

*The Polarized Spectrum of Anthracene. Part II.\* Weak Transitions and Second-order Crystal Field Perturbations.*

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Forces between molecules in aromatic crystals are small compared with intramolecular forces, allowing the energy levels and spectral intensities in crystals to be treated by perturbation methods. In intense molecular transitions the most important effect of a monoclinic crystal field is "Davydov" splitting of the upper state into two components giving two crystal absorptions, one polarized parallel and the other perpendicular to the *b* crystal axis. The Davydov splitting is proportional to the intensity and, in transitions of low intensity, it is not the only important effect, for the upper state of the weak transition in one molecule interacts with the upper states of strong transitions in neighbouring molecules to cause changes comparable to and perhaps exceeding it. These second-order perturbations alter the splitting and may upset the oriented-gas intensity ratios, especially if a weak and a strong band system are close together.

If vibrational sublevels share the intensity of a system each behaves as a separate upper state and has distinct values of splitting and intensity ratio. This leads to irregularities in progression spacings which, like the other effects, are characteristic of the properties of the parent, isolated molecule, excited states and may be used to identify them.

The theory of these effects is applied to anthracene with various assumptions. Values are calculated for band splittings and intensities in the 3800-Å system.

In the strong anthracene absorption near 2500 Å (Part I, *J.*, 1955, 539) the dominant effect of the crystal field is a resonance splitting of the double degeneracy due to the presence in the unit cell of two molecules with identical energy levels. The theory of this type of splitting was first studied by Davydov (*Zhur. eskp. teor. Fiz.*, 1948, 18, 210); it is properly called a first-order crystal field perturbation because its size is approximately calculable by first-order perturbation theory applied to wave functions of the isolated molecules. The splitting is proportional to the square of the transition moment, and in the intense transitions commonly found in aromatic molecules (*e.g.*, naphthalene 2200 Å, anthracene 2500 Å, tetracene 3000 Å) it may amount to some thousands of wave numbers, corresponding to transition moments of about 3 Å. Conditions in weak transitions are very different and we discuss in this Part the effect of crystal forces in the long-wave aromatic systems of intensity of about  $f = 0.1$ . The Davydov splitting is a few hundreds of wave numbers at most and may be much less; we shall show that second-order effects are comparable, especially where there is a strong transition near the weak one. Moreover, under these conditions the oriented-gas intensity ratios are seriously wrong: the upper states of separate free molecule transitions become mixed by crystal forces resulting in intensity transfers between weak transitions and stronger ones, with a superficial resemblance to the well-known Herzberg-Teller intensity-stealing by vibrational perturbations. The following discussion deals with second-order crystal field perturbations with special reference to the 3800-Å anthracene system which will be analyzed and assigned in Part III (following paper); it falls into two parts: (i) energy changes due to interactions between crystal wave functions based on different molecular-state wave functions, and (ii) intensity transfers between perturbed molecular transitions.

The notation used in Part I must now be adapted to describe several molecular excited states instead of one only. Superscripts attached to wave functions and energies as in the molecular wave functions  $\varphi^r$ , their energies  $w^r$ , and the crystal functions  $\Phi^r$ , refer to an upward energy sequence of molecular excited states; subscripts are used throughout as a means of distinguishing different molecules.

\* Part I, *J.*, 1955, 539.

*Second-order Energy Terms.*—According to the analysis given in Part I each excited molecular state of anthracene splits into two manifolds of crystal levels all with the same parity as the molecular state but transforming in other respects like different representations of the unit cell group  $C_{2h}$ . Table 1 of Part I (*loc. cit.*) gives the symmetries of the associated crystal and molecular states. One finds, for example, that a  $B_{2u}$  molecular state has a  $B_u$  crystal component (*ac* polarized) and an  $A_u$  component (*b* polarized). To a good approximation, optical transitions are allowed only to that one level of each manifold with zero values of the wave vectors  $k_a$ ,  $k_b$ , and  $k_z$  [Part I, Equation (14) *et seq.*] and in this case each band in the vapour spectrum splits into two spectral lines in the crystal (Part I, Fig. 2). These lines record transitions from the crystal ground state to two upper states, described approximately as products of molecule functions  $\phi$  and  $\phi^r$  for the ground and  $r$ -th excited state. We write for the first excited state ( $r = 1$ ),

