

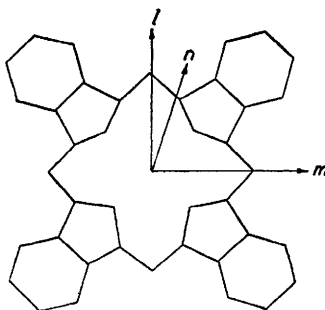
33. Phthalocyanine Crystal Spectra.

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The theory of the crystal splitting of the intense absorption bands in phthalocyanine crystals is used to make quantitative predictions of the spectra of the crystal. Experimental polarized spectra of single crystals of metal-free phthalocyanine are reported. Theory and experiment are compared, and the theory, even if the errors which arise from the point-dipole approximation and interaction with further excited states were completely removed, is found to be deficient in so far as it relies upon experimentally determined intensities and bands which are not of negligible width as required by the theory. The assignment of each pair of upper states near 15,000 cm^{-1} and 28,000 cm^{-1} to B_{1u} and B_{2u} symmetry in D_{2h} (E_u in D_{4h}) seems none the less to be reasonably certain for metal-free phthalocyanine and related compounds.

CRYSTALS of metal-free phthalocyanine exist in three forms,^{1,2} solutions of all of which give rise to the same spectrum. The conditions of formation of the α -, β -, and γ -forms are known. A transition temperature of 200°C between α and β has been reported.^{1,2} The β -form is the most stable at room temperature and is usually the form obtained by crystallization. Robertson³ has determined the crystal structure of the β -form, which is monoclinic prismatic. The space group is $P2_1/a$ with two largely planar centro-symmetric molecules in a unit cell.

FIG. 1. Molecular directions.



The unit-cell dimensions are $a = 19.85$, $b = 4.72$, $c = 14.8 \text{ \AA}$ (all $\pm 0.03 \text{ \AA}$); $\beta = 122^\circ 25'$. Molecular directions are shown in Fig. 1. The *l*-direction is actually the shorter in-plane axis in the crystal but, following Robertson, is called the long axis. With this assignment of molecular directions we use B_{1u} (in D_{2h}) to describe the symmetry of an upper state which terminates a transition which is polarized *m*, and B_{2u} for *l*.

The direction cosines connecting crystal and molecular directions are: la , 0.3532; lb , 0.0395; ld , 0.9347; ma , 0.6615; mb , 0.6960; md , -0.2794; na , -0.6617; nb , 0.7169; nd , 0.2197, where b is the crystal axis, a is perpendicular to b in the (001) plane, and d is perpendicular to both a and b .

The observed spectra⁴ of solutions are represented in Fig. 2 where also are shown the spectra of crystals (see below).

In free phthalocyanine solutions in α -chloronaphthalene absorption maxima are given by the relations, $\bar{\nu}_1 = 14,290 + 1585n_1$, $\bar{\nu}_2 = 15,060 + 1585n_2 \text{ cm}^{-1}$, where n_1 and n_2 are integers. 1585 cm^{-1} is readily interpreted as the frequency of a vibration which is

¹ Karasek and Decius, *J. Amer. Chem. Soc.*, 1952, **74**, 4716.

² Ebbert and Gottlieb, *J. Amer. Chem. Soc.*, 1952, **74**, 2806.

