364. *Structure of Benzene. Part X. Remarks on the Intensities of the Raman Lines in Benzene and Hexadeuterobenzene.*

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This paper deals with the theory of the effect of isotopic substitution on the intensities of Raman lines and infra-red absorption bands. In Parts III and IV quite irregular changes of intensity were found on passing from C_6H_6 to C_6D_6. They are now explained and the theory is quantitatively illustrated with respect to Raman intensities for which the experimental measurements have quantitative significance.

It is shown to be necessary for the calculation of intensity changes to consider collectively the dynamically inter-related vibrations of a symmetry class, including in each class any rotation thereto belonging, since, in general, rotations as well as vibrations can change the dipole moment vector and the polarisability tensor, on the variations of which absorption and scattering respectively depend.

The intensity changes in the A_{2u} infra-red vibration (relative parallel displacements of carbon and hydrogen hexagons along the six-fold axis), the two A_{1g} Raman vibrations (symmetrical expansion and contraction frequencies) and the E_g^- Raman vibration (relative rotation of carbon and hydrogen hexagons about a common axis in the ring-plane) are calculated in detail. The reason why the last, the only vibration of its class, gives rise to a stronger Raman line in C_6D_6 although the vibration amplitude must be smaller (a difficulty mentioned in Part III) is that the symmetry class includes a rotation. The effect of this rotation upon the variation in polarisability is taken into account in calculating the intensity change. The calculated intensities (and polarisations) agree well with experiment.

1. *General Remarks.*—The data of Angus, Ingold, and Leckie (Part III, J., 1936, 925) on the intensities and polarisations of the Raman lines in benzene and hexadeuterobenzene

furnish a means of testing quantitatively the general theory of intensities in the Raman effect. The infra-red absorption of these compounds has likewise been investigated (Bailey, Hale, Ingold, and Thompson, Part IV, J., 1936, 936), but since experimental absorption intensities in general have only qualitative significance, our discussion will be confined almost wholly to the Raman effect.

A glance at both the Raman and the infra-red data reveals a pronounced irregularity in the intensity changes produced by substitution of deuterium for hydrogen in benzene. In the infra-red, for example, the benzene frequency at 1485 cm.$^{-1}$ ($E_u^{-(c)}$) is of the same high intensity as the other active fundamentals, whereas in hexadeuterobenzene the corresponding band at 1333 cm.$^{-1}$ has become so weak that it is of the same intensity as several combination bands in its neighbourhood. The remainder of the active frequencies, on the other hand, exhibit about equal intensities in the two compounds. In the Raman effect, the 849 cm.$^{-1}$ line in benzene (E_g^-) is 35% *less* intense than the cognate line in hexadeuterobenzene, while the totally symmetrical ring vibration ($A_{1g}^{(c)}$) has about the same strength in both compounds. The two degenerate ring frequencies ($E_g^{+(c)}$), on the contrary, exhibit marked intensity decreases in hexadeuterobenzene.

Such irregularity is not surprising when one considers that the various Raman lines and infra-red bands arise from different modes of molecular vibration. The changes in polarisability α and in electric moment M of the molecule, which determine respectively the intensities of the molecule's Raman scattering and infra-red absorption, are directly dependent on the vibration forms. The several vibration forms may be altered variously by isotopic substitution, and in consequence the effect of substitution on intensities in the Raman effect and infra-red may differ considerably from one vibration type to the next. Investigation of the modes of vibration and of the functional dependence of α and M upon them is therefore a prerequisite to the determination of intensity relationships in isotopically related molecules.

This investigation is simple only for such normal vibrations as are alone in their symmetry classes, because the form of these vibrations is determined by symmetry. In most polyatomic molecules, however, nearly every vibration form has to share a symmetry class with one or more of the other forms. In benzene, for example, two modes share symmetry class A_{1g} (see Part VIII, J., 1936, 971), four share class E_g^+, two class E_u^+ and so on. Whenever several modes possess a common symmetry, these modes are dynamically inter-related, with the result that the amplitudes and frequencies of vibration cannot be calculated for each mode independently of the others, but rather must be calculated simultaneously for the entire class of modes. Since α and M depend on the amplitudes of vibrational motion, the intensities both of Raman scattering and of infra-red absorption due to vibration modes of a given symmetry class must also be inter-related. In studying intensity changes produced by isotopic substitution, we are thus compelled to consider changes in an entire class rather than in individual lines or bands.

It should be stated that one may also classify the various translational and rotational forms of molecular motion according to their symmetry properties, and in addition, that translation and rotation may share their symmetry classes with one or more vibration forms. The calculation of isotopic intensity shifts for such communal symmetry classes must then involve a consideration of the dependence of α and M on translation and rotation. Translation does not influence either α or M. Rotation, on the other hand, has a well-known effect on these quantities, so that the presence of a rotational type of motion in any symmetry class must be taken into account in the determination of the intensity relationship in that class.

