14. *The Role of* E_g^+ *Vibrations in the* 2600-A. *Benzene Band System.*

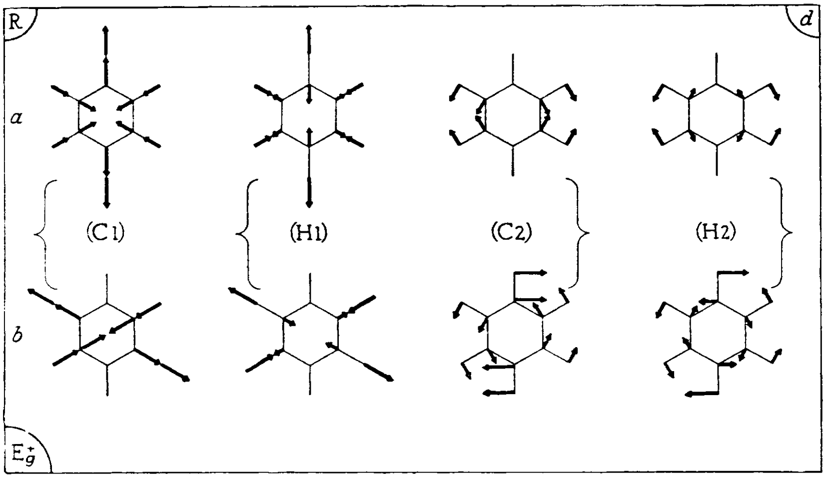
By D. P. Craig.

The observation by Garforth and Ingold (*J.*, 1948, 417) that the two E_g^+(C) vibrations differ strongly in their power to perturb the forbidden $\mathbf{A_{1g}} - \mathbf{B_{2u}}$ transition in benzene receives an explanation in terms of an assumed mechanism for the perturbation of electronic states by atomic vibrations. The mechanism, which in spite of a certain reasonableness must at present be treated as heuristic, is that each C atom in the benzene ring acts towards non-neighbours as a small positive charge but is completely screened from its neighbours. Electronic wave functions are approximated in terms of structures, and of these the polar ones here play the central part. The energy matrix components are changed in the course of vibrations by electrostatic action between the small charges already mentioned and the unit charges of polar structures. The 606-cm.$^{-1}$ vibration can then be calculated to be more effective, by a factor greater than 100 times, than the 1596-cm.$^{-1}$ vibration in causing the appearance of the forbidden transition. This agrees with the experimental finding.

Herzberg and Teller (*Z. physikal. Chem.*, 1933, *B*, **21**, 410) established the principles, so far as the demands of symmetry are concerned, which govern the disturbances caused to electronic states by atomic vibrations in polyatomic molecules. A spectral transition forbidden by electronic selection rules is made allowed if the symmetry properties of the atomic vibrations change during the transition by a component $\Gamma_{\text{vib.}}$ such that

$$\Gamma_{\text{Gd}} \times \Gamma_{\text{Exc.}} \times \Gamma_{\text{vib.}} \subset \Gamma_x, \Gamma_y, \text{ or } \Gamma_z$$

where Γ_{Gd} and $\Gamma_{\text{Exc.}}$ are the representations to which the ground and the excited electronic wave functions belong and Γ_x, for example, that of the x vector. However, Garforth and Ingold (*J.*, 1948, 417) showed that, of the four E_g^+ vibrations of benzene capable in principle of making the 2600 A. transition appear, only two actually do so and in these two the motions of the C skeleton are geometrically similar. The figure is part of a block of illustrations used by Bailey, Ingold, Poole, and Wilson (*J.*, 1946, 222) to show the vibration forms of benzene and it is reproduced here with their permission. It depicts a set of basic E_g^+ motions from which, by linear combination, all possible E_g^+ motions of benzene can be set up. Garforth and Ingold (*loc. cit.*) find that the two vibrations with a large component of either the C1 or the H1 motion—in which, that is, the C hexagon is distorted principally by angle bending and not by bond stretching—are effective, whereas those with a large component of C2 or H2 are ineffective. The latter equally with the former satisfy the symmetry demands but fail to appear on account of some more subtle detail of the atomic motions. To understand how this can happen a mechanism has to be assumed by which the electronic energy comes to depend on the nuclear motion, and this should make it plain how the observed differences come about. A very simple



E_g^+ *Vibration forms of benzene.*

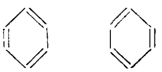
mechanism is applied in this paper to study those two vibrational motions, compounded from C1 and C2, in which the carbon atoms have large amplitudes, and it is found that one of these could be very much more effective than the other in this phenomenon. The effective one is the predominantly bending motion, as required by experiment.

