696. *The Spectrum of the Coronene Crystal.*

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First-order calculations of transition energies and oscillator strengths in the spectrum of the coronene crystal, using known data of crystal structure and the spectrum of the solution, are made.

CORONENE is a molecule of interest theoretically because it has a similar symmetry to that of benzene and yet the spectrum lies in a more convenient region than does that of benzene. No work has been reported on the spectrum of its crystal and so additional interest attaches to calculations of certain of its spectral properties. The experiments when done will then serve as a check on the theory and its basic assumptions. The theoretical methods used here are similar to those developed and used previously.[1-4] The theory has already met with some success,[5-7] but has not previously been applied to coronene. It should be noted that the application to coronene is limited to a certain extent by the use of the dipole term only in the series expansion of the interaction between molecules. However, this limitation should be little greater than in the case of anthracene where the theory works satisfactorily.[1,7]

The detailed crystal structure of coronene has been determined.[8] The crystal is monoclinic prismatic, the space group $P2_1/a$, and there are two planar centro-symmetric molecules in a unit cell. The position of one molecule can be transformed into that of the other by a translation through $b/2$ followed by a reflection in the ac plane and a translation through $a/2$. Molecular directions in the second molecule are therefore related to directions in the first molecule by this transformation. The unit cell dimensions are $a = 16{\cdot}10 \pm 0{\cdot}05$; $b = 4{\cdot}695 \pm 0{\cdot}005$; $c = 10{\cdot}15 \pm 0{\cdot}05$ Å; $\beta = 110{\cdot}8° \pm 0{\cdot}2°$. Direction cosines relating crystal and molecular directions are $la = 0{\cdot}0912$; $lb = 0{\cdot}0765$; $lc' = 0{\cdot}9928$; $ma = 0{\cdot}7174$; $mb = 0{\cdot}6865$; $mc' = -0{\cdot}1188$; $na = -0{\cdot}6905$; $nb = 0{\cdot}7233$; $nc' = 0{\cdot}0078$, where c' is perpendicular to a and b. In the coronene molecule the longer in-plane axis is denoted by l, the shorter by m (see Fig. 1).

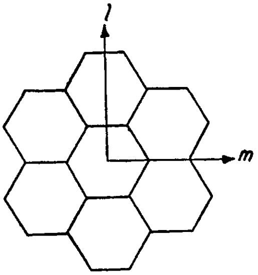

FIG. 1. *Directions in the coronene molecule.*

X-Ray evidence has shown that in the crystal the coronene molecule displays hexagonal symmetry although the various carbon–carbon bonds range in length from 1·385 to 1·430 Å. The appropriate symmetry group for the molecule is thus D_{6h}.

The spectrum [9] of the coronene solution between 28,000 and 34,000 cm.$^{-1}$ shows three transitions, I, II, and III, which bear a striking resemblance to those in benzene, having oscillator strengths, f, of I, 0·003; II, 0·24; III, 0·6. Transition III, which has a fairly

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[1] Craig and Hobbins, *J.*, 1955, 539.
[2] Lyons, *J.*, 1958, 1347 and references therein.
[3] Craig and Walsh, *J.*, 1958, 1613.
[4] Lyons, Walsh, and White, *J.*, 1959, in the press.
[5] Craig and Hobbins, *J.*, 1955, 2309.
[6] Lyons, *J. Chem. Phys.*, 1955, **23**, 1973.
[7] Lyons and Morris, *J.*, 1959, 1551.
[8] Robertson and White, *Nature*, 1944, **154**, 605; *J.*, 1945, 607.
[9] Clar, "Aromatische Kohlenwasserstoffe," Springer, Berlin, 1941.

sharp peak at about 32,800 cm.$^{-1}$, is presumably allowed, and the symmetry of the upper electronic state is therefore E_{1u}. In so far as the analogy with benzene is followed, transitions I and II are allowed by vibrational or other perturbation. In the free-electron terminology the upper states of transitions are described as I, ^1L_b; II, ^1L_a; III, ^1B_b.

