The Polarized Spectrum of Anthracene. Part I. The Assignment of the Intense Short Wave-length System.

By D. P. CRAIG and P. C. HOBBINS.

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Measurements have been made of the absorption spectrum of anthracene crystals between 2800 and 2300 Å, where absorption occurs related to the intense solution band system at 2500 Å. The molecular transition is assigned to the species A_g–B_{3u}, polarized parallel to the long axis.

The interpretation of aromatic crystal spectra is discussed using Davydov's application of Frenkel's exciton theory, and the theory is then used to predict the main features of the crystal band systems corresponding to possible molecular transitions in anthracene. Comparison of these results with the measured spectrum shows that the intense system which has its maximum in solution at about 2500 Å is split in the crystal into two components. One, at 2700 Å, is polarized along the *b* monoclinic axis. The other, which is much more intense, is polarized in the *ac* plane and has its maximum at a wave-length less than 2340 Å, the limit of the measurements.

The assignment to the species A_g–B_{3u} is based on (i) the much greater *ac* polarized absorption intensity than *b* polarized, (ii) the large Davydov splitting between oppositely polarized components, and (iii) the displacement to short wave-lengths of the mean crystal excitation energy relative to vapour and solution values. In all three there is good agreement between experiment and theoretical expectation for the proposed assignment.

The results agree with the predictions of molecular orbital theory in both LCAO form (Coulson, *Proc. Phys. Soc.*, 1948, **60**, 157) and free-electron form (Platt, *J. Chem. Phys.*, 1950, **18**, 1168). This will be discussed later, in conjunction with results on the long-wave system.

THEORY OF LIGHT ABSORPTION BY MOLECULAR CRYSTALS

1. *Davydov's Theory.*—Many of the outstanding problems in the spectra of aromatic molecules, such as the polarization directions of the light absorbed in the band systems, can in principle be solved by studying the spectra of the molecules in crystals in which they are held in known positions. However, the forces which hold the molecules in their places in the crystal are also responsible for the appearance of new features in the electronic spectra which affect their interpretation, especially in intense systems. This has recently been discussed by Davydov, and a statement of his theory is given in this paper as a preliminary to the analysis of the short-wave absorption spectrum of anthracene crystals in the region 2700—2000 Å. In a following paper the anthracene spectrum near 4000 Å will be analysed and assigned.

The theoretical problem of the energy levels of molecular crystals such as those formed by aromatic molecules was studied by Davydov (see, in particular, *Zhur. eksp. teor. Fiz.*, 1948, **18**, 210; *Akad. Nauk S.S.S.R., Pamyati S.I. Vavilov*, 1952, 197). The theory is an application, to molecular crystals, of Frenkel's exciton theory (*Phys. Rev.*, 1931, **37**, 17; *Phys.*

Z. Sowetjunion, 1936, **9**, 158). For the explanation of our results the theory will be set out briefly, for the original is rather inaccessible.

The simplest model of a molecular crystal is that the individual molecules do not act upon one another. In this *oriented gas model* the energy levels are the same as in an isolated molecule, except that rotational sublevels are missing. This model is useful in weak transitions, but more complex behaviour is manifest in many cases : for example, one finds that, not only the intensity of absorption, but also the wave-length varies for different directions of polarization of the absorbed beam. Davydov therefore discussed what may be called the *weak-coupling model* in which the interaction energy between molecules is assumed to be small compared to the intramolecular energy, so that the molecular electronic structure is essentially undisturbed by crystal formation.

The following notation is used :

φ_k, φ_k'	Antisymmetric wave functions for the k-th molecule in its ground state, and in an excited state, respectively.
$\mathbf{H}_k$	Hamiltonian for the isolated k-th molecule.
w_k, w_k'	Isolated molecule energies in the states φ_k, φ_k'.
$\mathbf{V}_{kl}$	Interaction potential energy between the k-th and l-th molecules.
Φ	Electronic wave function for the crystal.
E	Electronic energy of the crystal.

The interaction energy operator is :

$$\mathbf{V}_{kl} = -\sum_{f,j} Z_f e^2/r_{fj} - \sum_{g,i} Z_g e^2/r_{gi} + \sum_{i,j} e^2/r_{ij} + \sum_{f,g} Z_f Z_g e^2/r_{fg} \quad . \quad . \quad . \quad (1)$$

where f and g are the nuclei, Z_f and Z_g the nuclear charges, and i and j the electrons of the k-th and the l-th molecule respectively. Let the number of molecules be N. The energy levels E and the wave functions Φ are defined by the equation :

$$\sum_{k+1}^{N} (\mathbf{H}_k + \sum_{l>k} \mathbf{V}_{kl})\ \Phi = E\Phi$$

The crystal ground state, Φ_G, goes on infinite separation into N unexcited molecules. In harmony with the weak coupling assumption it is written as a simple product of molecular wave functions.*

$$\Phi_G = \varphi_1\varphi_2\varphi_3 \ . \ . \ . \ \varphi_N$$

According to first-order perturbation theory the energy of the ground state is :

$$E_G = \sum_{k=1}^{N} w_k + \sum\sum\int \varphi_l\varphi_k \mathbf{V}_{lk} \varphi_l\varphi_k \, d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The second-order terms are not negligible, but they play no important part in the energy-level splitting which we are to discuss, and their consideration is deferred.

