

Vibrational Intensities in Electronic Transitions

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1 Introduction

The electronic spectra of atoms are known to consist of single lines, each corresponding to the single transition between two electronic states.¹ The electronic spectra of molecules, on the other hand, are usually seen as broad regions of absorption with more or less detailed structure. However, recent technological advances have led to the observation of much more detail in these broad regions. In general, each of these regions of absorption corresponds to one, or possibly a superposition of two or more electronic transitions. Molecular electronic transitions cover rather broad areas, because electronic excitation is accompanied by changes in vibrational and rotational energy which are not present in single atoms. The increase of interest in medium- to high-resolution spectroscopy makes worthwhile a summary of what is well known² about the distribution of intensity among these various vibrational structures in an electronic transition. Most of the treatments readily available are rather specific to special cases or to specific small molecules. We have chosen here to outline the theory of the intensity distribution among the different vibronic components of electronic transitions, allowed or symmetry forbidden, with special attention to absorption. Thus, we have not examined fluorescence, or, more generally, 'the fate of the excited state',³ in any detail; also, we have omitted any reference to the rotational fine structure which further subdivides the vibronic bands and can be very useful in the interpretation of electronic spectra.

We must first describe a molecular state involving both electronic and nuclear motion. We will assume that we can apply the well-known Born–Oppenheimer (BO) approximation,⁴ in which one separates the motion of the electrons and of the nuclei. Therefore, we will write the total wavefunction as the product (1),

$$\Xi_{I\mu}(e, q) = \psi_I(e, q) X_I^\mu(q) \quad (1)$$

where $\psi_I(e, q)$, the electronic wavefunction, depends explicitly on the co-ordinates of the electrons, represented by e , and parametrically on the co-ordinates of the nuclei, represented by q : i.e., ψ_I is different for each set q . It is given as a solution of the electronic Schrödinger equation of the molecule [equation (2)];

¹ G. Herzberg, 'Atomic Spectra and Atomic Structure', Dover Publications, New York, 1944.

² G. Herzberg, 'Electronic Spectra of Polyatomic Molecules', Van Nostrand Reinhold Co., New York, 1966, Chapter 2.

³ M. Orchin and H. H. Jaffé, 'Symmetry, Orbitals, and Spectra', Wiley Interscience, New York, 1971, Chapter 11.

⁴ F. L. Pilar, 'Elementary Quantum Chemistry', McGraw-Hill, New York, 1968, p. 414.

$$H(e, q)\psi_I(e, q) = E_I(q)\psi_I(e, q) \quad (2)$$

$X_I^\mu(q)$ is the vibrational wavefunction, solution of the nuclear equation (3),

$$\left[- \sum_{\sigma} \frac{\hbar^2}{2M_{\sigma}} \nabla_{\sigma}^2 + V_I(q) \right] X_I^\mu(q) = E_{I\mu} X_I^\mu(q) \quad (3)$$

which is the Schrödinger equation for a set of nuclei σ moving in a potential field $V_I(q)$. We see that a different nuclear equation holds for each different electronic state I , which is the reason why the vibrational (or nuclear) wavefunctions have to be specified by the two quantum numbers I and μ . The set ($I\mu$) defines a vibronic state, of energy $E_{I\mu}$.

$V_I(q)$ has as many dimensions as there are vibrational degrees of freedom in the molecule ($3N - 6$ for a non-linear molecule, $3N - 5$ for a linear molecule, if N is the number of atoms of the molecule). The BO approximation is only valid if the state I is well separated from all the other states: otherwise a strong coupling occurs between *different* electronic states and the nuclear motions (Jahn–Teller and Renner effects⁵); throughout this review we shall assume the states with which we deal to be sufficiently well separated so that such couplings can be ignored.

Let us now consider an one-electron transition between two electronic states I and F . *A priori* there is nothing to indicate that the electron cannot jump from any initial vibronic state $I\mu$ to any final vibronic state $F\nu$, so that the spectrum corresponding to the electronic transition $F \leftarrow I$ could be composed of an infinity of lines (some of which might actually be superimposed). In this review we shall attempt to show qualitatively how the intensity of the absorption (or emission) of light may be distributed among these lines, or bands (because of the rotational structure, each line is in fact a band consisting of many lines and will be referred to as a vibronic band). First let us recall how we can determine theoretically the intensity of an electronic transition. Virtually all such transitions known from observation are electronic dipole transitions, and for the sake of simplicity we restrict ourselves to this case although the discussion can be extended to magnetic dipole and electric quadrupole transitions.

The intensity of the transition $F\nu \leftarrow I\mu$ may be expressed through the oscillator strength (4) where $|\Delta E_{I\mu, F\nu}|$ is the difference in energy between the two vibronic

$$f \propto |\Delta E_{I\mu, F\nu}|^2 \left| \vec{M}_{IF}^{\mu\nu} \right|^2 \quad (4)$$

states and $\vec{M}_{IF}^{\mu\nu}$ is the transition moment (5), where \vec{r}_i and \vec{r}_{σ} give the position

$$\vec{M}_{IF}^{\mu\nu} = \langle \vec{\mathcal{E}}_{I\mu} | \sum_i \vec{r}_i - \sum_{\sigma} Z_{\sigma} \vec{r}_{\sigma} | \vec{\mathcal{E}}_{F\nu} \rangle \quad (5)$$

of electron i and nucleus σ , respectively, and Z_{σ} the charge of nucleus σ . The difference $\Delta E_{I\mu, F\nu}$ can be expressed as the sum of an electronic difference ΔE_{IF}

⁵ G. W. King, 'Spectroscopy and Molecular Structure', Holt, Rinehart, and Winston, New York, 1965, pp. 410–418.

