271. *First-order Calculation of Factor Group Splittings in the Electronic Spectra of Durene, Ovalene, and Phthalocyanine Crystals.*

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Certain characteristics of crystal spectra of durene, ovalene, and phthalocyanine are predicted by first-order theory, using known X-ray crystal structures and the extinction coefficients of solutions.

Calculation of factor group splittings has followed Davydov's application [1] of Frenkel's exciton ideas.[2] Two methods have been used: (i) intermolecular integrals have been expressed in terms of transition-moment integrals which were then evaluated from experimental observations; and (ii) intermolecular integrals have been calculated from theory, after assumption of explicit forms for the molecular wave functions. Method (i) was worked out by Davydov and was used for calculations on anthracene [3] and naphthalene.[4] Method (ii) has been fully worked out for benzene by Fox and Schnepp.[5] Of the two methods, (i) is easier to apply, since (ii) becomes cumbersome for large molecules. Since the method involves a multipole expansion of intermolecular interactions, the expansion is not accurate when the interacting molecules are separated by distances comparable with molecular dimensions. However, by its use Bree and Lyons [6] have accounted almost quantitatively for the intensity of light absorption by an anthracene crystal and at least semiquantitatively for the splitting. In this paper integrals are calculated to the first-order for several crystals of $P2_1/a$ symmetry. Since the polarization of most of the electronic transitions in these molecules is not known the values of integrals and splittings are calculated for both in-plane directions, l (longer) and m (shorter). Second-order effects [7] are very important when considering polarization ratios but produce only a relatively small alteration in the splitting.[7, 8] Winston's criticism [9] of the original theory [1] does not apply to the procedure [3] here followed. A further criticism of the summation procedure has been answered [10] previously. In each crystal there are two molecules to the unit cell.[11] It follows that there will be two sets of electronic energy levels for each non-degenerate level in the isolated molecule. If allowed transitions are considered, then only one level of each set (with the excitation wave vector $K = 0$) need be considered. The energy difference between these levels, α and β, is the splitting, given [3] by:

$$E_\alpha - E_\beta = 2\sum_j I_{oj} \quad \ldots\ldots\ldots \quad (1)$$

where j denotes a molecule translationally equivalent to the unit cell partner of molecule o, and

$$I_{oj} \equiv \int \phi'_o \phi_j V_{oj} \phi_o \phi'_j \, dv$$

ϕ_o, ϕ'_j being ground- and excited-state molecular wave functions and V_{oj} the operator for the interaction between o and j, which may be expanded as a multipole series. In the expansion the dipole–dipole term is retained and the others assumed negligible, so that:

$$I_{oj} = [e^2/r_{oj}^3]F_{l(m)} \cdot \int \phi'_o(\textstyle\sum_p \rho_p)\phi_j \, dv \int \phi'_j(\textstyle\sum_q \rho_q)\phi_o \, dv \quad \ldots\ldots \quad (2)$$

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[1] Davydov, *Zhur. eksp. teor. Fiz.*, 1948, **18**, 210.

[2] Frenkel, *Phys. Rev.*, 1931, **37**, 17.

[3] Craig and Hobbins, *J.*, 1955, 539.

[4] Craig and Walsh, *J. Chem. Phys.*, 1956, **24**, 471.

[5] Fox and Schnepp, *ibid.*, 1955, **23**, 767.

[6] Bree and Lyons, *J.*, 1956, 2662.

[7] Craig, *J.*, 1955, 2302.

[8] McClure and Schnepp, *J. Chem. Phys.*, 1955, **23**, 1575.

[9] Winston, *ibid.*, 1951, **19**, 156.

[10] Craig and Walsh, *ibid.*, 1956, **25**, 588.