$$\phi_i^1 = \phi_1 \phi_2 \dots \phi_i^1 \dots \phi_N \dots \dots \dots (1)$$

and, by combining the product functions  $\phi$  according to representations of the unit cell group,

$$\begin{aligned} \gamma^{1\alpha} &= (1/\sqrt{2})(\phi_1^1 + \phi_2^1) \\ \gamma^{1\beta} &= (1/\sqrt{2})(\phi_1^1 - \phi_2^1) \end{aligned} \dots \dots \dots (2)$$

where the subscripts number the two molecules of one unit cell. The symmetry properties of  $\gamma$  depend on the symmetry of  $\phi$  and  $\phi^1$  in (1); in the case of most interest, where  $\phi^1$  is either of species  $B_{2u}$  or  $B_{3u}$  of  $D_{2h}$ ,  $\gamma^{1\alpha}$  transforms like  $B_u$  of  $C_{2h}$  and  $\gamma^{1\beta}$  like  $A_u$ .

The zero wave-vector crystal wave functions are

$$\Phi^{1\alpha, 1\beta} = (1/\sqrt{N/2}) \sum_{\mu, \nu, \omega} \gamma^{1\alpha, 1\beta}(\mu, \nu, \omega) \dots \dots \dots (3)$$

where the summation is over all the unit cells with co-ordinates  $(\mu, \nu, \omega)$ . The first-order splitting between  $\Phi^{1\alpha}$  and  $\Phi^{1\beta}$  is, from Part I, equation (17):  $2 \sum_m I_{lm}^1$  where

$$I_{lm}^1 = \int \phi_l \phi_l^1 \mathbf{V}_{lm} \phi_m \phi_m^1 d\tau$$

$\mathbf{V}_{lm}$  is the intermolecular potential [Part I, equation (1)] and  $m$  runs over molecules not translationally equivalent to  $l$ .

According to (2) we derive from each molecular excited state  $\phi^r$  two unit cell functions  $\gamma^{r\alpha}$  and  $\gamma^{r\beta}$  from which crystal wave functions (3) may be built. The first-order zero wave-vector crystal wave functions are formed by linear combination of the unperturbed functions (3) based on all the excited states  $r$  of the same parity with coefficients chosen to minimize the intermolecular energy. Proceeding conventionally we find that the excitation energy of the desired zero wave-vector crystal state is given by the lowest eigenvalue of an energy matrix of which the diagonal elements  $H^{rr}$  have the form of equation (17) of Part I, namely, for species  $B_u$ ,

$$H^{rr} = \Delta w^r + D^r + \sum_p I_{lp}^r + \sum_m I_{lm}^r \dots \dots \dots (4)$$

in which, as usual, the subscript  $l$  refers to molecules translationally equivalent to  $l$ , and  $m$  to the others. The non-diagonal elements  $H^{rs}$  are composed of integrals  $J$  and  $K$ , connecting two different molecular transitions:

$$H^{rs} = \sum_p K_{lp}^{rs} + \sum_m K_{lm}^{rs} + \sum_p J_{lp}^{rs} + \sum_m J_{lm}^{rs} \dots \dots \dots (5)$$

$$\left. \begin{aligned} K_{lp}^{rs} &= \int \phi_l^r \phi_l^s \mathbf{V}_{lp} \phi_p \phi_p \dots \\ J_{lp}^{rs} &= \frac{1}{2} \left( \int \phi_l^r \phi_l^s \mathbf{V}_{lp} \phi_p \phi_p^r \dots + \int \phi_l^r \phi_l^s \mathbf{V}_{lp} \phi_p \phi_p^s \dots \right) \end{aligned} \right\} \dots \dots \dots (6)$$

$\phi_p^s$  being the wave function for the  $p$ -th molecule in its  $s$ -th excited state. Expression (5), like (4), belongs to the  $B_u$  matrix; the elements of the  $A_u$  matrix are obtained by changing the signs of the last term in (4) and in (5).

