442. *The Franck–Condon Principle and the Size of the Excited Benzene Molecule.*

By D. P. Craig.

The Franck–Condon principle applied to the experimental intensity distribution in the 2600 A. band system of benzene gives the value 0·037 A. for the increase in equilibrium C–C distance in the excited electronic state. This agrees well with values deduced by Garforth, Ingold, and Poole (*J.*, 1948, 508) from empirical relations between force constant and bond length.

The calculation of changes in molecular dimensions by means of the Franck–Condon principle may be carried out in various simplified ways. Two of these are examined. The assumption that CH groups are concentrated in mass points gives the value 0·036 A. If, in addition, it is assumed that the force constants are unchanged in the excited state, a value 0·035—0·036 A. is obtained. The last calculation demands no detailed information about the excited electronic state, and so may be applied to study changes in dimensions of more complicated molecules whose excited-state elastic constants are not known.

The intensity of an electronic transition is distributed in the bands of its band system in a definite way. Apart from a small dependence on the change in elastic constants, the intensity distribution is governed predominantly by the change in molecular dimensions in the two electronic states, and thus by the Franck–Condon principle. Given the change in the dimensions, and the elastic constants for the two combining states, the Franck–Condon principle allows the intensity distribution to be calculated. In diatomic molecules this was first done by Hutchisson (*Physical Rev.*, 1930, **36**, 410), who compared values for molecular hydrogen with experiment and got fair agreement in view of the difficulties of the experimental measurement. In Hutchisson's case of hydrogen, and rather generally with diatomic molecules, the dimensions of the combining states can be derived with great precision from the rotational structure of the bands, so that there is no need to rely upon the Franck–Condon principle and upon difficult measurements of intensities. In polyatomic molecules, however, the situation is reversed. Here the rotational structure is usually not resolved, whereas the intensities of absorption can be measured, especially in solution, with fair accuracy. Thus the Franck–Condon principle in polyatomic molecules has a rôle that it does not have in diatomic ones. Given the intensity distribution in a band system and the elastic constants for the combining states, it allows a non-empirical estimate to be made of the change in molecular dimensions.

Herzberg and Teller (*Z. physikal. Chem.*, 1933, *B*, **21**, 410) first showed how the Franck–Condon principle was to be applied in polyatomic molecules. A change in molecular dimensions may be expressed as a change in the origins of some or all of the normal co-ordinates for nuclear vibrations. Those vibrations whose origins are so diplaced in an electronic transition appear in the spectrum in progressions. Every such vibration behaves as if it belonged to a diatomic molecule whose internuclear separation changed in an electronic transition. On the other hand, vibrations whose origins are not displaced behave as if they belonged to a diatomic molecule in which only the force constant, and not the equilibrium internuclear separation, changed in the transition; such vibrations appear strongly only in zero-quantum changes 0—0, 1—1, etc., and much more weakly in two-quantum changes.

The simplest situation exists when the polyatomic molecule, upon excitation, retains all its elements of symmetry. This is the case if it undergoes a symmetrical expansion or contraction, and the spectrum then shows progressions in the totally symmetrical vibrations alone. The 2600 A. band system of benzene is of this simple type, and the initial and the final state for one band may accordingly be written :

$$\left.\begin{aligned}\Psi(\mathbf{A}_{1g}) &= \psi(\mathbf{A}_{1g})\phi_0(A_{1g})\phi_0(E_g^+)\\ \Psi(\mathbf{B}_{2u}) &= \psi(\mathbf{B}_{2u})\phi_n'(A_{1g})\phi_1'(E_g^+)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Ψ stands for a vibrational-electronic wave function, ψ is a pure electronic wave function, and ϕ_n, ϕ_n' are *n*th quantum state harmonic oscillator * wave functions in the $\mathbf{A}_{1g}$ and $\mathbf{B}_{2u}$ electronic states respectively. The A_{1g} vibration is the totally symmetrical one, whose quantum number changes along the progressions; while the E_g^+ vibration is one which occurs with one

---

* Judged from the very slow convergence of successive A_{1g} vibrational levels (Garforth and Ingold, *J.*, 1948, 417) the assumption of harmonic forces is justified, in further contrast to diatomic molecules. The matter is examined in an Appendix.

quantum in the upper state of all the stronger bands of the absorption spectrum, as is noted below. The further but unspecified vibrational wave functions in (1) are to be the same in both states. We discuss the relation between the intensity of absorption associated with particular values of the quantum number n of (1) and the change in ring size between the two electronic states. A comparison with the experimental intensity distribution will then give a value for the size of the benzene ring in the $\mathbf{B}_{2u}$ state.