The vibrational type A_{2u} affords the simplest illustration of the foregoing discussion. This mode is infra-red-active, and to its symmetry class belongs only one other type of motion (translation along a line normal to the ring plane), which does not affect our discussion of intensities. We have therefore only to consider the relative changes in the M's due to this vibration in benzene and hexadeuterobenzene. The intensities are proportional to the squares of these changes. The changes in M are proportional to the amplitudes of vibration, which are in turn proportional to the square roots of the frequencies. The intensities should thus be in the same ratios as the frequencies, *i.e.*, 671 : 503. Actually this band appears, from the extinction coefficients, to be weaker in hexadeuterobenzene by about one-third, but as we have remarked, data on infra-red absorption intensities ordinarily have little quantitative significance.

2. *Intensity Change in Class* E_g^-.—The doubly degenerate Raman-active frequency of symmetry E_g^- offers a somewhat more complicated problem. In discussion with Professor Ingold one of us (E. T.) suggested that this frequency should have an intensity in hexadeuterobenzene lower than that in benzene by a factor equal to the ratio of the frequencies (Part VIII, *loc. cit.*). An intensity shift of this size and direction should certainly be expected if the vibration E_g^- were alone in its class. The degenerate vibration, however, shares the class with a " doubly degenerate " rotation, and the intensity discussion must take the latter into account.

The motion of class E_g^- consists of rotation of the carbon ring and of the hydrogen ring about a common axis, which may be either of two mutually perpendicular axes lying in the plane of the rings. If the carbon and hydrogen hexagons rotate in the same direction and through the same angle, the motion is a pure rotation. If the rings move in opposite directions so that the sum of their angular momenta is zero, the motion is vibrational (Part VIII, Fig. 1). The rotation of the two rings produces a distortion of α which leads to the presence of the vibration in the Raman effect. Let us call the magnitude of this distortion $\Delta\alpha$.

The intensity of Raman scattering is proportional to $(\Delta\alpha)^2$. We are interested in the ratio $(\Delta\alpha)^2/(\Delta\alpha')^2$. The prime (′) refers to hexadeuterobenzene. Our problem is to express $\Delta\alpha'$ in the terms of $\Delta\alpha$. To do this we remark that $\Delta\alpha$ may be regarded as the sum of two changes in polarisability, the one, $\Delta\alpha_H$, being caused by the rotation of the hydrogen ring when the carbon ring remains fixed, and the other, $\Delta\alpha_C$, caused by the rotation of the carbon ring with the hydrogen ring kept fixed. Thus

$$\Delta\alpha = \Delta\alpha_H + \Delta\alpha_C \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and for hexadeuterobenzene

$$\Delta\alpha' = \Delta\alpha'_H + \Delta\alpha'_C \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1')$$

The ratio $\Delta\alpha_C/\Delta\alpha'_C$ is given by the ratio of the angular amplitudes of the carbon ring in the two vibrations, and $\Delta\alpha_H/\Delta\alpha'_H$ by the hydrogen–deuterium amplitude ratio. If these respective ratios were equal, $\Delta\alpha/\Delta\alpha'$ would also have the same value and we could say immediately that the intensity in benzene should be larger by the square of the amplitude ratio. Actually, the ratios are not the same, and we are compelled to consider the variation of $\Delta\alpha$ in detail.

The angle *between* the carbon and hydrogen rings at maximum amplitude is smaller in hexadeuterobenzene than in benzene by the factor $\sqrt{\nu'/\nu}$, but neither the carbon nor the hydrogen ring amplitudes in the respective compounds will be related by this factor. The carbon amplitude, in fact, increases in hexadeuterobenzene, whereas the hydrogen amplitude is somewhat less than $\sqrt{\nu'/\nu}$ of its value in benzene. For purposes of calculation, however, it is helpful to consider a *hypothetical* " vibration " of the hexadeuterobenzene molecule in which both the carbon and hydrogen amplitudes *are* related to those in benzene by the same factor $\sqrt{\nu'/\nu}$. During this hypothetical " vibration " angular momentum is not conserved. In order to get the real vibration for hexadeuterobenzene, we have to add to the hypothetical one a libration, *i.e.*, a rotation through a small angle about the axis of vibration. The amplitude of the libration is chosen so that the angular momentum of the resulting vibration is zero. The contribution of our hypothetical " vibration " to $\Delta\alpha'$ is obtained from $\Delta\alpha$ by multiplication with $\sqrt{\nu'/\nu}$. It remains then to determine the contribution of the libration.

The contribution of libration to $\Delta\alpha'$ is given by the product of the libration angle, $\Delta\phi$, and the change in α, the polarisability of the whole molecule, upon rotation through unit angle about an axis in the ring plane. We remark that the polarisability of the molecule may be represented, as usual, by an ellipsoid. This ellipsoid is ordinarily not a sphere. If it were, rotation would not affect it and the contribution of libration would vanish. The contribution thus arises only from the anisotropy of the polarisability ellipsoid, and since the anisotropy is readily determinable from the Rayleigh scattering of the molecule, we have a means of finding the contribution of molecular rotation to $\Delta\alpha'$.

