106. *Excited States of Benzene. Part XII. The Effect of an Electronic Excitation on the Geometry, Elastic Properties, and Zero-point Energy of the Benzene Molecule: and the Effect of Isotopic Substitution on the Transition Energy.*

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Section A.—Conclusions concerning the geometry and dynamics of the first excited state of benzene are derived from the spectroscopic observations and considerations presented in the preceding papers.

The excited molecule has the full symmetry of a plane regular hexagon, but the C–C bonds are found to have expanded by 2·5% (from 1·39 A. to 1·43 A.), and the C–H bonds to have contracted by 1·0% (from 1·08 A. to 1·07 A.), in the course of the electronic excitation. These geometrical changes can be qualitatively understood on the well-established basis that the optical electron comes from the unsaturation shell. Its promotion produces a new orbital node, intersecting the geometrical bonds of the carbon ring, and thus decreases the bonding properties of the shell. Its excitation also increases the effective nuclear charge and unsaturation of the carbon atoms (which thus experience the beginnings of the development of carbonium ion character), and this shortens those bonds in which the unsaturation electrons do not participate.

The C–C stretching force-constant drops by 14% in the course of the electronic excitation, the bonds thus losing a considerable proportion of that part of their resistance to stretching which they derive from the bonding properties of the unsaturation electrons. The C–H stretching force-constant simultaneously increases by 6%. The electronic explanation of these dynamical changes closely corresponds to that of the associated geometrical changes.

The two elastic constants used to measure the resistance to angular deformation, in the plane of the molecule, of the three bonds of any one carbon atom drop substantially in the electronic excitation. Part of this form of resistance to deformation is not due to the unsaturation electrons: it would be there if they were removed, making every carbon atom a carbonium ion. The part which is due to the unsaturation electrons, and which therefore suffers reduction during the excitation, arises in three ways, *viz.*, by the repulsions exerted by the unsaturation electrons on the various saturated electron-pairs, by the shortening effect of the unsaturation electrons on the carbon bonds, with resulting increase in the repulsions between the saturated electron-pairs, and by the repulsion between the spin-coupled pairs of the unsaturation shell itself. All three effects act on the carbon-angle constant, which diminishes by 23%, but only the first two influence the hydrogen-angle constant, which drops by 17%, in the course of the electronic excitation.

Resistance to out-of-plane deformation is affected much more drastically by the electronic excitation, because such resistance comes almost entirely from the unsaturation shell. An elastic constant associated with the twisting of C–C bonds is reduced by 68%, and a constant connected with the out-of-plane bending of C–H bonds is diminished by 45%. The effect on the twisting constant is due partly to the increase of anti-bonding properties within the unsaturation shell, and partly also to the reduction of the non-bonding repulsions between the shell and other electron pairs. The effect on the out-of-plane bending constant is due essentially to the diminution in the non-bonding repulsions.

Section B.—The position of the electronic origin of the transition studied is not the same for the different isotopic forms of benzene: successive deuteration shifts the origin steadily towards the far-ultraviolet.

The energy of an electronic transition consists, not merely of the difference of electronic energy in the combining states, but of this plus the difference of nuclear-zero-point energy. In the case of benzene and hexadeuterobenzene, we know the vibration frequencies completely enough to be able to calculate the zero-point energy; and it turns out that, in relation to the energy of the electronic transition, the zero-point energy of these molecules is very substantial, being about one-half as large as the purely electronic part of the transition energy. The position of the electronic origin is thus considerably affected by the zero-point energy difference.

The isotope shift of the electronic origin is in principle the sum of the isotopic shifts in the purely electronic transition energy, and in the nuclear-zero-point transition energy. The former effect is negligible in relation to the observed shift, which amounts to 200 cm.$^{-1}$ from benzene to hexadeuterobenzene. This shift can be explained quantitatively on the basis of the zero-point energy effect. An analysis is given of the contributions made by the different types of zero-point vibrations to the total shift.

The shifts observed with the partly deuterated benzenes approximately agree with those which would be deduced by linear interpolation between benzene and hexadeuterobenzene, simply on the basis of the number of deuterium atoms present. This is discussed qualitatively, and is shown to follow plausibly from the known changes which are induced in vibrations by the dissymmetric loading of the molecule.

Correction for the zero-point transition energy leads to a purely electronic transition energy, which is the same for all benzenes.

In this paper we present such conclusions concerning the physics of the states and transitions of the benzene molecule as appear to us to follow from the studies of spectra described in the preceding eleven papers.