No transitions occur between the wave functions (1) unless, as the most likely possibility, the upper state becomes mixed with the $\mathbf{E}_u^-$ electronic state. E_g^+ vibrations may effect the necessary perturbation as follows :

$$\psi^*(\mathbf{B}_{2u})\phi_1'(E_g^+) = \psi(\mathbf{B}_{2u})\phi_1'(E_g^+) + \delta\psi(\mathbf{E}_u^-)\phi_0'(E_g^+) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

ψ^* depends on the nuclear motion as expressed in (2), whereas the unstarred electronic wave functions do not. δ is a small mixing coefficient, and when $\psi^*(\mathbf{B}_{2u})$ is used instead of $\psi(\mathbf{B}_{2u})$ in (1) the transition moment $\mathbf{D}_n$ is :

$$\begin{aligned}\mathbf{D}_n &= \int\phi_0(A_{1g})\phi_n'(A_{1g})\mathrm{d}\tau_{\text{nucl.}} \,.\, \delta\int\psi(\mathbf{A}_{1g})\sum_i e\mathbf{r}_i\psi(\mathbf{E}_u^-)\mathrm{d}\tau_{\text{elec.}} \\ &= k_1\int\phi_0(A_{1g})\phi_n'(A_{1g})\mathrm{d}\tau_{\text{nucl.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)\end{aligned}$$

since the second factor is a constant for the whole band system. The intensity of absorption is proportional to $(\mathbf{D}_n)^2$. The relative intensity distribution in a band system is governed by the expression

$$I_n = k_2(\nu_n/\nu_0)^4\left[\int\phi_0(A_{1g})\phi_n'(A_{1g})\mathrm{d}\tau\right]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where ν_n stands for the frequency of a transition ending at the nth quantum state of the A_{1g} vibration and k_2 includes the numerical constants. It is the case that the small Boltzmann factor for the ground-state A_{1g} 992 cm.$^{-1}$ frequency allows attention to be confined to those transitions starting from the zero-quantum state of that vibration. This was implied in (1).

If no change in ring size occurs on excitation, ϕ_0 and ϕ_n' are oscillator wave functions about the same point as origin, and only the integral for $n = 0$ is important (*i.e.*, only the 0–0 band appears strongly). If there is a change in ring size ϕ_0 and ϕ_n' refer to different origins and they overlap over a range of n, the spectral intensity associated with any one n value being given by (4). This is of course simply the expression of the Franck–Condon principle given by Condon (*Physical Rev.*, 1928, **32**, 858) and for polyatomic molecules by Herzberg and Teller (*loc. cit.*). The basic integrals in (4) were worked out by Hutchisson (*loc. cit.*) in forms specially convenient for diatomic molecules and they may be adapted to this case. A simple closed expression, however, becomes applicable when one of the oscillators is always in its lowest state and this will be given.

The mechanics of the low-frequency totally symmetrical vibration of benzene are that the carbon atoms and their attached hydrogen atoms move in phase and with roughly equal amplitudes. It is therefore a very good approximation to this mode of vibration to treat each CH group as a single mass point. The alternative, and superior, calculation is to allow for internal motion in the CH group by working with appropriate normal co-ordinates. The results of these two methods are to be compared, but the detail of the second calculation is reserved for the Appendix. The first and simpler calculation is surprisingly accurate and is alone likely to be manageable for larger molecules. In both cases a further simplification is to suppose the elastic constants to be the same in the upper as in the lower state. As will be shown, even this apparently drastic step introduces only a small error into the result.