(for example between the energies of the states I and F at their respective equilibrium positions) and of a vibrational energy $\Delta E_{\mu\nu}$, [equation (6)].

$$\Delta E_{I\mu, F\nu} = \Delta E_{IF} + \Delta E_{\mu\nu} \quad (6)$$

We shall see that usually the most intense vibronic bands arise from transitions between vibronic states having vibrational quantum numbers μ and ν which are not very different: taking into account that a quantum of vibrational energy is much smaller than one of electronic energy, we can neglect $\Delta E_{\mu\nu}$ in equation (6) and write

$$f \propto |\Delta E_{IF}| |\vec{M}_{IF}^{\mu\nu}|^2$$

For two definite electronic states I and F the intensity distribution thus depends only on $|\vec{M}_{IF}^{\mu\nu}|$. Using the product form for the Ξ , equation (1), we obtain equation (7). The second term on the right of this equation contains the

$$\vec{M}_{IF}^{\mu\nu} = \langle \psi_I X_I^\mu | \sum_i \vec{r}_i | \psi_F X_F^\nu \rangle - \langle \psi_I X_I^\mu | \sum_\sigma Z_\sigma \vec{r}_\sigma | \psi_F X_F^\nu \rangle \quad (7)$$

operator $\sum_\sigma Z_\sigma \vec{r}_\sigma$, which depends only on the nuclear co-ordinates; consequently, we can integrate first with respect to the electronic co-ordinates. $\psi_I(e, q)$ and $\psi_F(e, q)$ are orthogonal at any q since they are different solutions of the same electronic Schrödinger equation, and thus the second term vanishes. Accordingly, we have equations (8) and (9). The latter can be rewritten as equation (10),

$$\langle \psi_I X_I^\mu | \sum_\sigma Z_\sigma \vec{r}_\sigma | \psi_F X_F^\nu \rangle = \int X_I^\mu | \sum_\sigma Z_\sigma \vec{r}_\sigma | X_F^\nu \left[\int \psi_I \psi_F de \right] dq = 0 \quad (8)$$

$$\vec{M}_{IF}^{\mu\nu} = \langle \psi_I X_I^\mu | \sum_i \vec{r}_i | \psi_F X_F^\nu \rangle = \int X_I^\mu(q) \left[\int \psi_I(e, q) \sum_i \vec{r}_i \psi_F(e, q) de \right] X_F^\nu(q) dq \quad (9)$$

$$\vec{M}_{IF}^{\mu\nu} = \int X_I^\mu(q) \vec{M}_{IF}(q) X_F^\nu(q) dq \quad (10)$$

where the electronic transition moment $\vec{M}_{IF}(q)$ is given by equation (11) and

$$\vec{M}_{IF}(q) = \int \psi_I(e, q) \sum_i \vec{r}_i \psi_F(e, q) de \quad (11)$$

depends only parametrically on the nuclear configuration q .

Let us now consider all the transitions from the initial state $I\mu$ to the various vibrational levels ν of the final electronic state F . One can easily derive equation (12) by use of the so-called 'closure relation'.⁶ This equation means that the

$$\sum_\nu |\vec{M}_{IF}^{\mu\nu}|^2 = \int X_I^\mu(q) |\vec{M}_{IF}(q)|^2 X_I^\mu(q) dq \quad (12)$$

⁶ A. Messiah, 'Quantum Mechanics', Wiley, New York, 1965, Vol. 1, p. 269.

total intensity of all the transitions $Fv \leftarrow I\mu$ depends only on $X_I^\mu(q)$ and not on the actual form of the vibrational wavefunctions of the final state F . However, this total intensity still depends on the form of the potential surface V_F through $\vec{M}_{IF}(q)$.

2 Harmonic and Condon Approximations

Harmonic Approximation.—To try to gain some insight into the intensity distribution we must now introduce some approximation. *A priori* we do not have any idea of the form of the X , which depend on the form of the potential surfaces; our first approximation will thus concern the shapes of V_I and V_F .

Let us consider the potential surface V_I as an example. If ξ_I are the Cartesian displacement co-ordinates of the nuclei in a local axis system centred on the nuclei, we can expand V_I around the equilibrium geometry of the state I as a series (13). This series contains no linear terms because we assume the state I

$$V_I = \sum_{i,j} a_{ij} \xi_i \xi_j + \sum_{i,j,k} b_{ijk} \xi_i \xi_j \xi_k + \dots \quad (13)$$

to be stable, *i.e.*, $(\partial V_I / \partial \xi_j)_0 = 0$ for all j . We now introduce the assumption that the potential surface is harmonic, *i.e.* that all terms in equation (13) above second order may be neglected; thus

$$V_I = \sum_{i,j} a_{ij} \xi_i \xi_j$$

With this assumption, it is always possible to find a transformation which allows us to transform the ξ_i into a new set of co-ordinates Q_α such that V_I can be expressed as equation (14). In other words, the cross-terms are eliminated from

$$V_I = \frac{1}{2} \sum_\alpha \lambda_\alpha Q_\alpha^2 \quad (14)$$

the expression for V_I . In these co-ordinates, the nuclear Schrödinger equation may be rewritten⁷ as equation (15). Then a section through V_I along any Q_α

$$\left[-\frac{\hbar^2}{2} \sum_\alpha \frac{\partial^2}{\partial Q_\alpha^2} + \frac{1}{2} \sum_\alpha \lambda_\alpha Q_\alpha^2 \right] X_I^\mu(q) = E_{I\mu} X_I^\mu(q) \quad (15)$$

is a parabola, the concavity of which is proportional to λ_α . The Q_α are orthonormalized linear combinations of the mass-weighted Cartesian displacement co-ordinates $\sqrt{M_i} \xi_i$, and are called the 'normal co-ordinates' of the state I . We see that the nuclear Hamiltonian is now a sum of one-dimensional Hamiltonians [equation (16)], and we thus write $X_I^\mu(q)$ as a product of functions

$$H_\alpha = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_\alpha^2} + \frac{1}{2} \lambda_\alpha Q_\alpha^2 \quad (16)$$

⁷ See ref. 4, p. 417.