The integrals  $K$  vanish in the dipole approximation; however, although small, they are

of some interest and are discussed at the end of this section. The integrals  $J$  may be evaluated as described in Part I. Expanding  $\mathbf{V}_{lp}$  and retaining only the dipole-dipole term, we find (cf. I.15)

$$J_{lp}^{rs} = \frac{1}{2}(-e^2/r_{lp}^3)|\mathbf{M}^r||\mathbf{M}^s|\left\{2 \cos \theta_{11}^r \cos \theta_{p1}^s + 2 \cos \theta_{11}^s \cos \theta_{p1}^r - \cos \theta_{12}^r \cos \theta_{p2}^s - \cos \theta_{12}^s \cos \theta_{p2}^r - \cos \theta_{13}^r \cos \theta_{p3}^s - \cos \theta_{13}^s \cos \theta_{p3}^r\right\} \quad (7)$$

where  $r_{lp}$  is the distance between the  $l$ -th and  $p$ -th molecules and  $\theta_{11}^s$ , for example, is the angle between the transition moment for the  $s$ -th excited state of the  $l$ -th molecule and the line joining the centres of the  $l$ -th and  $p$ -th molecules. If the transitions to states  $s$  and  $r$  have the same polarizations, the numerical factors in the integrals are the same as quoted in Table 3 of Part I. Table 1 summarizes all the values to the dipole-dipole approximation including neighbouring molecules up to 20 Å separation in the crystal. For  $r = s$  one has  $J_{lp}^{rr} = I_{lp}^r$ .

TABLE 1. Intermolecular integral sums for anthracene ( $\text{cm.}^{-1} \text{Å}^{-2}$ ).

	Both transitions $A_g - B_{2u}$	Both transitions $A_g - B_{3u}$	Mixed polarizations $A_g - B_{2u}$ and $A_g - B_{3u}$
$\sum_p J_{lp}^{rs}/ \mathbf{M}^r  \mathbf{M}^s $ .....	-990	728	292
$\sum_m J_{lm}^{rs}/ \mathbf{M}^r  \mathbf{M}^s $ .....	96	1532	1284

If the perturbation conditions  $H^{rr} - H^{11} \gg H^{r1}$  hold we may write the excitation energy of the lowest excited crystal state in the second-order perturbation form:

$$\Delta E = H^{11} + \sum_r (H^{1r})^2 / (H^{11} - H^{rr}) \quad (8)$$

The labour of diagonalizing the energy matrix rigorously is not justified unless the inequality above is seriously disobeyed.

The quantities in Table 1, appropriately multiplied by the experimental transition moments, and taken together with the vapour excitation energies  $\Delta w$  allow all the quantities appearing on the right hand side of (8) to be calculated with the exception of the  $K$ 's, which are small, and of the  $D^r$  defined in equation (8) of Part I. It will be observed that where  $D^r$  occurs in (4) it does so in the same way for  $A_u$  and  $B_u$  states. If therefore we disregard the absolute excitation energies and calculate the splittings  $\Delta E(B_u) - \Delta E(A_u)$  the quantities  $D^r$  will cancel from the first-order terms and appear only in the denominator in the second-order terms, and there as differences ( $D^r - D^s$ ); moreover the denominator also contains the difference ( $\Delta w^r - \Delta w^s$ ) which will in most cases be much the larger term. This suggests that we might reasonably ignore differences between the  $D$  integrals and set ( $D^r - D^s$ ) = 0 throughout; alternatively the denominators in (8) might be taken directly from the observed spacings in the crystal spectrum. This latter has been adopted in the calculations reported on p. 2307.

