$^{-1}$, thus excluding assignment to any but out-of-plane vibrations. Even two of these, the vibrations E_u^+(H) and B_{2g}(H), are probably to be excluded on grounds of intensity, and a third, E_u^+(C), having known frequencies, is already excluded; so that we are left with the following possibilities, *viz.*, E_g^-(H), A_{2u}(H), and B_{2g}(C). The spectra themselves provide reason for the belief that the vibration concerned in these difference frequencies is degenerate, and thus the vibration E_g^-(H) is indicated.

Now any trial assignment can be checked by subtracting the observed difference frequencies from the known ground-state frequencies corresponding to the assignment, and applying the product rule to the upper-state frequencies thus computed. This use of the product theorem supports the choice of E_g^-(H), excludes A_{2u}(H), and has nothng immediately to say about B_{2g}(C). However, the B_{2g}(C) assignment can be excluded by a force-field calculation (Section B, 2); and a later application of the product rule assigns to the upper-state frequencies of this vibration, as well as of the vibration B_{2g}(H), values quite other than those they would have to possess if made responsible for the difference frequencies under discussion. The product theorem does not of itself exclude assignment of the difference frequencies to the vibration E_u^-(H); but if, in spite of the contrary indication of the intensities, we should try so to assign the differences, a force-field calculation would lead us back to almost the same E_g^-(H) frequencies as those which follow from our preferred assignment (Section B, 2).

This assignment leads to the E_g^-(H) frequencies 585 cm.$^{-1}$ for the upper state of benzene, and 454 cm.$^{-1}$ for that of hexadeuterobenzene. A final argument in favour of the assignment is that, just as in the fluorescence spectra of benzene and hexadeuterobenzene we observe prominent intervals representing the first overtones of the known ground-state frequencies of the E_g^-(H) vibration, so in the absorption spectra we find a corresponding appearance of intervals which, if interpreted as overtones, agree in both cases with the computed upper-state frequencies of this vibration.

The product ratio for the E_g^- symmetry class in the upper electronic states of benzene **and** hexadeuterobenzene is as follows :

$$\frac{\Pi E_g^-(C_6H_6{}^*)}{\Pi E_g^-(C_6D_6{}^*)} = \frac{585}{454} = 1{\cdot}288 \text{ (Harmonic value} = 1{\cdot}291)$$

A similarly close agreement between the observed and the calculated ratios for this symmetry class was found for the electronic ground state (Poole, *J.*, 1946, 252).

(6) *Excited States of* C_6H_6 *and* C_6D_6. *The* E_u^+ *Vibrations.*—The fundamental frequencies of the vibration E_u^+(C) in the lower and the upper states of benzene and hexadeutetobenzene are well established by the fluorescence and absorption spectra of these compounds (Part II, Section 4; Part III, Section 3; Part IV, Section 3; and Part V, Section 3). The difference frequencies 161 and 141 cm.$^{-1}$ have been proved to belong to this vibration (cf. Part I, Section 4), and its observed overtones of the ground state agree with the independently known fundamental frequencies in the ground state; furthermore, its observed overtones of the excited state agree with upper-state fundamental frequencies, as computed from the ground-state fundamentals and the difference frequencies.

Another out-of-plane vibration of which the upper-state frequencies may be regarded as well established is the vibration, E_g^-(H), discussed in the preceding sub-section. Therefore the next step in the assignment of upper-state frequencies to the out-of-plane vibrations is to base on the determined frequencies of these two vibrations a force-field calculation. In this way we may compute frequencies, in the upper state of benzene and hexadeuterobenzene, of the vibration E_u^+(H). Then having thus roughly located these frequencies (Section B, 2), we refer back to the absorption spectra of benzene and hexadeuterobenzene, in which the frequencies can now be recognised as overtones and in certain combinations, and thus more exactly determined (Part II, Section 8; Part IV, Section 10). Confirmation follows from the verified prediction that the benzene frequency should also belong to the upper state of the 1 : 4-dideuterobenzene, and thus reappear in the absorption spectrum of that substance; whilst the hexadeuterobenzene frequency should for similar reasons be found again in the absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene (Part VIII, Section 5; Part IX, Section 5). Further confirmation follows from an application of the product rule to the E_u^+ vibrations of the upper states of benzene and hexadeuterobenzene :

$$\frac{\Pi E_u^+(C_6H_6^*)}{\Pi E_u^+(C_6D_6^*)} = \frac{243 \times 706}{208 \times 590} = 1{\cdot}398 \text{ (Harmonic value} = 1{\cdot}414)$$

The ground-state frequencies gave the ratio 1·408 (harmonic value, 1·414) (Herzfeld, Ingold, and Poole, *J.*, 1946, 321).

(7) *Excited States of* C_6H_6 *and* C_6D_6. *The* A_{2u} *Vibration* (cf. Part II, Section 5; Part IV, Section 5; and Part V, Section 4).—The absorption and fluorescence spectra of hexadeuterobenzene contain the prominent sequence interval 114 cm.$^{-1}$. Its strength suggests low frequencies, probably belonging to an out-of-plane vibration. But no corresponding interval could be found in either the absorption or the fluorescence spectrum of benzene. The smaller Boltzmann factors associated with the lighter molecule seem an insufficient explanation of this. It appears much more probable that the vibration is a nearly pure hydrogen vibration, and that, in consequence, the sequence interval in benzene is considerably larger than in hexadeuterobenzene, and is, in fact, about 160 cm.$^{-1}$, with the effect that the resulting bands cannot be seen in the presence of the strong bands of the E_u^+(C) sequences.

This hypothesis suggests a trial assignment to the vibration A_{2u}(H). For the only other out-of-plane hydrogen vibration not excluded by previous assignments is the B_{2g}(H) vibration, and it would be difficult to reconcile this either with the observed intensities, or with the presumed difference between the sequence frequencies.† Computing upper-state A_{2u}(H) frequencies from the known lower-state fundamental frequencies and the differences, we obtain values which for both compounds are confirmed by the recognition of first overtones in the relevant spectra. The computed frequencies are consistent with force-field calculations based on the already discussed assignments to the upper electronic state (Section B, 2). An application of the product theorem to the A_{2u}symmetry class of the excited state supplies further confirmation :

$$\frac{\Pi A_{2u}(C_6H_6^*)}{\Pi A_{2u}(C_6D_6^*)} = \frac{513}{382} = 1{\cdot}343 \text{ (Harmonic value} = 1{\cdot}362)$$

In the ground state the observed ratio was 1·351, the harmonic value being 1·362 (Bailey, Carson, and Ingold, *J.*, 1946, 255).

(8) *Excited States of* C_6H_6 *and* C_6D_6. *The* B_{2g} *Vibrations* (cf. Part II, Sections 5 and 8; Part IV, Sections 8 and 9; and Part V, Sections 7 and 8).—The known low values, in excited benzene and hexadeuterobenzene, of the frequencies of the vibration E_u^+(C) lead us to expect upper-state frequencies between 300 and 400 cm.$^{-1}$ for the other out-of-plane carbon vibration B_{2g}(C). Force-field calculations confirm this, and locate the frequencies somewhat more closely (Section B, 2). In the absorption spectrum of benzene, we find a frequency for which the only obvious assignment is that of a first overtone, in the upper electronic state, of a fundamental frequency 365 cm.$^{-1}$. In both the absorption and the fluorescence spectrum of hexadeuterobenzene, we find similar evidence of a fundamental frequency, 306 cm.$^{-1}$, of the upper electronic state. And in confirmation, we are able to distinguish in the latter two spectra a sequence interval 295 cm.$^{-1}$, a frequency which, when added to the upper-state fundamental frequency 306 cm.$^{-1}$, gives correctly the known lower-state fundamental frequency, 601 cm.$^{-1}$, of the B_{2g}(C) vibration of hexadeuterobenzene (Herzfeld, Ingold, and Poole give 601 cm.$^{-1}$, *J.*, 1946, 332).