$\chi_I^{\mu\alpha}(Q_\alpha)$. The μ on X_I^μ now stands for the collection of μ_α , and the nuclear Schrödinger equation splits into $3N - 6$ (or $3N - 5$) equations (17). This is

$$\left[-\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_\alpha^2} + \frac{1}{2} \lambda_\alpha Q_\alpha^2 \right] \chi^{\mu\alpha}(Q_\alpha, \lambda_\alpha) = \epsilon_{\mu\alpha} \chi^{\mu\alpha}(Q_\alpha, \lambda_\alpha) \quad (17)$$

just the equation of the one-dimensional harmonic oscillator, the solutions of which are well known. We thus have equation (18), where μ_α refers to the

$$E_{I\mu} = \sum_\alpha \epsilon_{\mu\alpha} = \sum_\alpha \hbar \tilde{\mu}_\alpha (\mu_\alpha + \frac{1}{2}) \quad (18)$$

vibrational quantum number and $\tilde{\mu}_\alpha$ refers to the corresponding frequency. We do not need the exact expression of the $\chi^{\mu\alpha}(Q_\alpha, \lambda_\alpha)$, but it must be remembered that these functions form an orthonormal set, *i.e.*

$$\int \chi^{\mu\alpha} \chi^{\nu\alpha} dQ_\alpha = \delta_{\mu\alpha\nu\alpha}$$

where δ is the Kronecker symbol.

Analogous equations hold for the state F ; $X_F^\nu = \Pi_\alpha \chi^{\nu\alpha}(Q_\alpha', \lambda_\alpha')$, where the normal co-ordinates Q_α' of F are distinguished by a prime from the Q_α of I :

$$E_{F\nu} = \sum_\alpha \epsilon'_{\nu\alpha} = \sum_\alpha \hbar \tilde{\nu}_\alpha (\nu_\alpha + \frac{1}{2}) \quad (19)$$

Note that $E_{F\nu}$ is the energy above the minimum of V_F while $E_{I\mu}$ is the energy above the minimum of V_I . The difference $E_{F\nu} - E_{I\mu}$ represents $\Delta E_{\mu\nu}$ of equation (6).

Condon Approximation.—We now introduce a second hypothesis in order to simplify equation (10). As we have seen, $\vec{M}_{IF}(q)$ depends on the configuration of the nuclei. We assume that $\vec{M}_{IF}(q)$ can be approximated by a quantity independent of q : $\vec{M}_{IF}(q) \approx \vec{M}_{IF}(0)$, where $\vec{M}_{IF}(0)$ is the electronic transition moment at the equilibrium nuclear configuration 0 of the state I . This is called the 'Condon approximation'. Then

$$\vec{M}_{IF}^{\mu\nu} = \vec{M}_{IF}(0) \int X_I^\mu(q) X_F^\nu(q) dq = \vec{M}_{IF}(0) S_{\mu\nu} \quad (20)$$

3 Franck-Condon Factors and Vibrational Intensities in Allowed Transitions

Next we assume that $\vec{M}_{IF}(0) \neq 0$, *i.e.* we consider only *allowed* electronic transitions; the case of forbidden transitions will be treated later. With the Condon approximation the intensity distribution for allowed transitions depends only on the quantities

$$S_{\mu\nu}^2 = C_{\mu\nu}$$

Introducing the Condon approximation in equation (12) leads to equation (21),

$$\sum_{\nu} |\vec{M}_{IF}^{\mu\nu}|^2 = |\vec{M}_{IF}(0)|^2 \sum_{\nu} S_{\mu\nu}^2 = |\vec{M}_{IF}(0)|^2 \int X_I^{\mu}(q) X_I^{\mu}(q) dq = |\vec{M}_{IF}(0)|^2 \quad (21)$$

where the relationship (22) holds. At this point we have reduced the problem of

$$\sum_{\nu} S_{\mu\nu}^2 = \sum_{\nu} C_{\mu\nu} = 1 \quad (22)$$

the intensity distribution of the vibronic components of an allowed electronic transition to an evaluation of the integrals $S_{\mu\nu}$. The relative magnitudes of these depend on the relative shapes and positions of the potential surfaces V_I and V_F , and we can now investigate the different possible situations. In any case, we notice that because of our harmonic hypothesis, sections of V_I and V_F by vertical planes (assuming the energy axis to be vertical) are parabolas.

The simplest situation arises when not only the normal co-ordinates Q_{α} and Q_{α}' of initial and final states are the same, but also the associated λ_{α} [cf. equation (14)] are the same. This implies that the force constants for the various vibrations do not change upon excitation, and that the potential surfaces V_I and V_F are identical, except for displacement along the energy axis. This case is illustrated in Figure 1(a) where V_I and V_F are shown for a hypothetical case involving only two normal co-ordinates.

In this situation (Case 1) $C_{\mu\nu}$ can be factored into $3N - 6$ components, equation (23), one for each normal co-ordinate. The $C_{\mu_{\alpha}\nu_{\alpha}}$ are called the Franck-

$$C_{\mu\nu} = \prod_{\alpha} C_{\mu_{\alpha}\nu_{\alpha}} = \prod_{\alpha} S_{\mu_{\alpha}\nu_{\alpha}}^2 \quad (23)$$

Condon factors. It follows that the vibrational Schrödinger equations, and consequently the vibrational eigenvalues and eigenfunctions, are identical for the states I and F . As a consequence, the $\chi^{\nu_{\alpha}}$ and $\chi^{\mu_{\alpha}}$ are functions belonging to the same orthonormal set, $S_{\mu_{\alpha}\nu_{\alpha}} = \delta_{\mu_{\alpha}\nu_{\alpha}}$, and the only vibronic components of the transition $F \leftarrow I$ having non-zero intensity are those in which the sets of vibrational quantum numbers (μ and ν) are identical. Since the vibrational energy spacings are also identical, the spectrum will consist of a *single vibronic band*, which represents the superposition of all the degenerate transitions $F_{\mu} \leftarrow I_{\mu}$.