The system being supposed to be six CH " atoms " in a regular hexagon, a uniform expansion by a radial distance $q/\sqrt{6}$ moves the origin for the A_{1g} normal co-ordinate by q. We consider therefore two harmonic oscillators whose origins are q apart. These are distinguished by subscripts 1 and 2. Oscillator 1 is to be in its zeroth state (*i.e.*, it is to be the ground electronic state A_{1g} vibration) whereas 2 is to be excited to its nth quantum state.

$$\left.\begin{aligned}\phi_0(\sqrt{\beta_1}x_1) &= \left(\sqrt{\frac{\beta_1}{\pi}}\right)^{\frac{1}{2}}\mathrm{e}^{-\beta_1 x_1^2/2} \\ \phi_n'(\sqrt{\beta_2}x_2) &= \left(\sqrt{\frac{\beta_2}{\pi}}\Big/2^n n!\right)^{\frac{1}{2}}H_n(\sqrt{\beta_2}x_2)\mathrm{e}^{-\beta_2 x_2^2/2}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The expression $\beta = \frac{2\pi}{h}\sqrt{mk}$ and the H_n are Hermite polynomials. The overlap integral between these two functions, which appears in (3) and (4), may be shown to be :

$$\int\phi_0(\sqrt{\beta_1}x_1)\phi_n'(\sqrt{\beta_2}x_2)\mathrm{d}x = \mathrm{e}^{-\beta_1\{q^2/2(1+\rho)\}}\sum_r\left(\frac{\sqrt{\beta_2}q\rho}{1+\rho}\right)^{n-r}\left\{\frac{n!}{r!(n-r)!}\right\}^{\frac{1}{2}}\left\{\frac{2^{n-r}}{(n-r)!}\right\}^{\frac{1}{2}}\mathrm{S}_{0r} \quad . \quad (6)$$

In (6) $\rho = \beta_1/\beta_2$ and the S_{0r} are the elementary overlap integrals between oscillator wave functions about a common origin. These integrals vanish for odd values of r, and for even values are given by

$$\mathrm{S}_{0r} = \frac{1}{(r/2)!}\sqrt{\frac{r!}{2^r}}\left(\frac{2\sqrt{\rho}}{1+\rho}\right)^{\frac{1}{2}}\left(\frac{1-\rho}{1+\rho}\right)^{r/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For $\rho = 1$, $\mathrm{S}_{00} = 1$ and all others vanish. The values needed for benzene, in which $\rho = \nu_1/\nu_2 = 1{\cdot}075$, are : $\mathrm{S}_{00} = 0{\cdot}9997$, $\mathrm{S}_{02} = 0{\cdot}0255$, $\mathrm{S}_{04} = 7{\cdot}95 \times 10^{-4}$.

A constant multiplier being excluded, (6) together with values of (7) directly give the quantity $\mathbf{D}_n$ in terms of β_2, ρ, and q. Used in (4), they give the relative intensity distribution, in terms of the same quantities, between bands of different n. Table I gives sets of relative I_n values for a number of values of q. The approximation is that of CH mass points and the constants that enter are the frequencies $\nu_1 = 992$ cm.$^{-1}$, $\nu_2 = 923$ cm.$^{-1}$, and the isotopic masses C = 12, H = 1·008.

TABLE I.

Calculated relative intensity distributions.

$q/\sqrt{6}$ (A.).	0·0343.	0·0351.	0·0359.	0·0367.	0·0375.
I_0	1	1	1	1	1
I_1	1·38	1·45	1·52	1·59	1·66
I_2	0·90	0·99	1·09	1·20	1·31
I_3	0·37	0·43	0·50	0·57	0·66
I_4	0·11	0·13	0·16	0·20	0·24

Experimentally, the gross features of the intensity distribution are that bands $n = 1$ and $n = 2$ are stronger than $n = 0$, the former ($n = 1$) being considerably stronger and the latter ($n = 2$) stronger by a small margin. Later bands fall rapidly in intensity. This is enough, with use of Table I, to fix the change in equilibrium C–C separation between 0·0351 A. and 0·0376 A. These gross features are apparent in spectra taken in solution, as for example those of Mayneord and Roe (*Proc. Roy. Soc.*, 1935, *A*, **152**, 299). A closer study of the spectra is necessary for precise values of the intensity distribution.