(A) *Effect of the* $\mathbf{A_{1g}} \rightarrow \mathbf{B_{2u}}$ *Electronic Transition on the Geometry and Elastic Properties of the Benzene Molecule.*

(1) *Elastic Constants of the Lower and the Upper States.*—The Wilson–Bell potential-energy function provides a good basis for an assessment of the salient features of the effect of the $\mathbf{A_{1g}} \rightarrow \mathbf{B_{2u}}$ electronic transition on the elastic properties of the benzene molecule. In Table I we assemble the determined elastic constants, as they have emerged in the calculations reported in Part XI, Section B. The force-constants F and f are in the form already given: they express the restoring forces per unit change of length, r and s, of a C–C bond and of a C–H bond, respectively. However, bending and twisting force-constants are awkward concepts,* and we here replace the formerly used, carbon and hydrogen, planar-bending force-constants, D and d, as well as the out-of-plane carbon-bond twisting and hydrogen-bond bending, force-constants, Q and g, by the corresponding moment-constants, Δ, δ, Γ and γ, respectively. Each of these quantities expresses the restoring moment generated per unit angular deformation. For Δ, the deformation, ρ, is that of an internal ring-angle; for δ, it is the angular deviation, σ, in the plane of the ring, of a C–H bond from the bisector of the external ring-angle; for Γ, it is the angle, Φ, through which a C–C bond is twisted by the out-of-plane displacements of the adjacent atoms; and for γ, it is the angle, μ, by which the bond of a hydrogen atom deviates from the plane of the nearest three carbon atoms. In terms of these constants, the potential energy expression takes the form

$$2V = F\Sigma r^2 + f\Sigma s^2 + \Delta\Sigma\rho^2 + \delta\Sigma\sigma^2 + \Gamma\Sigma\Phi^2 + \gamma\Sigma\mu^2$$

where $\Phi = \phi_C + \phi_H$ (cf. Part XI, Section B, 1), and each sum extends over six like atoms or six like bonds. The relations between the moment-constants and the force-constants are $\Delta = Da^2$, $\delta = db^2$, $\Gamma = Qc^2$, and $\gamma = gb^2$, where a, b, and c are geometrical constants (cf. *loc. cit.*).

TABLE I.

Elastic Constants of the Benzene Molecule in its Normal and Excited States.

	Force-constants (dynes per cm.).		Moment-constants (dyne-cm. per radian).			
	10^{-5} F.	10^{-5} f.	10^{12} Δ.	10^{12} δ.	10^{12} Γ.	10^{12} γ.
Ground state	7·61	5·06	13·7	8·0	1·02	2·62
Excited state	6·53	5·35	10·5	6·6	0·32	1·43
% Drop	14	−6	23	17	68	45

(2) *Stretching Force-constant and Length of the* C–C *Bonds.*—As noted in Part I, Section 2, the electronic excitation $\mathbf{A_{1g}} \rightarrow \mathbf{B_{2u}}$ involves the promotion of one of the six unsaturation electrons from a molecular orbital of $\mathbf{e}_g^-$ symmetry to one of $\mathbf{e}_u^+$ symmetry. On an energy scale, the electron can be considered to have been raised just about half-way towards complete ionisation (ionisation potential, 9·19 electron-volts). From a stereo-electronic standpoint, the excited orbital has one additional nodal surface of indefinite orientation intersecting the geometrical bands, and therefore must have increased anti-bonding properties. From both points of view, one would expect the excitation to diminish both the strength of the C–C bonds and their resistance to stretching.

Consistently with its average content of three electrons, a C–C bond of normal benzene exhibits a degree of resistance to stretching which is intermediate between the degrees of resistance shown by the C–C bonds of normal ethane and ethylene:

Force-constants (F) of the normal molecules	ethane,	benzene,	ethylene.
10^{-5} F (with F in dynes/cm.).....................	4·5	7·6	9·8

It is the excess of resistance of the benzene bond, over that shown by the ethane bond, that we should expect to find considerably reduced as a result of the electronic excitation; and thus it seems very reasonable that 10^{-5} F for excited benzene should have a value 6·5, which is well bracketed between 4·5 and 7·6.

Badger's relation between the force-constants and the lengths of bonds (*J. Chem. Physics,*

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* The use of the term " bending force-constant " has often led to untidy notations, which its replacement by " moment-constant " would have avoided. Quantities which are really moment-constants have been called " bending force-constants ", and have even been expressed in incorrect units.

1934, **2**, 128) can be made the basis of a procedure for estimating the expansion which the benzene ring undergoes as a result of the electronic excitation. The relation takes the form

$$X = k(x - \kappa_{ij})^{-3}$$

where X is a force-constant in dynes/cm., x is the equilibrium bond-length in Ångström units, k is a universal constant, the best value of which, for general purposes, is $1{\cdot}85 \times 10^5$, and κ_{ij} is a constant which depends on the principal quantum numbers of the bonding electrons, and for a carbon–carbon bond has the value 0·68. If we make the plausible assumption that, for the bond of a benzene ring, the best value of k, though not exactly equal to the general average value, is, to a close approximation, the same for both electronic states, then, using our determined values of F, we can write the following expression for the precentage increase which the carbon bond-length undergoes as a result of the electronic excitation :

$$100(1{\cdot}39 - 0{\cdot}68)\{(7{\cdot}61/6{\cdot}53)^{1/3} - 1\}/1{\cdot}39 = 2{\cdot}7\%$$

Douglas Clark's relationship, $X = Cx^{-6}$ (*Phil. Mag.*, 1934, **18**, 459), gives a similar result. Taking the constant C to be the same in both states, the percentage enlargement becomes

$$100\{(7{\cdot}61/6{\cdot}53)^{1/6} - 1\} = 2{\cdot}6\%$$

Thus the C–C bond-length in the excited molecule is close to 1·43 A.