A more complicated situation (Case 2) exists when, although the Q_{α} and Q_{α}' are the same, one or more of the concavities λ_{α} of equation (13) differ between states I and F . This case is illustrated (again in the two-dimensional case), in Figure 1(b). Again, equation (23) holds. In this case the vibrational Schrödinger equations, although of equal *form*, are no longer identical, and different eigenvalues $E_{\mu_{\alpha}}$ and $E_{\nu_{\alpha}}$ result. Consequently, the overlap integrals $S_{\mu_{\alpha}\nu_{\alpha}} \neq \delta_{\mu_{\alpha}\nu_{\alpha}}$ and new vibronic bands become allowed. However, a selection rule arises from the nature of the vibrational wavefunctions in the harmonic approximation used here. These functions $\chi^{\nu_{\alpha}}(Q_{\alpha}, \lambda_{\alpha})$, are even or odd functions of Q_{α} , depending on whether μ_{α} is even or odd, and similarly for $\chi^{\mu_{\alpha}}(Q_{\alpha}', \lambda_{\alpha}')$. Consequently $S_{\mu_{\alpha}\nu_{\alpha}}$ vanishes unless μ_{α} and ν_{α} are of the same parity, and we obtain the selection rule (24).

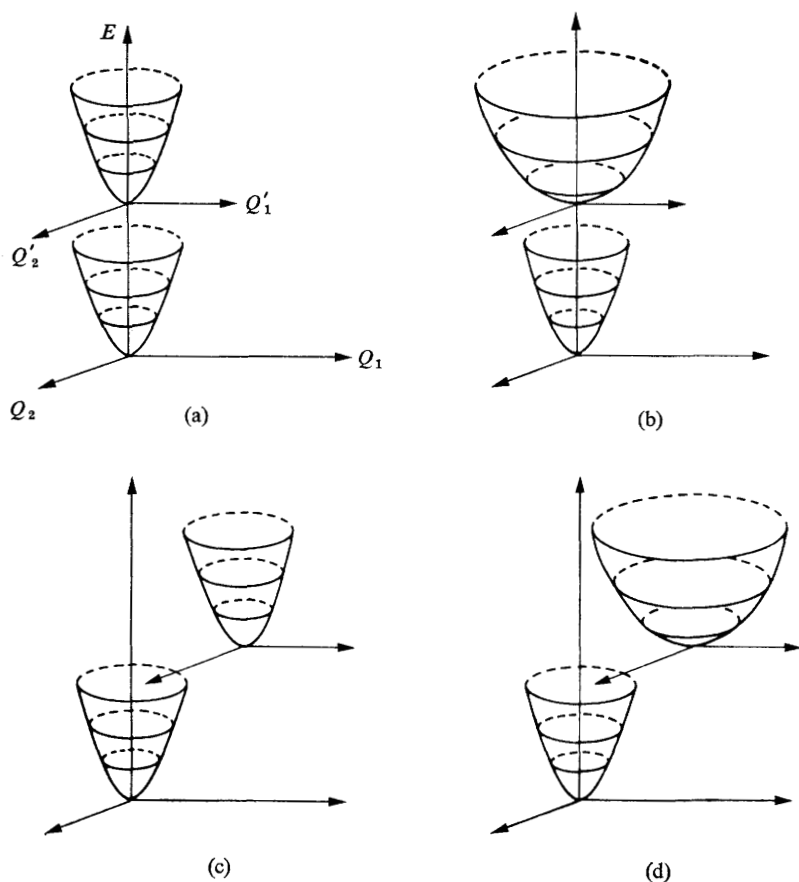


Figure 1 The relative shapes and orientations of potential surfaces (two-dimensional) for pairs of electronic states, (a) Case I, (b) Case II, (c) Case III, (d) Case IV

$$\Delta v_{\alpha} = \mu_{\alpha} - \nu_{\alpha} = 0, \pm 2 \quad (24)$$

The electronic spectrum of the molecule in the initial state I_{μ} should now be composed of various progressions of bands, each progression corresponding to a vibration α for which the surfaces are distorted (a single band corresponds to all the other Q_{α} for which no distortion occurs). At elevated temperatures, where a number of vibronic states I_{μ} are populated, a separate progression should appear for each significantly populated state. Since the spacing of vibrational levels is not the same in the two states, the progressions do not coincide but are offset from one another by $\tilde{\mu}_{\alpha} - \tilde{\nu}_{\alpha}$ [in units of \hbar : cf. equations (18) and (19)].

A study of the algebraic form of the Franck-Condon factors for diatomic

molecules⁸ shows that the band for which $\Delta\nu_\alpha = 0$ is by far the most intense and then the intensity decreases sharply with increasing $|\Delta\nu_\alpha|$. In absorption at room temperature or below, most of the molecules are in the vibrational ground state (all $\mu_\alpha = 0$) so that the most intense bands will result from transitions $F_v \leftarrow I_0$ (cold bands; $F_v \leftarrow I_\mu$ for some $\mu_\alpha > 0$ give the so-called hot bands). It can be shown that the Franck-Condon factor C_{00} for the 0-0 band is given by $C_{00} = 2\sqrt{\tilde{\mu}_\alpha \tilde{\nu}_\alpha} / (\tilde{\mu}_\alpha + \tilde{\nu}_\alpha)$. Even if $\nu_\alpha = \frac{1}{2} \mu_\alpha$, which corresponds to a strong distortion, $C_{00} = 0.94$, and the 0-0 band is most prominent among the cold bands.

In summary we can say that the distortion of the potential surfaces has a small effect on the spectrum, and generally speaking this spectrum will show the $\Delta\nu = 0$ bands very prominently and no clear progressions.

In a third situation [Case 3, Figure 1(c)] the potential surfaces are displaced relative to one another along one (or more) of the normal co-ordinates Q_α (as well as along the energy axis) by an amount ΔQ_α . $C_{\mu\nu}$ is still the product of $3N - 6$ $C_{\mu_\alpha \nu_\alpha}$ [equation (23)], so that we have to examine $C_{\mu_\alpha \nu_\alpha}$ for two displaced harmonic oscillators. There is no distortion, so that $C_{\mu_\alpha \nu_\alpha} = C_{\nu_\alpha \mu_\alpha}$; moreover when $\mu_\alpha = 0$, $C_{0\nu_\alpha}$ takes the simple form (25), where γ , the displacement parameter

$$C_{0\nu_\alpha} = \gamma^{\nu_\alpha} e^{-\gamma/\nu_\alpha}! \quad (25)$$

is given by (26). The main feature is that all $\Delta\nu_\alpha$ are now allowed. The ratio of

$$\gamma = \sqrt{\lambda_\alpha} \Delta Q_\alpha^2 / 2\hbar \quad (26)$$

two successive Franck-Condon factors is given by (27). Since γ can take any

$$C_{0\nu_\alpha+1}/C_{0\nu_\alpha} = \gamma/(\nu_\alpha + 1) \quad (27)$$

positive value, we see that the maximum value of $C_{\mu_\alpha \nu_\alpha}$ does not necessarily occur at C_{00} : it will be so only if $\gamma < 1$. For $\gamma = 1$, $C_{01} = C_{00}$, and for $\gamma = 2$, $C_{02} = C_{01} = 2C_{00}$.