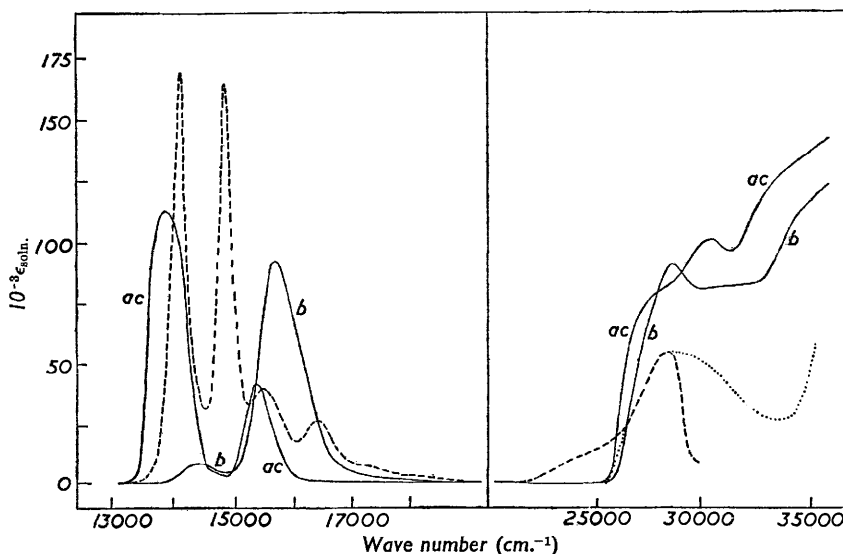
³ Robertson, *J.*, 1935, 615; 1936, 1195.

⁴ Fichen and Linstead, *J.*, 1952, 4846.

probably totally symmetric. The two series of intense peaks are replaced by one series in a number of metal phthalocyanines. It should be noted that, if use is made of Linstead's schematic representation of the spectra, account should be taken of the intensities of the various bands if this conclusion is to be seen easily. A similar simplification of the spectrum of porphyrin has been observed. The absorption in both series in the free phthalocyanine spectrum is very great; the oscillator strength of each peak in this spectrum is one half of that observed in a metal phthalocyanine peak.

At higher energies (about $28,000\text{ cm}^{-1}$) there occurs a further intense absorption which is the analogue of the Soret band in porphyrin spectra; in certain metal compounds this band appears split. At higher energy still, an even more intense absorption occurs.

FIG. 2. Spectra of solution (broken line) and polarized crystal (full line) of phthalocyanine. The dotted line is the absorption spectrum of a film; *ac* and *b* denote polarizations. The ordinates of the spectrum of the crystal are in arbitrary units.



Unpolarized spectra of crystals have been reported previously for various phthalocyanines.⁵ In both the free and the metal compounds the lower-energy system shows both a peak and a distinct shoulder.

Symmetry of the Molecule.—In the β -form of the crystal a molecule does not display D_{4h} symmetry, but either D_{2h} or a lower symmetry depending on the positions of the central hydrogen atoms. It seems reasonable to consider the molecule in D_{2h} (rather than in a lower symmetry group) when π -electronic spectra are being considered since the effect of the hydrogen atoms is then describable as a small perturbation which may be neglected. This was the assumption used in an earlier paper.⁶ However, as was there pointed out, an alternative approach is to regard the molecule in D_{4h} , and this must be approximately true. This assumption has been used in some molecular-orbital calculations by Basu.⁷ From the theory of atomic orbitals each nitrogen atom bonded to a hydrogen atom should be pyramidal and thus the hydrogen atoms would be non-planar.

Metal phthalocyanines such as those of copper or cobalt show in the crystal much less distortion from a D_{4h} symmetry than does the free phthalocyanine.

⁵ Fielding and Gutman, *J. Chem. Phys.*, 1957, **26**, 411.

⁶ Lyons, *J.*, 1958, 1347.

⁷ Basu, *Indian J. Phys.*, 1954, **28**, 511.

Kasha's suggestion⁸ that the $16,000\text{ cm}^{-1}$ bands in porphyrins involve at least two electronic transitions is consistent with the assumption of D_{2h} rather than D_{4h} symmetry.

Both absorption systems in metal phthalocyanines are so intense that it is reasonable to say that both denote allowed electronic transitions. In D_{4h} there are expected several allowed electronic transitions which arise from a ground state which is totally symmetrical. All the lower-energy allowed transitions correspond in D_{4h} to $E_u \leftarrow A_g$ transitions. The differences amongst them have been described in a simple molecular-orbital treatment and are indicated in Fig. 4, taken from Basu's results.