Kynch and Penney have made a quantum-mechanical calculation, using the electron-pair method, of some of the properties of the excited state of benzene (*Proc. Roy. Soc.*, 1941, *A*, **179**, 266). For the length of the C–C bond they found 1·44 A., in good agreement with the value given above. For the ring-breathing frequency they found 918 cm.$^{-1}$, remarking that " this agrees moderately well with the experimental measurement of 940 cm.$^{-1}$ ". Of course, it agrees much better with the correct experimental value, 923 cm.$^{-1}$ (of. Part II, Section 4; the value is 924 cm.$^{-1}$ when correction is applied for the anharmonicity of the vibration).

(3) *Stretching Force-constant and Length of the* C–H *Bonds.*—It might have been expected that the electronic excitation *increases* the vibration frequency and force-constant of the C–H bonds. If we could completely remove one unsaturation electron from a single carbon atom, the effect might well be to shorten the C–H bond considerably, and increase its resistance to stretching, both because of the increased effective nuclear charge of the carbon atom, and because of the incompleteness of its valency shell (Pauling, " Nature of the Chemical Bond ", Cornell Press, 1940, p. 169). A rough estimate, based on known bond-lengths, gives 0·1 A. as the probable order of magnitude of the contraction in this case. Actually, the excitation partly removes, from the near locality of each carbon nucleus, one-sixth of an unsaturation electron; and so one may plausibly suppose that the resultant contraction is likely to be only of the order of 0·01 A. This, however, is the correct order of magnitude for correlation with the determined increase of 6% in the force-constant f. Alternatively, we can use known force-constants in order to estimate directly the probable order of magnitude of the increase in force-constant (cf. Herzberg, " Infra-red and Raman Spectra ", van Nostrand, 1945, p. 192), and can thus discover that an increase of the order of 5% would be reasonable.

In an application of Badger's relation to a C–H bond, the constant κ_{ij} takes the value 0·34. Using this relation as before, together with the determined values of the force-constant f, we calculate the percentage shortening of the bond thus :

$$100(1{\cdot}08 - 0{\cdot}34)\{1 - (5{\cdot}06/5{\cdot}35)^{1/3}\}/1{\cdot}08 = 1{\cdot}3\%$$

Alternatively, using Douglas Clark's relation as before, we find for the contraction

$$100\{1 - (5{\cdot}06/5{\cdot}35)^{1/6}\} = 0{\cdot}9\%$$

Thus the C–H bond-length in excited benzene lies close to 1·07 A.

Sklar's theory of the electronic transition, and its ample verification in the spectra, establishes the plane-hexagonal (D_{6h}) symmetry of the equilibrium nuclear configuration of the excited benzene molecule. The above estimates of the equilibrium C–C and C–H bond-lengths in the excited state thus complete the determination of the geometry of the model of the excited molecule.

(4) *The Planar Bending Moment-constants.*—Since the planar variations of the three valency angles of any one carbon atom involve the relation that their sum is zero, the individual variations are expressible in terms of two parameters. The constant Δ measures the restoring moment which is produced when the CCC angle changes in one direction by a certain amount, and each CCH angle simultaneously changes in the other direction by half that amount. The

constant δ measures the moment which is called into operation when the two CCH angles simultaneously change in opposite directions by equal amounts, the CCC angle remaining unaltered.

Independently of the unsaturation electrons, the trigonal constitution of the carbon atomic orbitals of the three saturated electron-pair bonds tends to place the latter at angles of 120° to one another; and the repulsive forces of the three electron-pairs on one another tend to keep them close to these relative positions. However, the superposed effect of the unsaturation electrons in helping to maintain the structure is clearly shown by the observed weakening of the restoring moments, as measured by the moment-constants Δ and δ, when the unsaturation shell becomes attenuated as a result of the electronic excitation. We should note that the unsaturation electrons will exert their effect in at least two ways—partly through the repulsive forces which they themselves exert on the different saturated electron-pairs, and partly by shortening the C–C bonds, and thus enabling the three saturated electron-pairs of any one carbon atom to exert stronger repulsive forces on one another than they would otherwise. We cannot say much about the anticipated magnitude of the weakening which will be suffered, as a result of the electronic excitation, by the whole of this contribution of the unsaturation electrons to the angular rigidity of the system; though one might (somewhat naïvely) expect the percentage reduction of the moment-constants Δ and δ to be of the same order of magnitude as that of the stretching force-constant F—in so far as the changes in Δ and δ result from the effects considered. Actually, these should be the only major effects on the constant δ; and we notice (Table I) that the percentage change which it undergoes is, in fact, not very different from that of the force-constant F.