A set of excited states of the crystal may be specified by the property that upon infinite separation the N molecules go into $N - 1$ in their ground states and one in an excited state. The zeroth-approximation wave function is :

$$\phi_p = \varphi_1\varphi_2 \ . \ . \ . \ \varphi_p' \ . \ . \ . \ \varphi_N \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The symbol ϕ is used for the product wave function, and φ is reserved for single-molecule functions. Crystal wave functions based on the elementary product functions (3) take the form :

$$\Phi_r = \sum_{l=1}^{N} a_{rl}\phi_l ; \ \text{where} \sum_{l=1}^{N} a_{rl}^* a_{rl} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Φ_r is one of N crystal excited states all belonging in the weak coupling model to the excitation of one molecule to its excited state φ'. The quantity $a_{rp}^* a_{rp}$ is the probability

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* Davydov's formulation allows for electron exchange between molecules. We have omitted this refinement since the exchange terms in the energy are very small indeed.

that the p-th molecule is the excitation " site." Clearly if N is a small number, and the end molecules form a significant proportion of the whole, variations between end molecules and others will have to be allowed for, but if N is large as it is in the practical case we may impose cyclical boundary conditions. Then the coefficients a_{rl} will differ from one another only in their phase factors. Quite generally the coefficients may be obtained in the ordinary way from the secular equation :

$$\det\left\{(\phi_p|\sum \mathbf{H}_k + \sum\sum \mathbf{V}_{kl}|\phi_q) - (\phi_p|1|\phi_q)E\right\} = 0 \quad . \quad . \quad . \quad . \quad (5)$$

Overlap between the electronic orbits of different molecules being neglected, the diagonal elements are (6*a*) and the others (6*b*), where primed sums omit the excited molecule :

$$\sum_k{}' w_k + w_p{}' + \sum_k{}'\sum_{l>k}{}'(\varphi_k\varphi_l|\mathbf{V}_{kl}|\varphi_k\varphi_l) + \sum_l{}'(\varphi_p{}'\varphi_l|\mathbf{V}_{pl}|\varphi_p{}'\varphi_l) - E \quad . \quad . \quad (6a)$$

$$I_{pq} = (\varphi_p{}'\varphi_q|\mathbf{V}_{pq}|\varphi_p\varphi_q{}') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6b)$$

By subtracting the ground-state energy (2) from the diagonal elements of the energy matrix we derive a secular equation whose roots are the crystal excitation energies. The p-th diagonal element is

$$\Delta w_p + D - \Delta E \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $\Delta w_p = w_p{}' - w_p$ and

$$D = \sum_l{}' \left\{(\varphi_p{}'\varphi_l|\mathbf{V}_{pl}|\varphi_p{}'\varphi_l) - (\varphi_p\varphi_l|\mathbf{V}_{pl}|\varphi_p\varphi_l)\right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It is well known, following Frenkel, that the exchange of excitation between molecules is formally analogous to the motion of a spinless particle, which has been called the exciton. One might regard the functions ϕ as defining localized exciton sites or orbits and the functions Φ_r as delocalized orbits, corresponding to a range of exciton energies. In analogy with the molecular-orbital theory of electrons the integral D in equation (8) is an exciton " coulomb " energy term, and the off-diagonal integrals (6*b*) exciton " resonance " or " exchange " integrals for an exciton jumping fron one molecule to another.

2. *Application of the Rigid Lattice Theory to Anthracene.*—Again, by following Davydov, the discussion can be reduced to specific terms where the crystal structure is known. The crystals of anthracene belong to the space group $C^5{}_{2h}$. The well-defined cleavage plane contains the a and the b monoclinic axis. The c axis makes an angle $\beta = 124° 42'$ with the a axis and the unit-cell dimensions are $a = 8{\cdot}56$, $b = 6{\cdot}04$, and $c = 11{\cdot}16$ Å. Two molecules occupy the unit cell, at the corner and centre of the ab face. The unit cell group is C_{2h} and one molecule is transformed into the other by reflection in the ac plane followed by translation along the a axis by $a/2$. Fig. 1 shows one molecule of the unit cell projected on to the ab plane of the crystal; this is the cleavage plane normally developed. Fig. 1 also illustrates our convention for molecular axes : the x axis runs in the plane of the molecule parallel to its length and the z axis is perpendicular to the molecular plane. (Some writers reverse the convention.)