The polarisation of Rayleigh scattering can be interpreted by resolving the polarisability ellipsoid into two independent ellipsoids, one spherical and the other anisotropic. The spherical ellipsoid contributes only to the polarised component of the Rayleigh scattering, whereas all of the *depolarised* scattering is due to the anisotropic ellipsoid. The anisotropy of the molecular polarisability may thus be found from the intensity of the depolarised component of the Rayleigh line. We need not know its absolute intensity, for we are interested only in the relative values of $\Delta\alpha$ and $\Delta\alpha'$. It is therefore sufficient to know the ratio of the Rayleigh intensity to the intensity of the Raman line under consideration. This ratio has been measured for benzene (Carrelli and Went, *Z. Physik,* 1932, **76**, 236), and since we may assume that the molecular polarisabilities of benzene and of hexadeuterobenzene are essentially equal, we may find the anisotropy of hexadeuterobenzene in terms of $\Delta\alpha$ from the intensity measurements on benzene.

The actual calculation of the librational contribution is carried out below. We cannot say in advance, however, whether libration will lessen or increase $\Delta\alpha'$, *i.e.*, whether the ratio of Raman intensities $(\Delta\alpha')^2/(\Delta\alpha)^2$ will be less or more than ν'/ν. The ratio would be ν'/ν if libration made no contribution. Let us illustrate by two models.

(1) Suppose the motion of the hydrogen ring has no influence on the molecular polarisability. Rotation of the carbon ring through a given angle should cause, accordingly, a rotation of the polarisability ellipsoid through the same angle. In this case the Raman intensity will be greater for hexadeuterobenzene by a factor of 2·13, because the carbon hexagon vibrates in hexadeuterobenzene through an amplitude which is $\sqrt{2{\cdot}13}$ times larger than the amplitude in benzene.

(2) Suppose, on the contrary, that the motion of the carbon ring does not influence the polarisability. The polarisability ellipsoid then should rotate with the hydrogen ring, and the intensity should be smaller in hexadeuterobenzene by the square of the deuterium–hydrogen amplitude ratio, *i.e.*, by the factor 0·533. The observed increase in intensity indicates qualitatively that the first model more nearly corresponds to the actual state of affairs in benzene.

To place the foregoing discussion on a quantitative basis, we put

$$\Delta\alpha' = \Delta\alpha\sqrt{\nu'/\nu} + \Delta\phi(\partial\alpha/\partial\phi) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which the last term is the contribution of libration. The angle of libration $\Delta\phi$ may be determined from

$$M_{\mathrm{H}}\phi_{\mathrm{H}}\sqrt{\nu'/\nu} + (2M_{\mathrm{H}} + M_{\mathrm{C}})\Delta\phi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ϕ_{H} is the amplitude of the hydrogen ring in the benzene vibration, and M_{H} and M_{C} are the inertial momenta of the hydrogen and carbon hexagons around an axis lying in the plane of the hexagons.*

Equation (3) expresses the fact that the angular momentum of the actual hexadeuterobenzene vibration is zero, the first term giving the momentum of the hypothetical "vibration" and the second term the compensating momentum of the libration. From (2) and (3) we obtain

$$\frac{\Delta\alpha'}{\Delta\alpha} = \sqrt{\frac{\nu'}{\nu}}\left[1 - \frac{M_{\mathrm{H}}}{2M_{\mathrm{H}} + M_{\mathrm{C}}} \cdot \frac{(\partial\alpha/\partial\phi)}{\Delta\alpha} \cdot \phi_{\mathrm{H}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$\Delta\alpha$, $\Delta\alpha'$, and $(\partial\alpha/\partial\phi)$ represent tensors, and before proceeding we must explain what we mean by the quotient of two tensors. It follows from a symmetry argument that since $\Delta\alpha$, $\Delta\alpha'$, and $(\partial\alpha/\partial\phi)$ correspond to rotations through small angles about a common axis, they differ only by numerical factors. The quotients in (4) stand for the ratios of these numerical factors. For purposes of calculation it is simpler to find first the squares of these quotients, which we obtain when we replace each tensor by the sum of the squares of its components. These sums we denote by $(\Delta\alpha)^2$, $(\Delta\alpha')^2$, and $(\partial\alpha/\partial\phi)^2$ respectively.

Let us first calculate $(\partial\alpha/\partial\phi)^2$. If we select the six-fold axis of benzene as the z-axis, the principal values c_{xx}, c_{yy}, and c_{zz} of the polarisability tensor α may be denoted respectively by $\alpha_{\perp}$, $\alpha_{\perp}$, and $\alpha_{\parallel}$ (c_{xx} and c_{yy} are equal because of the symmetry of the benzene molecule).

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* $2M_{\mathrm{H}}$ is used for M'_{H}.

