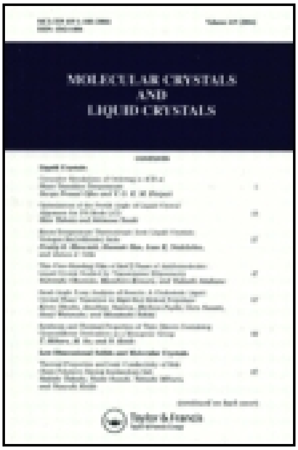

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Triplet Exciton Effects in Single Crystals of *p*-Diiodobenzene[†]

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Abstract—The singlet-triplet ($S \rightarrow T_1$) absorption spectrum of single crystals of *p*-diiodobenzene was measured in polarized light at 4.2°K. The crystal spectrum provides an example of intermediate to strong vibronic coupling. The three allowed factor group states B_{1u} (**a**), B_{2u} (**b**) and B_{3u} (**c**) are observed to bracket a range of 121 cm^{-1} with $E_a - E_b = -121$ cm^{-1}, $E_a - E_c = -6$ cm^{-1}. The forbidden level (A_u) was not identified.

The polarization ratios do not provide a unique molecular polarization, but it is likely that the transition is polarized in the plane of the long and normal molecular axes. This implies that only two spin-orbital coupling routes are active in the free molecule.

A theoretical account of our observations of the triplet exciton band is also described.

Introduction

The optical properties of organic molecular crystals have tended to manifest characteristics that relate to the electronic structure both of the molecules and of the crystal. Up to the present such studies have focussed on the readily obtainable spectra of multiplicity allowed states of the molecule, namely the singlet-singlet transitions that appear in the visible and near ultraviolet spectral regions. These transitions have oscillator strengths in the neighborhood of 1–10^{-3} and since molecular crystals are usually about 5 molar, pathlengths of *ca.* 0.01–1 μ are appropriate to their study. The polarized absorption and emission between singlet states of

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organic crystals has led to a variety of molecular information[1, 2, 3] such as the symmetries of the electronic wavefunctions and the vibrational-electronic coupling routes. Purely crystal effects such as, the correctness of the Davydov description of crystal wavefunctions, the approximate validity of a dipole-dipole model for the Coulomb interactions between aromatic molecules, and the usefulness of an exciton-like description of excitation energy in such crystals, have been confirmed in a large number of cases.[1, 2, 3]

No comparable studies have been reported for the singlet-triplet ($S \rightarrow T_1; \pi \rightarrow \pi^*$) transitions of aromatic hydrocarbons.† It is likely that the polarized absorption spectra of such single crystals will yield not only the same type of information as is being gathered for singlets, but also details of the spin-orbital coupling mechanisms that permit these transitions to occur.

The oscillator strengths for $S \rightarrow T_1$ transitions of aromatic hydrocarbons are in the range 10^{-8}–10^{-9} so crystals having thicknesses in the range 10 cm or longer will be required for direct absorption measurements of their triplet states. It has been known for some time that halogen substituents on polyacenes will enhance the absorption intensity of the $S \rightarrow T_1$ transitions by factors up to about 10^4.[4] The intensity enhancement derives from an increased spin-orbital coupling for aromatic optical π-electrons somehow associated with the heavy atom substituent. Even for the case of *p*-diiodobenzene the $S - T_1$ oscillator strength ($\sim 10^{-6}$) is very much less than for a spin-allowed transition. It was therefore apparent that a dipole-dipole description of the crystal exciton states would be inappropriate.