*Crystal Field Effect on Intensities.*—Crystal forces mix the crystal wave functions for different molecular states, and the transition intensities of the molecular spectrum are consequently redistributed in the crystal spectrum. The extent of this redistribution differs in the two crystal directions and so alters the intensity ratio from the oriented-gas value. To calculate magnitudes we start from the wave functions corrected to the first order. Aside from a normalizing multiplier very near to unity, these are

$$\Psi^1 = \Phi^1 + \left\{ H^{12} / (H^{11} - H^{22}) \right\} \Phi^2 + \dots + \left\{ H^{1r} / (H^{11} - H^{rr}) \right\} \Phi^r + \dots \quad (9)$$

in which the zero-order functions  $\Phi^1$  etc. are all of the same crystal symmetry species. The transition moment per unit cell from the ground state to  $\Psi^1$  may be expressed in terms of the free molecule moments  $\mathbf{M}_1^r$  and  $\mathbf{M}_2^r$  for the two molecules in the unit cell, as in (10). The upper signs refer to the  $B_u$ ,  $ac$  polarized species, and the lower to the  $A_u$ ,  $b$  polarized species.

$$\mathcal{M}^{\alpha, \beta} = (1/\sqrt{2}) \left[ (\mathbf{M}_1^1 \pm \mathbf{M}_2^1) + \sum_r \left\{ H^{1r} / (H^{11} - H^{rr}) \right\} (\mathbf{M}_1^r \pm \mathbf{M}_2^r) \right] \quad (10)$$

The experimental intensities to be reported and discussed in Part III may be related to the oscillator strength  $f$  of the molecular transition, which may in turn be related to the theoretically determined transition moment :

$$f = A \cdot \Delta E \cdot Q^2; eQ = \mathcal{M}/\sqrt{2} \quad . . . . . (11)$$

where  $A$  is a geometrical factor depending on the inclination of  $\mathcal{M}$  to the molecular and crystal axes;  $\Delta E$ , the transition energy, is measured in Rydbergs and  $Q$ , the dipole length, in atomic units. The ratio of oscillator strengths for absorption polarized along the two crystal axes is the *polarization ratio*. If the small difference in  $\Delta E$  for the  $a$  and  $b$  crystal transitions is ignored the polarization ratio is given as the ratio of the calculated quantities (12). This may be compared with the oriented-gas value (13) from which it differs by the presence of the first-order terms in equation (10) :

$$\left\{ \mathcal{M}^\alpha \cdot \mathbf{a} / |\mathcal{M}^\beta| \right\}^2 \quad . . . . . (12)$$

$$\left\{ (M_1^1 + M_2^1) \cdot \mathbf{a} / (M_1^1 - M_2^1) \right\}^2 \quad . . . . . (13)$$

where  $\mathbf{a}$  is a unit vector along the  $a$  crystal axis.

Quantitative examples of the application of formulæ (10) and (12) will be given later. We now consider some qualitative features of the crystal-induced intensity transfer. The meaning of the formulæ is clearer if there are just two transitions concerned, one weak and one strong. In the crystal each of these splits into  $ac$  and  $b$  polarized components which behave independently. According to (10) a fraction of the oriented-gas transition moment of the  $ac(b)$  component of the stronger transition is compounded with the  $ac(b)$  component of the weaker. If the matrix element  $H^{12}$  is positive and the crystal transition moments have the same sign the weak transition is strengthened; under other conditions it may be weakened. The magnitude of the transfer is greatest when the intense system has a large  $ac(b)$  component and  $H^{12}$  is large. Now  $H^{12}$  is itself a function of the molecular transition moments  $M^1$  and  $M^2$ ; we find that if the weak transition is very weak  $H^{12}$  is so small that transfer is negligible, on the other hand if the "weak" transition is in fact of comparable intensity with the strong the transferred transition moment is small compared with the transition moment already present and its effect is *relatively* small. In general, transfer should be most noticeable when the weak system is say 0.1 — 0.2 times as strong as the intense one, and greatest in the crystal direction in which the strong transition has its major component, *i.e.* in the  $ac$  plane for an  $A_g - B_{3u}$  system and along  $b$  for an  $A_g - B_{2u}$ . It follows from this last consideration that the transfer in the  $a$  and  $b$  directions will usually be very different, and therefore that the polarization ratio (12) will depart considerably from the oriented gas value.