If the molecule is rotated through the small angle $\delta\phi$ from its original position, the rotation taking place about the x-axis, the original polarisability tensor (I) will be changed to (II):

$$\underset{\text{(I.)}}{\begin{vmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha_{\|} \end{vmatrix}} \qquad \underset{\text{(II.)}}{\begin{vmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp \cos^2 \delta\phi & -(\alpha_\perp - \alpha_{\|}) \cos \delta\phi \sin \delta\phi \\ 0 & (\alpha_\perp - \alpha_{\|}) \cos \delta\phi \sin \delta\phi & \alpha_{\|} \cos^2 \delta\phi \end{vmatrix}}$$

In order to find $(\partial\alpha/\partial\phi)^2$ we subtract (I) from (II), divide each component of the resulting tensor by $\delta\phi$, square, and take the sum. For $\delta\phi \to 0$, we obtain

$$(\partial\alpha/\partial\phi)^2 = 2(\alpha_\perp - \alpha_{\|})^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We have previously remarked that the polarisability ellipsoid representing α may be resolved into a spherical and an anisotropic part:

$$\alpha = \alpha_{\text{sp.}} + \alpha_{\text{an.}}$$

The corresponding resolution of the tensor (I) is:

$$\underset{\text{(I.)}}{\begin{vmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha_{\|} \end{vmatrix}} = \underset{\text{(Spherical.)}}{\begin{vmatrix} \frac{2\alpha_\perp + \alpha_{\|}}{3} & 0 & 0 \\ 0 & \frac{2\alpha_\perp + \alpha_{\|}}{3} & 0 \\ 0 & 0 & \frac{2\alpha_\perp + \alpha_{\|}}{3} \end{vmatrix}} + \underset{\text{(Anisotropic.)}}{\begin{vmatrix} \frac{\alpha_\perp - \alpha_{\|}}{3} & 0 & 0 \\ 0 & \frac{\alpha_\perp - \alpha_{\|}}{3} & 0 \\ 0 & 0 & -2\frac{\alpha_\perp - \alpha_{\|}}{3} \end{vmatrix}} \quad (6)$$

From (5) and (6) we find

$$(\alpha_{\text{an.}})^2 = \tfrac{2}{3}(\alpha_\perp - \alpha_{\|})^2$$

and

$$(\partial\alpha/\partial\phi)^2 = 3(\alpha_{\text{an.}})^2$$

The intensity of the anisotropic part of the Rayleigh scattering by benzene (*i.e.*, the depolarised part of the undisplaced line) is proportional to $(\alpha_{\text{an.}})^2$.

Let $\Delta\alpha$, $\Delta\alpha'$, and $\Delta\phi$ in equation (2) denote the matrix elements * of these quantities for the 0—1 vibrational transition; $(\Delta\alpha)^2$ is then proportional to the intensity of the Raman line arising from the 0—1 transition. The proportionality constants relating $(\alpha_{\text{an.}})^2$ and $(\Delta\alpha)^2$ to the intensities of the depolarised parts of the Rayleigh and of the Raman scattering respectively are the same. Therefore the ratio $(\partial\alpha/\partial\phi)^2/(\Delta\alpha)^2$ can be obtained from the experimentally determined intensity ratio of the Rayleigh to the Raman line in benzene. The depolarised part of the Rayleigh line is found by multiplying its total intensity by the factor $\Delta/(1 + \Delta)$, where Δ is the depolarisation factor of the undisplaced line. In the same way the ratio $\rho/(1 + \rho)$ (ρ is the Raman depolarisation factor) converts the total intensity of the Raman line into its depolarised portion. If we denote by I_0/I_ν the ratio of total intensities of the Rayleigh and Raman lines scattered by benzene vapour, we may put

$$\frac{(\alpha_{\text{an.}})^2}{(\Delta\alpha)^2} = \frac{(\partial\alpha/\partial\phi)^2}{3(\Delta\alpha)^2} = \frac{\{\Delta/(1 + \Delta)\}I_0}{\{\rho/(1 + \rho)\}(I_\nu/2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

I_ν is divided by 2 because the double degeneracy of the Raman frequency in question has doubled I_ν. Since we are considering the matrix element of $\Delta\alpha$ for the 0—1 transition, I_ν is the Raman intensity observed at the absolute zero, at which temperature only the 0—1 transition can take place. I_ν at 0° K. is found from the observed intensity by multiplying by the factor $(1 - \varepsilon)$, where ε is $\exp(-h\nu/kT)$; ε is quite small ($\varepsilon = 0{\cdot}015$ at 290° K.), so this correction is not important. When we insert the temperature factor and rearrange, we obtain from (7)

$$\frac{(\partial\alpha/\partial\phi)}{\Delta\alpha} = \sqrt{\frac{6\Delta(1 + \rho)I_0}{\rho(1 + \Delta)I_\nu(1 - \varepsilon)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

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* The matrix element of $\Delta\alpha$, for example, is a tensor whose components are the matrix elements of the components of $\Delta\alpha$ (cf. Placzek, *Leipziger Vorträge*, 1931, pp. 74—75).

