322. *Calculations of the Crystal Spectra of Benzene and Naphthalene.*

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An E_{1u} state of benzene is split in the crystal into four components, three of them spectrally active. The splittings and intensity distribution for transitions to them are calculated according to perturbation theory by using methods discussed in earlier papers and now adapted to deal with a twofold degenerate upper state. Dipole sums have been found by two independent methods in good agreement with one another.

Calculations are reported for crystal transitions in naphthalene corresponding to band systems observed in solution at 2200 Å and 2750 Å. Their assignments as long-axis and short-axis polarised respectively are confirmed by comparison of the calculated results with experiment and by analogy with anthracene.

1. MOLECULES in crystals interact with forces which are small compared with intramolecular forces and accordingly the energy levels of crystals can be calculated from, and uniquely related to, those of free molecules by perturbation theory. A number of such studies have been made, beginning with Davydov's theoretical work[1] and including, for example, the weak A_g–B_{2u} system of benzene[2] and two transitions of anthracene.[3,4] Calculations are now reported for the intense system of benzene at 1790 and for two systems of naphthalene, at 2200 Å and 2750 Å. The crystal spectrum corresponding to the intense benzene system has not hitherto been discussed theoretically; our naphthalene results have already been briefly reported.[5]

We first restate the theory used briefly. It is derived so far as symmetry is concerned mostly from Seitz[6] and in other respects from Davydov and other authors already cited. A molecule will be supposed to have a ground state wave-function φ and a set of excited states φ^r. The transitions in the free molecules from the ground state have transition energies Δw^r measured in the equivalent wave numbers and transition dipole moments $\boldsymbol{M}^r = e\boldsymbol{Q}^r$ with the dipole lengths measured in Ångström units. In the crystal there will be h such molecules in a unit cell each occupying a *site* designated by a subscript $i =$ 1, 2, . . h, and if the crystal consists of N molecules there will be N/h unit cells numbered by a second subscript $m = 1, . . N/h$. Thus the symbol $\varphi_{lm}{}^s$ refers to a molecule in its s-th excited state placed on the l-th site of the m-th unit cell. Where specification of the unit

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[1] Davydov, *Zhur. eksp. teor. Fiz.*, 1948, **18**, 210.
[2] Fox and Schnepp, *J. Chem. Phys.*, 1955, **23**, 767.
[3] Craig and Hobbins, *J.*, 1955, 539, 2309.
[4] Craig, *J.*, 1955, 2302.
[5] Craig and Walsh, *J. Chem. Phys.*, 1956, **24**, 471; **25**, 588.
[6] Seitz, *Ann. Math.*, 1936, **37**, 17.

cell is unnecessary the second subscript is omitted. The Hamiltonian for the rigid lattice may be written

$$\sum_{k=1}^{N}\left(\mathbf{H}_k+\sum_{l>k}\mathbf{V}_{lk}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $\mathbf{H}_k$ is the Hamiltonian for the k-th molecule in isolation and V_{lk} is the interaction energy between the molecules k and l. Writing the crystal ground state wave function as a simple product of free molecule functions (2)

$$\Phi_G=\varphi_1\varphi_2\ldots\varphi_N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we find for the energy to the first order the expression (3):

$$E_G=Nw+\sum\sum\int\varphi_l\varphi_k\mathbf{V}_{lk}\varphi_l\varphi_k\mathrm{d}\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Excitation of the p-th molecule of the i-th set to its r-th excited state is represented in a localised excitation wave function (4):

$$\phi_{ip}{}^{r}=\varphi_{11}\varphi_{12}\ldots\varphi_{ip}{}^{r}\ldots\varphi_{h,N/h} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If all molecules are of one crystallographic species this belongs to an N-fold degenerate set with respect to the N-excitation sites: the overall degeneracy is the product of this site degeneracy and that of the molecule wave function. Where there is more than one crystallographic species the degeneracy of the functions (4) extends to the members of each species but not, of course, outside it. Approximate eigenfunctions for excited states of the crystal are linear combinations of the localised excitation functions (4), and the problem of finding the coefficients for them can always be partly solved, and sometimes completely, by using symmetry arguments.

2. *Symmetry Considerations.*—The Hamiltonian (1) is invariant under the operations of the space group and the setting up of crystal wave functions is simplified by making them transform like irreducible representations. The infinite crystal is simulated by applying cyclic boundary conditions to the finite crystal of N molecules, the group of which is the finite space group of Winston and Halford.[7] This contains as an invariant sub-group the finite translation group consisting of the lattice translations (5):

$$n_1\mathbf{t}_1+n_2\mathbf{t}_2+n_3\mathbf{t}_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the $\mathbf{t}$'s are primitive lattice vectors and the n's integers which, in (5), generate from a chosen molecule a set of molecules translationally equivalent to it.