Since the excited electronic state of the molecule is E_u in all these cases there is to be expected an interaction between the various states which would lead to, *inter alia*, a

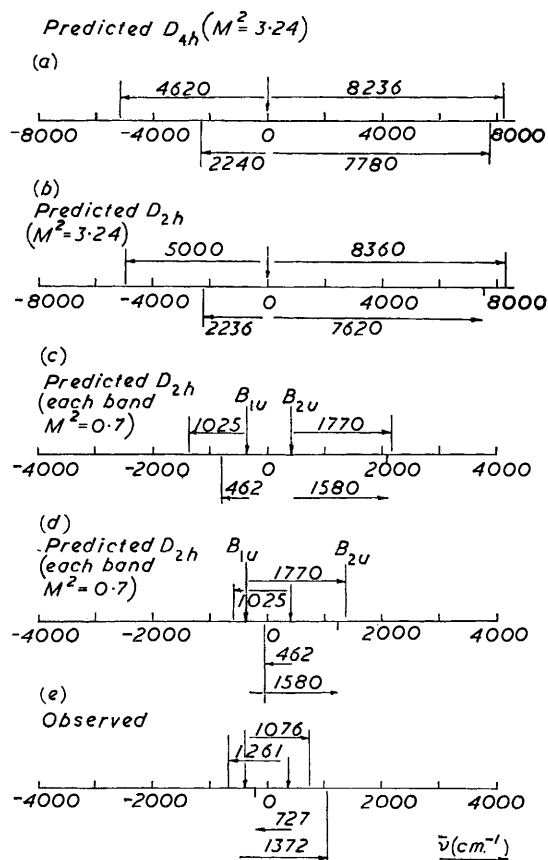


FIG. 3. Comparison of predicted spectra with that observed. The arrows denote the positions of the bands for the solution assumed or observed.

redistribution of intensity and an alteration in the band positions from those calculated for no interaction. It is clear that all allowed transitions of interest at present are likely to terminate in degenerate upper states.

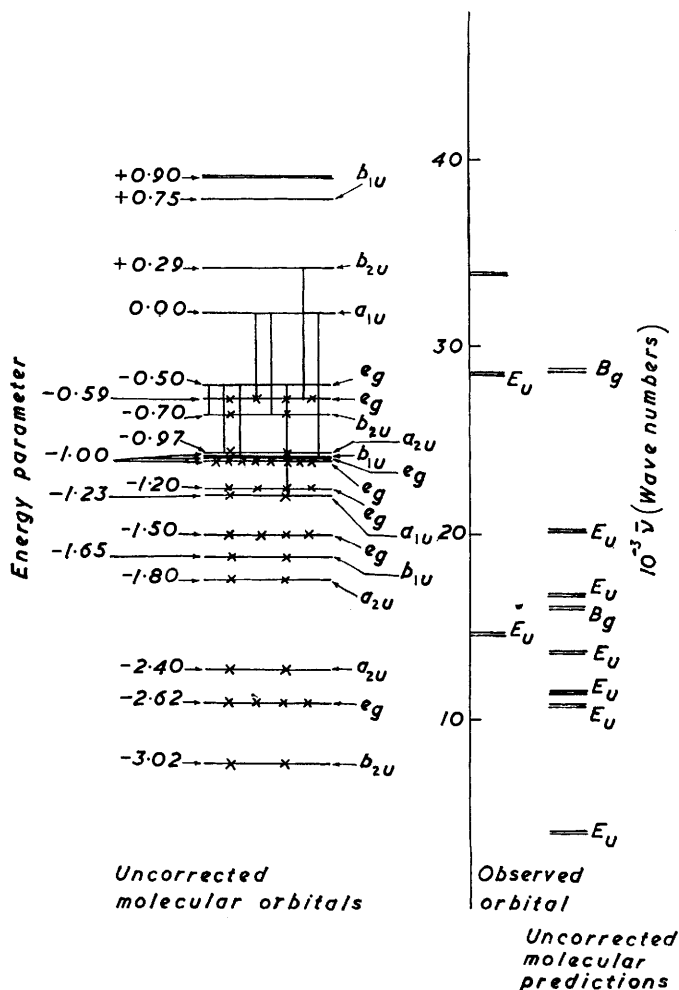
A reduction of symmetry from D_{4h} , e.g., to D_{2h} must lead to a splitting of a level degenerate in D_{4h} . In D_{2h} , B_{1u} and B_{2u} states would replace the E_u state in D_{4h} . The splitting between B_{1u} and B_{2u} states would be a measure of the departure from D_{4h} symmetry.