The notion of a triplet exciton band having a width comparable with a singlet band first arose through the theoretical work of Dexter[5] and subsequently by Merrifield.[6] The experimental results and theoretical estimates by Nieman and Robinson[7] then led to the conclusion that the exchange interactions in molecular

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† *Note added in proof*—Hanson and Robinson [*J. Chem. Phys.*, **43**, 4174 (1965)] have recently photographed a 4 cm thick melt of naphthalene at 4.2°K and have tentatively identified factor group components in the $S \rightarrow T^1$ absorption spectrum.

crystals should be on the order of a few cm^{-1}, and that triplet exciton band widths could be expected to be in the range 10–100 cm^{-1}. Recent calculations by Jortner, Rice, Katz and Choi,[8] in which the exchange interactions were computed for certain polyacene crystals, have indicated that Davydov splittings of *ca.* 1–10 cm^{-1} may be expected in the vibronic bands of the $S-T_1$ spectra of these crystals. It is assumed[8] that the exchange energy is distributed over the vibronic bands in the spectrum according to their vibrational overlap factors; i.e., a weak coupling model is assumed.

In the course of the present work we have examined the absorption spectra of *p*-dichloro, *p*-dibromo and *p*-diiodobenzene single crystals. The first two materials have very sharp spectra at 4.2° K but they do not exhibit any strong crystal effects other than band shifts;[9] the spectrum of *p*-diiodobenzene, which is the subject of this paper, is considerably broader but it does show some remarkable crystal effects. Thus the aim of this article is to describe the $S \rightarrow T_1$ absorption spectrum of the *p*-diiodobenzene single crystal; to compare this with the $S \rightarrow T_1$ spectrum of the isolated molecule; and to interpret the results on the basis of a factor group model for crystalline triplet states.

Crystal Structure

The crystal structure of *p*-diiodobenzene has been determined by Struchkov.[10] The crystal belongs to the space group $P_{bca} \equiv D_{2h}^{15} \equiv V_h^{15}$ with four molecules in the unit cell. The *ab* and *ac* projections of the unit cell are shown in Fig. 1. As can be seen from the figure, the molecular planes make only a small angle (20°) with the *ac* plane. The long axis of the molecule (through the halogens) makes a 32° angle with the *a* crystal axis.

The dimensions of the unit cell are: $a = 17.008$ Å, $b = 7.321$ Å, $c = 5.949$ Å. The squares of the projections of the long (L), short (M), and normal (N) molecular axes with the three crystallographic axes are given in Table 1.

TABLE 1

	a	b	c
L	0.722	0.0073	0.271
M	0.277	0.111	0.622
N	0.011	0.880	0.107

We will use the convention that the application of the factor group operations C_2^c, C_2^b, and C_2^a on the site I (0, 0, 0) generates the sites II ($a/2$, 0, $c/2$), III (0, $b/2$, $c/2$) and IV ($a/2, b/2$, 0), respectively.