Using the functions (4), we now set up normalised linear combinations (6) of translationally equivalent molecules with irreducible symmetry under the translation group:

$$\Phi_i{}^{r}(\mathbf{k})=\sqrt{(h/N)}\sum_{p}\exp\left(\mathrm{i}\mathbf{k}\,.\,\mathbf{r}_{ip}\right)\phi_{ip}{}^{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$\mathbf{r}_{ip}$ is the position vector of the p-th molecule of the i-th set, and $\mathbf{k}$ is a wave vector; $\mathbf{k}$ may be regarded as a vector in reciprocal space. Its components along the three crystal axes a, b, and c are limited, for example, along a, to $2\pi\sigma/(M_a\,.\,a)$ for $\sigma=0,\ \pm1,\ \pm2,\ldots M_a/2$ where a is the lattice spacing and M_a the number of translationally equivalent molecules along the a axis; $M_aM_bM_c=N/h$.

The invariant sub-group of translations is associated in the space group with the factor group or unit-cell group, and reference will be made also to two other groups, namely the site group and the group of the wave vector $\mathbf{k}$. The factor group consists of operations which leave the Hamiltonian for the molecules in a unit cell unchanged, either by interchanging the molecules or by mapping them on themselves or their translational

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[7] Winston and Halford, *J. Chem. Phys.*, 1949, **17**, 607.

equivalents. In the most general case each factor-group operation carries a chosen molecule into another crystallographically equivalent to it. Then, if all the molecules in the unit cell are crystallographically equivalent the order of the factor group equals the number of molecules in the unit cell.* In this case the site group, which consists of those factor-group operations which leave the Hamiltonian for one molecule unchanged, contains only the identity. In more special cases some factor-group operations permute the molecule Hamiltonians $\mathbf{H}_k$ while others leave them invariant; the latter operations constitute the site group. The number of molecules in the unit cell then equals the number of operations effecting distinct permutations in the factor group plus one, *i.e.*, its order divided by the order of the site group. Thus, in the naphthalene crystal there are two molecules per cell and the factor group C_{2h} is of order four. The identity and inversion operations self-transform the molecules, giving a site group C_i of order two.

To describe the group of the wave vector we must consider the transforms of the functions (6) by a factor-group operation **F**. In accordance with what has just been said, let us suppose that **F** carries a molecule of the *i*-th translationally equivalent set into the *j*-th and the *p*-th unit cell into the *q*-th. Then

$$\mathbf{F}\Phi_i^r(\mathbf{k}) = \sqrt{(h/N)} \sum_q \exp\,(\mathrm{i}\mathbf{k}\,.\,\mathbf{r}_{jq})\,\phi_{jq}^r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This is identical with the result of the operation **F** applied to the vector **k**, the **r** vectors being altered only to apply to the new site:

$$\mathbf{F}\Phi_i^r(\mathbf{k}) = \Phi_j^r(\mathbf{Fk}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Thus the factor-group operations generate a set of wave vectors from a chosen **k**. This set, radiating from a point of reciprocal space, is called a star by Wigner *et al.*[8] In general each factor-group operation generates a different **Fk** and, even if inversion of space co-ordinates is not a factor-group operation the negative of each wave vector is included in the star as a result of symmetry to time inversion. Thus the most general star consists of as many vectors as there are factor-group operations, or twice as many, depending upon whether space inversion is, or is not, an element of the factor group. In special cases the wave vector **k** is invariant to certain of the factor-group operations; these constitute a sub-group called the group of the wave vector. The functions (6) which transform like the **k** representation of the translation group can in addition be combined to transform like representations of the group of the wave vector. In the case $\mathbf{k} = 0$ the wave vectors on the left- and the right-hand side of (8) are the same, so the group of the wave vector is the point group isomorphous with the whole factor group, and crystal wave functions can be classified according to factor-group representations. This is of prime importance for optical transitions which are mainly to states of $\mathbf{k} = 0$. On the other hand, for the most general **k** the group of the wave vector consists only of the identity and time inversion and no subclassification of the functions (6) can be made.

The energy levels of the crystal are found by diagonalising the energy matrix of the Hamiltonian (1) in the basis of functions (6). It is somewhat more convenient to calculate directly the transition energies by subtracting the ground-state energy (3). The required transition energies to the first order can be found from the secular equation (9):

$$\mathit{det}\left\{[\Phi_i^r(\mathbf{k})|\sum\mathbf{H}_k + \sum\sum\mathbf{V}_{kl} - E_G|\Phi_j^r(\mathbf{k})] - [\Phi_i^r(\mathbf{k})|1|\Phi_j^r(\mathbf{k})]E\right\} = 0 \quad . \quad (9)$$

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* Where the unit cell contains more than one crystallographically distinct molecule each is considered separately in the same way under the factor-group operations.