We must now return to a consideration of the integrals  $K$  in (5), hitherto neglected. Like the terms in  $D^r$  these integrals vanish in the dipole approximation but their consideration cannot be avoided in the same way, *i.e.* by regarding the denominator in (8), in which the  $D^r$  occur, as an empirical parameter. It is necessary to form an estimate of the size of the  $K$  integrals and then to discuss their significance. The first contribution to the integral  $K_{ip}^{rs}$  in the expansion of  $\mathbf{V}_{ip}$  is the interaction between the static quadrupole moment of one molecule in its ground state with the transition quadrupole moment of another molecule for transitions between its  $r$ -th and  $s$ -th states. The practical upper limit to the product of components of the two moments is about  $1 \text{ \AA}^4$ , leading to interaction terms about  $(1/r_{ip})^2$  times the dipole terms, or about 1/25 for the nearest neighbours which provide the only significant terms. One arrives in this way at an upper limit to the sum of the  $K$  integrals of about 1/25 times the greatest of the  $J$  sums in Table 1, that is  $(1/25) \times (728 + 1532) \text{ cm.}^{-1}$ , giving  $90 \text{ cm.}^{-1}$ . Now it is easily verified that addition of a term of this size to  $H^{1r}$  in (8) for both  $A_u$  and  $B_u$  states makes a negligibly small difference to the splitting so long as the dipole moment product exceeds 0.2, a limit which is well below the actual value. This justifies our neglect of the  $K$  integrals in the calculations described on p. 2306 and 2307.

Having discussed the effect of a monoclinic crystal field in a strong transition (Part I)

and in a transition of medium intensity we now consider briefly the case of very weak transitions in which, as will be seen, the  $K$  integrals are quite important. In a band system as weak as the benzene 2600-Å or naphthalene 3200-Å systems the transition moment amounts to a few hundredths of an Å at most, so that even if the strong perturbing transition has a moment of 2 or 3 Å the product  $|M''||M'$  is probably not more than 0.10. Evidently the second-order splitting at its greatest is less than 5 cm.<sup>-1</sup>, and the first-order negligible; intensity transfer will be correspondingly small. The integrals  $K$  contributing to  $H''$  are independent of the transition dipole moments, and so under these conditions could be comparable to the dipole-dependent integrals  $J$ . This amounts to saying that, in very weak systems, the intermolecular resonance effects (splitting and intensity transfer) die out and one is left with a feeble van der Waals type of interaction. This gives no splitting, since the  $K$ -dependent part of  $H''$  is the same for  $A_u$  and  $B_u$  states, and its effect on intensities is intramolecular, *i.e.*, it causes a mixing of states of the same parity in one molecule. Naturally the selection rule for the mixing depends on the symmetry of the crystal field: in the monoclinic fields of aromatic crystals each molecule is at a centre of symmetry, and only states of the same parity are mixed. If we accept the estimate of 90 cm.<sup>-1</sup> for the  $K$  integral sum and suppose the two states eligible for mixing to be 10<sup>4</sup> cm.<sup>-1</sup> apart, the intensity-borrowing amounts to about 10<sup>-4</sup> the strong system's intensity, which is comparable to the borrowing caused by vibrational perturbations.