However, the above effects are expected to be reinforced by yet another in the case of the moment-constant Δ. This further effect arises from the repulsive forces between the different spin-coupled electron-pairs of the unsaturation shell itself. These pairs will tend to keep apart, and their repulsion will accordingly tend to open the internal ring-angles. The effect of this will be to steepen, on the side of small angles, the potential hollow which restricts the variation of a ring-angle. But even such a one-sided steepening of the potential hollow must make it narrower, and must therefore increase the angular vibration frequency, and the corresponding moment-constant. The decrease of this contribution to the moment-constant Δ, as the unsaturation shell becomes attenuated by excitation, must also be included amongst the causes of the observed reduction of this constant. We notice (Table I) that the percentage reduction of Δ is, in fact, appreciably larger than is that of the other planar moment-constant δ.

(5) *The Out-of-plane Moment-constants.*—As Table I shows, the two out-of-plane constants, Γ and γ, suffer much more drastic reductions, as a result of the electronic excitation, than do any of the planar elastic constants which we have been considering. This is not difficult to understand.

The constant Γ measures the harmonic resistance of a C–C bond to such torsion as arises from unequal out-of-plane displacements of the atoms attached on each side of it. Now according to our theories of chemical binding, practically the whole of such resistance to torsion must come from the unsaturation electrons; for the saturated electron-pair belonging to any bond is supposed to have full cylindrical symmetry about the line of the bond. It follows that any change in the state of the unsaturation shell must profoundly affect the constant Γ, and that, in particular, a replacement of bonding by antibonding character within the shell, such as occurs during the electronic excitation, must strongly reduce Γ. A second reason for the reduction of Γ consists in the diminution of the non-bonding repulsive forces exerted by the unsaturation shell on the neighbouring saturated electron-pairs.

The second out-of-plane constant, γ, measures the harmonic resistance to the bending of a hydrogen atom out of the plane of the nearest three carbon atoms. Since this type of hydrogen motion is tangential to the contours of electron density of the saturated electron-pairs belonging to the C–C bonds, these electron-pairs will contribute relatively slightly to the harmonic restoring moment. But since the hydrogen motion lies across the common nodal plane of the unsaturation electrons, and is directed as nearly as any bending motion can be towards their density gradients, these electrons will contribute largely to the restoring moment. Thus the harmonic restoring moment will owe its existence largely to the unsaturation electrons.* It should be noted that they exert their effect in this case solely by their repulsive action on the electrons of the C–H bond, and not indirectly through shortening the C–C bond. It follows that any change of state of the unsaturation shell must strongly influence the moment-constant γ; and that, in

* That the saturated electron-pairs can in principle make a finite, if small, contribution to the harmonic restoring moment is not intuitively obvious; but it can be established by an easy calculation.

particular, the attenutation of the shell, as a result of the electronic excitation, must very considerably reduce that constant.

We refer here to the attenuation of the unsaturation shell during excitation, but not to the increase of anti-bonding properties within it, because the latter effect is less important for interactions with outside electron-pairs than when the bonded character of the unsaturation shell itself is in question, as in the problem of the torsion constant Γ. That will be one reason why, although the out-of-plane bending constant γ is, indeed, much reduced, it is not, as Table I shows, so greatly reduced as is the torsion constant Γ.

Finally, a probable relationship between the two hydrogen-bending constants, δ and γ, may be pointed out. As we have seen, the planar-bending moment-constant δ can be considered as made up of two parts, one of which would still be present if the unsaturation shell could be removed, whilst the other is due to the unsaturation shell. Only the latter part is strongly reduced by the electronic excitation. It follows that we may take the observed value of $\delta_{\text{ground}} - \delta_{\text{excited}}$ as a lower limit to the value, in the electronic ground state, of that part of δ which depends on the unsaturation electrons. Now if the ground-state value of this part of δ were entirely determined by the repulsion between the unsaturation electrons and the electrons of the C–H bond, we could at once assert that it must be smaller than the ground-state value of γ, which is mainly determined by the type of electron repulsion specified. This follows because, in the planar motion, the denser parts of the electron cloud of the C–H bond move in the near neighbourhood of, and parallel to, the common nodal plane of the unsaturation electrons, and quite obliquely to their density gradients; whereas, on the contrary, the out-of-plane motion is directed across the nodal plane, and much more nearly towards the density gradients. The conclusion would thus be that a quantity which is substantially larger than $\delta_{\text{ground}} - \delta_{\text{excited}}$ is also substantially smaller than γ_{ground}. But we have noted before that the part of δ which depends on the unsaturation electrons, although it arises largely through the mechanism of direct repulsion between these electrons and the electrons of the C–H bond, must also to some extent be due to an indirect effect arising through the shortening influence of the unsaturation electrons on the C–C bonds. Our conclusion must therefore be modified to the following, *viz.*, that a quantity which is somewhat smaller than that mentioned above, and which, therefore, may not be very different from $\delta_{\text{ground}} - \delta_{\text{excited}}$, must be substantially smaller than γ_{ground}. That is to say, the quantity $\delta_{\text{ground}} - \delta_{\text{excited}}$ itself is likely to be definitely smaller than γ_{ground}. This expected relationship is fulfilled by the data of Table I.