Having replaced $\Delta\alpha$ by its matrix element, we must follow the same procedure with $\Delta\phi$. Since, according to equation (3), $\Delta\phi$ is related to ϕ_H by a constant factor, we may express the matrix element of $\Delta\phi$ in terms of the matrix element of ϕ_H, a transformation which has been made implicitly in equation (4). The evaluation of the matrix element of ϕ_H is facilitated by noting that ϕ_H is related to the angle between the hydrogen and carbon rings at maximum amplitude, $\phi_H - \phi_C$, thus :

$$\phi_H = (\phi_H - \phi_C)M_C/(M_C + M_H)$$

The matrix element of ϕ_H is therefore equal to the matrix element of $\phi_H - \phi_C$ multiplied by $M_C/(M_C + M_H)$. For the transition from the nth vibrational state to state $n + 1$ we have

$$\left|\phi_H - \phi_C\right|_n^{n+1} = \sqrt{\frac{(n+1)h}{8\pi^2\mu\nu}}$$

in which μ refers to the reduced moment of inertia of the carbon and hydrogen rings, *i.e.*, $1/\mu = 1/M_C + 1/M_H$. The matrix element for the 0—1 transition will therefore be

$$\left|\phi_H\right|_0^1 = \frac{M_C}{M_C + M_H}\sqrt{\frac{h}{8\pi^2\mu\nu}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

When we denote by $\Delta\alpha'$ in equation (4) the matrix element of $\Delta\alpha'$ for the 0—1 transition, and square both sides of the equation, we obtain I'_ν/I_ν, the ratio of intensities of the Raman lines in hexadeuterobenzene and in benzene at 0° K. The substitution of (8) and (9) in (4) thus leads to

$$I'_\nu/I_\nu = (1 - \delta)^2\nu'/\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where

$$\delta = \frac{\mu}{2M_H + M_C}\sqrt{\left[\frac{6\Delta(1+\rho)I_0}{\rho(1+\Delta)I_\nu(1-\varepsilon)}\right]\left[\frac{h}{8\pi^2\mu\nu}\right]}$$

I'_ν/I_ν must be converted into the ratio at 290° K. by multiplying I_ν by $1/(1 - \varepsilon)$ and I'_ν by $1/(1 - \varepsilon')$; ε' is $\exp(-h\nu'/kT)$. The temperature correction is, as before, unimportant.

For the numerical evaluation of δ we have adopted the following values : ortho-C–C distance in benzene, 1·40 A.; ortho-H–H distance, 2·48 A.; $\Delta = 0{\cdot}0445$; $\rho = 6/7$; $\nu = 848{\cdot}9$ cm.$^{-1}$; $\nu' = 661{\cdot}2$ cm.$^{-1}$.

A value for the intensity ratio I_0/I_ν for benzene vapour has been given by Carrelli and Went (*loc. cit.*). Their measurements were actually made with the liquid but have been converted by them to relate to the vapour. In their paper (Table 4, p. 248) they list the ratios in the gas of the whole Raman scattering to the isotropic (*i.e.*, polarised) part of the Rayleigh scattering for the various Raman-active frequencies. Since I_0 in our formula denotes the *entire* Rayleigh scattering, it is necessary to multiply their ratio for the 849 frequency by the factor $(1 - \frac{7}{6}\Delta)/(1 + \Delta)$. The value of Δ is that for the gas ($\Delta = 0{\cdot}0445$) and is not to be confused with Carrelli and Went's Δ_t, the depolarisation factor for the liquid. We obtain for the corrected ratio : $I_0/I_\nu = 3{\cdot}06 \times 10^4$.

Substitution of the foregoing numerical data in equation (10) leads to the value $\delta = \pm 0{\cdot}656$. The ratio I'_ν/I_ν corrected to 290° K. then becomes 0·095 for $+\,\delta$ and 2·18 for $-\,\delta$. The experimental ratio is 1·5. It is clear that we must take the negative sign for δ. The discrepancy between the calculated value 2·18 and the observed ratio is small enough to be due to experimental error in the measurements of I'_ν/I_ν or, more probably, of I_0/I_ν, particularly in view of the difficulty of measuring accurately the ratio of two intensities differing by a factor of thousands. It appears still more probable, however, that the discrepancy is due to uncertainty in the method of calculating the ratio I_0/I_ν in the vapour phase from intensities measured in the liquid. This is shown by the following discussion.

In order to find intensities in the vapour from those in the liquid, Carrelli and Went have assumed that the polarisabilities α and the vibrational changes in polarisability $\Delta\alpha$ are the same for the individual molecules both in the liquid and in the gas. This assumption is reasonable in the light of the experimental fact that Raman lines which are forbidden in the gas are observed only very weakly or not at all in the liquid.* Even under this assumption, however, the calculation of intensities in the vapour is not unequivocal. Carrelli and Went's formula for the intensity ratio, I_v/I_t, of Raman to Rayleigh scattering in the liquid is

$$\frac{I_v}{I_t} = \frac{n^4}{\left(\frac{n^2+2}{3}\right)^2} \cdot \frac{1-\frac{7}{6}\Delta_t}{1+\Delta_t} \cdot \frac{1}{kT\beta N} \left[\left(\frac{\lambda'}{\lambda}\right)^4 \frac{(5A^2{}_{vs} + 13\gamma^2{}_{vs})/45}{(A_0/3)^2}\right] \quad . \quad . \quad (11)$$

in which the quantity in square brackets is the ratio of Raman scattering to polarised Rayleigh scattering by the vapour; n designates the refractive index of the liquid, β its compressibility, and N the number of molecules per c.c.