*Influence of Vibrational Structure.*—Leaving the case in which the intensity of the absorption system is concentrated in one band, we must now deal with the common situation of a band system in which the intensity is spread over several bands to form a progression, or progressions, in one or more vibrations. Each of these sublevels must appear separately in the energy matrix formed from elements (4) and (5). To a good approximation the wave functions for these molecular vibronic states may be written as products  $\varphi^r \cdot \sigma^{r(n)}$  of an electronic function and a vibrational function  $\sigma^{r(n)}$  appropriate to the  $n$ -th quantum state of the vibration appearing in the progression. The vibration will in general differ from one electronic state  $r$  to another. For simplicity we shall examine the case in which only one strong progression occurs; in the ground state all molecules will be supposed to be in the zeroth quantum state  $\sigma^{0(0)}$  of the active vibration. The ground-state molecular wave function is now  $\varphi \cdot \sigma^{0(0)}$  and the upper states are  $\varphi^r \cdot \sigma^{r(n)}$  for as many electronic states  $r$  as are energetically significant. The integrals  $I$  and  $J$  are replaced by integrals over vibrational as well as electronic co-ordinates. These may be expressed:

$$J_{lm}^{r(n) \cdot s(n)} = \frac{1}{2} \left( \int \varphi_l \sigma_l^{0(0)} \varphi_l^r \sigma_l^{r(n)} \mathbf{V}_{lm} \varphi_m \sigma_m^{0(0)} \varphi_m^s \sigma_m^{s(n)} d\tau + \int \varphi_l \sigma_l^{0(0)} \varphi_l^s \sigma_l^{s(n)} \mathbf{V}_{lm} \varphi_m \sigma_m^{0(0)} \varphi_m^r \sigma_m^{r(n)} d\tau \right) \\ = \xi^{r(n)} \xi^{s(n)} J_{lm}^{rs} \quad \dots \quad (14)$$

where

$$\xi^{r(n)} = \int \sigma^{0(0)} \sigma^{r(n)} d\tau_{\text{vib.}}$$

The quantities  $\xi$  are the well-known Franck-Condon overlap factors. Values of  $(\xi^{r(n)})^2$  can be found from vapour and solution absorption spectra, where they are proportional to the intensities of the members of the progression in the vibration  $\sigma$ . In real examples, at any rate in simpler aromatic compounds, two circumstances simplify the problem. There is usually only one very intense transition within easy energy reach of the weaker transition, and in many cases this intense system shows no well-developed progression but has its intensity concentrated in one rather narrow band group. It is quite realistic therefore to simplify the problem to that of a ground state  $\phi$ , a weakly excited upper state  $\phi^1$  with accompanying vibrational sublevels, and an intensely excited upper state  $\phi^2$  without vibrational structure. The energy matrix for this problem is equal in order to the total number of vibronic levels of the two upper states. Two new types of matrix element occur. First, for the sublevels of one electronic level:

$$H^{1(n)1(n)} = \Delta w^1 + D^1 + (\xi^{1(n)})^2 \left\{ \sum_p I_{lp}^1 + \sum_m I_{lm}^1 \right\} \quad \dots \quad (15)$$

$$H^{1(n)1(m)} = \xi^{1(n)} \xi^{1(m)} \left\{ \sum_p I_{lp}^1 + \sum_m I_{lm}^1 \right\} \quad \dots \quad (16)$$

and secondly, joining the two electronic levels :

$$H^{1(n)2(0)} = \xi^{1(n)} \left\{ \sum_p J_{lp}^{12} + \sum_m J_{lm}^{12} \right\} \dots \dots \dots (17)$$

where the expressions refer to the  $B_u$  components. It may happen that the quantities in equation (16) are small compared to the interval  $\hbar\nu$  between vibrational sublevels. It is then a good approximation to write for the crystal excitation energy of the  $n$ -th sublevel of  $\varphi^1$  the expression, for the  $B_u$  component,

$$H^{1(n)1(n)} + \sum_m (H^{1(n)1(m)})^2 / (n\hbar\nu - m\hbar\nu) + (H^{1(n)2(0)})^2 / (H^{1(n)1(n)} - H^{22}) \dots (18)$$

To obtain the corresponding  $A_u$  excitation energy it is only necessary to change the signs of the last terms in each of expressions (15), (16), and (17). Since both  $B_u$  and  $A_u$  energies depend similarly on  $\xi^{1(n)}$  the splittings will be roughly proportional to the intensities along the progression and, because  $(\xi^{1(n)})^2 < 1$ , they will all be smaller than in the hypothetical case of a system in which the same total intensity is concentrated in one band.