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† The B_{2g}(H) vibration is *not* a nearly pure hydrogen vibration (cf. Bailey, Hale, Herzfeld, Ingold, Leckie, and Poole, *J.*, 1946, 261).

Force-field calculations, based on the previously assigned frequencies of out-of-plane vibrations of the excited electronic states of benzene and hexadeuterobenzene, have been used (Section B, 2) in order to locate approximately the frequencies, in these excited molecules, of the remaining out-of-plane vibration, B_{2g}(H). On referring back to the absorption spectrum of benzene, we find an overtone frequency belonging to an upper-state fundamental frequency 775 cm.$^{-1}$, in good agreement with the calculated B_{2g}(H) frequency for excited benzene. In both the absorption and the fluorescence spectrum of hexadeuterobenzene, we find similar evidence of an upper-state fundamental frequency 663 cm.$^{-1}$, also in good agreement with the calculated B_{2g}(H) frequency for excited hexadeuterobenzene. And in these two spectra we can find a sequence interval 165 cm.$^{-1}$, a frequency which, when added to the upper-state fundamental frequency 663 cm.$^{-1}$, gives correctly the known fundamental frequency, 828 cm.$^{-1}$, of the B_{2g}(H) vibration in the ground state of hexadeuterobenzene (Herzfeld, Ingold, and Poole give 827 cm.$^{-1}$, *loc. cit.*).

On the evidence presented, each of these pairs of assignments would seem fairly secure, but we can apply an additional check to the whole set by the use of the product theorem. We thus find :

$$\frac{\Pi B_{2g}(C_6H_6{}^*)}{\Pi B_{2g}(C_6D_6{}^*)} = \frac{365 \times 775}{306 \times 663} = 1{\cdot}394 \text{ (Harmonic value} = 1{\cdot}414)$$

In the electronic ground state the corresponding ratio was 1·393, the harmonic value again being 1·414 (Herzfeld, Ingold, and Poole, *loc. cit.*).

(9) *Excited State of* 1 : 3 : 5-$C_6H_3D_3$. *The E'' Vibrations* (cf. Part VI, Sections 2, 4, 5, and 6; Part VII, Sections 3 and 4).—This symmetry class contains one carbon and two hydrogen vibrations. The first-named, E''(C), corresponds very closely to the benzene and hexadeuterobenzene vibration E_u^+(C). Like the latter it is responsible for the strongest sequences in the absorption and fluorescence spectra, besides appearing as its upper- and lower-state overtones, and identifying itself as a degenerate vibration by the positions of some of the bands. The upper-state fundamental frequency, 223 cm.$^{-1}$, is well established, and its assignment cannot be doubted.

The vibration E''(H 1) roughly corresponds to the vibration E_g^-(H) of benzene and hexadeuterobenzene. Like the latter it appears as a rather strong sequence frequency in the absorption and fluorescence spectra of 1 : 3 : 5-trideuterobenzene, and also as an upper-state overtone in the absorption spectrum, besides confessing itself to be a degenerate vibration by the positions of some of the series. The upper-state fundamental frequency, 495 cm.$^{-1}$, is of the expected magnitude, and the evidence of analogy is so strong that the correctness of its assignment seems certain.

The third vibration, E''(H 2), is the approximate analogue of the benzene and hexadeuterobenzene vibration B_{2g}(H). In the absorption spectrum of 1 : 3 : 5-trideuterobenzene we find an overtone and a difference frequency, which point to an upper-state fundamental frequency 680 cm.$^{-1}$. It is of the expected magnitude for the vibration E''(H 2), and its participation in the difference frequency points to its belonging to a vibration of the E'' class. For confirmation we apply the product theorem :

$$\frac{\Pi E_u^+E_g^-(C_6H_6{}^*)}{\Pi E''(C_6H_3D_3{}^*)} = \frac{243 \times 585 \times 706}{223 \times 495 \times 680} = 1{\cdot}337 \text{ (Harmonic value} = 1{\cdot}346)$$

$$\frac{\Pi E''(C_6H_3D_3{}^*)}{\Pi E_u^+E_g^-(C_6D_6{}^*)} = \frac{223 \times 495 \times 680}{208 \times 454 \times 590} = 1{\cdot}347 \text{ (Harmonic value} = 1{\cdot}352)$$

The results evidently confirm the assignments.

(10) *Excited State of* 1 : 3 : 5-$C_6H_3D_3$. *The A_2'' Vibrations* (cf. Part VI, Section 7; and Part VII, Section 5).—This symmetry class also contains one carbon and two hydrogen vibrations. The carbon vibration, A_2''(C), is a close analogue of the benzene and hexadeuterobenzene vibration, B_{2g}(C). In the absorption spectrum of 1 : 3 : 5-trideuterobenzene we find a frequency which can scarcely be assigned otherwise than as the first overtone of an upper-state fundamental frequency 360 cm.$^{-1}$. Such a frequency could only belong to the B_{2g}(C) vibration.

The hydrogen vibration, A_2''(H 1), is very roughly analogous to the benzene and hexadeuterobenzene vibration, A_{2u}(H). We find in the absorption spectrum of 1 : 3 : 5-trideuterobenzene an overtone of an upper-state fundamental frequency 411 cm.$^{-1}$, which is of about the expected magnitude for the upper-state frequency A_2''(H 1). We also find in the spectrum a sequence interval 119 cm.$^{-1}$, which one would in any case be tempted to try to correlate with the sequence interval 114 cm.$^{-1}$ of the A_{2u}(H) vibration of hexadeuterobenzene.

And the frequency 119 cm.$^{-1}$, when added to the upper-state fundamental frequency 411 cm.$^{-1}$, gives correctly the known lower-state frequency of the vibration A_2''(H 1). An active overtone gives the value 531 cm.$^{-1}$ for this lower-state frequency, and it is independently known from infra-red measurements. Thus our identification of the upper-state frequency of the vibration A_2''(H 1) seems certain.