The interpretation of the free-phthalocyanine bands at $14,290$ and $15,050\text{ cm}^{-1}$ can therefore be made in terms of the replacement of an E_u state in D_{4h} by two states, $B_{1u} + B_{2u}$

⁸ Kasha, quoted by Longuet-Higgins, Rector, and Platt, *J. Chem. Phys.*, 1950, **18**, 1174.

in D_{2h} . The evidence from oscillator strengths is consistent with this interpretation. The possibility of tautomerism has not been excluded completely, but if tautomers were responsible for the two spectral series near $15,000 \text{ cm.}^{-1}$ it is necessary that the tautomers should be present in equal amount. In the absence of evidence that tautomers are indeed present, the lower-energy transition in the visible spectrum provides evidence that the

FIG. 4. Molecular orbitals⁷ and predicted electronic states of the phthalocyanine molecule with the lowest-energy allowed transitions indicated with vertical lines.



effective molecular symmetry is D_{4h} for metal phthalocyanines and D_{2h} (or lower) for free phthalocyanine.

Earlier calculations⁶ considered phthalocyanine in D_{2h} and used a direct summation method. The question of the effect of molecular symmetry when this involved degenerate levels was not then investigated. The present calculations provide evidence on this question by extending the theory to the D_{4h} case. The method of direct summation has the advantage of giving individual interactions between various molecule pairs but is subject to some error when the total interaction is desired, unless the number of molecules

considered is inconveniently large. Consequently the Ewald-Kornfeld method of summation⁹ was used here. It gives the total interaction, and all the spectroscopically observable quantities can then be calculated. Both methods are limited in validity by their assumption of point dipoles. An increasing error is introduced as the molecular dimensions become larger in comparison with the intermolecular spacings. The larger the molecule the larger are the intermolecular spacings, but none the less the error is expected to be larger for big molecules and it is probably appreciable for any aromatic molecular crystal.

The approximation of point dipoles is expected to be good in the case of phthalocyanines for all pairs of inequivalent molecules, and for all pairs of equivalent molecules except the pair of nearest neighbours separated along the b direction. In this instance an estimate of the error showed that the point dipole result of $2458 \text{ cm.}^{-1} \text{ \AA}^{-2}$ for an $l-l$ interaction (Table 1) between equivalent molecules is likely to be high by several hundred $\text{cm.}^{-1} \text{ \AA}^{-2}$, but the error should be rather less than 50%. The splitting between components of the same band is not affected by such errors, although the spread of the four levels from a degenerate molecular level, as given in Fig. 3, will be high. The estimate of error was made by consideration of dipoles placed on the extremes of the molecular framework instead of concentrated at the molecular centre. In phthalocyanine the effective molecular dimension is the 18-membered conjugated ring which is to some extent shielded from neighbouring molecules by the outer atoms of the molecule. This has the effect of reducing the error.

The theory and the methods have been described previously¹⁰ and will not be discussed here except for one or two new points.

The symbolism and expressions for the crystal wave-functions γ^α and γ^β follow previous usage.¹⁰ Transitions to γ^α from the ground state are ac polarized, to γ^β b polarized. The energy E of a crystal transition is given by $E = w + D + S$, where w denotes the energy of the free molecule transition, D denotes a shift due to a change of phase, and S denotes a sum of various intermolecular integrals.¹⁰ The present calculations give values for E relative to $w + D$.