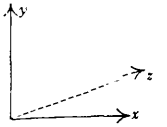
The intense absorption band of benzene at 1700 A. records an $\mathbf{A_{1g}} - \mathbf{E_u^-}$ transition, and any forbidden transition which appears at longer wave-lengths does so mainly by borrowing intensity from this strong band. We concentrate therefore on finding to what extent E_g^+ vibrations cause mixing of the final $\mathbf{B_{2u}}$ state of the forbidden transition with the final $\mathbf{E_u^-}$ state of the allowed one. The coefficient for this mixing is, in perturbation theory,

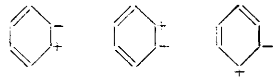
$$\frac{\int \psi(\mathbf{B_{2u}})(EH_g^+)\psi(\mathbf{E_u^-})d\tau}{E(\mathbf{B_{2u}}) - E(\mathbf{E_u^-})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

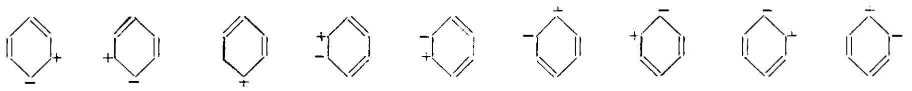
in which ψ and E respectively denote unperturbed wave functions and energies, and $H(E_g^+)$ is the perturbing potential of a hexagon distorted in an E_g^+ vibration. The intensity of the transition ending at the $\mathbf{B_{2u}}$ state will bear the same ratio to the allowed $\mathbf{A_{1g}} - \mathbf{E_u^-}$ intensity as the square of the expression (1) bears to unity; hence to compare the perturbing powers of the two E_g^+ vibrations (*i.e.*, the two C vibrations) we have to compare the squares of (1) evaluated for them.

We may write approximate forms for $\psi(\mathbf{E_u^-})$ and $\psi(\mathbf{B_{2u}})$ in terms of the following structures :






A B C


D E F G H I J K L

Two $\mathbf{E_u^-}$ wave functions may be made up from these and both involve only the polar structures A to L. Of the two the following one alone may be the final state for intense transitions :

$$\psi(\mathbf{E_u^-}) = (1/\sqrt{24})(2\mathrm{A} - 2\mathrm{B} + \mathrm{C} - \mathrm{D} - \mathrm{E} + \mathrm{F} - 2\mathrm{G} + 2\mathrm{H} - \mathrm{I} + \mathrm{J} + \mathrm{K} - \mathrm{L}) \quad . \quad (2)$$

A degenerate partner to (2), chosen orthogonal to it, is inactive in the mechanism we consider and hence may be neglected. The $\mathbf{B_{2u}}$ state which, to appear in the spectrum, has to become mixed with $\psi(\mathbf{E_u^-})$ has non-polar as well as polar components. We follow in detail only the polar part, $\psi(\mathbf{B_{2u}})$. The contribution by the non-polar part is in the same sense and proportional, but is smaller because it appears multiplied by the overlap integral between neighbouring atomic orbitals. We therefore take

$$\psi(\mathbf{B_{2u}}) = (1/\sqrt{12})(\mathrm{A} + \mathrm{B} - \mathrm{C} - \mathrm{D} + \mathrm{E} + \mathrm{F} - \mathrm{G} - \mathrm{H} + \mathrm{I} + \mathrm{J} - \mathrm{K} - \mathrm{L}) \quad . \quad . \quad (3)$$

If H be the Hamiltonian for the undistorted hexagonal shape it follows from the symmetry of the problem that

$$\int \psi(\mathbf{E_u^-})H\psi(\mathbf{B_{2u}})d\tau = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