[8] Bouckaert, Smoluchowski, and Wigner, *Phys. Rev.*, 1936, **50**, 58.

and to higher order of approximation by including in the basis functions corresponding to different free-molecule excited states as discussed in ref. 4. In the diagonal places in the determinant we find

$$\Delta w^r + D^r + \sum_q{}' \exp\,[\mathbf{ik}\,.\,(\mathbf{r}_{ip} - \mathbf{r}_{iq})]I_{ip,iq}{}^{rr} - \Delta E \quad . \quad . \quad . \quad . \qquad (10a)$$

and in the non-diagonal

$$\sum_q (\exp\,[\mathbf{ik}\,.\,(\mathbf{r}_{ip} - \mathbf{r}_{jq})]I_{ip,jq}{}^{rr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10b)$$

where

$$D^r = \sum_q{}' \left\{(\varphi_p{}^r\varphi_q|\mathbf{V}_{pq}|\varphi_p{}^r\varphi_p) - (\varphi_p\varphi_q|\mathbf{V}_{pq}|\varphi_p\varphi_q)\right\}$$

$$I_{ip,jq}{}^{rr} = (\varphi_{ip}{}^r\varphi_{ip}|\mathbf{V}_{ip,jq}|\varphi_{jq}{}^r\varphi_{jq})$$

and the primed sums omit $p = q$. The degree of the secular equation is equal to the number of molecules in the unit cell but it can be factorised into smaller blocks by using the group of the wave vector and, in the case $\mathbf{k} = 0$, using the factor group.

3. *Application to Benzene.*—Benzene crystals are orthorhombic with four molecules in the unit cell. These will be numbered as follows: I is at (0, 0, 0) and the others are generated from it by applying the factor-group operations as defined in Table 1. A set of rectangular axes is assigned to I: the z axis is normal to the molecular plane with its positive direction making acute angles with the positive directions of the crystal axes a, b, and c; the y axis is the intersection of the molecular plane with the ab crystal plane with positive direction making an acute angle with the positive b axis, and the x axis is perpendicular to y and z and makes acute angles with a and b but not c. The axes in the other molecules are the transforms of those in I by the factor-group operations. Table 1 sets out the direction cosines of molecular to crystal axes derived in this way from the results of Cox and Smith.[9]

TABLE 1. *Direction cosines of molecular axes with respect to crystal axes in benzene crystals.*

Molecular type	Method of generation	Crystal axes	Direction cosines x	y	z
I	E	a	0·6365	−0·2992	0·7109
		b	0·2000	0·9541	0·2229
		c	−0·7450	0	0·6671
II	$C_2{}^c$	a	−0·6365	0·2992	−0·7109
		b	−0·2000	−0·9541	−0·2229
		c	−0·7450	0	0·6671
III	C_2	a	−0·6365	0·2992	−0·7109
		b	0·2000	0·9541	0·2229
		c	0·7450	0	−0·6671
IV	$C_2{}^a$	a	0·6365	−0·2992	0·7109
		b	−0·2000	−0·9541	−0·2229
		c	0·7450	0	−0·6671

For the calculation of optical transitions the energy levels belonging to $\mathbf{k} = 0$ are the important ones. The corresponding wave functions transform like representations of the factor group, as explained in the last section, and are given in the basis of the functions (4) by the following expressions (11):

$$\begin{aligned}\gamma^\alpha &= (1/2)(\phi_{\mathrm{I}}{}^r + \phi_{\mathrm{II}}{}^r + \phi_{\mathrm{III}}{}^r + \phi_{\mathrm{IV}}{}^r)\\ &= (++++)\\ \gamma^\beta &= (+-+-)\ \gamma^\delta = (+--+)\ \gamma^\epsilon = (++--) \quad . \quad . \quad . \qquad ((11)\end{aligned}$$

The functions γ transform under the twofold rotations in the same way for any molecular state φ^r and, because the site group contains inversion, the g or u character is the same as

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[9] Cox and Smith, *Nature*, 1954, **173**, 75.

that of the molecule wave function. The complete crystal wave functions for $\mathbf{k} = 0$ are sums of the expressions γ over all unit cells. The factor-group representations for a molecular u wave function are set out in Table 2.

TABLE 2. *Factor-group representations and polarisations for crystalline benzene* ($\mathbf{k} = 0$).

Wave function	D_{2h} representation	Transition dipole direction
γ^{α}	A_{1u}	(Forbidden)
γ^{β}	B_{2u}	b
γ^{δ}	B_{1u}	a
γ^{ϵ}	B_{3u}	c

The transitions referred to are from the ground state which is g, and there are no allowed transitions leading to excited states of the crystal corresponding to g excited molecular states. For a non-degenerate molecular wave function φ^r there is just one crystal wave function belonging to each factor-group representation, but for a doubly degenerate molecule wave function there will be two, and these two will be split by the crystal field as we shall see for the E_{1u} state of benzene.