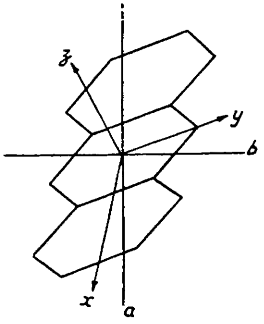

FIG. 1. *Projection of an anthracene molecule on the ab crystal plane.*

(Data from Sinclair, Robertson, and Mathieson, *Acta Cryst.*, 1949, **3**, 251.)

The molecular symmetry of anthracene is $\boldsymbol{D}_{2h}$; the character table for this group is readily accessible and not reproduced here. In the crystal each molecule is at a point in the lattice where the only element of local symmetry is inversion (site group $\boldsymbol{C}_i$), but the important structural element is now the unit cell and not the molecule, and we shall make no further mention of the site symmetry. The symmetry of the unit cell (group $\boldsymbol{C}_{2h}$) has the characters given in Table 1. In accordance with the approximation of building crystal wave functions from those for the isolated molecules, combinations of molecular wave functions are formed which transform like representations of the unit-cell group. The necessary relations between the representations of the molecule group $\boldsymbol{D}_{2h}$ and the unit-cell group are also given in the Table. We find, for example, that a molecular B_{2u} state is associated with unit-cell states of both A_u and B_u symmetries.

TABLE 1. *Representations of the unit-cell group* $\boldsymbol{C}_{2h}$.

	E	C_2^b	i	σ^b	Associated $\boldsymbol{D}_{2h}$ representations
A_g	1	1	1	1	A_g, B_{1g}
$A_u(\boldsymbol{r}_b)$	1	1	−1	−1	B_{2u}, B_{3u}
B_g	1	−1	1	−1	A_g, B_{1g}
$B_u(\boldsymbol{r}_a)$	1	−1	−1	1	B_{2u}, B_{3u}

$\boldsymbol{r}_a$ and $\boldsymbol{r}_b$ denote vectors along the a and the b crystal axis. We now proceed to define unit-cell wave functions γ in terms of the product wave functions ϕ which correspond (3) to excitation of the two molecules in the unit cell individually. The co-ordinate system in one molecule having been chosen, the other is derived from it by glide reflection in the ac plane. We have :

$$\left.\begin{aligned}\gamma^{\alpha} &= (1/\sqrt{2})(\phi_1 + \phi_2)\\ \gamma^{\beta} &= (1/\sqrt{2})(\phi_1 - \phi_2)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

α and β unit-cell functions formed by combining g molecular wave functions transform like the A_g and B_g crystal species respectively; and those from B_{2u} and B_{3u} molecular functions like B_u and A_u.* N is now assumed large, so that cyclical boundary conditions apply. Wave functions (4) having the symmetry of the three-dimensional space group are :

$$\Phi^{\alpha,\beta}(k_a, k_b, k_c) = (1/\sqrt{N/2}) \sum_{\mu,\nu,\omega} e^{i(k_a a\mu + k_b b\nu + k_c c\omega)}\, \gamma^{\alpha,\beta}(\mu, \nu, \omega) \quad . \quad . \quad (10)$$

k_a, k_b, and k_c are wave vectors. μ, ν, and ω respectively number the M_a unit cells along the a axis, M_b along b, and M_c along c; $M_aM_bM_c = N/2$. The wave vector k_a takes the values $2\pi\sigma/(M_a \,.\, a)$ for $\sigma = 0, \pm 1, \pm 2, \ldots +M_a/2$. For each pair of values of k_b and k_c there is thus a manifold of M_a states, of which those belonging to $k_a = 0$ and $M_a/2$ † are non-degenerate and the others doubly degenerate.

To give a simple illustration of the effects of environment in molecular crystals, we consider one single sheet of molecules in the ab plane and limit ourselves to interactions between nearest-neighbour molecules. As is pointed out below, these restrictions must be relaxed in actual calculations. Denoting the excitation energy of a unit cell by ΔE_u we find :

$$\Delta E^{\alpha,\beta}(k_a, k_b) = \Delta E_u{}^{\alpha,\beta} + 2\cos(k_a \,.\, a)H_a{}^{\alpha,\beta} + 2\cos(k_b \,.\, b)H_b{}^{\alpha,\beta} + 2\cos(k_a \,.\, a + k_b \,.\, b)H_{ab}{}^{\alpha,\beta}$$

where H_a and H_b are the interactions between neighbour *cells* translationally equivalent along the a and b axes, and H_{ab} is the interaction between neighbour cells displaced along the diagonal. If A, B, and C denote values of the interaction integral (6b) between translationally equivalent *molecules* along the a and the b axis and between the

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* Davydov does not use the symmetry properties of the unit-cell wave functions explicitly, and he has a different system of molecular axes. As a result the symmetry species of his α and β combinations are reversed from ours for molecular species B_{1g} and B_{2u}.