For any normal co-ordinate Q_α , for which the minimum of V_F is displaced relative to the minimum of V_I , we then expect to see a progression of vibronic components; usually the progressions are not very long, since the $C_{0\nu_\alpha}$ decrease rapidly for large values of ν_α . The maximum intensity in such a progression then occurs usually not at $\nu_\alpha = 0$, but at some relatively small value of this quantum number. The appearance of these progressions is the rationale for the statement frequently found in the literature that those vibrations appear prominently in the vibronic spectrum which transform the molecule from the equilibrium geometry of its ground state to that of the excited state.

In actual molecules, of course, we usually do not encounter any of these first three limiting cases in pure form. Thus the deformations of Case 2 usually accompany the distortions of Case 3, and we have to deal with Case 4 where we find both distortion and displacement along one (or more) of the normal co-

⁸ C. Manneback, *Physica*, 1951, 17, 1001.

ordinates [Figure 1(d)]: equation (23) is still valid and it is possible to evaluate the $C_{\mu\alpha\nu\alpha}$.

As indicated above, the deformations of the potential energy surface usually have relatively little effect on the Franck–Condon factors, so that Case 4 is very similar to Case 3. Often, the displacement of V_F relative to V_I occurs along several normal co-ordinates. Since the total Franck–Condon factor $C_{\mu\nu}$ is the product of individual $C_{\mu\alpha\nu\alpha}$ for individual vibrations, the effects are readily predicted, and mixed progressions (corresponding to combination bands in the i.r.) between the displacing normal co-ordinates are expected to show weakly in absorption or emission.

In all the above situations of Figure 1, we have assumed that the normal co-ordinates remain unchanged upon excitation, although their origin may have been displaced. To provide a general treatment, we must consider changes in going from the Q_α to the Q'_α . Since the vibrational degrees of freedom are the same in the ground and excited states, it is always possible to express the normal co-ordinates Q'_α as linear combinations of the Q_α :

$$Q'_\alpha = \sum A_{\alpha\beta} Q_\beta + B_\alpha \quad \alpha = 1, 2, \dots, 3N - 6$$

We may now distinguish two basically different situations: if all $A_{\alpha\beta}$ (except $A_{\alpha\alpha}$) vanish, the co-ordinate axes in the two states are parallel. If any $A_{\alpha\beta}$ ($\alpha \neq \beta$) is non-vanishing, some Q'_α axes are rotated with respect to the Q_α axes; this situation is referred to in the literature as the Duschinsky effect.⁹ The difference between these two situations is illustrated in Figure 2 where again we suppose that there are only two normal co-ordinates ($\alpha, \beta = 1, 2$). We note that the sections of V_I and V_F by horizontal planes are ellipses with principal axes directed along the axes of the normal co-ordinates; such ellipses are represented in Figure 2. In Figure 2(a), with no Duschinsky effect, $Q'_1 = Q_1 + B_1$ and $Q'_2 = Q_2 + B_2$; $\tilde{\nu}_1 = \tilde{\nu}_1$ but $\tilde{\nu}_2 \neq \tilde{\nu}_2$. This corresponds to Case 3 of the previous discussion for Q_1 , and to Case 4 for Q_2 . On the other hand, Figure 2(b) represents the same surfaces, but in addition to displacements and distortions, there is a rotation of Q'_1 and Q'_2 with respect to Q_1 and Q_2 .

The factorization of equation (23) is not possible when a Duschinsky effect is present, and the calculation of the intensity distribution requires the evaluation of more involved integrals than simply the overlap

$$\int \chi^{\mu\alpha}(Q_\alpha, \lambda_\alpha) \chi^{\nu\alpha}(Q_\alpha + B_\alpha, \lambda'_\alpha) dQ_\alpha$$

between two displaced and/or distorted harmonic oscillators.

A Duschinsky effect is probably present in many actual spectra and is likely to alter significantly the vibrational intensities if the rotation of the normal co-ordinates is important. Although it has been studied in some particular

* F. Duschinsky, *Acta Physiochim. U.R.S.S.*, 1937, **1**, 551.