The energies of the crystal levels relative to those of free molecules depend, at least when the levels give rise to intense absorption systems, on resonance effects between molecules. These have been discussed in Section 1 and more fully in refs. 1 and 3. For $\mathbf{k} = 0$ the magnitudes depend on sums of integrals of the intermolecular potential energy $\mathbf{V}_{kl}$ between all molecule pairs kl. The symmetry relations in Table 1 reduce the integrals to a small number of different types each involving a selected molecule which we choose to be a member of the set translationally equivalent to I. Written in full a representative integral sum is (12):

$$\sum_{j=1}^{N/4} I_{i\mathrm{I},j\mathrm{K}}{}^{xx} = \sum_{j} (\varphi_{i\mathrm{I}}{}^{x}\ \varphi_{i\mathrm{I}}|\mathbf{V}_{i\mathrm{I},j\mathrm{K}}|\varphi_{j\mathrm{K}}{}^{x}\ \varphi_{j\mathrm{K}}) \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The superscripts refer to the x component of the degenerate excited state φ^r as will be explained later. The integral sums occur in combinations determined by the appearance of the functions ϕ in (11) and defined below; the expressions are simplified by giving only that subscript which refers to the set of molecules over which the sum is taken.

$$\left.\begin{aligned} \mathscr{I}_{\alpha}{}^{xx} &= \sum I_{\mathrm{I}}{}^{xx} + \sum I_{\mathrm{II}}{}^{xx} + \sum I_{\mathrm{III}}{}^{xx} + \sum I_{\mathrm{IV}}{}^{xx} \\ \mathscr{I}_{\alpha}{}^{xy} &= \sum I_{\mathrm{I}}{}^{xy} + \sum I_{\mathrm{II}}{}^{xy} + \sum I_{\mathrm{III}}{}^{xy} + \sum I_{\mathrm{IV}}{}^{xy} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad 13$$

Analogous combinations occur in the energies of, and have the same sequences of signs as, the wave functions specified by subscripts β, δ, and ε.

For the doubly degenerate E_{1u} state of benzene there are two primitive crystal wave functions of each factor-group representation, and hence two distinct crystal energy levels, found by diagonalising a two-rowed secular equation. The elements of the four such secular equations are formally the same. For the A_{1u} factor group representation for example:

$$\begin{vmatrix} \mathscr{E} + \mathscr{I}_{\alpha}{}^{xx} & \mathscr{I}_{\alpha}{}^{xy} \\ \mathscr{I}_{\alpha}{}^{yx} & \mathscr{E} + \mathscr{I}_{\alpha}{}^{yy} \end{vmatrix} = 0 \qquad \mathscr{E} = \Delta w^r + D - \Delta E$$

For the mean energy displacement from a reference zero equal to $\Delta w^r + D$ we have $(1/2)(\mathscr{I}^{xx} + \mathscr{I}^{yy})$, and the two components are each separated from this by

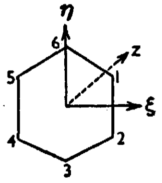
$$(1/2)\left\{(\mathscr{I}^{xx} - \mathscr{I}^{yy})^2 + 4(\mathscr{I}^{xy})^2\right\}^{1/2}$$

In the dipole–dipole approximation [3] the expression for a representative term occurring in the sum $\mathscr{J}^{xy}$ is as follows, for molecules l and m:

$$-(1/2)(1/r_{lm}^3)|\boldsymbol{M}^x||\boldsymbol{M}^y|\Big\{2\cos\theta_{l1}^x\cos\theta_{m1}^y +$$
$$2\cos\theta_{l1}^y\cos\theta_{m1}^x - \cos\theta_{l2}^x\cos\theta_{m2}^y - \cos\theta_{l3}^x\cos\theta_{m3}^y$$
$$- \cos\theta_{l2}^y\cos\theta_{m2}^x - \cos\theta_{l3}^y\cos\theta_{m3}^x\Big\}\ . \qquad (14)$$

r_{lm} is the distance between the centres of the molecules, $\boldsymbol{M}^x$ is the transition dipole moment for the transition to φ^x, and θ_{l1}^x is the angle between the transition moment and the line of centres of the molecules. Axes 2 and 3 are perpendicular to the line of centres.

We must now consider the transition moments for the free molecule. It is well known that an E_{1u} wave function in group $\boldsymbol{D}_{6h}$ can be expressed in two orthogonal functions which depend on the angle round the z axis according to the sine and cosine of $2\pi k/6$ when k numbers the vertices of the hexagon from 1 to 6. With the numbering in the diagram the transition dipole moments from the ground state lie respectively along the η and ξ directions for the sine- and cosine-dependent functions. By taking general linear combinations in terms of an angle parameter χ, we get two orthogonal functions with angle dependence given by $(\cos\chi\,.\cos 2\pi k/6 + \sin\chi\,.\sin 2\pi k/6)$ and $(-\sin\chi\,.\cos 2\pi k/6 + \cos\chi\,.\sin 2\pi k/6)$, the transition dipoles for which are rotated through χ from those for the original. Thus in an isolated molecule the transition moment to the degenerate E_{1u} state can be regarded as having components along any two axes at right angles in the molecular plane. We shall take the wave-function component φ^y to be that which has its transition dipole moment along the line of intersection of the molecular plane with the *ab* plane of the crystal, *i.e.*, the y axis already defined, and φ^x similarly.