[11] Robertson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 659; Donaldson and Robertson, *ibid.*, 1953, *A*, **220**, 157; Robertson and Woodward, *J.*, 1937, 219.

where $F_{l(m)}$ is the " angle factor " for a long (short) axis transition given by

$$F_l = 2lz\,.\,lz' - lx\,.\,lx' - ly\,.\,ly' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In (3) lz (or lz') denotes the cosine of the angle, $\angle lz$, between the molecular direction l (or l') and z, the intermolecular line drawn from l to j; $\rho_{p(q)}$ denotes the co-ordinate of electron $p(q)$ in molecule o(j). The integrals in equation (2) are the usual transition dipole-moment integrals, M, of absorption spectroscopy. Reference directions in the crystal are such that d is perpendicular to both the a and b crystal directions. The x direction is drawn perpendicular to z in the (001) plane from the centre of molecule j; y is perpendicular to both x and z. Directions within molecule o are indicated by l, m, and n, all mutually perpendicular; in molecule j by l', m', and n'. The matrix $(l'a)$ is defined as:

$$(l'a) = \begin{pmatrix} l'a & l'b & l'd \\ m'a & m'b & m'd \\ n'a & n'b & n'd \end{pmatrix}$$

From the symmetry of the crystal,

$$(l'a) = (la)\,.\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Also, $(lx) = (la)\,.\,(ax)$, and $(l'x) = (l'a)\,.\,(ax)$.
By means of these relations it may be shown that:

$$F_l = lb^2(2bz^2 - bx^2 - by^2) - la^2(2az^2 - ax^2 - ay^2) - ld^2(2dz^2 - dx^2 - dy^2) - 2la\,.\,ld\,(2az\,.\,dz - aydy - ax\,.\,dx) \quad . \quad (4)$$

where lb^2 denotes $\cos^2 \angle lb$; etc.

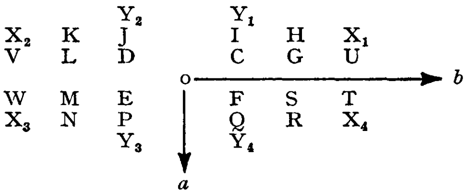
A similar expression holds for F_m.

For molecules in the same (001) plane, equation (4) simplifies to

$$F_l = lb^2(2\sin^2 \angle az - az^2) - la^2(az^2 - \sin^2 \angle az) + ld^2 \quad . \quad . \quad . \quad (5)$$

For two molecules in the same (001) plane it is necessary to evaluate interactions only for one quadrant; for molecules in different planes interactions over a half-plane must be calculated. The remainder follow by symmetry. With reference to molecule o, other non-equivalent sites are designated as in Fig. 1. A prime indicates the corresponding molecule in the adjacent plane (*e.g.*, C′ and C).

FIG. 1. *Designation of sites in* (001) *plane.*



The molecules are so labelled that F′ lies nearer to o than does C′. Calculations were made for all molecule pairs for which $r_{\text{oj}} < 20$ Å.

The values calculated for $[e^2/r_{ij}{}^3]F_{l(m)}$ are given for various molecule pairs in Tables 1 and 2. The unit of cm.$^{-1}$ Å^{-2} is convenient if M, the transition-moment integral, is expressed in Å. For $M = 1$, the sum of the interactions between inequivalent molecules in the same (001) plane is given by $4\sum$; in the two adjacent planes, one above and one below, by $4\sum'$. Thus the total interaction is $4(\sum + \sum')$.

Values of $4(\sum + \sum')$ for anthracene were calculated by the formulæ used for the other substances, as l 1737; m 144. Craig and Walsh [10] obtained 1796 and 152; the slight discrepancy arises because the sign of az is taken differently for molecule pairs such as oF′.

Since $\sum_j I_{oj} = 4(\sum + \sum') = \sum_j [e^2/r_{oj}^2] F_{l(m)}$ equation (3) was used to find $F_{l(m)}$: then by equation (1), the splitting was calculated. The results are given in Table 3. When $\sum_j I_{oj}$ is negative, the *a* component should appear at lower energies than the *b*, and *vice versa*.