The internal spectral evidence concerning the remaining vibration A_2''(H 2) is less complete. This vibration is roughly analogous to the benzene and hexadeuterobenzene vibration B_{2g}(H). In the absorption and fluorescence spectra of 1 : 3 : 5-trideuterobenzene, we find a sequence interval of 200 cm.$^{-1}$, and an argument of exclusion (Part VI, Section 7) shows that this can only belong to the vibration A_2''(H 2). The ground-state fundamental frequency of this vibration, 915 cm.$^{-1}$, is found as an overtone in the fluorescence spectrum, and it is known from infra-red measurements. One deduces that the upper-state fundamental frequency must be $915 - 200 = 715$ cm.$^{-1}$. The figure is of the expected magnitude, but the direct support which would follow from an observation of its overtone in the absorption spectrum is unfortunately not available. For a confirmatory test we have therefore to rely on the product theorem, which confirms the assignment :

$$\frac{\Pi B_{2g}A_{2u}(C_6H_6{}^*)}{\Pi A_2''(C_6H_3D_3{}^*)} = \frac{365 \times 513 \times 775}{360 \times 411 \times 715} = 1{\cdot}372 \text{ (Harmonic value} = 1{\cdot}387)$$

$$\frac{\Pi A_2''(C_6H_3D_3{}^*)}{\Pi B_{2g}A_{2u}(C_6D_6{}^*)} = \frac{360 \times 411 \times 715}{306 \times 382 \times 663} = 1{\cdot}362 \text{ (Harmonic value} = 1{\cdot}388)$$

(11) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The* A_g *Vibrations* (cf. Part VIII, Sections 2, 3, and 8; and Part IX, Sections 2, 3, and 8).—The six vibrations of this symmetry class correspond collectively, and to a large extent individually, to the two A_{1g} and four E_g^+ vibrations of benzene or hexadeuterobenzene. Of the six upper-state A_g fundamental frequencies of 1 : 4-dideuterobenzene, five have been directly and definitely identified in the absorption spectrum of that substance : (A_{1g}-like) 909 and 3132; (E_g^+-like) 511, 1489, and 2355 cm.$^{-1}$. Five fundamental frequencies of 1 : 2 : 4 : 5-tetradeuterobenzene have been identified with equal certainty in the corresponding spectrum : (A_{1g}-like) 895 and 2355; (E_g^+-like) 509·5, 1414, and 3133 cm.$^{-1}$. In each case the missing frequency is that of the hydrogen-bending vibration A_g(H), corresponding to the E_g^+(H 2) vibration of a D_{6h} benzene.

These missing frequencies we now calculate, using the various product ratios between the relevant frequencies of benzene, 1 : 4-dideuterobenzene, 1 : 2 : 4 : 5-tetradeuterobenzene, and hexadeuterobenzene. The results are as follows :

For 1 : 4-$C_6H_4D_2$:—$A_g(\mathrm{H})_{\mathrm{excited}} = 1075$ cm.$^{-1}$
For 1 : 2 : 4 : 5-$C_6H_2D_4$:—$A_g(\mathrm{H})_{\mathrm{excited}} = 820$ cm.$^{-1}$

These values may involve an error due to the circumstance that the other frequencies from which they are calculated include some which, as has been pointed out, are probably perturbed by a resonance displacement of certain upper-state energy levels. The corresponding ground-state frequency of 1: 4-dideuterobenzene is 1173·4 cm.$^{-1}$, and of 1 : 2 : 4 : 5-tetradeuterobenzene is 862·2 cm.$^{-1}$, according to the evidence of Raman spectra (Herzfeld, Hobden, Ingold, and Poole, *J.*, 1946, 379).

(12) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The* A_u *Vibrations* (cf. Part VIII, Sections 4 and 5; and Part IX, Sections 4 and 5).—In theory, the two A_u frequencies of excited 1 : 4-dideuterobenzene are individually identical with the upper-state E_u^+ frequencies of benzene, whilst the corresponding A_u frequencies of 1 : 2 : 4 : 5-tetradeuterobenzene are identical with the E_u^+-frequencies of excited hexadeuterobenzene. The observed exact (or very close) identity of the relevant pairs of frequencies is an important part of the basis on which the A_u frequencies are recognised in the absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene. We therefore expect the product theorem to be satisfied by these frequencies, as, indeed, the following figures illustrate :

$$\frac{\Pi E_u^+(C_6H_6{}^*)}{\Pi A_u(C_6H_4D_2{}^*)} = \frac{243 \times 706}{243 \times 706} = 1{\cdot}000 \text{ (Harmonic value} = 1{\cdot}000)$$

$$\frac{\Pi A_u(C_6H_4D_2{}^*)}{\Pi A_u(C_6H_2D_4{}^*)} = \frac{243 \times 706}{208 \times 591} = 1{\cdot}395 \text{ (Harmonic value} = 1{\cdot}414)$$

$$\frac{\Pi A_u(C_6H_2D_4{}^*)}{\Pi E_u^+(C_6D_6{}^*)} = \frac{208 \times 591}{208 \times 590} = 1{\cdot}002 \text{ (Harmonic value} = 1{\cdot}000)$$

(13) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The* B_{2g} *Vibrations* (cf. Part VIII, Section 6; and Part IX, Section 6).—This case is similar to the last, except that the involved symmetry classes, B_{2g} for 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene and E_g^- for benzene and hexadeuterobenzene, each contain only one vibration. The upper-state product ratios are as follows :

$$\frac{\Pi E_g^-(C_6H_6^*)}{\Pi B_{2g}(C_6H_4D_2^*)} = \frac{585}{585} = 1{\cdot}000 \text{ (Harmonic value} = 1{\cdot}000)$$

$$\frac{\Pi B_{2g}(C_6H_4D_2^*)}{\Pi B_{2g}(C_6H_2D_4^*)} = \frac{585}{452} = 1{\cdot}291 \text{ (Harmonic value} = 1{\cdot}291)$$

$$\frac{\Pi B_{2g}(C_6H_2D_4^*)}{\Pi E_g^-(C_6D_6^*)} = \frac{452}{454} = 0{\cdot}996 \text{ (Harmonic value} = 1{\cdot}000)$$

(14) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The* B_{1u} *Vibrations* (cf. Part VIII, Sections 4 and 5; Part IX, Sections 4 and 5).—This symmetry class contains one carbon and two hydrogen vibrations, collectively related to the two E_u^+, and the single A_{2u}, vibrations of benzene, and of hexadeuterobenzene. The carbon vibration, B_{1u}(C), is a close analogue of the E_u^+(C) vibration of benzene and hexadeuterobenzene; and it can readily be identified in the absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene by its generation of strong sequences and overtone series, closely corresponding to those given by the E_u^+(C) vibration of benzene and hexadeuterobenzene. The upper-state fundamental frequencies are 222 cm.$^{-1}$ for 1 : 4-dideuterobenzene, and 233 cm.$^{-1}$ for 1 : 2 : 4 : 5-tetradeuterobenzene. These figures are of about the estimated magnitude : they stand in the unusual numerical order, because, in this vibration, the hydrogen motion tends to concentrate in the isotope present in smaller proportion (cf. Bailey, Carson, Gordon, and Ingold, *J.*, 1946, 292).

The vibration B_{1u}(H 1) of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene is an approximate analogue of the A_{2u}(H) vibration of benzene and hexadeuterobenzene. In the absorption spectrum of 1 : 4-dideuterobenzene we find the overtone of an upper-state fundamental frequency 435 cm.$^{-1}$. This is of about the magnitude one would associate with the B_{1u}(H 1) vibration, but the spectrum itself provides no further evidence of identity. On the other hand, the absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene contains the overtone of an upper-state fundamental frequency 419 cm.$^{-1}$, which is likewise of about the magnitude to be expected for the frequency of the B_{1u}(H 1) vibration; and this frequency is rather clearly identified as such by the internal evidence of the spectrum. For we find a sequence frequency, 128 cm.$^{-1}$, which, when added to the upper-state frequency 419 cm.$^{-1}$, gives correctly the known lower-state frequency, 547 cm.$^{-1}$, of the vibration B_{1u}(H 1) (Bailey, Carson, Gordon, and Ingold's infra-red observations gave 548 cm.$^{-1}$; *loc. cit.*); and one of the other combinations in which the frequency 419 cm.$^{-1}$ appears points to its belonging to the B_{1u} symmetry class.