† $\sigma = M_a/2$ is non-degenerate for reasons discussed fully by Bethe (*Ann. Physik*, 1929, **3**, 133). Real functions being used, the cosine function $\Sigma \cos a\mu \,.\, \pi/a$, etc., defines a proper function, but the sine function vanishes identically. Evidently the state $\sigma = M_a/2$ has zero momentum, as has the state $\sigma = 0$.

two molecules of a unit cell we find: $H_a^{\alpha,\beta} = A \pm C/2$, $H_b^{\alpha,\beta} = B \pm C/2$, $H_{ab}^{\alpha,\beta} = \pm C/2$, and $\Delta E_u^{\alpha,\beta} = \Delta w + D \pm C$, where the upper sign applies to α and the lower to β. It now follows that:

$$\begin{aligned}\Delta E^{\alpha,\beta}(k_a, k_b) = {} & \Delta w + D + 2\cos(k_a \,.\, a)A + 2\cos(k_b \,.\, b)B \\ & \pm \left\{1 + \cos(k_a \,.\, a) + \cos(k_b \,.\, b) + \cos(k_a \,.\, a + k_b \,.\, b)\right\} C \quad . \quad . \quad (11)\end{aligned}$$

For a chosen set of wave vectors k_a and k_b and a chosen molecular excited state there are two crystal states separated by (12):

$$E^{\alpha}(k_a, k_b) - E^{\beta}(k_a, k_b) = 2C\left\{1 + \cos(k_a \,.\, a) + \cos(k_b \,.\, b) + \cos(k_a \,.\, a + k_b \,.\, b)\right\} \quad (12)$$

We shall refer to this interval, calculated for zero values of the wave vectors, as the *Davydov splitting*.

There is a further quantity associated with the energy of the crystal band systems which is of some importance in assigning the transitions and in correlating the crystal absorptions with their vapour and solution analogues. This is the displacement of the mean value of the components ΔE^{α} and ΔE^{β} from the excitation energy in vapour and solution spectra. Anticipating section 3, we note that in the rigid lattice approximation transitions are allowed only for $k_a = k_b = k_c = 0$, and that when lattice vibrations are permitted these transitions will usually still be the most intense. For this case of zero values for the wave vectors the mean transition energy is:

$$(\Delta E^{\alpha} + \Delta E^{\beta})/2 = \Delta w + D + 2A + 2B$$

Δw, the energy of the transition in the isolated molecule, is the vapour transition energy, so that the shift from vapour to crystal is $D + 2A + 2B$. The integral D is capable of approximate calculation. It is the difference between two quantites [see equation (8)] each of which is, in intense transitions, small compared to A and B. We may therefore write for the *crystal shift* the approximate relation:

$$(\Delta E^{\alpha} + \Delta E^{\beta})/2 - \Delta w \cong 2A + 2B \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

We shall apply a relation like (13), suitably generalized to include non-neighbours, only to intense transitions where A and B are of dominating importance compared to D. In weak transitions inclusion of D would be essential.

Table 2 shows that the sum $(2A + 2B)$ can be either positive or negative, leading to the expectation that the crystal shift, in some cases quite large, may be to shorter or longer wave-lengths from the vapour absorption maximum.

3. *Selection Rules and Polarizations.*—The unit cell has a centre of symmetry and, as in the single molecule, the $g \rightarrow u$ selection rule applies. It follows that only those crystal transitions are allowed which correlate with allowed molecular transitions, and their polarizations may be read from the $\boldsymbol{C}_{2h}$ group table. Crystal transitions related either to molecular transitions A_g–B_{2u} (short axis polarized) or A_g–B_{3u} (long axis polarized) have their α components polarized in the *ac* crystal plane, and their β components polarized along the *b* crystal axis. Accordingly the Davydov splitting appears as a separation between a transition polarized along the *b* axis and the corresponding one in the *ac* plane.