Calculations were made in three ways: (1) For an E_u upper state in D_{4h} ; these results are most applicable to metal derivatives and also to the metal-free derivatives for consideration of the Soret band which is relatively insensitive to metal substitution. (2) For a B_{1u} upper state in D_{2h} (m -polarized). (3) For a B_{2u} upper state in D_{2h} (l -polarized). The results of (2) and (3) can be corrected for crystal mixing of upper states of similar crystal symmetry. When the B_{1u} and B_{2u} upper states have the same energy this procedure then becomes identical with the D_{4h} method.¹

The formal relation between the D_{4h} and D_{2h} methods is made clear in the Appendix (p. 174). It is seen later that, as far as the location of the crystal components is concerned, there is little to choose between the methods. Of the two, the D_{2h} method is the simpler and is therefore to be preferred. However, when intensities are to be considered there is a

TABLE 1. Dipole sums for phthalocyanine calculated by the Ewald-Kornfeld method ($\text{cm.}^{-1} \text{ \AA}^{-2}$).

Interaction type	Equivalent molecules	Inequivalent molecules	Interaction type	Equivalent molecules	Inequivalent molecules
$l-l$	2458	60	$l-n$	-291	256
$m-m$	-1121	-430	$n-l$		
$n-n$	-1328	-460	$n-m$	-3654	29
$l-m$	-118	-291	$m-n$		
$m-l$					

small difference between the two methods. Of course, when the components are split by intramolecular forces the D_{2h} method can be used.

The results for the dipole sums are given in Table 1. Calculated energies and relative

⁹ Born and Bradburn, *Proc. Camb. Phil. Soc.*, 1943, **39**, 104.

¹⁰ Craig and Walsh, *J.*, 1958, 1613; and references therein.

TABLE 2. *Calculated energies and relative intensities of bands in a metal-free phthalocyanine crystal.* (The energy is expressed in $\text{cm.}^{-1}/M^2$ and is relative to $w + D$).

Polarization	In D_{4h} (E_u molecular level)			In D_{2h}	
	Energy	Relative intensity	Molecular level	Energy	Relative intensity
<i>a</i>	2560	0.04	B_{2u}	2518	0.06
<i>c</i>	"	0.46	B_{2u}	"	0.44
<i>a</i>	-1592	0.24	B_{1u}	-1551	0.22
<i>c</i>	"	0.02	B_{1u}	"	0.04
<i>b</i>	2408	0.003	B_{2u}	2398	0.001
<i>b</i>	-700	0.24	B_{1u}	-691	0.24

intensities of crystal bands are given in Table 2. The *a* and *c* polarized bands fall at the same energy in each case.

EXPERIMENTAL

The polarized spectra of phthalocyanine crystals have been observed at 90° and 300°K . The crystals were prepared by vacuum-sublimation and were mounted on fused silica discs. Because of the small dimensions of suitable crystals, the spectra were taken with the aid of a microscope with reflecting optics. For the spectra taken at liquid-air temperature the crystals were mounted in a cell which could be attached to the microscope stage. The light from the microscope was collimated and passed through a Wollaston prism before reaching the slit. In this way two oppositely polarized components of the spectrum were recorded on the plate. On use of a high-intensity carbon arc as the source and slit widths of 50μ , exposure times on the E1 Hilger large quartz spectrograph varied from 5 to 40 min. For the Soret band a 150-watt high-pressure xenon lamp was used as the source, and exposure times were between 10 sec. and 3 min. The third system was not penetrated. The plates were microphotometered on a Hilger Recording microdensitometer. A neon arc was used for calibration.

Relative crystal thicknesses were measured with an Ehringhaus rotatable compensator.

RESULTS

Microphotometer traces of the spectra are shown in Fig. 2. No sharpening of the bands occurred at liquid-air temperature.