The vibration B_{1u}(H 2) of the 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene is roughly analogous to the E_u^+(H) vibration of benzene and hexadeuterobenzene. In the absorption spectrum of 1 : 4-dideuterobenzene we find the overtone of an upper-state fundamental frequency 655 cm.$^{-1}$. The absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene yields similar evidence of an upper-state fundamental frequency 665 cm.$^{-1}$. In each case the frequency is of about the magnitude we should expect for the vibration B_{1u}(H 2), the order of the two frequencies again being explicable by the concentration of much of the hydrogen motion in the isotope present in smaller proportion (*idem, ibid.*). But in neither case does the spectrum itself yield any further evidence of the identity of the frequencies. The main support for our assignments of these upper-state frequencies to the vibration B_{1u}(H 2), and of the upper-state frequency 435 cm.$^{-1}$ of 1 : 4-dideuterobenzene to the vibration B_{1u}(H 1), is therefore that these three initially tentative assignments, in combination with the three secure B_{1u} assignments already mentioned, give correct B_{1u} frequency products for both excited 1 : 4-dideuterobenzene and excited 1 : 2 : 4 : 5-tetradeuterobenzene. The following product ratios establish this :

$$\frac{\Pi E_u^+ A_{2u}(C_6H_6^*)}{\Pi B_{1u}(C_6H_4D_2^*)} = \frac{243 \times 513 \times 706}{222 \times 435 \times 655} = 1{\cdot}391 \text{ (Harmonic value} = 1{\cdot}396)$$

$$\frac{\Pi B_{1u}(C_6H_4D_2^*)}{\Pi B_{1u}(C_6H_2D_4^*)} = \frac{222 \times 435 \times 655}{233 \times 419 \times 665} = 0{\cdot}974 \text{ (Harmonic value} = 0{\cdot}988)$$

$$\frac{\Pi B_{1u}(C_6H_2D_4^*)}{\Pi E_u^+ A_{2u}(C_6D_6^*)} = \frac{233 \times 419 \times 665}{208 \times 382 \times 590} = 1{\cdot}385 \text{ (Harmonic value} = 1{\cdot}396)$$

(15) *Excited States of* 1 : 4-$C_6H_4D_2$ *and* 1 : 2 : 4 : 5-$C_6H_2D_4$. *The* B_{3g} *Vibrations* (cf. Part VIII, Section 7; and Part IX, Section 7).—This symmetry class possesses one carbon and two

hydrogen vibrations. They are collectively related to the two B_{2g}, and the single E_g^-, vibrations of benzene and hexadeuterobenzene. The carbon vibration is quite a close analogue of the vibration B_{2g}(C) of benzene and hexadeuterobenzene. In the absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, we find, as overtones, the upper-state fundamental frequencies 357 cm.$^{-1}$ and 351 cm.$^{-1}$, respectively. Both are of about the expected magnitude for the vibration B_{2g}(C) ; and they could hardly belong to any other fundamental vibration.

The absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene also contain overtones of the upper-state fundamental frequencies 457 cm.$^{-1}$ and 535 cm.$^{-1}$, respectively. Each is of about the magnitude to be expected of the lower of the two B_{3g} hydrogen frequencies in each excited molecule. But the respective spectra provide no additional evidence of the identity of these frequencies.

The same situation prevails in relation to the higher of the B_{3g} hydrogen frequencies. The absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene contain overtones of the upper-state fundamental frequencies 775 cm.$^{-1}$ and 649 cm.$^{-1}$, respectively. Each of these is of about the expected magnitude, but the spectra yield no further evidence of identity. The one additional check which we have is that, for each compound, the two initially provisional assignments, in combination with the secure assignment of the carbon frequency, give a correct B_{3g} frequency product. This is established by the following product ratios for the upper electronic state :

$$\frac{\Pi B_{2g}E_g^-(\mathrm{C_6H_6}^*)}{\Pi B_{3g}(\mathrm{C_6H_4D_2}^*)} = \frac{365 \times 585 \times 775}{357 \times 457 \times 775} = 1{\cdot}309 \text{ (Harmonic value } = 1{\cdot}326)$$

$$\frac{\Pi B_{3g}(\mathrm{C_6H_4D_2}^*)}{\Pi B_{3g}(\mathrm{C_6H_2D_4}^*)} = \frac{357 \times 457 \times 775}{351 \times 535 \times 649} = 1{\cdot}038 \text{ (Harmonic value } = 1{\cdot}031)$$

$$\frac{\Pi B_{3g}(\mathrm{C_6H_2D_4}^*)}{\Pi B_{2g}E_g^-(\mathrm{C_6D_6}^*)} = \frac{351 \times 535 \times 649}{306 \times 454 \times 663} = 1{\cdot}323 \text{ (Harmonic value } = 1{\cdot}331)$$

(15) *Excited State of* C_6H_5D. *The* A_2 *Vibrations* (cf. Part X, Sections 4 and 6).—According to theory, the three upper-state A_2 frequencies of monodeuterobenzene are individually identical with the two E_u^+, and the single E_g^-, frequencies of excited benzene, and also with the two A_u, and the single B_{2g}, frequencies of excited 1 : 4-dideuterobenzene. Naturally, the relevant product ratios are unity. Two of the three monodeuterobenzene frequencies, 243 and 585 cm.$^{-1}$, can be found and identified in the absorption spectrum of that substance : the values are just those we expect. The third has not been so identified, but we know its value from its identified equivalents in the spectra of the two isotopically isomeric compounds. Another form of the same statement is that we can calculate the missing frequency from the observed frequencies and the product theorem :

$$\text{For } \mathrm{C_6H_5D} :\!—A_2(\mathrm{H})_{\text{excited}} = 706 \text{ cm.}^{-1}$$

The corresponding frequency of the electronic ground state is 970 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *loc. cit.*).