The first stage of the numerical work is the computation of the dipole–dipole sums, given in Table 3 for a transition dipole length of 1 Å. Values in the Table have been computed in two distinct ways. The results marked (*a*) are sums over an infinite sphere by the Ewald–Kornfeld [10] method, and (*b*) are obtained by direct molecule-by-molecule evaluation over a sphere of radius 20 Å. We discuss and compare these methods of evaluation later. The sums (*a*) are used in the calculations of the crystal energy levels given in Table 4. These are characterised by the displacement of each level from a zero given by $\Delta w^r + D$ which is expected to be close to the free-molecule excitation energy. There are two levels belonging to each symmetry species labelled (i) and (ii), separated by an amount which measures the degree to which the crystal field splits the free-molecule degeneracy in the several symmetries.

TABLE 3. *Benzene crystal dipole–dipole sums* (cm.$^{-1}/Q^2$).

Dipole	Molecule sites				Dipole	Molecule sites			
axes	I, I	I, II	I, III	I, IV	axes	I, I	I, II	I, III	I, IV
(x, x)	(*a*) −386	−112	−791	−729	(x, y)	(*a*) 205	−947	−25	275
	(*b*) −415	− 92	−769	−771		(*b*) 233	−934	− 8	289
(y, y)	(*a*) 727	−2679	−1723	1341	(x, z)	(*a*) 207	1340	−738	795
	(*b*) 790	−2629	−1713	1405		(*b*) 181	1306	−818	833
(z, z)	(*a*) −341	185	−955	−553	(y, z)	(*a*) 228	−1058	−27	307
	(*b*) −375	220	−950	−587		(*b*) 260	−1041	− 7	323

The transition intensities in the crystal are conveniently considered in two steps: first, the sharing of the total intensity between the three axes of polarisation, and secondly,

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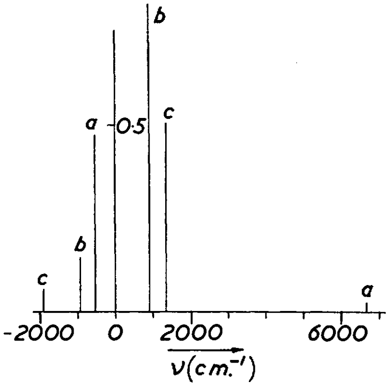
[10] Kittel, " Introduction to Solid State Physics," John Wiley, New York, 2nd edn., 1954, p. 347.

the subdivision between the two components polarised along each axis. In first-order theory the partition between the three axes is determined by their projections on the active molecular axes. Denoting the transition dipole length projected along the crystal axes by Q_a, Q_b, and Q_c, we find that the squares of these quantities are in the ratios 1 : 1·92 : 1·12. If the splittings are taken to be small compared with the transition energy Δw^r, these are also the ratios of oscillator strengths along the axes. To determine absolute intensities we use the formula for f, the oscillator strength, $f = A \cdot \Delta E \cdot Q^2$, where ΔE is the transition energy in Rydberg units, Q the transition dipole length in atomic units, and A the square of the cosine of the angle between Q and the polarisation direction of the incident light. In solution, A averages at 1/3; in the crystal it can be found from Table 1. The total f value summed over the three axes is evidently three times the solution value.

TABLE 4. *Calculated positions of crystal levels of benzene for* $\mathbf{k} = 0$ *relative to* $\Delta w^r + D$ (cm.$^{-1}$/Q^2).

$\alpha(A_{1u})$	$\beta(B_{2u})$	$\delta(B_{1u})$	(B_{3u})	$\alpha(A_{1u})$	$\beta(B_{2u})$	$\delta(B_{1u})$	(B_{3u})
−2693	−914	−514	−1906	−1659	+920	+6772	+1358

The calculated structure of the crystal spectrum corresponding to a vapour A_{1g}–E_{1u} *system of benzene, showing splittings, polarisation directions and transition dipole lengths in* Å. *The values apply to a transition of intensity with dipole length* 1Å *in each of the two degenerate components.*



The partition of these intensities between the two components along each axis can be determined from the solutions of the two-rowed secular equations (13) which give the coefficients for the mixing of φ^x and φ^y in the crystal eigenfunctions. The results are expressed as the ratios of the squares of transition moments. The values found (the higher frequency first) are: *a* polarised 0·057 : 1; *b* 5·94 : 1; *c* 8·72 : 1. The Figure illustrates the results, showing the splittings and intensity distribution in an intense A_{1g}–E_{1u} system. The frequency zero is $\Delta w^r + D$.