A schematic representation of the observed $15,000 \text{ cm.}^{-1}$ system is shown in Fig. 3(e) in which the bands for the crystal are shown in the correct relationship with the bands for solutions, indicated by arrows.

In order to compare the calculated values with experiment it is necessary to determine the effective transition moment to be associated with each transition. The total intensity under each of the first two peaks in the free phthalocyanine spectrum corresponds to an oscillator strength $f = 0.52$, $|M| = 1.27 \text{ \AA}$, $M^2 = 1.62 \text{ \AA}^2$. The use of the total oscillator strength, $2f$, is most justified when the band in solution is not split. When, as in the $15,000 \text{ cm.}^{-1}$ region of the spectrum of the metal-free phthalocyanine, there are two distinct bands in the spectrum of solutions it seems best to consider each band separately, *i.e.*, each with $f = 0.52$. This results in a much lower separation of the components in the spectrum of the crystal than that calculated with a strength of 1.04.

The results of the calculations may be applied to the group of compounds having similar crystal structures to the metal-free phthalocyanine, *e.g.*, to various metal derivatives. In addition to the system near $15,000 \text{ cm.}^{-1}$ the Soret band can also be considered. In this work only the metal-free compound is discussed in detail, but the results in Tables 1 and 2 can be applied to the other compounds without great difficulty.

The predictions for the $15,000 \text{ cm.}^{-1}$ system in metal-free phthalocyanine are shown in Fig. 3.

Figs. 3(a) and 3(b) assume that the total intensity is concentrated at a point and, as expected, the predicted spread ($13,000 \text{ cm.}^{-1}$) of the bands is much greater than that observed (1860 cm.^{-1}).

From Table 2, as from Figs. 3(a) and 3(b), it is clear that very little change is brought about by adopting the D_{4h} rather than the simpler D_{2h} approach. Thus, in Fig. 3 the separation of

the *ac* polarized transitions is increased from 4069 cm^{-1} in (*b*) to 4152 cm^{-1} in (*a*); the separation of the *b* polarized transition is increased from 3089 cm^{-1} in (*b*) to 3108 cm^{-1} in (*a*). When intensities in the crystal are considered, Table 2 shows that the two methods again give very similar results. This adequacy of the D_{2h} treatment to discuss a D_{4h} case is expected to be moderately general and to be valid whenever there is an appreciable separation of energy between similarly polarized crystal transitions arising from oppositely polarized molecular transitions. As expected on general grounds, the effect of changing from D_{2h} to D_{4h} is to push similarly polarized transitions very slightly further apart.

When the intensity is divided between the two bands of the spectra of the solution, two predictions are possible depending upon whether the lower-energy transition is to B_{1u} or to a B_{2u} upper state. With $M^2 = 0.7$ for each band (as taken previously⁶) the predictions for the two possibilities are shown in Figs. 3(*c*) and 3(*d*). Although neither prediction agrees exactly with the observed spectrum, the better agreement is obtained if the lower-energy transition for the solution is to an upper state which is of B_{2u} symmetry. It must be remembered that in compiling Fig. 3 it has not been possible to determine the variation in D on going from solution to crystal, and this correction must be made when the information becomes available. Since the effect would be to shift all the predicted bands equally to different energies the comparison with experiment may still be made safely. For an intense transition the change due to D is expected to be small compared to S (Craig¹¹).

The differences between the predicted [Fig. 3(*d*)] and observed [Fig. 3(*e*)] spectra are three-fold: (i) the order of the four bands, (ii) the energy separating the bands, and (iii) the intensity of the bands.

(i) The two components of lower energy appear in the predicted sequence but the other two do not. The further refinement of the theory, by taking into account interactions between appropriate upper states arising from the 15,000 cm^{-1} and the 28,000 cm^{-1} systems (and possibly higher-energy systems also) may remove this discrepancy.