In the application of the theory to coronene, attention was confined to excited states having the excitation wave-vector equal to zero. Wave functions which transform as irreducible representations of the factor group are:

$$\gamma^{\alpha(\beta)} = (1/\sqrt{2})\,(\phi_{\mathrm{I}} \pm \phi_{\mathrm{II}})$$

where α is to be read with the plus sign, β with the minus; subscripts I and II refer to the sites of a unit cell; ϕ refers to a product of molecular wave functions when one molecule of the crystal is excited to an E_{1u} degenerate level. In this case the solution of the Schrödinger equation leads to the secular equation

$$\begin{vmatrix} x + \mathscr{I}_{\alpha}^{ll} & \mathscr{I}_{\alpha}^{lm} \\ \mathscr{I}_{\alpha}^{lm} & x + \mathscr{I}_{\alpha}^{mm} \end{vmatrix} \begin{vmatrix} x + \mathscr{I}_{\beta}^{ll} & \mathscr{I}_{\beta}^{lm} \\ \mathscr{I}_{\beta}^{lm} & x + \mathscr{I}_{\beta}^{mm} \end{vmatrix} = 0 \quad . \quad (1)$$

where $x = w + D - E$; w denotes the energy of excitation of an isolated molecule; $D = \sum_{i \neq j} \int (\phi_i'\phi_j V_{ij} \phi_i'\phi_j - \phi_i\phi_j V_{ij}\phi_i\phi_j)\mathrm{d}\tau$; ϕ_i' refers to the excited state of molecule i; E is the energy of excitation in the crystal :

$$\mathscr{I}_{\alpha(\beta)}^{ll} = \sum I_{\mathrm{I}}^{ll} \pm \sum I_{\mathrm{II}}^{ll}$$
$$\mathscr{I}_{\alpha(\beta)}^{lm} = \sum J_{\mathrm{I}}^{lm} \pm \sum J_{\mathrm{II}}^{lm}$$

I and II denote the sites in the unit cell. Again, α is to be read with the plus sign on the right hand side, β with the minus.

$\sum I_{\mathrm{I}}^{ll}$ refers to the sum over molecules on sites of type I.

I^{ll} refers to an integral of the type

$$\int \phi_i^l \phi_i V_{ij} \phi_j^l \phi_j \, . \, \mathrm{d}\tau$$

where ϕ_i^l is the wave function which is the lth component of the degenerate excited state of the molecule (see 3).

ϕ_j is the wave function of the jth molecule in its ground state. J^{lm} differs from I^{ll} only in that one of the superscripts l is replaced by m.

The choice of the in-plane axes as l and m has been shown [3] to be permissible.

Interactions between inequivalent molecules were calculated on the dipole–dipole approximation and are given in Table 1, where the molecules are designated as in Fig. 2.

TABLE 1. *Interactions* (cm.$^{-1}$ Å^{-2}) *between inequivalent molecules separated by less than* 20 Å.

Same (001) plane			Adjacent (001) plane		
Molecule paired with O	$l - l$	$m - m$	Molecule paired with O	$l - l$	$m - m$
$C, D, E,$ *or* F	190	−251	C' *or* D'	−14	−19
G, L, S, M	90	−19	G', L'	5	−16
U, T, V, W	40	22	U', V'	2	3
I, J, P, Q	8	−12	F', E'	−105	−33
H, K, N, R	7	−9	S', M'	−31	8
X_1, X_2, X_3, X_4	6	−6	T', W'	−1	22
Y_1, Y_2, Y_3, Y_4	2	−3	Q', N'	*	*
Total interaction in one (001) plane (up to 20 Å)	1366	−1111		−288	−70

The means of intermolecular interactions on the same approximation are listed in Table 2. Those for the complete crystal were obtained by the Ewald–Kornfeld method and include

TABLE 2. *Sum of intermolecular interactions.*

Interaction type	Equivalent molecules	Inequivalent molecules	Interaction type	Equivalent molecules	Inequivalent molecules
l–l	1971	508 (790 *)	*l–n* *n–l*	−678	295
m–m	−828	−902 (−1251 *)			
n–n	−1145	−978	*n–m* *m–n*	−3691	260
l–m *m–l*	−31	−443			

* Denotes sum up to 20 Å radius. Other figures refer to complete crystal.

cross terms, *i.e.*, terms of the type *l–m* and are given for sets of both equivalent and inequivalent molecules. It is seen from Table 2 that the error from limiting the summation to a sphere of 20 Å radius, although not overwhelming, is appreciable.

The solutions to (1) are

$$E_\alpha = w + D + (\mathscr{J}_\alpha^{ll} + \mathscr{J}_\alpha^{mm})/2 \pm (1/2)\{(\mathscr{J}_\alpha^{ll} - \mathscr{J}_\alpha^{mm})^2 + 4(\mathscr{J}_\alpha^{lm})^2\}^{1/2}$$

with a similar expression for the β state.

Numerical values were calculated and are given in Table 3, in units of cm.$^{-1}/M^2$, where M denotes the transition moment.

TABLE 3. *Calculated positions of crystal levels for $k = 0$ relative to $w + D$.*

α (*ac* polarized)	2533	−1783
β (*b* polarized)	1576	−39

The polarizations of the four transitions to γ^α and γ^β were obtained by a consideration of the factor group, C_{2h}. When subjected to the operations of this group, γ^α behaved as a reducible representation, $B_u + B_u$. Therefore there are expected in the spectrum two transitions, each polarized in the *ac* plane. From γ^β there are expected two further transitions, each polarized *b*.