The selection rule for the wave vectors k may be deduced from the transition moment integral (14). When expression (10) is used, then

$$\int \Phi_G \sum_i \boldsymbol{r}_i \Phi^{\alpha,\beta}(k_a, k_b, k_c)\mathrm{d}\tau = \sum_{\mu,\nu,\omega} \mathrm{e}^{i(k_a a\mu + k_b b\nu + k_c c\omega} \,.\, (2/N)^{\frac{1}{2}} \int \Phi_G \sum_i \boldsymbol{r}_i \,.\, \gamma^{\alpha,\beta}\, \mathrm{d}\tau \quad . \quad (14)$$

The transition moment vanishes unless $k_a = k_b = k_c = 0$. This selection rule applies to the rigid lattice and in this case the crystal band widths suggested by a consideration of the possible ranges of the wave vectors given after (10) are only of formal interest since each molecular transition between pairs of vibronic states gives rise simply to two crystal lines.

Some crystal spectra seem to be of this simple kind but others show evidence of finite band width on account of the excitation of lattice vibrations.

If we use expression (14) to calculate the relative intensities of the *a* and the *b* polarized component of a crystal transition we find that the intensity ratio is unaltered from the oriented-gas model value, and is given by the ratio of the squares of the projections of the active molecular axis upon the crystal axes. This over-simple result is a consequence of the use of first-order perturbation theory. However, the precision of our measured intensities is not enough to justify a more elaborate calculation at this stage.

4. *The Energy Terms.*—We now consider the integrals which occur in the expressions for the splitting and crystal shift. These are of the form (6*b*)

$$I_{lk} = \int \varphi_l' \varphi_k V_{lk} \varphi_l \varphi_k' \, d\tau$$

By expanding the potential (1) in a series of poles of increasing order, and discarding all but the dipole–dipole interactions we obtain (Davydov, *loc. cit.*):

$$I_{lk} = -(e^2/r^3_{lk})|M|^2 \left\{2 \cos \theta_{l1} \,.\, \cos \theta_{k1} - \cos \theta_{l2} \,.\, \cos \theta_{k2} - \cos \theta_{l3} \,.\, \cos \theta_{k3}\right\} \quad . \quad (15)$$

in which M is the molecular transition moment and r_{lk} the distance between the centres of the two molecules. θ_{l1}, θ_{l2}, and θ_{l3} are the angles made by the transition moment of the *l*-th molecule with a set of rectangular axes erected at its centre; θ_{l1} refers to an axis along the line of the centres of the *l*-th and *k*-th molecules. Values of *A*, *B*, and *C* according to equation (15) are given for anthracene in Table 2. The units are cm.$^{-1}$ with the length of the transition moment measured in Å. It is to be noted that according to expression (12) a positive value of *C* means that the *b* polarized component of a transition lies at lower energy than the *ac* component, and *vice versa.*

TABLE 2. *Neighbour intermolecular integrals for crystalline anthracene.*

Integral	Molecular transition Species A_g–B_{2u} (cm.$^{-1}$ Å^{-2})	Molecular transition Species A_g–B_{3u} (cm.$^{-1}$ Å^{-2})
$A/\lvert M\rvert^2$	128	49
$B/\lvert M\rvert^2$	−739	504
$C/\lvert M\rvert^2$	−8	399

It is easy to generalise the results to include non-neighbour interactions. For the allowed transition $k_a = k_b = k_c = 0$ we have, from (10):

$$\Phi^{\alpha,\beta} = (2/N)^{\frac{1}{2}} \sum_{\mu,\nu,\omega} \gamma^{\alpha,\beta} (\mu, \nu, \omega) \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The energy of the transition to this state may be written in terms of the integrals (6*b*) in the form:

$$\Delta E^{\alpha,\beta} = \Delta w + D + \sum_p I_{lp} \pm \sum_m I_{lm} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where *p* runs over all molecules translationally equivalent to the *l*-th, and *m* runs over the others. As before, the upper sign refers to the α wave function and the lower to β. The first sum in equation (17) replaces (and includes) the term (2*A* + 2*B*) and the second 4*C* in (12); and both have contributions from non-neighbour interactions. The integrals fall off as the inverse cube of the intermolecular distance and there is some cancellation, leading to a satisfactory convergence when molecules separated by up to 20 Å are included. The individual integrals were evaluated by using expression (15), and the appropriate sums are listed in Table 3, compared with the nearest-neighbour values (shown in square brackets). As in expression (17) the first sum in Table 3 is taken over all translationally equivalent molecules within 20 Å, and the second over the others.

There is a source of error in our values for integrals arising from the fact that the molecules are not small compared to the lattice spacings, showing that the conditions for cutting off the multipole expansion after the dipole terms are not well realized. Other methods of evaluation, however, are open to the serious objection that they depend on assuming specific forms of molecular wave functions; this is an additional uncertainty which it seems best to avoid.