The factor $1/(kT\beta N)$ gives the density fluctuations which determine the Rayleigh scattering of the liquid, and the factor $(1 - \frac{7}{6}\Delta_t)/(1 + \Delta_t)$ reduces this scattering to its isotropic part. Such a reduction is necessary because the randomness of molecular orientation will give rise to an anisotropic scattering when the molecular polarisability is anisotropic. This anisotropic scattering is not due to density fluctuations and must be eliminated before the theory of density fluctuations can be applied to the calculation of Rayleigh scattering by the liquid. It is tacitly assumed in the derivation of equation (11) that only the isotropic part of the molecular polarisability contributes to the isotropic part of the Rayleigh scattering of the liquid. This assumption is not strictly valid, since the anisotropic part of the molecular polarisability may give rise, under the influence of anisotropic density fluctuations, to isotropic scattering.

The most uncertain feature of equation (11), however, is the coefficient $n^4/[(n^2 + 2)/3]^2$. This factor takes into account the effect of polarisation of the dielectric medium on scattering. In a liquid such as benzene, composed of non-spherically symmetric molecules, the electric field acting on an individual molecule will be strongly influenced both by the position and by the orientation of the dipoles which are induced in the surrounding molecules by the incident light wave. In general, there will be no simple expression for taking this influence into account. On the other hand, if the molecules are spherically symmetric (as in carbon tetrachloride) the principal effect of the polarisation of the dielectric will be the same both for Rayleigh and for Raman scattering, the only difference being that in the former there is also interaction between the additional induced dipoles which arise from density fluctuations. This interaction, however, will contribute only to the anisotropic part of the Rayleigh scattering, and has already been eliminated from consideration by the depolarisation term. The $n^4/[(n^2 + 2)/3]^2$ factor should therefore be replaced by unity for spherically-symmetric molecules.

If the $n^4/[(n^2 + 2)/3]^2$ factor is omitted for the calculation of I_0/I_v in benzene vapour, we find for this ratio $1{\cdot}22 \times 10^4$ rather than $3{\cdot}06 \times 10^4$. We then obtain $\delta = -0{\cdot}412$ and I'_v/I_v at 290° K. is 1·59, which is practically the measured value. In the absence of further information about the theory of liquids, the omission of the factor $n^4/[(n^2 + 2)/3]^2$ is no less justified than its inclusion. The uncertainty in the calculation of I'_v/I_v is therefore of about the same magnitude as the discrepancy with experiment. The whole matter could be cleared up by making accurate measurements of I_0/I_v in the vapour.

3. *Intensities of the Totally Symmetrical Frequencies.*—The above information concerning the relative importance of the carbon and hydrogen hexagons in determining $\Delta\alpha$ for the molecule may be used as a basis for qualitative statement about intensity relationships in the class A_{1g}. The amplitudes through which the carbon atoms move during the vibration $A_{1g}^{(\mathrm{C})}$ are slightly larger in benzene than in hexadeuterobenzene, while in $A_{1g}^{(\mathrm{H})}$ the carbon amplitudes are considerably greater in hexadeuterobenzene. We have found for the E_g^- vibration that $\Delta\alpha$ (and thus the intensity) is chiefly dependent on the motion of the carbon atoms: $A_{1g}^{(\mathrm{C})}$ should therefore be a little more intense, and $A_{1g}^{(\mathrm{H})}$ noticeably less intense, in benzene. Actually, both are about 2% more intense.

The carbon atoms participate very little in vibration $A_{1g}^{(\mathrm{H})}$, but have quite considerable amplitudes in $A_{1g}^{(\mathrm{C})}$. The latter frequency should therefore be the stronger both in benzene and in hexadeuterobenzene. Experimentally, the former is 6% more intense in both

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* It must be borne in mind, however, that changes in $\Delta\alpha$ brought about by change of state may give rise to considerable intensity changes in allowed lines, even though changes in $\Delta\alpha$ for forbidden vibrations will result only in very small intensities in the liquid. For example, if $\Delta\alpha$ for a particular allowed vibration is 1·0 in the vapour and changes to 1·1 in the liquid, the intensity will change to 1·2 (*i.e.*, $1{\cdot}1^2$). On the other hand, if $\Delta\alpha$ for a forbidden vibration changes from zero in the vapour to 0·1 in the liquid, the intensity of the forbidden line in the liquid will be only 0·01.

compounds. This disagreement of experiment with our qualitative expectations indicates that the dependence of $\Delta\alpha$ on amplitude is less simple than we have assumed. It is thus essential to consider the amplitude and intensity relationships of the class A_{1g} in a quantitative manner.