We have discussed the influence of crystal forces on the degenerate E_{1u} state of benzene without referring to Jahn and Teller's theorem[11] which shows that electronic degeneracy and a non-linear nuclear arrangement are incompatible. According to Jahn and Teller the regular hexagonal shape of a free benzene molecule must collapse in a degenerate state into an elongated hexagon with dimensions governed by the balance reached between σ-electron forces tending to preserve regularity and π-electron forces opposing it. In the crystal we treat the levels appropriate to molecules in which the regular hexagon is preserved, for the following reason. The degeneracy having been removed by crystal forces even in the regular shape, there will be no first-order Jahn–Teller effect, and its vestigial influence on shape will be of the same order as that of the crystal forces themselves and therefore properly to be neglected in the present approximation, the essence of which is that the time constant for nuclear displacements is long compare with that for

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[11] Jahn and Teller, *Proc. Roy. Soc.*, 1937, *A*, **161**, 220.

exciton transfer; this being so, the crystal levels are predominantly determined by the molecular dimensions in the ground state.

4. *Application to Naphthalene.*—The considerations of molecule and crystal symmetry for naphthalene are identical with those for anthracene already given in detail.[3] Moreover, calculations for naphthalene have already been reported briefly and will here only be summarised. The space group is C_{2h}^5 with two molecules in the unit cell; for each **k** value a free molecule state gives rise to two crystal levels. For $\mathbf{k} = 0$ transitions are allowed to both components of a *u* state, polarised in the one case in the *ac* plane and in the other along the *b* axis. Since naphthalene crystallises with a prominent (001) plane, measurements are made along the *a* and *b* monoclinic axes. Their energies may be calculated in relation to the free-molecule transition energy by using the intermolecular integral sums given in Table 5, computed in the dipole–dipole approximation. The in-plane transitions in naphthalene have their moments parallel to the longer in-plane axis (*y*-polarised A_g–B_{2u}) or along the shorter (*z*-polarised A_g–B_{1u}) in the recommended convention.[12] The left-hand column of Table 5 lists the combinations of transition moment directions in the two molecules, and the sums taken over equivalent and non-equivalent molecule pairs are given in the right-hand columns; values labelled (*a*) are Ewald–Kornfeld (EK) sums taken over the infinite sphere, and those labelled (*b*) are direct sums (DS) over a 20 Å sphere.

TABLE 5.* *Naphthalene crystal dipole sums* (cm.$^{-1}$/Q^2).

Dipole axes	Molecule sites		Dipole axes	Molecule sites		Dipole axes	Molecule sites	
	I, I	I, II		I, I	I, II		I, I	I, II
(*y*, *y*)	(*a*) 555	(*a*) 1350	(*z*, *z*)	(*a*) −789	(*a*) 84	(*y*, *z*)	(*a*) 323	(*a*) 1160
	(*b*) 581	(*b*) 1450		(*b*) −854	(*b*) 90		(*b*) 366	(*b*) 1164

* Calculations based on the crystal structure reported by Abrahams, Robertson, and White, *Acta Cryst.*, 1949, **2**, 238.

TABLE 6.*

Assignment	ΔE^α (cm.$^{-1}$)	ΔE^β	Splitting ΔE^α–ΔE^β	Shift $(\Delta E^\alpha + \Delta E^\beta)/2$
Long-axis (*y*) poln. A_g–B_{2u}	+6570	−2740	+9310	+1910
Short-axis (*z*) poln. A_g–B_{1u}	−2430	−3010	+580	−2720

* The minor differences between these results and those given in reference (5) are due to the substitution of EK values for the slightly different DS ones.

Naphthalene has three known singlet band systems in the quartz ultraviolet region, at 2200 Å ($f = 1{\cdot}7$), at 2750 Å ($f = 0{\cdot}11$), and at 3200 Å ($f = 0{\cdot}002$), of which the last is too weak to be treated in the dipole–dipole approximation. Table 6 refers to the first of the three systems and gives values of the Davydov splitting and shift based on the EK values in Table 5 and measured relative to $\Delta w + D$ as in expression (10*a*). The superscripts α and β refer respectively to *a* and *b* polarised absorption. Experimental evidence to determine the polarisation of this system is not available but analogy with the strongly similar anthracene absorption system and indirect evidence to be discussed based on the influence of the strong system on the weaker one at 2750 Å make it evident that the 2200 Å system is long-axis polarised.

In the weaker system at 2750 Å there are two features of the crystal spectrum not found in strong systems, again as in the similar system of anthracene at 3800 Å. The transition dipole length calculated from the observed oscillator strength in solution is 0·53 Å, so that the Davydov splitting will not exceed 400 cm.$^{-1}$ whatever the assignment. This is substantially smaller than the vibrational spacing of the progression, so that one cannot treat the electronic intensity as concentrated at one frequency but must consider each vibrational-electronic level of the progression separately. When the splitting energy

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[12] Report of Joint Commission for Spectroscopy, *J. Chem. Phys.*, 1955, **23**, 1997.