To calculate the actual value of the splitting it is necessary to evaluate M from experiment. When the band system marks a strongly allowed transition the total integrated intensity of the whole system may be used, the numerical value being derived from the solution spectrum. This approximation is reasonable when there is a relative absence of vibrational structure. However, as has been shown,[7] the presence of vibrational structure results in the various bands' each being split. To apply the previous method would give a result which would represent the sum of the splittings of the individual bands.

TABLE 1. *Same* (001) *plane*: *interactions between non-equivalent molecules.*

Pair: o and	Durene *l*	Durene *m*	Ovalene *l*	Ovalene *m*	Metal-free phthalocyanine *l*	Metal-free phthalocyanine *m*
C, D, E, or F	−352	414	−133	85	70	−124
G, L, S, or M	67	103	−24	56	48	−22
U, T, V, or W	36	31	10	30	26	10
I, J, P, or Q	−28	21	−6	3	3	−6
H, K, N, or R	−13	15	−5	3	3	−5
X_1, X_2, X_3, or X_4	2	10	−3	3	2	−3
Y_1, Y_2, Y_3, or Y_4	−7	5	−1	1	1	−1
$\sum$	−295	599	−163	182	151	−150

TABLE 2. *Adjacent* (001) *plane*: *interactions between inequivalent molecules*: *and total interaction* (cm.$^{-1}$ Å^{-2}).

Molecule paired with o	Durene *l*	Durene *m*	Ovalene *l*	Ovalene *m*	Metal-free phthalocyanine *l*	Metal-free phthalocyanine *m*
C′ or D′	−80	24	−41	9	(11) *	(−4) *
G′ or L′	− 3	24	−20	9	*	*
U′ or V′	12	14	− 8	9	*	*
F′ or G′	43	−338	−12	−86	−63	−17
S′ or M′	69	−8	20	−35	−31	2
T′ or W′	34	13	20	−5	−7	11
Q′ or N′	−31	−7	*	*	*	*
$\sum'$	46	−278	−50	−99	−101	−4
$4\sum'$	184	−1112	−200	−396	−404	−16
$4\sum$	−1180	2394	−652	726	607	−601
$4\sum + 4\sum'$	−996	1282	−852	330	203	−617

* Molecule separation greater than 20 Å.

TABLE 3. *Splittings for l and m polarized molecular transitions* (cm.$^{-1}$).

	ν (cm.$^{-1}$)	Region considered (cm.$^{-1}$)	f	M^2 (Å)^2	$E_\alpha - E_\beta$ *l* [cm.$^{-1}$]	$E_\alpha - E_\beta$ *m* [cm.$^{-1}$]
Durene	36,000	35,000—41,000	0·008	0·022	−40	60
	49,300	45,000—46,000	*ca.* 0·13	0·27	−540	700
Ovalene	21,900	21,700—22,700	0·08	0·35	−600 *	230 *
	23,100	22,700—23,800	0·055	0·22	−380 *	150 *
	24,600	23,800—25,600	0·05	0·20	−340 *	130 *
	21,900	21,300—26,300	0·22	0·8	−1400	500
	28,700	26,300—33,400	1·2	0·34	−600	220
Metal-free phthalocyanine	14,290	14,100—14,400	0·1	0·7	280 *	−860 *
	15,060	14,900—15,200	0·1	0·7	280 *	−860 *

* Denotes vibrational bands considered separately.

Allowance for vibrational structure demands that if I_{oj} is defined in terms of purely electronic functions ϕ, the splitting given by equation (1) should be multiplied by ξ^2 where $\xi = \int \sigma(0) \cdot \sigma'(n)\, dv_{\text{vib}}$ in which σ, σ' refer to vibrational functions of the ground and excited electronic states and the quantum state of the vibration is given in parentheses.

The quantities ξ^2 are evaluated from the solution spectrum. This approach has been used in those cases which are denoted in Table 3 by an asterisk. There will be an interaction between different vibrational quantum states of the one electronic level as well as between different electronic levels. These refinements have been discussed by Craig [7] but may be neglected when the splitting is small compared with the vibrational spacing.