TABLE 3. *Intermolecular integral sums for crystalline anthracene.*

	Molecular transition Species A_g–B_{2u} (cm.$^{-1}$ Å^{-2})	Molecular transition Species A_g–B_{3u} (cm.$^{-1}$ Å^{-2})
$\sum_p I_{lp}/\|M\|^2$	−990 [−1222]	728 [1106]
$\sum_m I_{lm}/\|M\|^2$	96 [−32]	1532 [1596]

To summarize these results we give in Fig. 2 diagrams of the crystal spectra of molecular transitions of the long- and the short-axis polarized types as deduced by calculation in the dipole–dipole approximation. The molecular transition is assumed to be of intensity $f = 1$, corresponding to $|M|^2 = 2{\cdot}3$.

THE OBSERVED CRYSTAL SPECTRUM OF ANTHRACENE

5. *Preliminary Considerations.*—In solution the two singlet–singlet absorption systems of anthracene in the quartz ultraviolet fall at about 3900 and 2500 Å. The intensity of the first corresponds to an oscillator strength $f = 0{\cdot}1$, and that of the second to $f = 2{\cdot}3$.

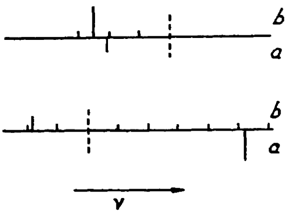

FIG. 2. *Calculated crystal absorption in anthracene corresponding to a single band in the vapour spectrum of a system of intensity $f = 1$. The crystal components are shown by full lines, with the more intense drawn longer; the vapour band is indicated by the broken line. The upper spectrum (showing a red shift and small splitting) is for a short-axis molecular transition and the lower (violet shift and large splitting) is for a long-axis transition. The frequency unit is 1000 cm.$^{-1}$.*

It is not to be expected that the properties of the two systems will be entirely independent. The upper state of the weaker system at 3900 Å will be perturbed because the upper state of the stronger gives the weaker band system a composite character, having some properties " stolen " from the more intense system as well as those characteristic of its pure, isolated molecule, species. We believe that the 3900-Å system actually displays such a mixed character, and to distinguish between the two components it is convenient to have established first the properties of the intense system, because this allows the forbidden component to be recognized. For this reason we deal with the intense system first, even though the crystal spectrum is much richer in the 3900-Å region, as will be discussed in a later paper.

6. *Polarization of Absorption Systems.*—The intense system is certainly allowed and may have a transition moment parallel to the x or the y axis, it being assumed to be of the π-π type. At wave-lengths of absorption a single molecule would show strong dichroism; light polarized along the active axis would be absorbed while that polarized at right angles would be transmitted. In crystals the behaviour is less simple because the symmetry elements of the crystal do not coincide with those of the molecules, and because intermolecular forces may change the pattern of energy levels. The purely geometrical effect has already been referred to (Fig. 1). The projection seen by the spectrograph is that shown in Fig. 1, since the *ab* plane is the strongly developed face.* Thus the spectra record absorption of a light beam incident normal to the page with electric vector either parallel to the *b* crystal axis (*b* spectra) or perpendicular to it (*a* spectra). The features to be expected from the effect of intermolecular forces have been discussed in section 1.

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* We are indebted to Dr. Philip Knight for several X-ray examinations of crystal flakes of different thicknesses and from different batches. In every case the orientation was found to be (001).

Our method of measurement amounts to finding the optical densities of a thin crystal for light traversing normal to its face and polarized parallel or perpendicular to the *b* axis. The absorption in the 3900-Å system extends to about 3500 Å. Between 3500 Å and the onset of the next system near 2700 Å there is no appreciable structure, but weak and apparently continuous absorption rises to a maximum near 2680 Å, then falls and rises again to a second, lower, maximum at 2595 Å and after that falls slowly. This behaviour is illustrated in Fig. 3. Measurements of these wave-lengths, but not of the optical densities of the absorption maxima, were reported by Obreimov and Prikhotjko (*Phys. Z. Sowetjunion*, 1936, **9**, 49). Their values are in excellent agreement with ours. The *a* absorption shows no definite maximum in this region, but begins to rise near 2600 Å and crosses the *b* absorption near 2540 Å.

Fig. 3. *The weak crystal absorption. Crystal thickness* ~0·1 μ.