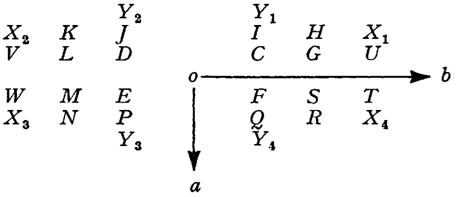

FIG. 2. *Designation of sites in the* (001) *plane.*

The intensity of the solution transition will be divided in the crystal amongst the four components. The total intensity along the three crystal directions, *a*, *b*, and *c′*, was calculated from the direction cosines relating the molecular and crystal directions as

$$I_a : I_b : I_{c'} = 1{\cdot}10 : 1{\cdot}00 : 2{\cdot}10$$

The total intensity along each crystal direction will be divided in each case between the two components of similar polarization. The method described previously[3] was used to show that in *a* polarization the ratio of the intensity of one component to that of the other will be only (1/5900). Similarly, in *c′* polarization, the ratio is (32,000/1) and in *b* polarization 1/6·3. In a given crystal therefore only one of the *a* components is likely to be observable, and one of the *c′* components, although both of the *b* components should appear. The weaker *a* component is that of lower energy, the weaker *c′* component that of higher energy. Both *a* and *c′* components appear at the same energies.

The crystal spectrum has not yet been observed but may now be predicted. It is necessary to assume the oscillator strength of the transition in solution. This was taken as $f = 1{\cdot}52$, corresponding to $M = 1{\cdot}46$ Å. The predicted spectrum is shown in Fig. 3 and Tables 4 and 5.

The " Davydov " splitting is the difference between oppositely polarized components arising from a molecular transition of given polarization. For l and m polarized molecular transitions the Davydov splittings were calculated as 957 and -1744 cm.$^{-1}/M^2$. On using a simpler approach, in which coronene is considered in the group D_{2h}, the Davydov splittings were 1580 and -2502 cm.$^{-1}/M^2$. The fuller more accurate treatment therefore shows that, although the simpler treatment gives the correct sizes and order of magnitude for the splitting yet it should be corrected by about -30%.

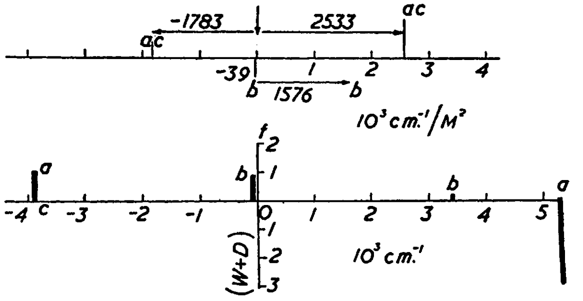

FIG. 3. *Predicted band positions in the crystal. Upper: for unit transition moment. Lower: for* $M = 1{\cdot}46$ Å *concentrated at one frequency.* f *denotes the oscillator strength.* a, b, c *denote the polarization of the bands.*

TABLE 4. *Energies of transitions in the crystal corresponding to the* 33,130 *cm.*$^{-1}$ *transition in the free molecule.*

α (*ac* polarized)		β (*b* polarized)	
38,530 cm.$^{-1}$	2597 Å	36,494 cm.$^{-1}$	2740 Å
29,337	3412	33,052	3026

TABLE 5. *Values of* f *calculated for crystal transitions corresponding to* 33,130 *cm.*$^{-1}$ *transition in the free molecule.*

	α		β
	a polarized	*c* polarized	*b* polarized
Higher-frequency component	0·0002	2·67	0·17
Lower frequency component	1·06	0·00006	0·94

Total f value in crystal $= 4{\cdot}84$.

Whilst the present theory in the form used in this paper is correctly applied to molecular transitions which are allowed and therefore intense, it is none the less possible to make at least qualitative remarks about the other transitions. In particular the upper state of transition II in benzene has been assigned $^1E_{2g}$[10] and $^1B_{1u}$,[11] and is presumably similar in coronene.

Coronene crystal forces should produce four components in the case of the E_{2g} assignment and two components in the case of B_{1u}. A complete analysis of a well-resolved crystal spectrum should therefore enable a decision between the alternatives to be made. The magnitude of the splitting in both cases is expected to be much smaller than for the allowed transition due to the necessary presence of vibrations. Experiments on the spectrum of the crystal are being conducted. All predictions are subject to the limitations discussed elsewhere.[4]

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[11] *E.g.*, Goeppart-Meyer and Sklar, *J. Chem. Phys.*, 1938, **6**, 645.