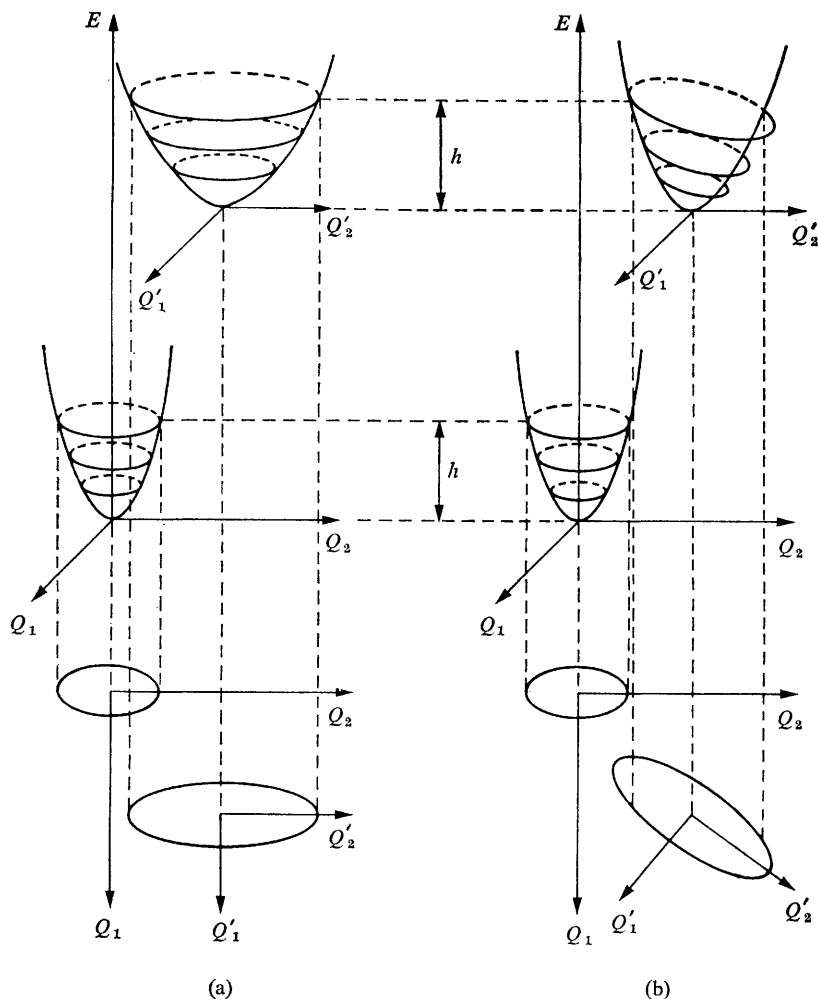


Figure 2 Potential surfaces illustrating the Duschinsky effect

cases,^{10,11} it has not yet been fully investigated; apparently most spectra can be understood with sufficient accuracy without taking it into account.

We have thus examined the different cases and seen why more than one band appears in the electronic spectra of molecules; observation of only a single band would correspond to the ideal Case 1 of identical potential surfaces, a case which is virtually never encountered.

¹⁰ B. Sharf and B. Honig, *Chem. Phys. Letters*, 1970, 7, 132.

¹¹ G. J. Small, *J. Chem. Phys.*, 1971, 54, 3300.

The above discussion presupposed a knowledge of V_I and V_F . Unfortunately, theoretical calculation of potential surfaces, even for ground states, although in principle feasible, is not yet a practical reality. While information about ground-state potential energy functions is readily available from i.r. and Raman spectroscopy, and other physical measurements, the vibronic structure of electronic transitions is about the only experimental avenue to excited-state potential functions.

We are now in a position to apply the above arguments to obtain information about the relation of V_F to V_I from the vibronic structure of spectra. For example, if no progressions are observed, implying that all bands correspond to $\Delta v = 0$, this strongly suggests that V_I and V_F are practically not displaced with respect to each other. On the other hand, the appearance of progressions in one or several frequencies shows that the surfaces are displaced along the corresponding normal co-ordinates. The intensity distribution depends on the extent of the displacements. If one knows the normal co-ordinates, one can calculate approximately the displacements by fitting the bands with calculated Franck-Condon factors. In absorption at low temperatures we expect, for each displaced co-ordinate Q_α' , a progression of band with maximum intensity generally occurring at some $\Delta v_\alpha > 0$; *i.e.* the most intense band generally is not the 0-0 band (*all* the μ_α and *all* the ν_α equal to zero). At higher temperatures, several new progressions of weaker intensity may appear, their intensity increasing with temperature (hot bands). At sufficiently high temperatures, the cold bands may even noticeably lose intensity. The spacing of the successive terms is a measure for the vibrational frequencies ν_α of the excited state in absorption and μ_α of the ground state in emission.

Such simple rules form a useful tool for the analysis of experimental spectra and the study of the potential surfaces of excited states. Symmetry arguments can also serve as a powerful tool in the analysis of experimental spectra and the study of excited states. The reader is referred to standard texts for the use of group theory in spectroscopy.¹² Let it suffice here to say that the transition $F_\nu \leftarrow I_\mu$ can have non-vanishing intensity only if $X_I^\mu(q)X_F^\nu(q)$ [*cf.* equation (20)] is invariant under all symmetry operations of the molecule; in other words, if the product of the X is totally symmetric. This requirement immediately eliminates many vibronic transitions but never the 0-0 band: the 0-0 band is always present in an allowed transition.

It is now time to look back to our two basic approximations, the assumption of a harmonic potential surface and the Condon approximation. In particular, the discussion of the Condon approximation will lead us to the consideration of symmetry-forbidden electronic transitions.

Harmonic Approximation.—Potential surfaces are not in reality harmonic except in a small region around the equilibrium geometry. The anharmonicity becomes important for high vibrational excited states, and these in turn are important

¹² See for example: M. Orchin and H. H. Jaffé, 'Symmetry in Chemistry', Wiley, New York, 1967, Chapter 5, section 5.3.

when the potential surfaces are largely displaced; in such rather rare cases dramatic changes in the spectrum can occur for which the above discussion is totally invalid. Such a case is, *e.g.*, the phenomenon of dissociation upon excitation.¹³ In a rigorous treatment it is to be noted that, with the introduction of higher-order terms in V_I (and/or V_F), the nuclear Schrödinger equation cannot be factored into $3N - 6$ unidimensional ones and consequently the normal coordinates do not exist as such. However, for small translations of the potential surfaces, only those levels appear in the spectrum for which μ_α and ν_α are small, and therefore anharmonicity will have little effect; under these circumstances anharmonicity can be treated as a perturbation.

Condon Approximation.—So far we have assumed that $\vec{M}_{IF}(q)$ is approximately constant and we have replaced it by $\vec{M}_{IF}(0)$, where 0 stands for the equilibrium geometry of I . In a better approximation we can expand $\vec{M}_{IF}(q)$ in a series around 0 [equation (28)]. Substitution in equation (10) leads to equation (29).

$$\vec{M}_{IF}(q) = M_{IF}(0) + \sum_{\alpha} \left(\frac{\partial \vec{M}_{IF}(q)}{\partial Q_{\alpha}} \right)_0 Q_{\alpha} + \dots \quad (28)$$

$$\vec{M}_{IF}^{\mu\nu} = M_{IF}(0) S_{\mu\nu} + \sum_{\alpha} \left(\frac{\partial \vec{M}_{IF}^{\mu\nu}(q)}{\partial Q_{\alpha}} \right)_0 \int X_I^{\mu} Q_{\alpha} X_F^{\nu} dq \quad (29)$$