(16) *Excited State of* C_6H_5D. *The* B_2 *Vibrations* (cf. Part X, Sections 4, 5, 6, and 7).—This symmetry class contains two carbon and four hydrogen vibrations, collectively corresponding to the six out-of-plane vibrations of benzene. Four of the upper-state frequencies of monodeuterobenzene, those of the vibrations which correspond more or less nearly to the benzene vibrations E_u^+(C), B_{2g}(C), A_{2u}(H), and E_g^-(H), can be not only found, but also identified with fair certainty, in the absorption spectrum of monodeuterobenzene. Two other frequencies are found which can be assigned to the remaining vibrations, namely, those vibrations which are most closely allied to the benzene vibrations E_u^+(H) and B_{2g}(H). The frequencies have the approximate magnitudes to be expected for upper-state frequencies thus assigned, but the spectrum offers no further evidence of their identity. In adopting the assignments suggested, we therefore rely on the circumstance that these two frequencies, in conjunction with the four more securely assigned frequencies already mentioned, produce the correct frequency product for the B_2 symmetry class of excited monodeuterobenzene. This is established by the following product ratios *inter alia* :

$$\frac{\Pi E_u^+B_{2g}A_{2u}E_g^-(\mathrm{C_6H_6}^*)}{\Pi B_2(\mathrm{C_6H_5D}^*)} = \frac{243 \times 365 \times 513 \times 585 \times 706 \times 775}{230 \times 360 \times 476 \times 552 \times 690 \times 720} = 1{\cdot}348 \text{ (Harmonic value} = 1{\cdot}359)$$

$$\frac{\Pi B_2(\mathrm{C_6H_5D}^*)}{\Pi B_{1u}B_{3g}(\mathrm{C_6H_4D_2}^*)} = \frac{230 \times 360 \times 476 \times 552 \times 690 \times 720}{222 \times 357 \times 435 \times 457 \times 655 \times 775} = 1{\cdot}351 \text{ (Harmonic value } = 1{\cdot}362)$$

$$\frac{\Pi B_2(\mathrm{C_6H_5D}^*)}{\Pi E''A_2''(\mathrm{C_6H_3D_3}^*)} = \frac{230 \times 360 \times 476 \times 552 \times 690 \times 720}{223 \times 360 \times 411 \times 475 \times 680 \times 715} = 1{\cdot}360 \text{ (Harmonic value } = 1{\cdot}375)$$

(17) *Partial Summary.*—This section completes the theoretical basis of our assignments of frequencies to the upper-state vibrations of the planar symmetry classes A_{1g}, B_{1u}, and E_g^+ of benzene and hexadeuterobenzene, and of the corresponding symmetry classes of the partly deuterated benzenes studied. It also extends, though it does not complete, the theoretical arguments on which we rely in our assignments of frequencies to all the out-of-plane vibrations of the upper electronic states of the benzenes studied, *i.e.*, the vibrations of the symmetry classes A_{2u}, B_{2g}, E_u^+ and E_g^- of benzene and hexadeuterobenzene, and of the related symmetry classes of the partly deuterated benzenes.

Two matters therefore remain to be treated. The first need is to complete the discussion of the upper-state out-of-plane vibrations. The second is to consider the upper-state planar vibrations of those symmetry classes of benzene and hexadeuterobenzene which have been left aside hitherto, *viz.*, the three symmetry classes A_{2g}, B_{2u}, and E_u^-. These are the subjects of the following Section.

(B) *Force System for the Excited State.*

(1) *The Wilson–Bell Potential-energy Function for Benzene.*—The simplest normal co-ordinate treatment which has been applied to the benzene molecule is that of Wilson (*Physical Rev.*, 1934, **45**, 706), who adopted a valency-force potential-energy function containing six constants, and from this derived a complete set of equations for the twenty fundamental frequencies in terms of the six constants. Wilson's function may be written thus :

$$2V = F\Sigma r^2 + f\Sigma s^2 + D\Sigma a^2\rho^2 + d\Sigma b^2\sigma^2 + G\Sigma c^2\phi^2 + g\Sigma b^2\mu^2 \quad . \quad . \quad . \quad (1)$$

Here V is the potential energy of deformation of the molecule; r, s, ρ σ, ϕ, and μ are the geometrical variables in terms of which the deformation is expressed; F, f, D, d, G, and g are the force-constants (Kohlrausch's notation); and a, b, and c are geometrical constants. The geometrical variables are defined as follows : r is the deviation of the length of a C–C bond, and s of that of a C–H bond, from their respective equilibrium lengths; ρ is the angular deformation of an internal ring angle, and σ is the angular deviation, in the plane of the ring, of a C–H bond from the bisector of an external ring angle; ϕ is the angle through which a C–C bond is twisted by out-of-plane displacements of the carbon atoms attached to the atoms forming the bond, and μ is the angle by which the bond of a hydrogen atom is bent out of the plane of the nearest three carbon atoms. The force-constants correspond : F is the carbon-stretching, and f is the hydrogen-stretching, constant, and D is the carbon-bending, and d the hydrogen-bending, constant, all with reference to motion in the plane of the molecule; whilst G is the carbon-twisting, and g the hydrogen-bending, constant, both relating to out-of-plane motion. The geometrical constants have the following meanings : a is the equilibrium C–C bond-length, and b is the equilibrium C–H bond-length, whilst c is an abbreviation for $\sqrt{3}a/2$. Each summation extends over six similar terms, one for each of six like atoms or six like bonds.

It is not necessary to quote the frequency equations which follow from equation (1). There are ten, one for each of the ten symmetry classes which possess vibrations, the order of each equation, and the number of its roots, corresponding to the number of frequencies belonging to the symmetry class. The equations are separable into two sets : the six which give the fourteen planar frequencies involve only the force-constants F, f, D, and d; whilst the four which give the six out-of-plane frequencies involve only the force-constants G and g.

These equations have been compared with spectrally determined frequencies for the electronic ground states of benzene and hexadeuterobenzene by Kohlrausch (*Z. physikal. Chem.*, 1935, **30**, 307) and Lord and Andrews (*J. Physical Chem.*, 1937, **41**, 149); and further spectral data have since become available for the comparison. As regards the planar frequencies, there are no discrepancies greater than 17% : here the agreement seems to be about as good as one should expect for a potential function without cross terms. But for the out-of-plane vibrations, the discrepancies are much greater, ranging up to 50%. However, Bell (*Trans. Faraday Soc.*, 1945, **41**, 293) has proposed to modify equation (1) in a manner which not only is physically very reasonable, but also has the effect of making the out-of-plane portion of the potential energy function at least as successful as the in-plane portion. He remarks that it cannot be right to take into account only the effect, on the twisting of a C–C bond, of the out-of-plane displacements of the two carbon atoms attached to the atom-pair, neglecting the similar effect of the out-of-plane displacements of the two hydrogen atoms. He observes that, if only one torsional force-constant is to be used, the best measure of the torsion about a given C–C bond is $\phi_C + \phi_H$, where ϕ_C and ϕ_H are the relative angular twists, about the given bond, of the two attached C–C bonds and the two attached C–H bonds, respectively. This modifies the potential-energy function, and leads to a new set of equations for the out-of-plane frequencies. Bell has given these equations, and has shown that they satisfactorily represent the out-of-plane frequencies of the ground state of benzene.

In calculating relationships between the fundamental frequencies of the electronically excited states of benzene and hexadeuterobenzene, and in comparison calculations on the electronic ground states of these molecules, we have accordingly used Bell's equations for the out-of-plane frequencies and Wilson's equations for the planar frequencies, the complete potential energy function being $V = V_o + V_p$, where

$$2V_o = Q\Sigma c^2(\phi_C + \phi_H)^2 + g\Sigma b^2\mu^2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$2V_p = F\Sigma r^2 + f\Sigma s^2 + D\Sigma a^2\rho^2 + d\Sigma b^2\sigma^2 \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

The constant Q is the new torsional force-constant, which takes into account the twisting of a carbon bond by the motion of the hydrogen atoms as well as by the motion of other carbon atoms. The physical data employed in the calculations, apart from universal constants, are the isotopic weights, H = 1·008, D = 2·014, and C = 12·00, and the internuclear distances, C–C = 1·39 A. and C–H = 1·08 A. for the ground state, and C–C = 1·43 A. and C–H = 1·07 A. for the excited state (cf. Part XII).