is small compared with the progression interval, the splitting actually observed depends, not on the total intensity of the band system, but on that part of it present in the particular vibronic transition. For somewhat greater splittings, interactions between different vibrational sub-levels become significant, leading to observed values between the limiting case just mentioned and those for large intermolecular interaction in which the band system behaves as if it were concentrated at a single frequency. This is the first of the new features of weaker systems; the second is that, first-order effects becoming rapidly very small, second-order disturbances caused by nearby strong systems become relatively important, leading to modified splittings and transfers of intensity between the weak and the strong system. Now, however, in contrast to the first-order term, and because the vibrational spacing in one system is usually less than the separation of two electronic systems, the magnitude of the second-order term depends mainly on the total intensities in the electronic systems. Thus one sees that such effects will rapidly overtake first-order effects in weak systems, especially when there is a widely spread vibrational structure. Furthermore, the intensity ratios for different crystal axes are unaffected in the first order and so show a sharp dependence on the second-order terms. All of these features were recognised and discussed in connection with the spectrum of anthracene[4] and in the preliminary report on naphthalene[5] and need not be insisted upon here. They have also been discussed recently by Simpson and Peterson[13] in a more general context.

TABLE 7. 2750 Å *System assigned* A_g–B_{2u} (*y polarised*).

n	First-order splitting	a Component (cm.$^{-1}$)	b Component (cm.$^{-1}$)	Splitting to the second order	Polarisation ratio, $a : b$
0	115	39	$-\ 54$	93	1 : 1·2
1	205	$h\nu + 75$	$h\nu - 93$	168	1 : 1·5
2	196	$2h\nu + 78$	$2h\nu - 87$	165	1 : 2·1
3	154	$3h\nu + 61$	$3h\nu - 73$	134	1 : 3·4
4	99	$4h\nu + 37$	$4h\nu - 61$	98	1 : 7·8
Conc. system	767	306	$-\ 320$	626	1 : 1·5

TABLE 8. 2750 Å *System assigned* A_g–B_{1u} (*z polarised*).

n	First-order splitting	a Component (cm.$^{-1}$)	b Component (cm.$^{-1}$)	Splitting to the second order	Polarisation ratio, $a : b$
0	9	$-\ 57$	$-\ 60$	3	1 : 3·1
1	14	$h\nu - 96$	$h\nu - 102$	6	1 : 2·8
2	11	$2h\nu - 87$	$2h\nu - 95$	8	1 : 2·4
3	8	$3h\nu - 67$	$3h\nu - 81$	14	1 : 2·0
4	5	$4h\nu - 45$	$4h\nu - 67$	12	1 : 1·2
Conc. system	48	$-\ 336$	$-\ 352$	16	1 : 2·8

The intensity ratio $a : b$ is 4·2 : 1 for a long-axis transition, and 1 : 7·3 for a short-axis transition, from the projections of molecular axes on crystal axes. The measured value[14] for the onset of the system is about 1 : 3. This value depends both on the polarisation properties of the transition at 2750 Å and on that at 2200 Å which under the influence of neighbour molecules imparts its own polarisation to the weaker system to some extent. One readily finds[5] that neither assignment for the *weak* system, coupled with a short-axis *intense* system, can lead to an intensity ratio near 1 : 3. The intense system must therefore be long-axis polarised as is its analogue in anthracene.[3] Accordingly, we list results in Tables 7 and 8 calculated for the members of the main progression ($h\nu = 1430$ cm.$^{-1}$) in the 2750 Å naphthalene system separately for the two in-plane polarisation directions, but assuming in the derivation of both a long-axis intense system at 2200 Å.

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[13] Simpson and Peterson, *J. Chem. Phys.*, 1957, **26**, 588.

[14] Craig and Lyons, *Nature*, 1952, **169**. 1102.

Values of the first-order splitting given in the second column for the several vibrational sub-levels may be compared with that for a concentrated system which has the same total intensity at a single frequency; their sum is equal to the concentrated-system value, but individually they are, of course, very much less, and the change in the second order (col. 5) is relatively a small one. Thus, in accordance with the earlier qualitative considerations, the concentrated-system approximation breaks down completely for weaker systems, particularly for the calculations of splitting; the average intensity ratio, on the other hand, differs much less from the concentrated-system value.

Experimental values of the splitting in the 2750 Å system are not known, but the measured polarisation ratio [14] of 1 : 3 indicates the assignment A_g–B_{1u} short-axis polarised, as for the corresponding anthracene system.

5. *The Dipole Sums.*—The quantitative results, as distinct from the qualitative features of intermolecular interactions in crystals, depend on the values of the dipole sums listed in Tables 3 and 6. Two important matters need to be mentioned in relation to them, one concerned with the method of evaluation and the other with the shape of the region over which the sum is taken. We postpone the second, and consider how the summation can be made for the special case of a sphere. Individual terms are given in expression (14), and the term may be found by term-by-term evaluation through a sphere of some chosen radius. If the radius of this sphere is big enough, the effect of a spherical shell of molecules external to it becomes that of a uniformly polarised shell which, according to classical electrostatics, contributes nothing to the field at the centre. In practice a radius of 20—30 Å gives an adequate convergence to the limiting value of the sum except in certain cases where a molecule which happens to make an exceptionally large contribution lies very close to the surface of the spherical region. The direct summation (DS) procedure is, of course, highly susceptible to such accidents of structure, and the Ewald–Kornfeld (EK) method for summation over an infinite sphere by a transformation leading to a rapidly convergent summation is in principle to be preferred. In practice the EK method is a little more laborious to apply than direct summation within a 20 Å sphere, but certainly less so than a 30 Å summation; moreover, the errors of the DS summation accumulate with the number of individual interactions included, so that no purpose is served in extending it to a large radius. The comparisons between the two methods in Tables 3 and 6 show a satisfying agreement which confirms the general correctness of the values given; for calculations of the crystal spectra we have used the EK values.