4 Perturbations due to Vibronic Coupling

The derivatives $\vec{M}_{\alpha} = [\partial \vec{M}_{IF}^{\mu\nu}(q) / \partial Q_{\alpha}]_0$ do not generally all vanish and hence the second term on the right of equation (29) generally makes some contribution to $\vec{M}_{IF}^{\mu\nu}$. This second term appears because the electronic wavefunctions vary with q , and will be referred to as the ‘vibronic coupling’ term or simply ‘perturbing’ term; in turn we call $\vec{M}_{IF}(0)S_{\mu\nu}$ the ‘Condon term’. Again group theory provides rigorous symmetry selection rules for the perturbing term in symmetrical molecules, and an important remark can be made similar to the one we have made for the Condon term: for the perturbing term to be non-zero, $X_I^{\mu} Q_{\alpha} X_F^{\nu}$ must be totally symmetric. Now if Q_{α} is totally symmetric, this means that $X_I^{\mu} X_F^{\nu}$ must be totally symmetric; in other words if Q_{α} is totally symmetric, the same vibronic transitions are allowed for the Condon term and the perturbing term. On the other hand, if Q_{α} is not totally symmetric, $X_I^{\mu} X_F^{\nu}$ must *not* be totally symmetric: in other words, if Q_{α} is not totally symmetric the vibronic transitions allowed for the Condon terms are forbidden for the perturbing term, and some of the vibronic transitions forbidden for the Condon term can be made allowed by the perturbing term.

We will keep this remark in mind in looking at the possible effects of the

¹³ See ref. 2, p. 445.

vibronic coupling terms in electronic transitions. First we rewrite equation (29) in a more convenient way as equation (30), assuming as before that the harmonic approximation is valid and that there is no Duschinsky effect. It can be shown¹⁴

$$\int X_I^\mu Q_\alpha X_F^\nu dq = \int \chi^{\mu\alpha} Q_\alpha \chi^{\nu\alpha} dQ_\alpha \cdot \prod_{\beta} S_{\mu\beta\nu\beta} \quad (\beta \neq \alpha) \quad (30)$$

that the recurrence relationship (31) holds for the harmonic functions $\chi^{\nu\alpha}$.

$$Q_\alpha \chi^{\nu\alpha} = a \chi^{\nu\alpha-1} + b \chi^{\nu\alpha+1} \quad (31)$$

With the use of this relation, equation (29) then takes the form (32), where

$$\vec{M}_{IF}^{\mu\nu}(q) = \vec{M}_{IF}(0) S_{\mu\nu} + \sum_{\alpha} \vec{M}_{\alpha} (a S_{\mu\alpha\nu\alpha-1} + b S_{\mu\alpha\nu\alpha+1}) \cdot \prod_{\beta} S_{\mu\beta\nu\beta} \quad (\beta \neq \alpha) \quad (32)$$

a and b are constants; in equation (32) we have the same type of integrals S as in our previous discussion of the Franck–Condon factors.

Perturbing terms due to Q_α which are not totally symmetric give rise to bands which are forbidden in the Condon approximation. In the cases of potential surfaces illustrated by Figures 1(a) and (b) (Cases 1 and 2), the coefficients of \vec{M}_{α} are very small unless $\mu_{\alpha} = \nu_{\alpha} \pm 1$; in these cases no progressions in α will be observed, but only the $0 \rightarrow 1$ bands in the cold, and $1 \rightarrow 0$ and $1 \rightarrow 2$ as hot bands. Thus we may expect progressions in any vibration β for which V_I and V_F are strongly displaced relative to one another. In the cases of Figures 1(c) and (d) (Cases 3 and 4) we may expect progressions in α . The effect of these perturbing terms due to non-totally symmetric Q_α differ depending on whether the electronic transition is allowed [$\vec{M}_{IF}(0) \neq 0$] or symmetry forbidden [$\vec{M}_{IF}(0) = 0$]. In the allowed case, the perturbations cause new weak bands to appear in addition to the much more intense Condon term allowed bands. In the forbidden case these perturbation bands are the only bands appearing in the spectrum, as will become apparent from the following argument: a totally symmetric distortion, by definition, does not change the symmetry of the molecule or of the electronic state of this molecule; consequently, if $\vec{M}_{IF}(0) = 0$ for symmetry reasons $\vec{M}_{IF}(Q_\alpha)$ vanishes for any value of Q_α if Q_α is totally symmetric; as a result, vibronic coupling by totally symmetric vibrations vanishes, and only non-totally symmetric vibrations can bring intensity to symmetry-forbidden transitions.

From what we have said before, we can then conclude that the vibronic bands that would be allowed in an allowed transition are forbidden in such a symmetry-forbidden transition; in particular, the 0–0 band is forbidden. The absence of the 0–0 band along with the weak intensity of the spectrum is characteristic of symmetry-forbidden transitions (another feature is a distinct vibrational structure in the spectrum, even in solution, due to the fact that in general only a few

¹⁴ E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations', McGraw-Hill, New York, 1955, p. 38.

bands are allowed). In many molecules, there is no change of symmetry upon excitation, which means that V_I and V_F may only be displaced along totally symmetric vibrations. These do not contribute to the intensity but may show up as progressions. On the other hand, the transitions which make the transition allowed generally do not show up as progressions.

The perturbing terms due to totally symmetric vibrations contribute intensity in allowed transitions. The effect of such terms is not readily observable since the intensity they contribute is much smaller than typical Condon terms on which they are superimposed; thus they only result in a change of the intensities of the Condon term bands. It has been shown that such perturbation may be responsible for a lack of 'mirror symmetry' between absorption and fluorescence, even when such a symmetry would be expected according to the Condon approximation.¹⁵

5 Example of Symmetry-forbidden Transitions

We shall conclude this elementary review with a discussion of some of the most prominent features of the absorption band system of benzene vapour near 260 nm. The overall weak intensity and pronounced vibrational structure, even in solution, suggest a symmetry forbidden transition. From its energy it appears obvious that it is a $\pi \rightarrow \pi^*$ transition. We shall limit ourselves to two of the numerous progressions exhibited by the real spectrum: the progression A which is by far the most intense of all, and the progression B of weaker intensity. The intensities of A and B have been estimated by Sponer *et al.*,¹⁶ and are presented in Figure 3. Both progressions are in the same vibration β (frequency 925 cm^{-1}).