(6) *Note on the Assignments of Planar Hydrogen-bending Frequencies to the Excited State.*—In so far as our assignments of upper-state frequencies to the planar hydrogen-bending vibrations of benzene in its different isotopic forms rest on evidence of a direct spectral nature, they are less well supported than are the spectrally-based assignments to vibrations of other types. However, the preceding argument provides some general confirmation of the assignments we have adopted. For essentially it is these assignments which determine the moment-constant δ_{excited}. The above conclusion, that δ_{excited} should fall below δ_{ground} by an amount which is substantially less than γ_{ground}, means that $10^{12}\,\delta_{\text{excited}}$ should fall well within the range $6{\cdot}7 \pm 1{\cdot}3$. Since frequencies shift comparably to the square-roots of moment-constants, this in turn means that the planar hydrogen-bending frequencies should not lie many units per cent. away from the values we have assigned to them. A further argument pointing to the same conclusion is mentioned later (Section B, 5).

(B) *Effect of the* $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Electronic Excitation on the Zero-point Energy of the Benzene Molecule; and the Effect of Isotopic Substitution on the Energy of the* $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Electronic Transition.*

(1) *The Isotopic Shift of the Electronic Origin.*—Since the transition $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ is forbidden, no 0—0 band appears to mark the position of the electronic origin of the band-system, and thus to give directly the energy of the electronic transition. However, Sklar's identification of the upper electronic state, and Nordheim, Sponer, Sklar, and Teller's explanation of the mechanism through which the transition becomes observable, are so well proven that the position of the origin in the spectrum of any of the isotopically isomeric benzenes which have been studied can be fixed with as much certainty as if it were marked by a visible band. In Parts II—X the positions of the origins of the various band-systems are given. These figures are now assembled in Table II. It is unlikely that any of the figures is in error by more than 2 cm.$^{-1}$.

One notices that the different isotopically isomeric benzenes have not all the same electronic origin: that of hexadeuterobenzene lies 200 cm.$^{-1}$ further out towards the far-ultraviolet than that of benzene. Furthermore, the shift with isotopic substitution is an approximately linear function of the number of deuterium atoms present in the molecule. A finer point is that the departures from linearity appear to be systematic, in the sense that the origin frequencies of the middle members of the series, those with two, three, and four deuterium atoms, lean slightly towards lower values than the linearly interpolated ones, the deviation being greatest for the central member, 1 : 3 : 5-trideuterobenzene.

TABLE II.

Frequencies (cm.$^{-1}$) of the Electronic Origins of the First Ultraviolet Band-systems of the Isotopically Isomeric Benzenes, as observed in either Fluorescence or Absorption.

	Origin frequency.	Difference.	Deviation from linearity.
Benzene	38090		± 0
Monodeuterobenzene	38124	34	+ 1
1 : 4-Dideuterobenzene	38154	30	− 3
1 : 3 : 5-Trideuterobenzene	38184	30	− 6
1 : 2 : 4 : 5-Tetradeuterobenzene	38219	35	− 4
Pentadeuterobenzene	—	2 × 35	—
Hexadeuterobenzene	38290		± 0

(2) *The Contribution of Vibrational Zero-point Energy to the Transition Energy.*—We shall show that practically the whole of the observed shift is due to vibrational zero-point energy. The energy of an electronic transition is not simply the difference between the electronic energies of the two combining states : it is this, *plus* the difference between their nuclear-zero-point energies. To a very close approximation the electronic energy of each state remains the same in an isotopic substitution, and therefore the difference between the electronic energies of the two states remains the same. However, the vibrational zero-point energy of each state will be changed by isotopic substitution, and, if the changes are different, then the contribution of the zero-point energy to the transition energy will be different for the isotopically isomeric molecules.