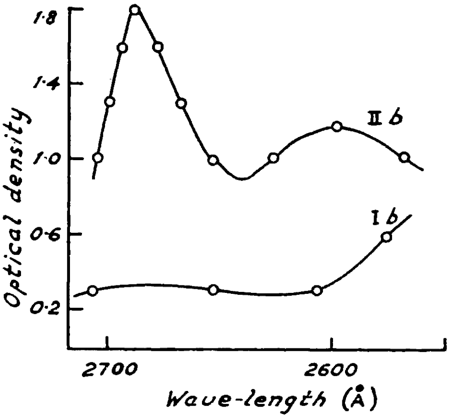
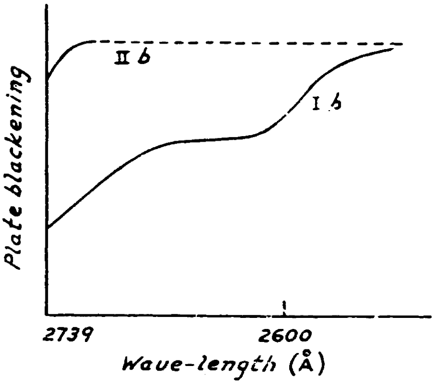


Fig. 4.



I *b*, Perpendicular to *b*; II *b*, parallel to *b*.

Measurements of two crystals of approximately equal thickness are given in the Table.

Optical densities		Wave-lengths (Å)	
E_b	E_a	1st peak	2nd peak
1·79	0·34	2680	2594
1·71	0·29	2678	2595

The optical densities include some loss of light due to reflections from the crystal surfaces. The apparent optical density of a crystal in regions clear of absorption bands is not greater than 0·1 unit, but is too small for accurate measurement by our technique. If a 5—10% reflection loss per surface is assumed, the apparent optical density is in the range 0·04—0·1. We then see that the ratio of absorption optical densities at the maxima is in the region of 7—8 : 1 (the significance of this will be discussed in section 7). The crystals used were about 0·1 μ thick, as determined by microscopy. The spectrum of a crystal several times thicker (Fig. 4) was examined for evidence of an absorption maximum in the *a* spectrum, but none was found.

Toward shorter wave-lengths again, the *a* absorption continues to increase until a cut-off is reached; this happens at about 2300 Å in the thinnest crystals (~0·1 μ). Between 2540 Å and this cut-off point the *b* absorption is less than the *a*, but is rising toward shorter wave-lengths, suggesting the presence of another *b* polarized absorption outside the range of observation. Measurements of the absorption of tetracene crystals, in which the analogous band systems are somewhat shifted to longer wave-lengths, confirm the presence of an intense *b* absorption in this region.

The intensities of absorption in the *b* polarization at 2700 Å and in the *a* polarization at 2300 Å are of considerable importance for the analysis. Values for the former have already been given, but crystals could not be grown thin enough to enable the maximum at 2300 Å to be located, even with a high intensity arc of the Allen type and very long exposures. In every attempt no more than the onset of the *a* system was penetrated. A conservative estimate is that the *a* system is not less than five times the *b* in optical density.

7. *Discussion.*—To the first order the intensity ratios in crystal spectra are unchanged from the oriented gas values, and the total intensity is the same as that in solution, there being due allowance for random molecular orientation. A satisfactory theory of the crystal absorption must fit both these requirements. We consider first the relation between the solution extinction coefficient of 2×10^5 and the crystal optical densities. Knowing the dimensions of the unit cell and the arrangement of molecules within it we can calculate the optical density per micron thickness of crystal as a function of the solution extinction coefficient for either of the two molecular transition directions, *viz.*:

Crystal axis	Molecular transition	Optical density per micron ($10^{-4}E_s$)
a	Short axis	2·17
b	Short axis	16·9
a	Long axis	5·18
b	Long axis	0·316

The quantity E_s used here is the extinction coefficient in solution, and the conversion factors assume that the shapes of the band systems are not affected by the change from solution to crystal. Setting $E_s = 2 \times 10^5$ we calculate for a short molecular axis transition a *b* crystal optical density of 340 per micron, and for a long axis transition 6·4 per micron. The measured *b* optical density of a crystal about 0·1 micron is 1·8 minus an estimated 0·1 for reflection loss, giving, per micron, the value 17. This is evidently incompatible with the short-axis assignment (calc. 340), but if some error is allowed for in the crystal thickness it agrees as well as can be expected with the 6·4 per micron of a long-axis assignment; moreover the latter leads to the expectation of a much more intense *a* component, again in agreement with experiment, since the long axis has a projection on the *a* crystal axis four times as great as on the *b*, and the intensity ratio should therefore be 16 : 1 in favour of the *a* axis.