The experimental intensities in most polyatomic molecules must be taken from solution spectra alone, but in benzene the exhaustive analysis and assignments in the vapour spectrum by Garforth, Ingold, and Poole (*J.*, 1948, 406) allow a most valuable check. Indeed, the intensities in the vapour spectrum are to be preferred where an analysis has been made. Broadly, in the vapour spectrum, the intensities of individual bands in a progression may be compared, whereas in solution only the summed intensities of a large number of such members of progressions are available in broad band groups. The former comparison is in principle the better, but is much hampered by the widespread occurrence of intensity transfers between bands by Fermi resonance. Garforth and Ingold (*loc. cit.*, p. 421) have examined a striking case of this and elsewhere brought to light many definite examples. In general, a strong band loses a part of its proper (harmonic approximation) intensity to weaker bands which fall near to it in frequency. Neither the strong nor the weak bands in these alliances furnish material for the comparison of intensities in progressions, because each member of a progression is affected by the proximity of other bands, and by amounts which vary in a very irregular way. Two bands however may perturb one another in this way only if their final states have the same symmetry properties. There is in the assignments of Garforth, Ingold, and Poole (*loc. cit.*) a single long progression which, upon these grounds, is likely to be free from intensity disturbances. All except this one have final states whose vibrational symmetry includes one or all of A_{1g}, A_{2g}, and E_g^+ representations. None of these is useful for the present purpose. The unique progression is denoted by Ingold as the M progression and its transitions start and end at states having one quantum of the E_g^- vibration. The members are given by :

$$\nu = 38090 + E_g^{+\prime} + (E_g^{-\prime} - E_g^-) + p' \, 923 \text{ cm.}^{-1} \; (p' = 0,\ 1,\ 2,\ 3,\ 4).$$

The final states of this progression belong to B_{1g}, B_{2g}, and E_g^-. There are no other progressions with more than two members whose final states match these, and it follows that intensity transfers must be small. The vapour spectrum intensity distribution given in Table II has been calculated from this progression by using the experimental intensities found by Radle and Beck (*J. Chem. Physics*, 1940, **8**, 507).

In solution, the measurement of intensities as proportional to the area under the extinction curve is not suitable to the present purpose because the area includes a contribution by a continuous absorption which increases towards higher frequencies. This continuous absorption records transitions ending at dissociating molecules. It might properly be regarded as belonging to the band system as a whole but has no reference to particular values of the vibrational quantum numbers. To make the comparison of intensities, therefore, this continuous absorption would have in some way to be subtracted and the remainder analysed. Instead, the solution spectrum values given in Table II are based on the maximum values of extinction coefficients in the distinct band groups in the solution spectrum. These measure the relative areas of the band groups provided the shapes are the same. The effect of the continuous absorption is much less in this measurement because it appears only as a small addition to each maximum, and it might fairly safely be corrected for. Its influence is negligible in the first few maxima and no correction has in fact been made to the figures given in Table II. These have been obtained from the spectrum in alcohol solution given by Mayneord and Roe (*loc. cit.*).

TABLE II.

Experimental relative intensity distributions.

	Vapour spectrum. (Radle and Beck, *loc. cit.*).	Solution spectrum.* (Mayneord and Roe, *loc. cit.*).
I_0	1	1
I_1	1·46	1·45
I_2	1·12	1·12
I_3	0·42	0·65
....	0·17	—

* A new experimental study by Mr. I. G. Ross using a Cary Recording Spectrophotometer gives the values: 1, 1·48, 1·18, 0·69. The differences between these figures and those quoted in the table are not significant in the subsequent comparison with Table I.

The best agreements between the experimental values and the calculated ones of Table I are for $q/\sqrt{6}$ not less than 0·0359 A. and not greater than 0·0367 A. Thus in the approximation of CH mass points the increase in the C–C distance in the $\mathbf{B}_{2u}$ electronic state is 0·036 A.

When, in the more precise calculations already referred to, account is taken of relative motion within each C–H unit the increase in C–C distance is found to be 0·037 A., and this should be correct to 0·001 A. The calculation is outlined in the Appendix. Here the C and H atoms are allowed to have different motions and the calculation involves two unknown quantities, instead of one as formerly. These are the increase in the C–C distance as before, and the change in the C–H distance. Previously the C–H distance was, in effect, taken as unchanged. Now, however, a value must be assigned to it in order to calculate the change in C–C distance. If the change is taken to be zero, then the refined calculation gives the same result, to within 1%, as the simple one did. The procedure we have adopted is to use a value for the change in C–H bond length deduced by Garforth, Ingold, and Poole (*J.*, 1948, 508) by applying Badger's rule to the observed force constants. This gives a shortening of the C–H bond length by 0·01 A. in the $\mathbf{B}_{2u}$ state. With this the Franck–Condon calculation gives the value 0·037 A. for the increase in C–C distance. It will be noticed that the change in calculated C–C distance due to a C–H change of 0·01 A. is 0·001 A.; thus the incorporation of this empirical quantity in the working does not have a critical effect on the accuracy of the result.