For simplicity, let us consider a vibration of benzene which is alone in its symmetry class, *e.g.*, the vibration E_g^-(H). We can then discuss it independently of the other vibrations. Since it is doubly degenerate, its contribution to the zero-point energy ($h\nu/2$ in each of two degrees of freedom), if expressed in frequency units, is equal to its fundamental frequency. For the electronic ground state, this is 849 cm.$^{-1}$. In the electronic excitation the forces are loosened and the frequency drops, so that the contribution of this vibration to the zero-point energy of the upper electronic state is only 585 cm.$^{-1}$. The difference between these two quantities, -264 cm.$^{-1}$, is the contribution of the zero-point energy of the vibration to the energy of a transition from one " vibrationless " electronic state to the other. Its sign is opposite to that of the electronic energy difference, so that its effect is to shift the electronic origin to a lower frequency than that which the origin would have if there were no zero-point energy. Starting again in the ground state, we make the isotopic substitution which converts benzene into hexadeuterobenzene, thus reducing the fundamental frequency, and therefore the zero-point energy contribution, of the vibration by a factor which is given by the product rule. This energy is, in fact, reduced to 662 cm.$^{-1}$. In the upper electronic state also, the zero-point energy contribution becomes reduced by a factor, which is likewise given by the product rule, and is very nearly the same as before. This energy accordingly becomes 454 cm.$^{-1}$. The difference between these two quantities, -208 cm.$^{-1}$, could obviously be calculated by reducing the former difference, -264 cm.$^{-1}$, by almost the same factor. (The various factors can be considered identical, if we agree to neglect anharmonicity and the small difference in the size of the molecule in its two electronic states.) Each of the differences, -264 cm.$^{-1}$ for benzene, and -208 cm.$^{-1}$ for hexadeuterobenzene, is a negative contribution to the energy of electronic excitation of the relevant molecule : each shifts the origin towards lower frequencies, but the reduction of frequency is greater for benzene than for hexadeuterobenzene. Thus the difference between the differences, $+56$ cm.$^{-1}$, represents the contribution of the zero-point energy of this vibration to the upward displacement of the excitation energy of hexadeuterobenzene relatively to that of benzene.

Only three vibrations of benzene are alone in their symmetry classes, and it is not theoretically rigorous to discuss the other seventeen on similar lines. But to quite a reasonable degree of approximation one may do so. For it has been shown empirically that the electronic excitation not only reduces, as the product theorem necessitates, the products of frequencies of the same symmetry class by substantially the same factor for benzene and hexadeuterobenzene : it also reduces each individual frequency by approximately the same factor for both compounds (cf. Part XI, Section B, 3, especially Table IV). This fact is sufficient to ensure that any vibration whose frequency is considerably reduced by the conversion of benzene into hexadeuterobenzene, and is also considerably reduced by the electronic excitation, will act like the E_g^-(H) vibration considered above : it will supply to the energy of the electronic excitation of each compound a contribution, consisting of a difference of zero-point energies, which displaces the electronic origin towards lower frequencies, but does so in such a way as to leave the electronic origin of hexadeuterobenzene at a higher frequency than that of benzene.

The great majority of the vibrations of benzene have their frequencies reduced both by complete deuteration of the molecule and by the electronic excitation, although in some cases the changes are not very large. All these, if they have any decided effect on the relative positions of the electronic origins, will act in the way described. Thus it is not unnatural that the total contribution of the zero-point energy of all the vibrations to the energy of the electronic excitation should be of the kind illustrated; and that, accordingly, we should, as we do, find that the electronic origin of the hexadeuterobenzene transition lies at a higher frequency than that of the benzene transition.

One group of vibrations is anomalous, *viz.*, the hydrogen-stretching vibrations. These have their frequencies reduced (obviously) by deuteration, but increased quite appreciably by the electronic excitation. It will be evident from the foregoing discussion that the zero-point energy contribution of such vibrations will be in the direction of raising the energy of the electronic excitation; and furthermore, that the magnitude of the contribution will be greater for benzene than for hexadeuterobenzene. It follows that, if this difference were the dominating one, the electronic origin of the transition of benzene would lie higher than that of the transition of hexadeuterobenzene. However, the effect of the hydrogen-stretching vibrations is, in fact, not powerful enough to prevail against the contrary action of all the other vibrations.