The application of the results is chiefly to predict features of the crystal spectra from the known molecular (solution) spectra. When the crystal spectra become available it should be possible to use Table 3 to determine the polarization of the molecular transitions. This may be done on two bases: (*a*) The sign of the splitting varies with the polarization of the molecular transition. A determination of whether the *a* or the *b* component lies at longer wavelengths is in the case of non-degenerate levels therefore sufficient to find the polarization. (*b*) The magnitude of the splitting gives an indication of how far apart in the spectrum related bands may be found. This is not so necessary for weak bands where the relation should be obvious, but as is seen in Table 3 strong bands may have components separated by hundreds of Ångström units and their relation is not likely to be obvious. (This was the case with anthracene and interpretation of the crystal spectrum was hindered for a long time as a result.)

Durene and ovalene are considered to have a molecular symmetry described by the group D_{2h}. In these cases the use of the integrals to calculate the splitting is not complicated by the presence of degenerate levels.

In durene the first two electronic transitions become electronically allowed if the corresponding transitions in benzene are $B_{2u} \longleftarrow A_{1g}$ and $B_{1u} \longleftarrow A_{1g}$. The expected polarizations are *l* and *m* respectively. In the crystal therefore the two transitions should be split differently, by -40 and $+700$ cm.$^{-1}$ respectively. However, if the 2000 Å benzene transition is $E_{2g} \longleftarrow A_{1g}$, made allowed by vibrations,[12] then four components should appear in the crystal, involving both molecular polarizations. The presence of vibrational structure reduces the expected splitting. At 90° K seven main peaks appear [13] in the 2800 Å transition. The splitting in each of these is, therefore, expected to be only a few tenths of an Ångström unit. Certainly no splitting appreciably larger than this appeared at 90° K but the actual value has not yet been measured.

In ovalene the *l* direction passes through the centres of several C–C bonds, the *m* direction through four C atoms. The splitting of a vibrational level is expected to be of the order of 100 cm.$^{-1}$ whatever the polarization of the molecular transition. From the polarization of the longer-wavelength component it should be possible to determine the transition polarization.

The spectra of metal phthalocyanines in general resemble the spectrum of metal-free phthalocyanine, which in solution shows a series of absorption maxima. It has been suggested [14] that two electronic transitions are present with origins at 14,290 and 15,060 cm.$^{-1}$. It is not clear that this must be the case and that a 770 cm.$^{-1}$ vibrational interval is not responsible. A further possibility arises from a consideration of the molecular symmetry. At least in the crystal the molecular symmetry either, most strictly, is described by C_{2h} or, if the two hydrogen atoms are ignored, by D_{2h}. The departure from D_{4h} symmetry is not great, but is quite definite. The significance of the departure from D_{4h} is hard to determine quantitatively. It is roughly estimated in cm.$^{-1}$ from the separation of the four central nitrogen atoms as of the order of a molecular vibration. It may be suggested tentatively that the 14,290 and 15,060 cm.$^{-1}$ bands are components of a transition which in D_{4h} would be terminated by a degenerate level. The question of the splitting of a degenerate level in phthalocyanine and in coronene will be discussed in a later paper. The similar problem in the case of benzene has been treated by Craig and Walsh.[15] The

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[12] Craig, *Proc. Roy. Soc.*, 1950, *A*, **200**, 401; Dunn and Ingold, *Nature*, 1955, **176**, 65.

[13] Lyons and Walsh, unpublished work.

[14] Anderson, Bradbrook, Cook, and Linstead, *J.*, 1938, 1152.

[15] Craig and Walsh, *J.*, in the press.

splittings quoted in Table 3 will be relevant to observation only if the effective molecular symmetry is D_{2h} and not D_{4h}. The *l* polarized splitting is rather less than the 14,290—15,060 interval, but the *m* polarized splitting is comparable in magnitude with this interval and is therefore but a first approximation. Observation of the spectrum should be able easily to differentiate between *l* and *m* polarization.

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