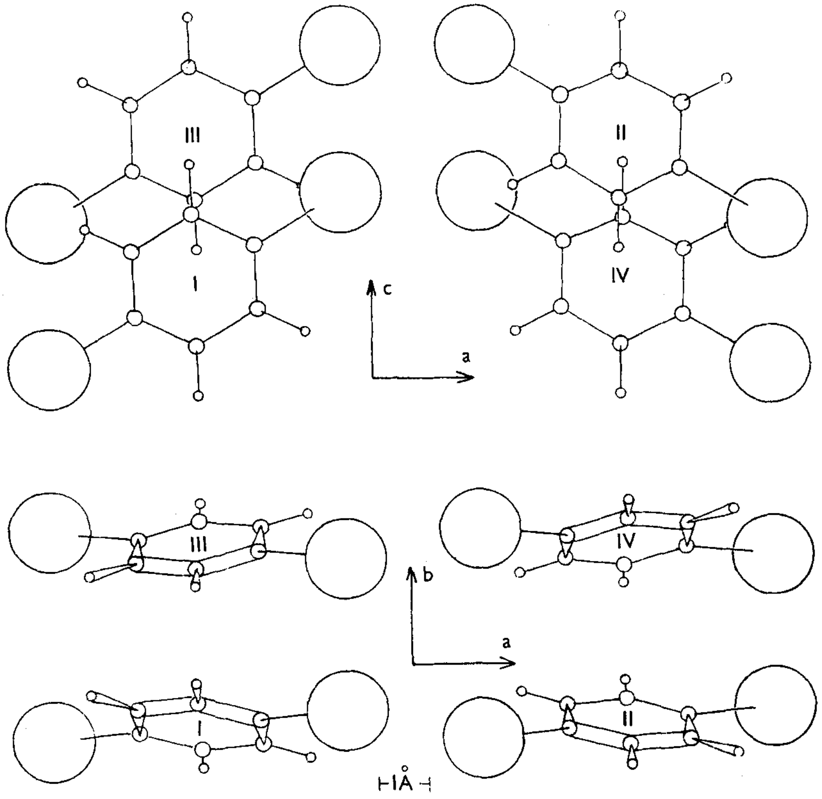


Figure 1. Crystal structure of *p*-diiodobenzene. Upper, projection on *ac*. Lower, projection on *ab*.

Factor Group Analysis

In an orthorhombic crystal having space symmetry P_{bca} the wave-functions for $\mathbf{k}=0$ states belong to representations of the factor group D_{2h}. The molecular site symmetry is C_i. The site functions, transforming like the jth representation of C_i have the following form:

$$\Phi^j_m(R) = \sum_{\mu} \mathbf{A}\psi^{(m)}(R_\mu)\,\psi^{(0)}(S_\mu)\ldots\psi^{(0)}(W_\mu)\prod_{R\nu\neq R\mu}^{n(u-1)}\psi^{(0)}(R_\nu) \tag{1}$$

where $R_\mu, S_\mu, \ldots W_\mu (\equiv n)$ are the n sites of the μth unit cell of a crystal containing u unit cells. The product is assumed to be antisymmetric to the interchange of electrons amongst the molecular wavefunctions ψ. The mth molecular state $\psi^{(m)}$ is the one that correlates with the appropriate site state j. In this particular case m could not be a u-state if j were a g-state. The molecular ground state function for molecule R_ν is written as $\psi^{(0)}(R_\nu)$ The factor group state, Ψ^α_{jm}, that belongs to the αth representation of the factor group and is derived from the mth molecular state which in turn becomes a site of type j, is given by:

$$\Psi^\alpha_{jm} = N^{-\frac{1}{2}}\sum_{F}\chi^{(\alpha)}(F)\,\mathbf{T}_F\Phi^j_m(R_\mu) \tag{2}$$

where $\chi^\alpha(F)$ is the character of the αth factor group representation for the symmetry operation F in the factor group. $\mathbf{T}_F$ is the operator corresponding to the symmetry operation F. The effect of the operator $\mathbf{T}_F$ on a product function such as (1) is as follows:

$$\mathbf{T}_F\Phi^j_m(R) = A\psi^{(m)}(FR_\mu)\,\psi^{(0)}(FS_\mu)\ldots\psi^{(0)}(FW_\mu)\prod_{R\nu\neq R\mu}\psi^{(0)}(FR_\nu) \tag{3}$$

$$= \Phi^{(j)}_m(FR) \tag{4}$$

The operation F acting on the site R transforms it in three ways depending on the nature of F:

(a) If F belongs to the site group s, then:

$$\Phi^j_m(FR) = \chi^{(j)}_s(F)\,\Phi^{(j)}_m(R) \tag{5}$$

(b) If F does not belong to the site group, then:

$$\Phi^j_m(FR) = +\Phi^j_m(S) \tag{6}$$

in this case F is a *rotational symmetry operation* and Eq. (6) is a definition of phase.

(c) If F does not belong to the site group, but F corresponds to a *reflection plane*, then:

$$\Phi^{j}_{m}(FR) = \chi^{(m)}_{M}(\mathrm{i})\,\Phi^{(j)}_{m}(T) \tag{7}$$

The results (5), (6) and (7) assume that the molecular ground state is totally symmetric. $\chi^{(m)}_{M}(\mathbf{i})$ is the character of the mth representation in the molecular point group under the operation of inversion, **i**.