The final variation in method is that of supposing the elastic constants in the two electronic states to be the same. Practically, this means that the calculation can be made without any detailed information about the excited state. The starting point is a knowledge of the elastic constants of the ground state, together with the experimental intensity distribution in the spectrum. In benzene the experimental results are now fitted about equally well by values of the C–C increase of 0·0355 A. and 0·0359 A. From this simplest model therefore the result is between 0·035 A. and 0·036 A. It is striking how closely this agrees with the more precise calculations. In more complicated molecules this last method, on its present showing, may be used with some confidence. The largest single correction to it is likely to be that for the change in equilibrium C–H distance.

Finally, Table III displays values for the increase in C–C distance upon excitation to the $\mathbf{B}_{2u}$ state from three different sources. The first is a theoretical value obtained by Kynch and Penney (*Proc. Roy. Soc.*, 1941, *A*, **179**, 266) in the electron-pair approximation. The second and third are due to Garforth, Ingold, and Poole (*J.*, 1948, 508) and are based upon empirical relations between force constants and bond lengths. The remainder are Franck–Condon values. The value in heavy type is recommended. The agreement throughout these independent estimates, and especially between those based immediately upon elastic constants and spectral intensities, is satisfactory.

TABLE III.

Values for the increase in C–C *distance in the* $\mathbf{B}_{2u}$ *electronic state.*

Theoretical calculation (Kynch and Penney)	0·05 A.	
Badger's rule (Garforth, Ingold, and Poole)	(0·0375 A.) *	2·7%
Douglas Clark's rule (Garforth, Ingold, and Poole)	(0·0361 A.) *	2·6%
Franck–Condon principle	**0·037** A.	
Franck–Condon principle with CH groups as single mass points	0·036 A.	
Same, with elastic constants unaltered in the upper state	0·035—0·036 A.	

* Worked out from the published percentages by using 1·39 A. for the ground state C–C distance.

APPENDIX 1.

The Inclusion of Internal C–H *Motion.*—The force constants given by Garforth, Ingold, and Poole (*loc. cit.*, p. 491) being used, the following are the normal co-ordinates for the motion of a single CH group.

Ground electronic state :

$$\left.\begin{aligned}\xi_1 &= 0{\cdot}9503\,p_C + 0{\cdot}3114\,p_H\\ \xi_2 &= 0{\cdot}3114\,p_C - 0{\cdot}9503\,p_H\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Excited state :

$$\left.\begin{aligned}\xi_1' &= 0{\cdot}9525\,p_C + 0{\cdot}3046\,p_H\\ \xi_2' &= 0{\cdot}3046\,p_C - 0{\cdot}9525\,p_H\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The p's are mass-reduced co-ordinates and the x's displacements :

$$p_C = \sqrt{12/1{\cdot}008}\;x_C$$
$$p_H = x_H$$

The first co-ordinate in each of (8) and (9) is that for the desired low-frequency motion, and when the system is oscillating in this mode $\xi_2(\xi_2') = 0$. Thus in the ground state

$$\left.\begin{aligned}&0{\cdot}3114\,p_C = 0{\cdot}9503\,p_H \text{ and } \xi_1 = 1{\cdot}0523\,p_C = 13{\cdot}1825\,x_C\\ &\text{and in the excited state } \quad \xi_1' = 1{\cdot}0499\,p_C = 13{\cdot}1225\,x_C\end{aligned}\right\} \quad . \quad . \quad . \quad (10)$$

It will be noticed, in passing, that the hydrogens are displaced about 1·1 times as far as the carbons, and in the same phase, in this mode. The relations (10) show that the motion of the carbon atoms in the actual system is equivalent to the oscillations of mass points of masses 13·1825 and 13·1225, respectively. This enables the work to be linked with that given in the text. The oscillator constants β in the two states are $3{\cdot}908 \times 10^{18}$ (ground) and $3{\cdot}608 \times 10^{18}$ (excited) ; $\rho = 1{\cdot}0834$. Values for the S_{0r} and of intensity distributions for chosen values of q may be found from these. q now refers directly only to the separation between the origins of normal co-ordinates and not to the actual displacements of the carbon atoms. Table IV gives a few such calculated intensity distributions.