(2) *Excited States of* C_6H_6 *and* C_6D_6. *The Out-of-plane Vibrations* (cf. Section A, Sub-sections 5, 6, 7, and 8).—The two out-of-plane vibrations for the assignments of upper-state frequencies to which the strongest cases can be presented, purely on the internal evidence of the absorption and fluorescence spectra of benzene and hexadeuterobenzene, are the vibrations E_u^+(C) and E_g^-(H). It was therefore an obvious step to employ these frequencies, either of benzene or of hexadeuterobenzene, in order to determine the force-constants Q and g of equation (2), and from these to calculate the remaining out-of-plane frequencies of the upper electronic states of the two molecules. It makes little difference which of the pairs of frequencies we employ initially, and the results of a calculation, in which we have started from the two hexadeuterobenzene frequencies, are shown in the upper part of Table II.

As a control, a similar calculation starting from the corresponding pair of frequencies of hexadeuterobenzene in the electronic ground state, has been carried through for the ground states of benzene and hexadeuterobenzene. The results are given in the lower part of Table II. In both parts of the Table, the columns headed " Obsd." contain the spectrally determined frequencies, whilst the columns headed " Corrn." record the percentage corrections which would convert the calculated frequencies into the spectrally determined values.

TABLE II.

Calculated Out-of-plane Frequencies (cm.$^{-1}$) for Excited and Normal Benzene and Hexadeuterobenzene. Comparison with Spectrally Observed Values.

(a) *Excited state.*

Starting frequencies : those marked * below.
Force constants : Q = 2090 dynes/cm., and g = 12500 dynes/cm.

	Benzene.			Hexadeuterobenzene.		
Vibration.	Calc.	Obsd.	Corrn., %.	Calc.	Obsd.	Corrn., %.
A_{2u}(H)	478	513	+ 7·3	351	382	+ 8·8
B_{2g} (C)	387	365	– 5·7	328	306	– 6·7
(H)	774	775	+ 0·1	637	663	+ 4·1
E_g^-(H)	585	585	± 0·0	—	454 *	—
E_u^+ (C)	238	243	+ 2·1	—	208 *	—
(H)	726	706	– 2·8	588	590	+ 0·3

(b) *Ground state.*

Starting frequencies : those marked † below.
Force constants : Q = 6700 dynes/cm., and g = 22900 dynes/cm.

	Benzene.			Hexadeuterobenzene.		
Vibration.	Calc.	Obsd.	Corrn., %.	Calc.	Obsd.	Corrn., %.
A_{2u}(H)	646	671	+ 3·9	475	496·5	+ 4·1
B_{2g} (C)	638	703	+10·2	572	601	+ 5·1
(H)	1136	985	–12·4	898	827	– 7·9
E_g^-(H)	851	849	– 0·2	—	662 †	—
E_u^+ (C)	390	405	+ 3·8	—	352 †	—
(H)	1075	970	– 9·8	844	793	– 6·0

The general agreement between the calculated upper-state frequencies and those assigned on the basis of the spectral observations is evidently satisfactory. In particular the assignments of the A_{2u}(H) and B_{2g}(C) frequencies are confirmed. Since the calculations were used in order roughly to locate the E_u^+(H) and B_{2g}(H) frequencies, prior to their identification in the spectra, these frequencies automatically agree with the calculated values.

We have carried out similar calculations starting from the well-established upper-state E_u^+(C) frequency of either benzene or hexadeuterobenzene and a second upper-state frequency given by the use of some trial assignment in place of the adopted assignment of the E_g^- frequency. For instance, one of our earlier ideas was that the fairly strong sequence frequencies, 265 cm.$^{-1}$ of benzene and 208 cm.$^{-1}$ of hexadeuterobenzene, which we now assign to the vibration E_g^-(H) might belong to the vibration B_{2g}(C). But either of the upper-state B_{2g}(C) frequencies of benzene and hexadeuterobenzene, which would then follow, produces quite absurd results when, in combination with the E_u^+(C) frequency, it is made the basis of a calculation such as that illustrated above. We have been unable to find any scheme, other than that now proposed, of spectral assignments to out-of-plane vibrations of the upper electronic state, which is consistent both with the product rule and with the force-field calculations. This completes our case for the out-of-plane assignments.

(3) *Excited States of* C_6H_6 *and* C_6D_6. *The* A_{2g}, B_{2u}, *and* E_u^- *Planar Vibrations.*—Our application of force-field calculations to the determination of planar vibration frequencies of the upper electronic states of benzene and hexadeuterobenzene has followed different lines from those already illustrated, because of the different situation prevailing with regard to the planar vibrations. On the one hand, the upper-state frequencies of all the vibrations of the planar symmetry classes A_{1g}, B_{1u}, and E_g^+ have already been determined with greater certainty and precision than could have been achieved by force-field calculations. On the other hand, we as yet know nothing about any of the upper-state vibration frequencies of the other three planar symmetry classes, A_{2g}, B_{2u}, and E_u^-. Therefore, as an initial step towards the evaluation of these frequencies of excited benzene and hexadeuterobenzene, we first used the known planar frequencies of the upper electronic states of these molecules in order to determine the force constants, F, f, D, and d, of equation (3), and then employed these constants for the calculation of the unknown planar frequencies.

The calculation was carried out as follows. First, the carbon- and hydrogen-stretching force-constants, F and f, were derived from the upper-state A_{1g} frequencies. With the aid of these constants, a mean value of the carbon-bending constant, D, was then calculated from the upper-state B_{1u} frequencies and the E_g^+ frequencies, in the latter case by the use of those coefficients in the frequency equation which give the sum and product of the squares of the four frequencies. Then, with the aid of these three constants, a value of the hydrogen-bending constant, d, was derived from the upper-state E_g^+ frequencies, employing for this purpose the expression for the product of the squares of the frequencies. The above procedures were carried through independently for benzene and hexadeuterobenzene, with the results shown in the upper left-hand part of Table III. The consistency is good for F and f, but poor for D and d. The mean values listed were used for the calculation of those upper-state frequencies which are entered under the heading " Calc." in the top right-hand part of Table III. The significance of the adjacent figures under the heading " E.A." is explained below.

As a control on the values thus obtained, the calculation was repeated for the electronic ground states of benzene and hexadeuterobenzene. The resulting force-constants are given in the lower left-hand portion of Table III. These force-constants are almost certainly not the best that could be obtained by making use of all that is known about the frequencies of benzene and hexadeuterobenzene in their electronic ground states. However, we particularly wanted values which would be comparable to those obtained for the upper electronic state, and subject to similar errors. As before, we used mean values for the calculation of the frequencies of both molecules. These frequencies are contained in the columns headed " Calc." in the lower right-hand part of the Table. We are able to compare them with values derived from spectral observations, and such values, taken from Herzfeld, Ingold, and Poole's list (*J.*, 1946, 332), are given in the neighbouring columns headed " Obsd.". The deviations, entered in the columns headed " Corrn.", are expressed as the percentage corrections which would have to be applied to the calculated frequencies in order to produce the observed values.

Our object in making the frequency calculations for the electronic ground state was to obtain a set of correction factors, with the aid of which we might hope to improve our estimates of the A_{2g}, B_{2u}, and E_u^- frequencies of benzene and hexadeuterobenzene in their electronically excited states. It is true that, as one sees from Table II, there is no very close correspondence between

TABLE III.