To deal with changes in the polarization ratio we consider the transition moments for excitation to the  $n$ -th vibrational quantum level of  $\varphi^1$ . In the  $B_u$  component

$$\mathcal{M}^\alpha(n) = 2^{-1} \left\{ \xi^{1(n)} (M_1^1 + M_2^1) + \xi^{1(n)} H^{12} / (H^{1(n)1(n)} - H^{22}) \cdot (M_1^2 + M_2^2) \right\} \dots (19)$$

An analogous expression holds for  $\mathcal{M}^\beta(n)$ . The polarization ratio is evidently independent of the Franck-Condon factors, which cancel, and it changes from member to member of the progression only through the slowly varying energy difference  $H^{1(n)1(n)} - H^{22}$ . Indeed if variations in this were neglected the polarization ratio would be constant along the progression and equal to the value for a concentrated system. In actual examples however the variation in ratio is not negligible, but it is true that the polarization ratio is much less sensitive to details of the vibrational structure than is the splitting.

*Application to Anthracene.*—In this section we shall apply the theory to see how second-order crystal perturbations affect the spectrum of anthracene. The intense system, denoted on p. 2306 by  $\varphi^2$ , is now the anthracene absorption at 2500 Å assigned to the species  $A_g - B_{3u}$  in Part I.  $\varphi^1$  is the system at 3800 Å (oscillator strength  $f = 0.1$ ) which appears in the vapour in a progression of five or more members with a spacing of 1400  $\text{cm}^{-1}$ . Discussion of the measured crystal spectrum and comparison with theory is left to Part III; here we are concerned only with calculating the crystal energy levels and polarization ratios corresponding to the weak vapour system using the theory developed earlier under each of the two plausible assignments for the system. The starting data include the solution intensity distribution along the progression, the relative values of which we equate to the quantities  $(\xi^{1(n)})^2$  as follows:  $n = 0 : 0.324, n = 1 : 0.316, n = 2 : 0.218, n = 3 : 0.093, n = 4 : 0.050$ . The interaction integrals are otherwise determined by the values in Table 1 and by the transition moments  $|M^1| = 0.61 \text{ Å}$  and  $|M^2| = 2.3 \text{ Å}$  found in the solution spectrum.

For Table 2 and Fig. 1 it is assumed that the 3800 Å system has the same polarization as the intense system, *i.e.*, belongs to the species  $A_g - B_{3u}$ . Table 3 and Fig. 2 assume, contrariwise, that the polarization is  $A_g - B_{2u}$ . In order that the individual terms of the energy may be compared the Tables show separately the splitting calculated with and without the last term of equation (18), which measures the second-order effect of  $\varphi^2$  on  $\varphi^1$ .

TABLE 2. Assumption : Weak system assigned  $A_g - B_{3u}$ .

$n$	First-order splitting ( $\text{cm}^{-1}$ )	$B_u$ component* by (18) ( $\text{cm}^{-1}$ )	$A_u$ component* by (18) ( $\text{cm}^{-1}$ )	Splitting by (18) ( $\text{cm}^{-1}$ )	Polarization ratio $a/b$
0	300	+71	-146	217	2.3 : 1
1	364	+ $\hbar\nu$ + 142	+ $\hbar\nu$ - 140	282	1.9 : 1
2	281	+ $2\hbar\nu$ + 127	+ $2\hbar\nu$ - 98	225	1.5 : 1
3	121	+ $3\hbar\nu$ + 55	+ $3\hbar\nu$ - 44	99	1.1 : 1
4	50	+ $4\hbar\nu$ + 10	+ $4\hbar\nu$ - 29	39	0.7 : 1
Concentrated system	1133	+444	-422	866	2.3 : 1