(ii) The separations of the various bands are of the right order of magnitude, especially for the lower-energy pair and the overall spread of the four bands. This is almost all that can be expected of the theory in its present form. The prediction of both the spread and the separations of the bands varies directly with the value chosen for M^2 . The total intensity in the 15,000 cm^{-1} region corresponds to $M^2 = 3.2$, and this choice for M^2 results in a spread such as is shown in Figs. 3(*a*) and 3(*b*) which would be reduced by perhaps 1000 cm^{-1} upon removing the point-dipole approximation. However, the spread would still be in excess of that observed. Consideration of this and of the splitting of the lowest-energy band shows that the choice of $M^2 = 0.7$ for each band gives better agreement with the observed spectrum [Fig. 3(*c*), 3(*d*), and 3(*e*)]. This choice for M^2 was based upon the rather arbitrary conclusion drawn from the appearance of the spectrum of the solution in which each band appeared to be about 300 cm^{-1} wide. The remaining intensity was distributed over other regions of the spectrum and was disregarded. Since the phthalocyanine spectrum has two very sharp peaks, the choice for M^2 was made more easily than would have been the case for a system which showed only one broader band.

The separation of purely electronic from vibronic bands has been discussed by others.¹¹ The occurrence of both lattice and intramolecular vibrational broadening in the crystal makes exact predictions of the spectrum of the crystal difficult, as does the use of values for M^2 based purely on spectra taken in solution. The numerical application of the theory in its present form is limited by the difficulty in assigning a value to M^2 .

(iii) Differences between predicted and observed intensities occur in both polarizations and in this respect the present theory is inadequate. The further refinement mentioned in (i) should lessen the discrepancies, but is not expected to remove them completely.

In the 28,000 cm^{-1} system in the metal-free phthalocyanine crystal (Fig. 2), three components are observed, spread over 2900 cm^{-1} . The fourth (*b* polarized) component is presumably at higher energies and buried beneath the next system. The total spread is therefore likely to be greater than 2900 cm^{-1} , *i.e.*, rather greater than that observed in the 15,000 cm^{-1} system. The splitting in the two systems appears to be in the same sense, *e.g.*, the component at lowest energy is *ac* polarized, the next *b*, and the next *ac* polarized. This is consistent with the assignment of the upper states of both systems as $B_{1u} + B_{2u}$ in D_{2h} . Only the beginning of the

¹¹ Winston, *J. Chem. Phys.*, 1951, **19**, 156; Craig, *J.*, 1955, 2302; Simpson and Peterson, *J. Chem. Phys.*, 1957, **26**, 588.

system at energies greater than about 31,000 cm^{-1} has been observed. The observations are again consistent with a pair of upper states which are similar to the lower-energy states in symmetry. Such conclusions agree with the expectations based on molecular-orbital theory (Fig. 4).

A comparison is possible between the factor-group (Davydov) splittings calculated in the present work by using the Ewald-Kornfeld summation over the whole crystal and those calculated previously⁶ by using a direct summation method over a sphere of 20 Å radius. On taking $M^2 = 0.7$ (as was done previously) the factor-group splittings between oppositely polarized components are now calculated as 196 and -595 cm^{-1} ; previously they were found to be 280 and -860 cm^{-1} . In view of the large variations which result from varying choices for M^2 , this difference between the two methods of summation is small. The sense of the previous results is confirmed, as is the magnitude to less than 50%. However, the hope expressed earlier⁶ that the calculations by the present theory of the sign of the factor-group splitting would provide a criterion for the experimental assignment of the polarization of the transition has now been shown to be false. In one of the present cases the calculated sign is opposite to that observed. In this respect also the theory needs to be improved.

In conclusion, it is clear that the theory in the form used, without consideration of the interaction between the various systems at 15,000 cm^{-1} , 28,000 cm^{-1} , etc., is at best semi-quantitative. The greatest difficulty arises in determining what value is to be given to M^2 , and the resulting errors may be greater than 100%. Errors also arise from the point-dipole approximation and from the neglect of the interaction with systems of higher energy. However, even if these were completely eliminated the difficulty over M^2 still remains and would still be the cause of greatest inaccuracy.