Some Calculated Planar Frequencies (cm.$^{-1}$) of Excited and Normal Benzene and Hexadeuterobenzene. Comparison of Calculated Ground-state Frequencies with Spectrally Determined Values.

(a) *Excited state.*

[Starting frequencies : those of A_{1g}, B_{1u}, and E_g^+ symmetry classes given in Table V.]

Force constants.

(F, f, D and d in dynes/cm.).

	C_6H_6.	C_6D_6.	Mean.
10^{-5} F	6·54	6·53	6·53
10^{-5} f	5·30	5·40	5·35
10^{-5} D	0·58	0·46	0·52
10^{-5} d	0·50	0·64	0·57

Frequencies (cm.$^{-1}$).

	C_6H_6.		C_6D_6.	
Vibration.	Calc.	E.A.	Calc.	E.A.
A_{2g}(H)	1103	1210	857	940
B_{2u} (C)	1700	1510	1668	1440
(H)	961	1010	683	750
E_u^- (C)	1632	1470	1697	1320
(H 1)	1024	940	754	740
(H 2)	2984	3130	2025	2300

(b) *Ground state.*

[Starting frequencies : those of A_{1g}, B_{1u}, and E_g^+ symmetry classes given in *J.*, 1946, 332.]

Force constants

(F, f, D, and d in dynes/cm.).

	C_6H_6.	C_6D_6.	Mean.
10^{-5} F	7·65	7·58	7·61
10^{-5} f	5·02	5·10	5·06
10^{-5} D	0·77	0·59	0·68
10^{-5} d	0·60	0·79	0·69

Frequencies (cm.$^{-1}$).

	C_6H_6.			C_6D_6.		
Vibration.	Calc.	Obsd.	Corrn., %.	Calc.	Obsd.	Corrn., %.
A_{2g}(H)	1214	1326	+ 9·1	942	1037	+ 10·1
B_{2u} (C)	1837	1648	− 10·3	1833	1571	− 14·3
(H)	1053	1110	+ 5·4	750	825	+ 10·0
E_u^- (C)	1734	1485	− 14·3	1638	1333	− 18·4
(H 1)	1118	1037	− 7·3	838	813	− 3·0
(H 2)	2870	3080	+ 7·3	2130	2294	+ 7·7

the correction factors applying to the different out-of-plane vibrations in the two electronic states. All that can be said is that the order of magnitude of the deviations between the calculated and observed frequencies of these vibrations is the same for both states, and that, on the whole, the errors for the upper state are smaller than for the lower. On the other hand, in the case of the planar vibrations, it seems reasonable to assume a much closer correlation between the errors involved in the calculation of corresponding frequencies of the two electronic states—for two reasons. The first is that, whereas the force-constants for the out-of-plane vibrations are greater by factors of two and three in the electronic ground state than in the excited state, the force-constants for the planar vibrations differ by less than 25% in the two states; which therefore behave as much more closely similar dynamical systems with respect to planar vibrations than they do with respect to out-of-plane vibrations. The second reason is that, although the determined values of the planar force-constants are not all independent of whether they are obtained from the frequencies of benzene or from those of hexadeuterobenzene, the percentage deviations between the values obtained in these two ways for the electronic ground state are repeated very closely in the values applying to the excited state. Therefore we presume that the errors inherent in our calculations of the planar frequencies are similar for the two electronic states; so that we may expect generally to improve our estimates of those planar frequencies which cannot be directly observed, by applying to the calculated values correction factors deduced from a comparison of similarly calculated ground-state frequencies with data derived from spectral observation.

Several other empirical, or partly empirical, guides to the upper-state frequencies of the symmetry classes A_{2g}, B_{2u}, and E_u^- are available. A comparison of the frequencies, in the lower and upper electronic states, of those vibrations of benzene and hexadeuterobenzene, whose frequencies in the upper state are most closely and definitely determined by spectral observation, shows that the percentage drop of frequency, which a given vibration undergoes when the molecule is electronically excited, is essentially a characteristic of the vibration, and is nearly independent of whether the frequencies belong to benzene or to hexadeuterobenzene. Only a partial explanation of this effect can be given in simple terms, but its reality, which the figures of Table IV illustrate, cannot be doubted. This, then, is one guide; for we should certainly expect those frequencies which we are not able directly to observe, to conform to the rule which all the other frequencies follow.

Again we know empirically, and there is also a theoretical explanation of the fact, that, for a given electronic system, all protium-stretching frequencies lie within a certain narrow range, whilst all deuterium-stretching frequencies lie within another narrow range. These frequency ranges of the upper electronic state are well defined by the spectral observations, not only on benzene and hexadeuterobenzene, but also on all the partly deuterated benzenes. The symmetry class E_u^- of benzene and hexadeuterobenzene contains a hydrogen-stretching vibration, and we may expect its frequencies to conform to the general rule.

Finally, the upper-state frequencies of each of those symmetry classes, A_{2g}, B_{2u}, and E_u^-, of benzene and hexadeuterobenzene with which we are concerned must satisfy the product theorem.

TABLE IV.

Percentage Reduction undergone by Some Fundamental Frequencies (cm.$^{-1}$) of Benzene and Hexadeuterobenzene on Electronic Excitation.

	A_{1g}.		E_g^+.			
C_6H_6 (ground state)	992	3062	606	3047	1596	1178
C_6H_6 (excited state)	923	3130	521	3080	1470	1130
% Drop (C_6H_6)	7·0	– 2·2	14·0	– 1·1	7 ·9	4·9
C_6D_6 (ground state)	943	2293	577	2265	1551	867
C_6D_6 (excited state)	879	2340	499	2320	1403	830
% Drop (C_6D_6)	7·3	–2·2	15·7	–2·5	9·5	4·3

	A_{2u}.	B_{2g}.		E_u^+.		E_g^-.
C_6H_6 (ground state)	671	703	985	405	970	849
C_6H_6 (excited state)	513	365	775	243	706	585
% Drop (C_6H_6)	23·6	48·0	21·3	40·0	27·2	31·1
C_6D_6 (ground state)	496	601	827	352	793	662
C_6D_6 (excited state)	382	306	663	208	590	454
% Drop (C_6D_6)	23·0	49·0	19·8	40·9	25·6	31·4

It seemed desirable to offer, for those upper-state vibrations of benzene and hexadeuterobenzene on which we have no direct spectral information, a set of frequencies which have been fixed as closely as possible with the aid of our empirical, as well as theoretical, resources; and that is why, alongside of the calculated frequencies given in the top right-hand section of Table III, two further columns of figures, headed " E.A.", have been added. The heading means that they are empirically adopted frequencies, which we have fixed as described above, in the first stage roughly, by adjusting the crude, calculated values with the aid of parallel calculations on the ground state, and then more closely by reference to the indications or requirements of all the guiding rules mentioned. The figures are given in rounded form, for, though it is difficult to estimate their accuracy, it would clearly be inappropriate to quote units. However, they satisfy all the tests we are able to apply, including one to be considered in Part XII.