A distortion from hexagonal shape replaces H in (4) by $H + H'$, H' being a perturbing potential having the symmetry of the distortion. When H' transforms like E_g^+ the matrix component analogous to that in (4) has a part which transforms like A_{1g} and is not therefore necessarily zero. Small terms being neglected, the totally symmetrical part is

$$\begin{aligned} \int \psi(\mathbf{E_u^-})H'\psi(\mathbf{B_{2u}})d\tau &= (1/12\sqrt{2})\{2(\mathrm{A}H'\mathrm{A}) - 2(\mathrm{B}H'\mathrm{B}) - (\mathrm{C}H'\mathrm{C}) + (\mathrm{D}H'\mathrm{D}) \;.\;.\; \text{etc}\} \\ &= (1/2\sqrt{2})\{(\mathrm{A}H'\mathrm{A}) - (\mathrm{B}H'\mathrm{B})\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5) \end{aligned}$$

where $\qquad (\mathrm{A}H'\mathrm{A}) = \int \mathrm{A}H'\mathrm{A}d\tau$

the second line following from the first because H' transforms like E_g^+. The value of this expression, put in (1), determines the intensity of the forbidden band system. Evidently its value depends on the development of energy differences under the perturbing vibration between structures in pairs like A and B which have opposite charge displacements. We therefore have to investigate the right-hand side of (5) by seeing how the energies of oppositely charged structures are split by atomic motions of specified types.

The energies of these polar structures change during the course of vibrations because the internuclear distances change, and this alters the mutual energy of the charged atoms and the other nuclei. Since at distances greater than a bond length the field of an atom is dominantly electrostatic (the exchange terms being negligibly small) the energy changes we wish to study may be taken to arise from the electrostatic action between the unit positive and negative charges in the structure, and the field of the incompletely screened nuclear charge of the other atoms. Now screening is most complete in the directions of maximum electron density (*i.e.*, bond directions) so it is evident from the outset that a distinction must be made between neighbour and non-neighbour interactions, the former being smaller than the latter by virtue of the more complete screening along the line of the σ bonds. Accordingly we propose, as the simplest reasonable model, that any nucleus acts toward a non-neighbour as a small positive charge qe, but is completely shielded from its immediate neighbours by the bonding electrons. Interest throughout centres on energy differences developed between oppositely charged structures, so that no attention need be paid to the interaction between the charged atoms which changes by the same amount in the two structures. We thus suppose that in any structure there are on the non-charged atoms small residual charges qe, and that energy changes in distorted molecules are a consequence of interactions between the two charged atoms and these small charges on non-neighbours.

We now proceed with the calculation of the perturbation energies. Since the displacements are small compared with a bond length we use the differential expression for change in electrostatic energy :

$$\delta E = (qe^2/r^2)\delta r \equiv \mathcal{A}(r_b^2/r^2)\delta r, \text{ where } \mathcal{A} = qe^2/r_b^2 \text{ and } r_b = 1{\cdot}40 \text{ A}.$$

Since $\psi(\mathbf{B}_{2u})$ is symmetric, but $\psi(\mathbf{E}_u^-)$ antisymmetric, to rotation about the x axis, antisymmetry in the vibrational motion will be necessary to cause mixing. Only the lower forms of C1 and C2 need therefore be studied. We suppose the atoms in the lower form of C1 to be displaced a distance $\delta r/2$, and in the lower form of C2 the clockwise displacements are δr and the anticlockwise ones $\delta r/2$. This choice is merely a convenient one for the next step, and the composite motions have later to be normalised to unit kinetic energy. The distortion energies are :

Structure A, distorted according to C1 (lower form)

$$\Sigma\delta E = -2\mathcal{A}(1/4 + \sqrt{3}/12)\delta r$$

Structure A, distorted according to C2 (lower form)

$$\Sigma\delta E = \tfrac{1}{2}\mathcal{A}\delta r$$

Substituting in (5), we have

$$\left.\begin{aligned} \int \psi(\mathbf{B}_{2u})H(\mathrm{C1})\psi(\mathbf{E}_u^-)d\tau &= -\sqrt{2}(1/4 + \sqrt{3}/12)\,\mathcal{A}\delta r = -0{\cdot}558\,\mathcal{A}\delta r \\ \int \psi(\mathbf{B}_{2u})H(\mathrm{C2})\psi(\mathbf{E}_u^-)d\tau &= 1/2\sqrt{2}\mathcal{A}\delta r \qquad\qquad\quad = 0{\cdot}354\,\mathcal{A}\delta r \end{aligned}\right\} \quad . \quad . \quad . \quad (6)$$