In order to calculate the intensities of the totally symmetrical frequencies, we express the hexadeuterobenzene vibration $A_{1g}^{(C)\prime}$ in terms of a linear superposition of the benzene vibrations $A_{1g}^{(H)}$ and $A_{1g}^{(C)}$ by means of suitable coefficients ξ_1 and η_1 :

$$A_{1g}^{(C)\prime} = \xi_1 A_{1g}^{(H)} + \eta_1 A_{1g}^{(C)}$$

The detailed meaning of this symbolic equation is that

$$\left.\begin{array}{l} \chi'_{1H} = \xi_1 \chi_{1H} + \eta_1 \chi_{2H} \\ \chi'_{1C} = \xi_1 \chi_{1C} + \eta_1 \chi_{2C} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where χ'_{1H} and χ'_{1C} are the amplitudes of the hydrogen atoms and of the carbon atoms respectively in the hexadeuterobenzene vibration $A_{1g}^{(C)\prime}$; whilst χ_{1H} and χ_{1C} are the hydrogen and carbon amplitudes in the benzene vibration $A_{1g}^{(C)}$, and χ_{2H} and χ_{2C} are the corresponding quantities for the benzene vibration $A_{1g}^{(H)}$. For the vibration $A_{1g}^{(H)\prime}$ we have similarly :

$$A_{1g}^{(H)\prime} = \xi_2 A_{1g}^{(H)} + \eta_2 A_{1g}^{(C)}$$

which means

$$\left.\begin{array}{l} \chi'_{2H} = \xi_2 \chi_{1H} + \eta_2 \chi_{2H} \\ \chi'_{2C} = \xi_2 \chi_{1C} + \eta_2 \chi_{2C} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The coefficients ξ and η are pure numbers which can be evaluated readily by inserting in equations (12) and (13) the amplitudes obtained from the equation of motion.

The components of the tensor $\Delta\alpha$ for a given frequency are proportional to the amplitudes of the vibration. The transformation of these components from benzene to hexadeuterobenzene is therefore given by the transformation coefficients ξ and η of the amplitudes. The relation of Raman intensity to the components of $\Delta\alpha$ is furnished by the well-known equation

$$I = \text{const.}\,(5A^2 + 13\gamma^2) I_{ex} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

in which I is the intensity of the Raman scattering observed at right angles to the monochromatic, non-polarised incident beam of intensity I_{ex}, and

$$A = d_{xx} + d_{yy} + d_{zz}$$
$$\gamma^2 = \tfrac{1}{2}[(d_{xx} - d_{yy})^2 + (d_{yy} - d_{zz})^2 + (d_{zz} - d_{xx})^2]$$

The d's are the three principal components of the tensor $\Delta\alpha$. Owing to the symmetry of the A_{1g} vibrations, A and γ are linear functions of the amplitudes χ, and therefore they will transform in the same way as the amplitudes themselves :*

$$\left.\begin{array}{ll} A_1' = \xi_1 A_1 + \eta_1 A_2 \,; & A_2' = \xi_2 A_1 + \eta_2 A_2 \\ \gamma_1' = \xi_1 \gamma_1 + \eta_1 \gamma_2 \,; & \gamma_2' = \xi_2 \gamma_1 + \eta_2 \gamma_2 \end{array}\right\} \quad . \quad . \quad . \quad . \quad (15)$$

The subscripts 1 and 2 refer, as before, to vibrations $A_{1g}^{(C)}$ and $A_{1g}^{(H)}$ respectively.

The calculation of intensities in hexadeuterobenzene is thus reduced to the problem of determining the A's and γ's for benzene. These are obtained with the help of the familiar depolarisation formula

$$\rho = 6\gamma^2/(5A^2 + 7\gamma^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

By combining equations (14) and (16) with experimental data for ρ and I, A and γ may be evaluated on a relative intensity scale. Since we are interested only in relative intensities, absolute values of A and γ are not essential. It is possible to determine A and γ absolutely,

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* $\Delta\alpha$ may be decomposed into a spherical and an anisotropic part, $\Delta\alpha_{sp.}$ and $\Delta\alpha_{an.}$. For $\Delta\alpha_{sp.}$ we have : $A \neq 0$, $\gamma = 0$; for $\Delta\alpha_{an.}$: $A = 0$, $\gamma \neq 0$. Owing to symmetry, $\Delta\alpha_{an.}$ (and of course also $\Delta\alpha_{sp.}$) can differ only by a numerical factor for different vibrations of the A_{1g} type. From this and the definition of A and γ, it follows that A and γ are linear functions of the amplitudes.

however, from the experimental ratio $(5A^2 + 13\gamma^2)/5A_0^2$ which is given in Carrelli and Went's table (*loc. cit.*); $A_0/3$, the polarisability of the non-vibrating molecule, may be calculated directly from the index of refraction (cf. Carrelli and Went, *loc. cit.*, p. 245; Stuart, "Molekülstruktur," Chap. 7).

When only two vibrations occupy a symmetry class, the most general expression for the potential energy of the vibrations contains three constants. In our case these three constants correspond to the interaction between hydrogen atoms, between carbon atoms, and between carbon and hydrogen atoms. Among the four observed A_{1g} frequencies (two in benzene and two in hexadeuterobenzene), there exists one relation, namely, the product rule (Part VIII, *loc. cit.*). We have used the three remaining independent values to determine from the equation of motion the three force constants, and from these the amplitudes of motion. The amplitudes substituted in equations (12) and (13) yield the ξ and η values, from which in turn the several A''s and γ''s have been determined. The following table lists the calculated values of A and γ in absolute units (c.c.). The amplitudes of vibration correspond to vibrational quantum number 3/2.