Thus, only in its qualitative features is the present theory completely successful (*i.e.*, the number of components in the crystal is correctly predicted) and for this no numerical computation is necessary. Improvements in the theory should include quantitative consideration of (i) the interaction in the crystal of all molecular systems, (ii) an exact consideration of the effect of removing the point-dipole approximation, and (iii), most importantly, the factors which broaden the absorption bands.

APPENDIX

The method of treating a doubly degenerate level in D_{4h} may be regarded as composed of two stages: (i) in which the two levels are regarded as independent and as terminating transitions which are oppositely polarized in D_{2h} , followed by (ii) interaction between crystal levels of similar symmetry. In this way the relation between the D_{2h} and D_{4h} methods becomes clear.

For an excited degenerate state the wave function Φ_i can be written

$$\Phi_i = c_1\gamma_l^\alpha + c_2\gamma_l^\beta + c_3\gamma_m^\alpha + c_4\gamma_m^\beta \quad ; \quad i = 1, 2, 3, 4,$$

where γ^α denotes a crystal function for the state which arises in a transition polarized along the l axis. The energies of the four levels, Φ_i , are given by the roots of the equation

$$\begin{vmatrix} X + I_{ll}^\alpha & 0 & J_{lm}^\alpha & 0 \\ 0 & X + I_{ll}^\beta & 0 & J_{lm}^\beta \\ J_{lm}^\alpha & 0 & X + I_{mm}^\alpha & 0 \\ 0 & J_{lm}^\beta & 0 & X + I_{mm}^\beta \end{vmatrix} = 0 \quad \dots \quad (1)$$

where $X = w + D - E$

$$I_{ll}^\alpha = \sum_{\text{equiv.}} I_{ll} + \sum_{\text{inequiv.}} I_{ll}$$

$$I_{ll}^\beta = \sum_{\text{equiv.}} I_{ll} - \sum_{\text{inequiv.}} I_{ll}$$

$$J_{lm}^\alpha = \sum_{\text{equiv.}} J_{ml} + \sum_{\text{inequiv.}} J_{ml}$$

and

$$J_{lm}^\beta = \sum_{\text{equiv.}} J_{ml} - \sum_{\text{inequiv.}} J_{ml}$$

Equation (1) can be rewritten

$$\begin{vmatrix} X + I_u^\alpha & J_{lm}^\alpha \\ J_{lm}^\alpha & X + I_{mm}^\alpha \end{vmatrix} \begin{vmatrix} X + I_u^\beta & J_{lm}^\beta \\ J_{lm}^\beta & X + I_{mm}^\beta \end{vmatrix} = 0 \quad \dots \quad (2)$$

In equation (2) $X (= w + D - E)$ will differ slightly in one factor from its value in the other owing to changes in w , which have been allowed for in compiling Fig. 3, and changes also in D , which can be neglected.¹⁰ When the J terms are negligible, the solutions for X are given by I_u^α , I_{mm}^α , I_u^β , and I_{mm}^β and these are just the values obtained from a treatment which consists only of stage (i). Stage (ii) alters the results obtained from stage (i) by an amount which depends on the magnitudes of J_{lm}^α and J_{lm}^β . Numerical values of the I and J terms may be derived from Table 1, *e.g.*, $I_u^\alpha = 2518$; $I_{mm}^\alpha = -1551$, but $J_{lm}^\alpha = -409$ only, and this is not large enough to affect the energy values greatly.

In order to calculate intensities it is necessary to find c_1 , c_2 , c_3 , and c_4 in each case. For α states the ratio of the intensities of the a polarized components is given by

$$(c_1.la + c_3.ma)^2 / (-c_3.la + c_1.ma)^2$$

where la denotes the cosine of the angle between the l molecular and the a crystal axis.

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