TABLE IV.

q (A.).	0·087.	0·088.	0·089.
I_0	1	1	1
I_1	1·51	1·55	1·58
I_2	1·08	1·13	1·19
I_3	0·49	0·52	0·56
I_4	0·16	0·17	0·19

Here 0·087 A. and 0·088 A. fit the experimental distributions about equally well.

If d is the increase in the C–C distance and f the shortening of the C–H bond, then, a term which is very small for small f being neglected, it may be shown that the relation between q and these quantities is :

$$q \cong \sqrt{6}(0{\cdot}99d - 0{\cdot}084f)$$

Use of this expression gives $d = 0{\cdot}037$ A. for $f = 0{\cdot}01$ A.

APPENDIX 2.

Anharmonicity in the Vibrations.—If the potential field for the A_{1g} vibrations were strongly anharmonic, the working would become really very complicated. This happens in diatomic molecules such as H_2 (Hutchisson, *loc. cit.*) but is not expected so much in polyatomic molecules. It may be neglected altogether in benzene for reasons now to be given.

Suppose the potential function to contain a cubic and a quartic term as the principal anharmonicities :

$$V(x) = \tfrac{1}{2}kx^2 + ax^3 + bx^4$$

The quartic term has a first-order effect upon the energy levels and we may set an upper limit to it by assuming that it causes the whole of the observed convergence. The anharmonic correction to the seventh quantum state of the A_{1g} vibration is 7 cm.$^{-1}$ (Garforth and Ingold, *J.*, 1948, 417) and by first-order perturbation theory this leads to $b/\beta^2 = 1{\cdot}64 \times 10^{-17}$ dynes cm.$^{-4}$. The fourth-power term causes intensity transfers between a band of a progression and the second and fourth bands on either side of it. The correction to the intensity of a band for $n = 2$, for example, is easily found by first-order perturbation theory to be in the order 10^{-8} for the value of b/β^2 given. Evidently the fourth-power term is negligible.

The cubic term has no first-order effect upon the energy levels but only a second-order one. It is possible to form an upper estimate of the cubic term (an improbably high upper estimate) by supposing the whole of the observed convergence to be due to its second-order effect upon the energy levels. Where there is no first-order term, the second order correction to the energy of the nth state is a sum of contributions from all states joined to it by matrix components of the perturbing potential :

$$W_n = \sum_{m \neq n} \frac{(H_{mn})^2}{\nu_n - \nu_m}; \quad H_{mn} = \frac{a}{\beta^{3/2}} \int \phi_n'(A_{1g})\beta^{3/2}x^3\phi_m'(A_{1g})\mathrm{d}x$$

Four matrix components exist, joining the nth state to states $n \pm 1$ and $n \pm 3$. The higher frequency states depress, and the lower raise, the perturbed state, with the former predominating. Again, by use of the fact that the seventh quantum level is depressed by 7 cm.$^{-1}$ the relations given above lead to $a/\beta^{3/2} \cong 1{\cdot}1 \times 10^{-15}$ dynes cm.$^{-1}$. The magnitude of the intensity transfer due to this may now be calculated. The largest matrix component joins the nth to the $(n + 1)$th state. The coefficient of the $(n + 1)$th wave function in the perturbed nth is :

$$\frac{a/\beta^{3/2} \times 3/(2\sqrt{2}) \times (n + 1)^{3/2}}{1{\cdot}835 \times 10^{-13}} \cong 6{\cdot}4 \times 10^{-3}(n + 1)^{3/2}$$

For $n = 2$, which is important in the interpretation of the experimental intensities, the coefficient is about $3{\cdot}3 \times 10^{-2}$. The fraction of the intensity transferred is the square of this, and so it may be said that 0·1% is an upper limit to the intensity transfers by anharmonicity in the bands whose intensities are critical. For $n = 5$ the transfer approaches only 1%, which is still negligibly small. The anharmonicity of the A_{1g} potential may therefore be altogether neglected.

My thanks are due to Dr. Edward Teller and to Professor C. K. Ingold, F.R.S., for discussions about this subject. The work has been carried out during tenure of a Turner and Newall Research Fellowship in the University of London.

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

[*Received, May 1st*, 1950.]