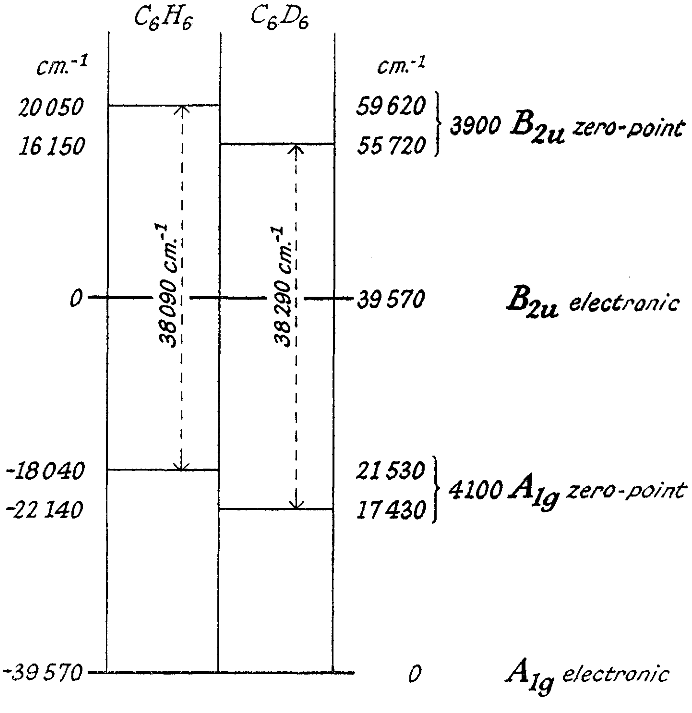
We now turn to the partly deuterated benzenes. One might have expected that their electronic origins would space themselves out according to the number of deuterium atoms; and that, in rough approximation, the spacing would correspond to a linear interpolation between the electronic origins of benzene and hexadeuterobenzene. It is true that, as symmetry is reduced by the isotopic loading of the partly deuterated benzenes, with the consequence that certain vibrational symmetry classes become fused together, many of the vibrations which are characteristic of benzene and hexadeuterobenzene become mixed. But when two vibrations thus mix, even when they do so rather completely, as do, *e.g.*, the ring-swelling, and plane-trigonal ring-bending, vibrations of benzene or hexadeuterobenzene in forming the two totally symmetrical carbon vibrations of 1 : 3 : 5-trideuterobenzene (cf. *J.*, 1946, 259, 260), the effect on the frequencies is merely to push them apart in such a way that their sum, and therefore the sum of their zero-point energies, is not very different from what it would have been if the isotopic loading of the molecule had been so levelled out as to stop the mixing, *i.e.*, if, in this example, the molecule had been supplied with six hydrogen atoms of atomic weight 1·5. In short, the sum of the frequencies will not differ greatly from a linearly interpolated sum. Many of the mixings which occur when successive deuterium atoms are introduced into benzene are more complicated than this, and, in particular, involve more than two vibrations; but such mixings may be analysed into successive two-component mixings, and thus the rough principle of a linear shift of summed frequencies may be expected still to hold. Furthermore, the deviations shown by particular groups of mixed vibrations, due to the dissymmetric pushing apart of frequencies, are likely to occur about equally often in either direction, so that for the complete sum of all the vibration frequencies, and therefore for the total vibrational zero-point energy, the law of linear interpolation might be expected to hold rather well. Now all this is true not only for the ground state, but also for the excited state. Therefore linear interpolation should hold, not only for each state separately, but also for the difference between the zero-point energies of the ground and the excited states. In short, it should hold for the contribution of zero-point energy to the energy of excitation, and for the effect of zero-point energy on the position of the electronic origin.

We can offer no correspondingly simple treatment of the small, but apparently systematic, deviations from the linear relationship which the observational figures disclose, because the errors introduced by the simplifications tried cannot be shown to be of a smaller order of magnitude than that of the deviations themselves.

(3) *The Isotope Effect on the Electronic Part of the Transition Energy.*—The second conceivable cause of isotope shifts in the electronic origins of the band systems is the occurrence in the molecular case of the effect, with which we are familiar in atoms, arising from the altered reduced masses of the electrons. Although we cannot calculate this effect in molecules, it is easy to show that it must be too small to have any relevance to the present observations.

The Rydberg constants for a protium atom and a deuterium atom differ as 1 differs from $1 + 1/(2 \times 1835)$. Therefore, if the benzene transition, amounting as it does to 38090 cm.$^{-1}$, consisted in the excitation of an electron which belonged entirely to one hydrogen atom, or entirely to all the hydrogen atoms, and not to any of the carbon atoms, we should expect the electronic energy of the transition to be altered in hexadeuterobenzene, on account of the altered reduced mass of the electron, by a quantity of the order of $38090/3670 = 10$ cm.$^{-1}$. But we believe that the optical electron has actually very little to do with the hydrogen atoms, and that it belongs essentially to the carbon atoms. For this reason we do not expect the isotope shift in the purely electronic part of the excitation energy to be of a greater order of magnitude than 1 cm.$^{-1}$—which is the order of the experimental error.

(4) *Quantitative Comparisons for Benzene and Hexadeuterobenzene.*—From the last paragraph it follows that, in seeking to establish a quantitative connexion between theory and experiment, we can confine attention to the isotope shift in the zero-point energy contribution to the transition energy. A quantitative test is possible for benzene and hexadeuterobenzene, because for these molecules we have complete sets of vibration frequencies, not only for the electronic ground state (Herzfeld, Ingold, and Poole, *J.*, 1946, 332), but also for the upper electronic state (Part XI, Tables V and VI, this vol., pp. 506, 507). The cases of the partly deuterated benzenes can then be allowed to rest on the discussed rule of linear interpolation.



Electronic and zero-point energy levels (cm.$^{-1}$) of the **A_{1g}** *and* **B_{2u}** *states of benzene and hexadeuterobenzene.*

The results of the test, applied to benzene and hexadeuterobenzene, are shown in Table III; in which, for convenience, we express energies in wave-numbers. The calculated isotopic shift of the electronic origin is 208 cm.$^{-1}$, whilst the observed shift is 200 cm.$^{-1}$. The agreement is closer than one had any right to expect, having regard to the errors to which the frequencies are liable.

Attention may be directed to the considerable magnitude of the zero-point energy of benzene. It appears that one would have to heat that substance to more than 1300° c. in order to add as much energy again, or to more than 1500° c. to add as much vibrational energy, as the molecule already possesses at the absolute zero of temperature. A remarkable fact is that the zero-point energy in either state is of the order of one-half of the energy of the electronic transition. This is shown in the figure, which is a graphical expression of the data for benzene and hexadeutero-

TABLE III.