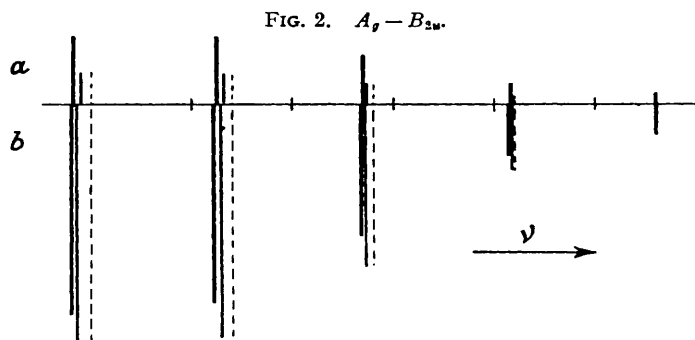
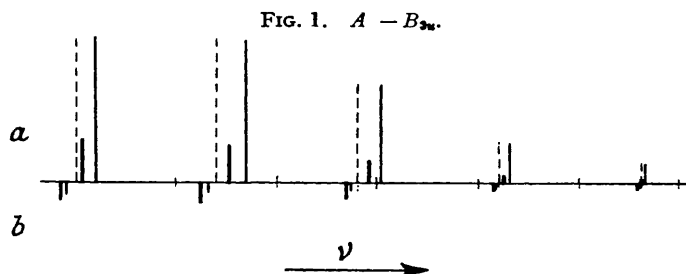
\* Omitting throughout the constant  $\Delta w^1 + D^1$ .

TABLE 3. Assumption: Weak system assigned  $A_g - B_{2u}$ .

$n$	First-order splitting (cm. <sup>-1</sup> )	$B_u$ component * by (18) (cm. <sup>-1</sup> )	$A_u$ component * by (18) (cm. <sup>-1</sup> )	Splitting by (18) (cm. <sup>-1</sup> )	Polarization ratio $a/b$
0	28	-180	-209	29	1 : 3.0
1	22	+ $h\nu - 165$	+ $h\nu - 196$	31	1 : 2.8
2	13	+ $2h\nu - 112$	+ $2h\nu - 137$	25	1 : 2.6
3	3	+ $3h\nu - 50$	+ $3h\nu - 64$	14	1 : 2.4
4	3	+ $4h\nu - 29$	+ $4h\nu - 42$	13	1 : 2.0
Concentrated system	71	-476	-589	123	1 : 3.0

\* Omitting throughout the constant  $\Delta w^1 + D^1$ .

Without this term the splitting is comparable to the Davydov splitting of a concentrated system, with the exception of additional interaction terms in our case between different vibronic (electronic  $\times$  vibrational) levels of the same electronic state.



Crystal spectra of a transition with the intensity and vibrational structure of the anthracene 3800 Å system, assumed to belong to the long axis-polarized species  $A_g - B_{3u}$  (Fig. 1) or the short-axis polarized species  $A_g - B_{2u}$  (Fig. 2).

Dotted lines: oriented gas model. Faint full lines: weak-coupling model with first-order energy corrections only. Full lines: weak-coupling model including intensity transfers and second-order energy corrections. The vertical lines are proportional to intensities with the  $a$  component above and the  $b$  below the horizontal line. The vertical scale is doubled in Fig. 2. The horizontal axis is marked in thousands of wave numbers. The neglected integrals  $D$  would if included, displace the crystal spectra bodily to lower frequencies.

The progression intervals in vapour and solution are constant except for a very slow change due to anharmonicity which is in any case negligible in the first few members. Crystal forces distort the intervals enough to be detectable experimentally, and do so to different degrees in the two assumed polarizations. The calculated splittings are equally characteristic, as also are the striking changes in polarization ratio; the values in the Tables should be compared with oriented-gas values of 16 : 1 and 1 : 7.8, respectively. These three quantities, the resonance splittings, the progression intervals, and the polarization ratios, are the essentially crystalline spectral properties, and they should enable the assignment of molecular transitions in anthracene and in other cases of favourable crystal structure.