(C) *Summary of Fundamental Frequencies of Excited Benzenes.*

Having now exploited most of the methods by which it seems possible to extract, from observations on the ultraviolet absorption and fluorescence spectra of the various isotopically isomeric benzenes, information about their fundamental vibration frequencies in the upper electronic state, we give, in Tables V and VI, a conspectus of the determined frequencies. Two tables are necessary in order to show how the values shift with the different modes of isotopic substitution. This is because the symmetry of benzene and hexadeuterobenzene can be degraded to that of monodeuterobenzene either by way of the symmetry of 1 : 3 : 5-trideuterobenzene, or through that of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene; and the vibrations group themselves in different ways, and their symmetry classes coalesce in different patterns, according to the route taken.

Many interesting effects of isotopic substitution can be seen amongst these frequencies of the upper electronic state. However, we omit discussion of this matter, because it would be lengthy, and because much of the argument runs parallel to that which has already been fully given with reference to the effects of isotopic substitution on the vibration frequencies of the same molecules in their electronic ground states (*J.*, 1946, 222, *et seq.*). It is thought that the following pages from the papers cited, if read in conjunction with the present Tables, will furnish a sufficient indication of what might have been written about the forms of the vibrations which the excited electronic system controls, and about the ways in which they modify one another when the molecule is loaded with extra neutrons in the different ways studied : *loc. cit.*, pp. 259—265, 268 and 269, 278 and 279, 284—287, 292 and 293, 298 and 299, 312, and 315. It is to be noted that some rather marked differences are exhibited in this connexion between the two electronic states in relation to their out-of-plane vibrations.

The frequencies which appear in Roman type in Tables V and VI, without any added indications, are those which are based directly on spectral observations, and on well-supported assignments of the observed bands. The frequencies which are printed in Roman type in parentheses are also based on observed bands, but with assignments which, so far as the internal spectral evidence is concerned, are still somewhat provisional, though they are supported by theoretical considerations, including some mentioned in Part XII. The frequencies printed in italics, without an additional indication, are calculated from related observed frequencies with the help of the product rule. The italicised frequencies in parentheses are deduced from observed vibration frequencies by consideration of the relevant normal co-ordinates. Finally, the italicised figures in square brackets are the frequencies which have been obtained by a combination of calculation and the application of partly empirical rules, as described above.

TABLE V.

Correlation of Fundamental Frequencies (cm.$^{-1}$) of the Upper Electronic State (**B$_{2u}$**) *of Benzenes of the Symmetry Types D_{6h}, D_{3h}, and C_{2v}.*

Description of vibration.	D_{6h}.			D_{3h}.		C_{2v}.	
	Class.	C_6H_6.	C_6D_6.	Class.	$C_6H_3D_3$.	Class.	C_6H_5D.
C-stretching	A_{1g}	923	879	A_1'	893	A_1	920
H-stretching		3130	*2340*		3135		3129
C-bending	B_{1u}	*985*	*940*		988		990
H-stretching		(*3130*)	(*2340*)		2300		3081
C-bending	E_g^+	521	499	E'	513		517
H-stretching		3080	2320		3085		2348
C-stretching		1470	1403		1428		1472
H-bending		*1130*	(830)		(824)		—
C-deformation	E_u^-	[*1470*]	[*1320*]		—		—
H-bending		[*940*]	[*740*]		—		—
H-stretching		[*3130*]	[*2300*]		2330		—
Out-of-plane	E_u^+	243	208	E''	223	A_2	243
Out-of-plane		706	590		680		(*706*)
Out-of-plane	E_g^-	585	454		495		585
H-bending	A_{2g}	[*1210*]	[*940*]	A_2'	—	B_1	—
C-stretching	B_{2u}	[*1510*]	[*1440*]		—		—
H-bending		[*1010*]	[*750*]		—		—
C-bending	E_g^+	521	499	E'	513		517
H-stretching		3080	2320		3085		3072
C-stretching		1470	1403		1428		1446
H-bending		*1130*	(830)		(824)		—
C-deformation	E_u^-	[*1470*]	[*1320*]		—		—
H-bending		[*940*]	[*740*]		—		—
H-stretching		[*3130*]	[*2300*]		2330		—
Out-of-plane	A_{2u}	513	382	A_2''	411	B_2	476
Out-of-plane	B_{2g}	365	306		360		360
Out-of-plane		775	663		715		720
Out-of-plane	E_u^+	243	208	E''	223		230
Out-of-plane		706	590		680		690
Out-of-plane	E_g^-	585	454		495		552

TABLE VI.

Correlation of Fundamental Frequencies (cm.$^{-1}$) of the Upper Electronic State ($\mathbf{B_{2u}}$) *of Benzenes of the Symmetry Types* D_{6h}, V_h, *and* C_{2v}.

Description of vibration.	D_{6h}.			V_h.			C_{2v}.	
	Class.	C_6H_6.	C_6D_6.	Class.	$C_6H_4D_2$.	$C_6H_2D_4$.	Class.	C_6H_5D.
C-stretching	A_{1g}	923	879	A_g	909	895	A_1	920
H-stretching		3130	*2340*		3132	2355		3129
C-bending	E_g^+	521	499		511	509·5		517
H-stretching		3080	2320		2355	3133		2348
C-stretching		1470	1403		1489	1414		1472
H-bending		*1130*	(830)		*1075*	*820*		—
C-bending	B_{1u}	*985*	*940*	B_{2u}	—	—		990
H-stretching		(*3130*)	(*2340*)		—	—		3081
C-deformation	E_u^-	[*1470*]	[*1320*]		—	—		—
H-bending		[*940*]	[*740*]		—	—		—
H-stretching		[*3130*]	[*2300*]		—	—		—
Out-of-plane	E_u^+	243	208	A_u	243	208	A_2	243
Out-of-plane		706	590		706	591		(*706*)
Out-of-plane	E_g^-	585	454	B_{2g}	585	452		585
H-bending	A_{2g}	[*1210*]	[*940*]	B_{1g}	—	—	B_1	—
C-bending	E_g^+	521	499		516·5	505		517
H-stretching		3080	2320		3075	2333		3072
C-stretching		1470	1403		1469	1414		1446
H-bending		*1130*	(830)		—	—		—
C-stretching	B_{2u}	[*1510*]	[*1440*]	B_{3u}	—	—		—
H-bending		[*1010*]	[*750*]		—	—		—
C-deformation	E_u^-	[*1470*]	[*1320*]		(787)	—		—
H-bending		[*940*]	[*740*]		—	—		—
H-stretching		[*3130*]	[*2300*]		—	—		—
Out-of-plane	A_{2u}	513	382	B_{1u}	435	419	B_2	476
Out-of-plane	E_u^+	243	208		222	233		230
Out-of-plane		706	590		655	665		690
Out-of-plane	B_{2g}	365	306	B_{3g}	357	351		360
Out-of-plane		775	663		775	649		720
Out-of-plane	E_g^-	585	454		457	535		552

In our opinion, the most uncertain of all these frequencies are those of the B_{2u} C-stretching vibration of benzene and hexadeuterobenzene. From their mode of derivation, these two upper-state frequencies are almost bound proportionally to reproduce any considerable error that may affect Herzfeld, Ingold, and Poole's values of the corresponding ground-state frequencies. As these authors emphasized, their assignment of frequencies to the B_{2u}(C) vibration rests on an argument of such a kind that the possibility of error cannot be excluded.

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