Zero-point Energies (cm.$^{-1}$) of the States and Transitions of Benzene and Hexadeuterobenzene, interpreting the Isotope Shift of the Electronic Origin of their Band Systems.

	C_6H_6.	C_6D_6.	Isotope shift.
Excited state ($\mathbf{B_{2u}}$)	20050	16154	− 3896
Ground state ($\mathbf{A_{1g}}$)	21535	17431	− 4104
Transition ($\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$)	− 1485	− 1277	+ 208

benzene, contained in Tables II and III, the units of wave-numbers having been rounded off in order to secure consistency. The figure shows that the electronic transitions actually take place rather far from those positions in the energy diagram in which we usually think of them.

The change of purely electronic energy associated with the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ transition of either benzene or hexadeuterobenzene is

$$39570 \text{ cm.}^{-1} = 4{\cdot}88 \text{ electron-volts.}$$

It is of interest to examine how the various types of vibrations contribute to the shift of the electronic origin. For this purpose we divide the vibrations into four groups. The first consists of all the planar carbon vibrations, stretching, bending, and deformation, the frequencies of which are not greatly altered by the isotopic substitution. The second is the group of hydrogen-stretching vibrations. The third consists of the planar hydrogen-bending vibrations. The fourth comprises all the out-of-plane vibrations, in most of which hydrogen and carbon types of motion are not at all sharply separated from one another (cf. *J.*, 1946, 261, *et seq.*). An analysis of the effects attributable to these four sets of vibrations is set out in Table IV. One sees that the carbon vibrations have very little effect on the isotopic displacement of the transition energy; that the out-of-plane vibrations could account for the whole of the observed effect; but that the hydrogen-stretching and planar hydrogen-bending groups of vibrations make significant contributions, which, however, largely cancel each other.

TABLE IV.

Analysis of the Contributions made by Four Groups of Vibrations to the Zero-point Energies (cm.$^{-1}$) of the States and Transitions of Benzene and Hexadeuterobenzene, and to the Shift of the Electronic Origin.

		C_6H_6.	C_6D_6.	Isotope shift.
Excited state	Planar C	5170·0	4851·5	318·5
	„ H-stretching	9340·0	6960·0	2380·0
	„ H-bending	3180·0	2415·0	765·0
	Out-of-plane	2360·5	1927·5	433·0
Ground state	Planar C	5511·4	5200·5	310·9
	„ H-stretching	9187·7	6850·3	2337·4
	„ H-bending	3433·0	2611·3	821·7
	Out-of-plane	3403·4	2768·9	634·5
Transition	Planar C	− 341·4	− 349·0	− 7·6
	„ H-stretching	+ 152·3	+ 109·7	− 42·6
	„ H-bending	− 253·0	− 196·3	+ 56·7
	Out-of-plane	− 1042·9	− 841·4	+ 201·5
Transition (total)		− 1485·0	− 1277·0	+ 208·0

The reason why the nine carbon vibrational degrees of freedom make no significant contribution to the displacement of the origin is because this appears as a second difference, and the carbon frequencies, although they are appreciably reduced by the electronic excitation, are not greatly shifted by the isotopic substitution. All the other groups of frequencies are considerably shifted by the isotopic substitution; but the reason why the out-of-plane vibrations, with their nine degrees of freedom, exert so very much more influence on the displacement of the origin than do either of the planar hydrogen groups, each with six degrees of freedom, is that the out-of-plane vibrations suffer a much larger diminution of frequency as a result of the electronic excitation than do the planar vibrations. The contrary signs of the moderate contributions made by the hydrogen-stretching and planar hydrogen-bending groups of vibration are evidently to be correlated with the circumstance that the stretching frequencies are increased, whilst the bending frequencies are decreased, by the excitation.

(5) *Further Note on the Upper-state Assignments of Planar Hydrogen-bending Frequencies.*—The preceding analysis provides some further confirmation of the conclusion (cf. Section A, 6) that our assignments of planar hydrogen-bending frequencies, in the upper electronic states of the various isotopically isomeric benzenes, are substantially correct; and all such confirmation is welcome, because the direct spectral evidence on which that particular series of assignments originally rested was somewhat slender. The present argument is as follows. Since the zero-point energy of the out-of-plane vibrations, the frequencies of which are well supported, could by itself account for the whole of the observed shift of the electronic origin, and since the planar carbon vibrations can make very little contribution to the shift, it is evident that the contributions of the planar hydrogen-stretching and hydrogen-bending vibrations have got, roughly, to balance. Isotopic substitution reduces the hydrogen-stretching and hydrogen-bending frequencies by similar factors. Electronic excitation increases the hydrogen-stretching frequencies, and the order of magnitude of the increase is well-documented. It follows that the electronic excitation must decrease the hydrogen-bending frequencies by an average amount, that can be roughly computed from the condition that it must produce the balancing described. This computed average decrease is in fairly good agreement with our assignments of the hydrogen-bending frequencies.

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