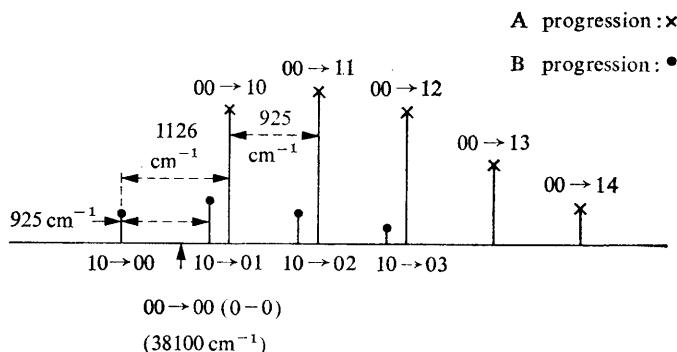


Figure 3 Two progressions in the absorption spectrum of benzene vapour

The vibronic bands are represented by $ab \rightarrow a'b'$ where a and a' are the quantum numbers of the vibration α (see below) in the ground and excited states, respectively,

¹⁵ D. P. Craig and G. J. Small, *J. Chem. Phys.*, 1969, **50**, 3827.

¹⁶ H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, *J. Chem. Phys.*, 1939, **7**, 207.

and b and b' are the corresponding quantum numbers for the vibration β . The intensities of the B bands are found experimentally to increase with temperature: they are thus hot bands. The rather long progressions in ν_β show that V_I and V_F are displaced along the corresponding normal co-ordinate Q_β . The vibrations of the ground state I are known¹⁷ from i.r. and Raman spectra but not the vibrations of F , and in order to identify Q_β we have to make some reasonable hypotheses and see whether the experimental spectrum is in agreement with them. We will assume that, at equilibrium, I and F have the same symmetry (D_{6h}). Then Q_β has to be totally symmetric; benzene has only two totally symmetric vibrations, one involving mostly the carbon ring at 993 cm^{-1} , the other involving mostly the C—H bonds at 3073 cm^{-1} . Now a $\pi \rightarrow \pi^*$ transition will certainly affect primarily the C—C bonds so that we can assume that V_I and V_F are distorted and displaced along the 'ring-breathing' totally symmetric normal co-ordinate. The distortion is not significant ($993\text{ cm}^{-1} \rightarrow 925\text{ cm}^{-1}$); the displacement has been estimated to correspond approximately to an increase of 0.04 \AA in the C—C bond distances;¹⁸ this is enough to make the $\Delta\nu_\beta = 1$ bands more intense than the $\Delta\nu_\beta = 0$ bands.

Next, we shall try to understand the 1126 cm^{-1} separation between the A and B bands. Since the first are cold bands, and the second hot bands, the frequency would have to correspond to one of the vibrations of the *ground* state; however, no such vibration exists in benzene. This is another argument to assign the band system to a forbidden transition, which is then made allowed by some non-totally symmetric vibration. In this case, we have seen that the cold bands will correspond to a $0 \rightarrow 1$ transition in α and the hot bands to a $1 \rightarrow 0$ or $1 \rightarrow 2$ transition in α ; in fact, two systems of hot bands, one for $1 \rightarrow 0$ and one for $1 \rightarrow 2$ are expected to show with comparable intensities, the second being displaced with respect to the first *toward the high frequencies* by $2\tilde{\nu}_\alpha$; a more detailed analysis of the spectrum shows that there is another progression of hot bands similar to the B progression at higher frequencies¹⁶ and we will then assign B to the $1 \rightarrow 0$ transition in α . If this is so, Figure 4 shows immediately that the separation between the A and B bands is $\tilde{\mu}_\alpha + \tilde{\nu}_\alpha$. Let us attempt to find among the vibrations of benzene the vibration α which can contribute the most to the intensity. An out-of-plane vibration will not significantly change the π wavefunctions involved

in this $\pi \rightarrow \pi^*$ transition, and the derivatives \vec{M}_α will be small for such a vibration. Therefore, we have to look for α among the in-plane vibrations. Examination of the corresponding frequencies shows that the only reasonable choice for α is the 606 cm^{-1} vibration (E_{2g}); hence $\nu_\alpha = 1126 - 606 = 520\text{ cm}^{-1}$ in the excited state. The frequencies of all the other in-plane non-totally symmetric vibrations lie above 1000 cm^{-1} , which would lead to an estimate of less than 150 cm^{-1} for $\tilde{\nu}_\alpha$, and would imply a tremendous and very unlikely distortion of V_F with respect to V_I . The 606 cm^{-1} vibration is mainly a ring vibration, the most likely to affect the π electrons and the intensity of the spectrum. With this

¹⁷ G. Varsanyi, 'Vibrational Spectra of Benzene Derivatives', Academic Press, New York, 1969, pp. 70—71.

¹⁸ F. M. Garforth, C. K. Ingold, and H. G. Poole, *J. Chem. Soc.*, 1948, 406.

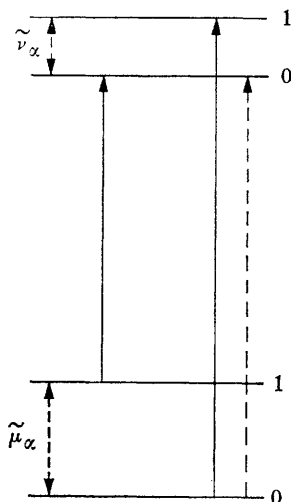


Figure 4 Vibronic transitions from ground to excited state in benzene

choice for α , we see that V_I and V_F are only slightly distorted and not displaced along Q_α , so that there is no progression in α . The 0–0 band is of course absent, and, if allowed, would be situated at $38\,100\text{ cm}^{-1}$ (Figure 3).

In summary, we have given a satisfactory interpretation of the spectrum as a symmetry-forbidden transition and have identified the vibronic bands. We have at the same time gained some insight into the shape of the potential surface of the excited state.