The actual molecular motions in E_g^+ vibrations are combinations of C1 and C2 in proportions determined by the force system opposing distortions of the equilibrium hexagon. To find these actual motions we proceed in the simplest way, by supposing the C–H groups concentrated in mass points and taking a valence-force field with C–C stretching and C–C–C planar bending force constants as found by Ingold and his collaborators (*J.*, 1948, 491). Referred to the lower forms of the illustrated motions, the actual motions after being normalised to equal kinetic energies are :

$$0{\cdot}90\mathrm{C1} - 0{\cdot}25\mathrm{C2} : \text{ calc. } 616 \text{ cm.}^{-1} \text{ (exptl. } 606 \text{ cm.}^{-1})$$
$$0{\cdot}44\mathrm{C1} + 0{\cdot}52\mathrm{C2} : \text{ calc. } 1657 \text{ cm.}^{-1} \text{ (exptl. } 1596 \text{ cm.}^{-1})$$

Using (6), we now find the matrix components for the mixing of $\mathbf{B}_{2u}$ and $\mathbf{E}_u^-$ states by these two vibrations.

$$606 \text{ cm.}^{-1} : \int \psi(\mathbf{B}_{2u})\{0{\cdot}90H(\mathrm{C1}) - 0{\cdot}25\,H\,(\mathrm{C2})\}\psi(\mathbf{E}_u^-)\,d\tau$$
$$= -0{\cdot}591\,\mathcal{A}\delta r$$

$$1596 \text{ cm.}^{-1} : \int \psi(\mathbf{B}_{2u})\{0{\cdot}44H(\mathrm{C1}) + 0{\cdot}52H(\mathrm{C2})\}\psi(\mathbf{E}_u^-)\,d\tau$$
$$= -0{\cdot}063\,\mathcal{A}\delta r$$

The relative effectiveness of the vibrations per unit excursion of the nuclei is the ratio of the squares of these quantities. Since the low-frequency motion has a larger amplitude than the high, the ratio of squares has to be increased in favour of the 606-cm.$^{-1}$ vibration by a factor (1596/606), making the final result:

$$\frac{\text{Intensity in } \mathbf{A}_{1g} - \mathbf{B}_{2u} \text{ due to 606 cm.}^{-1}}{\text{Intensity in } \mathbf{A}_{1g} - \mathbf{B}_{2u} \text{ due to 1596 cm.}^{-1}} = \frac{(-0{\cdot}591)^2}{(-0{\cdot}063)^2} \times \frac{1596}{606} = 230 : 1$$

We do not wish to insist on the numerical magnitude of the ratio, which is rather sensitive to the elastic constants chosen to determine the motions. However, in making the forbidden transition allowed, the 606-cm.$^{-1}$ vibration is certainly more effective, by a factor greater than 100 times, than the 1596 cm.$^{-1}$, and this agrees with the observation by Garforth and Ingold (*loc. cit.*) that the latter vibration is actually inactive, or very weak, in the spectrum.

An estimate of the intensity $\mathbf{A}_{1g} - \mathbf{B}_{2u}$. With one further assumption it is possible to form an estimate of the stolen intensity in the 2600-A. band system. Such a calculation, compared with experiment, gives a partial check of the mechanism of perturbation that has been assumed. The quantity required for evaluating (1) is qe, from which $\mathcal{A}$ can be found. For this we use Slater's rules for atomic screening constants, and suppose that at remote points a nucleus has the field expected outside the atomic configuration $(1s)^2(2s, 2p)^4$. This gives $qe = -0{\cdot}6$ electron. The root mean square excursion of a nucleus in the 606-cm.$^{-1}$ vibration is 0·064 A., and the coefficient of $\psi(\mathbf{B}_{2u})$ in the full wave function for the $\mathbf{B}_{2u}$ state (including non-polar as well as polar structures) is about 0·5. The perturbation matrix component is

$$\int \psi(\mathbf{B}_{2u}) H \psi(\mathbf{E}_u^-) d\tau = 0{\cdot}09 \ e\text{V}.$$

and this, through (1), gives f (calc.) = 0·0014 as the calculated stolen intensity. The experimental value is f (exptl.) = 0·002. The close agreement is fortuitous. The important thing is the agreement in order of magnitude and the calculation is satisfactory to that extent.

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