It was pointed out by Fox and Yatsiv [15] that the dipole–dipole summation for $\mathbf{k} = 0$ is identical with a problem familiar in electrostatics in relation to permanent rather than transition dipoles, namely, that the sum depends on the shape of the region over which interactions are considered, and therefore that some care must be taken in interpreting experimental results by comparing them with calculations of what is a special case, namely a sphere. However, in the one case (anthracene) in which results are available for an intense system the interpretation is unambiguous because the effects of change of shape on the calculated spectrum are too small to blur the distinction between long- and short-axis polarisations [5] and, this fact being noted, we can further see that in this case the experimental results are fitted better by calculations for a sphere than for any substantially different shape. These facts are evident in the results collected in Table 9 for the crystal spectrum related to the intense system of anthracene observed at 2500 Å in the vapour. To deal with the change of shape we proceed conventionally to consider the field acting on a molecule to be made up of three parts: first, the cavity field produced by the molecules contained in a large spherical cavity, then the fields associated respectively with the inner and outer surfaces of a uniformly polarised medium surrounding the cavity, the outer surface being that which defines the volume through which the summation is taken. The polarisation $\boldsymbol{P}$ of the medium is $\boldsymbol{M}/\Gamma$ where $\boldsymbol{M}$ is the transition dipole moment and Γ the volume of the unit cell of the crystal. The field of the inner (spherical) surface is $4\pi\boldsymbol{P}/3$,

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[15] Fox and Yatsiv, *J. Chem. Phys.*, 1956, **24**, 1103.

that of the outer depends on its shape; for a sphere it is $-4\pi\boldsymbol{P}/3$, for a thin slab with $\boldsymbol{P}$ normal to the plane sides it is $-4\pi\boldsymbol{P}$, and with $\boldsymbol{P}$ parallel to the sides it is zero. For a transition dipole length of 1 Å and with use of the anthracene unit cell volume of 474·2 Å^3, we find that the energy of a dipole of length 1 Å in the polarising field is $-1026 \cos \theta$ in wave-number units, where θ is the angle between the dipole and field directions. This allows the results for cases A and C in Table 9 to be built from those for B. The experimental results are those of Craig and Hobbins,[3] and the calculations refer to shapes as follows: A and C are thin slabs with polarisation normal and parallel respectively to the plane sides, and B is a sphere. ΔE^{α} refers to the displacement of the *a*-polarised component from the vapour value and the splitting is made positive when the *a* component is at higher frequencies than the *b*. The values in parentheses refer to short axis polarised molecular absorption. It is apparent that the observed value of the splitting is incompatible with a short-axis transition irrespective of assumption about shape, and, moreover, the sphere values fit better than either extreme departure from the spherical.

TABLE 9.

Shape	ΔE^{α} (cm.$^{-1}$)	ΔE^{β} (cm.$^{-1}$)	Splitting $\Delta E^{\alpha} - \Delta E^{\beta}$ (cm.$^{-1}$)	Shift $(\Delta E^{\alpha} + \Delta E^{\beta})/2$ (cm.$^{-1}$)
		Anthracene		
A	+33,300(−380)	−3900(+11,600)	+37,300(−12,000)	+14,700(+5600)
B	+12,000(−4700)	−4250(−5700)	+16,200(+1000)	+3850(−5200)
C	+1260(−6900)	−4400(−14,400)	+5700(+7500)	−1600(−10,700)
Exptl. (2500 Å system)	~+13,000	~−3000	~+16,000	~+5000
		Naphthalene		
A	+24,400(+2100)	−1900(+11,200)	+26,300(−9100)	+11,300(+6600)
B	+6600(−2400)	−2700(−3000)	+9300(+600)	+1900(−2700)
C	−2300(−4700)	−3200(−10,100)	+800(+5400)	−2800(−7400)

We are inclined to think that the difficulty over shape dependence will not arise when allowance is made for the fact that, at distances comparable to the length of the absorbed light wave, the intermolecular potential energy is not the static but the retarded potential.[16] It is certain that at such distances the interaction energy will not follow the static inverse-cube law and therefore that the analogy with the problem of permanent dipoles breaks down. The explanation may involve a cutting-off of the interaction at distances of the order of a wavelength, leading to a shape-independent sum. This is to be taken up in a later paper.

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[16] Heitler, "The Quantum Theory of Radiation," 3rd edn., Oxford, 1954, p. 233.