We next consider the magnitude of the Davydov splitting, which powerfully supports the long-axis assignment. According to Table 2 and the illustrated spectra of Fig. 2 the splitting is very much greater for a long- than for a short-axis transition. Calculated for an intensity $f = 2{\cdot}3$, the values are 16,000 and 1000 cm.$^{-1}$ respectively. The former agrees satisfactorily with the spectrum: the *b* maximum being taken at 2680 Å, the calculated *a* maximum falls at 1900 Å, which is compatible with *a* absorption beginning strongly near 2300 Å, as is observed. The true maximum is probably a little to longer wave-length of this calculated position. This account of the spectrum implies that in the two regions of crystal absorption the polarization is wholly *b* and wholly *a* respectively. The observed spectrum (Fig. 3) does, however, show some *a* absorption at 2680 Å. We believe that this is not intrinsic to the crystal absorption, but arises from slight distortion of the crystal flakes in the process of mounting (such strains were occasionally seen under the polarizing microscope) and from small errors in aligning the crystal axes with the polarizing directions of the optical system. The alternative explanation of the presence of *a* absorption, that the 2680 Å absorption is a weak short-axis system with little or no Davydov shift, is only doubtfully compatible with the polarization ratio already quoted of 7—8 : 1, as well as being open to objections on other grounds. A value of 7·8 : 1 would indeed be found for a short-axis transition if the molecules were held rigidly in the lattice, but is unattainable in practice. Both torsional oscillations in the lattice and inevitable small errors in alignment reduce the expected value. Torsional oscillations alone (Jablonski, *Acta Phys. Polon.*, 1950, **10**, 193; D. A. Levy, unpublished work) reduce the value to about 7 : 1, and taking account as well of the probable aligning error we consider that 6·5 : 1 is an upper limit to the ratio in a genuine short-axis system. The decisive objection to the short-axis assignment, however, arises from the necessity of accounting in the crystal spectrum for the same total intensity as in solution. A short-axis system has four-fifths of its intensity in the *b* crystal component and, since the measured *b* optical density per micron is about 17 we could account only for one-twentieth of the solution intensity in this way. There might in fact be a small reduction in intensity in the crystal, but it seems impossible to explain a reduction by a factor 1/20 by using interaction terms of reasonable size.

Finally we consider the wave-lengths of the crystal bands in relation to the vapour and the solution maxima, both of which fall nearly enough at 2500 Å (40,000 cm.$^{-1}$). According to the calculations illustrated in Fig. 2 a long-axis transition is associated with a crystal shift to higher energies, and a short-axis transition to lower energies. There is no doubt that the former agrees with the measured spectrum. The *b* component appears at 37,000 cm.$^{-1}$ and the *a* probably near 50,000 cm.$^{-1}$. The experimental crystal shift is therefore to be measured in thousands of wave numbers, and is toward higher energies. The calculated shift for a long axis system is $+4000$ cm.$^{-1}$ and for a short axis system -5200 cm.$^{-1}$. The agreement for the former is good, confirming the assignment A_g–B_{3u}.

Our results have a bearing on a problem which has often arisen in discussions of crystal spectra. It has been reported many times that systems which are intense in solution and vapour are greatly weakened in the crystal. Anthracene at first appears to be an example because the weak 2700-Å crystal system lies close to the intense solution absorption and so could be mistaken for the same absorption system simply shifted to the red and much weakened. The explanation is, as we have shown, that the major component of the crystal absorption is found at a wave-length so far displaced that its relation to the solution absorption is not at once suspected. Only the minor crystal component is left close to the solution absorption. An entirely similar explanation applies to the apparent weakening in naphthalene and tetracene, and probably to many of the other cases in the literature.

EXPERIMENTAL

The spectra were recorded on a Hilger large quartz spectrograph E492. Light from a Beckman-type hydrogen lamp was focused on to a crystal of chromatographically purified anthracene mounted over a 1-mm. hole. The transmitted beam was made parallel and passed through a Wollaston prism, then focused on to the slit. The plate recorded two images separated by about 3 mm. for each exposure, corresponding to the two perpendicular directions of plane polarization. The orientation of the anthracene crystal axes was determined with a polarizing microscope, and the crystal was mounted in the optical path with its *a* and its *b* axis respectively parallel and perpendicular to the slit. The crystal holder could be turned through 90° so that errors due to discrimination within the spectrograph between the two beams could be avoided.

The optical densities were measured by sector photometry. On the same plate as the crystal spectrum a series a blank exposures were recorded, each having the same exposure time but different settings of a rotating sector. The blanks recorded optical densities of 0·2, 0·3, up to 1·5, and these were used to determine crystal optical densities essentially by a match-point technique. The crystal spectrum was recorded photographically from the plate on a Zeiss microphotometer, and on the same record traces of the blanks were superposed. Match points corresponded to points of intersection of the blank and the crystal trace. Where necessary, a sector was interposed in the weaker crystal absorption in order to bring the optical density into a more readily measurable range.

DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF SYDNEY,
N.S.W., AUSTRALIA.
WILLIAM RAMSAY AND RALPH FORSTER LABORATORY, UNIVERSITY COLLEGE,
GOWER STREET, LONDON, W.C.1.

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