		Amplitudes, in 10^{-10} cm.		Transformation coefficients.		Change of polarisability, in 10^{-25} c.c.		Intensity.		Depolarisation ρ.	
Frequency.		C.	H.	ξ.	η.	A.	γ.	Obs.	Calc.	Obs.	Calc.
C_6H_6	$A_{1g}^{(\mathrm{C})}$	3·56	4·03	—	—	6·01	1·74	10·0	—	0·09	—
	$A_{1g}^{(\mathrm{H})}$	−0·66	7·01	—	—	−4·22	−3·33	10·6	—	0·4	—
C_6D_6	$A_{1g}^{(\mathrm{C})\prime}$	3·42	4·31	0·9696	0·0576	5·56	1·50	9·8	8·4	0·08	0·08
	$A_{1g}^{(\mathrm{H})\prime}$	−1·14	5·35	−0·1607	0·8565	−4·58	−3·14	10·4	10·5	0·35	0·34

The calculation of A and γ from equations (14) and (16) leaves the signs of both quantities indeterminate, since only their squares appear in the equations. A knowledge of the signs is essential if A' and γ' are to be determined from equation (15), and therefore the signs of the corresponding amplitudes must be considered. The signs in the table were so chosen for benzene that the calculated values of A' and γ' lead to agreement with the observed hexadeuterobenzene intensities. This agreement would not be affected if all the values of A or of γ or of both were to be multiplied by -1.

It is noteworthy that, although the amplitude ratio $x_{1\mathrm{C}}/x_{2\mathrm{C}}$ in benzene is about -5, the experimental ratio of A_1 to A_2 is only $-1{\cdot}5$, and γ_1/γ_2, $-0{\cdot}5$. The fact that A and γ are relatively large in $A_{1g}^{(\mathrm{H})}$, despite the much smaller amplitude of the carbon atoms, indicates that the influence of the hydrogen atoms on $\Delta\alpha$ is considerable. The small amplitude of the carbon atoms in $A_{1g}^{(\mathrm{H})}$ is offset by the fact that the hydrogen atoms augment rather than counteract the portion of $\Delta\alpha$ due to the carbon ring, and there results the considerable intensity observed for $A_{1g}^{(\mathrm{H})}$. On the other hand, when the hydrogen atoms move in phase with the carbons (in $A_{1g}^{(\mathrm{C})}$) they tend to counterbalance the contribution of the latter to $\Delta\alpha$.

The effect produced on the polarisability of the expanding carbon ring by concomitant alteration of the carbon–hydrogen distance is rather contrary to the expected one, namely, that an increase in polarisability should result when a bond is stretched. This unusual behaviour may be due to the peculiar electronic structure of the carbon hexagon.* In the E_g^- vibration, the motion of the hydrogen ring affects $\Delta\alpha$ in more orthodox fashion. As we should anticipate, the contrary motion of the two ellipsoids in E_g^- results in the subtraction of the one contribution to $\Delta\alpha$ from the other.

4. *Intensities in the Class* E_g^+.—In principle, the difficulty of calculating intensity shifts by means of transformation coefficients is no greater for the four E_g^+ frequencies than for the two totally symmetrical frequencies. In practice, however, a quantitative calculation is out of the question, because a perfectly general potential system introduces into the secular determinant for E_g^+ more constants than one can evaluate from the observed E_g^+ frequencies. Intensity changes can be predicted qualitatively, however, from the behaviour of the polarisability during the A_{1g} vibrations. We may expect from analogy with the A_{1g} vibrations

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* This singular electronic structure manifests itself also in the influence which the first chemical substituent in the benzene ring has on subsequent substitution (see Huckel, *Z. Physik*, 1931, **72**, 310; Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362, 606).

that the two carbon frequencies of E_g^+ symmetry will have smaller carbon amplitudes and somewhat greater in-phase hydrogen amplitudes in hexadeuterobenzene. We have found that each of these changes leads to lower intensity, and therefore predict decrease in intensity for the two carbon frequencies. Experimentally, both are about 40% less intense in hexadeuterobenzene. It should be remarked in this connection that the intensity of the E_g^+ carbon frequency at 1596 cm.$^{-1}$ must be taken as the sum of the intensities of the two components of the resonance doublet, inasmuch as this sum must be equal to the sum of the intensity of the unperturbed fundamental frequency and the negligibly small intensity of the combination tone responsible for the perturbation.

In the E_g^+ hydrogen frequencies in hexadeuterobenzene, the effect of the larger carbon amplitudes on $\Delta\alpha$ will be offset by decrease in the out-of-phase hydrogen amplitudes. Which effect will predominate we cannot say without quantitative calculation. In $A_{1g}^{(\pi)}$ the two were about equal, and the same is apparently true of the lower of the two E_g^+ hydrogen frequencies, for an intensity increase of less than 5% is observed. The effect of increased carbon amplitudes seems to be greater in the higher frequency, however, since this line is one-fourth more intense in hexadeuterobenzene.

The irregularity of the intensity changes produced by deuterium substitution is thus quite understandable. Qualitatively, and quantitatively where calculation is possible, the intensity shifts are just what we should expect from the intensity relationships in the Raman spectrum of benzene itself.

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