For the diiodobenzene crystal the factor group is isomorphous with the point group D_{2h}, and consists of the symmetry operations shown in Table 2; that table also shows the molecular interchanges

TABLE 2 Interchanges of Molecules Occurring Under The Various Factor Group (D_{2h}) Symmetry Operations

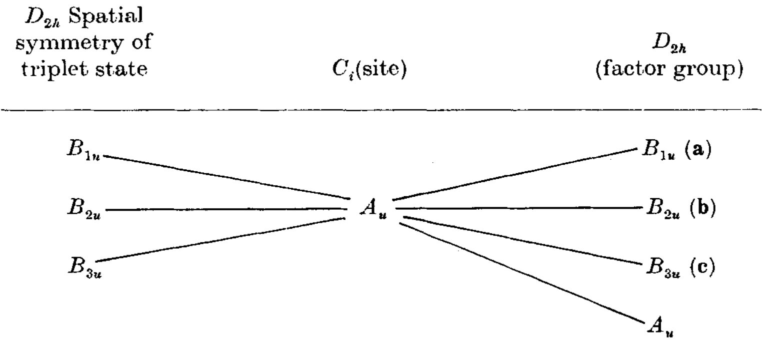
Symmetry operation		Interchanges of molecules
E	screwaxes	$\mathrm{I} \rightleftarrows \mathrm{I}$; $\mathrm{II} \rightleftarrows \mathrm{II}$
$C_2^{(a)}$		$\mathrm{I} \rightleftarrows \mathrm{IV}$; $\mathrm{II} \rightleftarrows \mathrm{III}$
$C_2^{(b)}$		$\mathrm{I} \rightleftarrows \mathrm{III}$; $\mathrm{II} \rightleftarrows \mathrm{IV}$
$C_2^{(c)}$		$\mathrm{I} \rightleftarrows \mathrm{II}$; $\mathrm{III} \rightleftarrows \mathrm{IV}$
i		$\mathrm{I} \rightleftarrows \mathrm{I}$; $\mathrm{II} \rightleftarrows \mathrm{II}$
σ_{bc}	glide planes	Same as for screwaxes normal to crystal planes
σ_{ac}		
σ_{ab}		

that occur on application of these unit cell operations. The correlations between the molecular point group (D_{2h}), the site group (C_i), and the factor group (D_{2h}) are given in Table 3. From Eq. (2), and the information in Table 3 the $\mathbf{k} = 0$ factor group functions belonging to molecular states m (of ungerade parentage) can be written down as follows:

$$\Psi_{a_u m}\begin{bmatrix} B_{1u} \\ B_{2u} \\ B_{3u} \\ A_u \end{bmatrix} = \tfrac{1}{2}\left[\Phi^{a_u}_{m}(\mathrm{I}) \begin{array}{c} - \\ - \\ + \\ + \end{array} \Phi^{a_u}_{m}(\mathrm{II}) \begin{array}{c} - \\ + \\ - \\ + \end{array} \Phi^{a_u}_{m}(\mathrm{III}) \begin{array}{c} + \\ - \\ - \\ + \end{array} \Phi^{a_u}_{m}(\mathrm{IV})\right] \tag{8}$$

TABLE 3 Correlations Between Electric Dipole Allowed States of the Molecule and the Resulting Factor Group States

The factor group states that give electric dipole allowed transitions to the A_g ground state are indicated by **a**, **b** or **c** according to their polarization



The foregoing treatment follows the approach of Craig and Walsh[11] but is different from that used by Fox and Schnepp,[12] and later by Nieman and Robinson.[7] The splitting between any two states belonging to factor group representations Γ_i and Γ_j is:

$$\Delta E_{ij} = \langle \Psi_m^{a_u}(\Gamma_i)|\mathscr{H}|\Psi_m^{a_u}(\Gamma_i)\rangle - \langle \Psi_m^{a_u}(\Gamma_j)|\mathscr{H}|\Psi_m^{a_u}(\Gamma_j)\rangle \tag{9}$$

where $\mathscr{H}$ is the full crystal Hamiltonian without spin but including the pair-wise electrostatic potential V that takes into account the interactions between electrons in different molecules. The substitution of (8) into (9) yields, in this case:

$$\left.\begin{aligned} \Delta E_{\mathbf{ab}} &= 2\langle \Phi_m(\mathrm{I})|V|\Phi_m(\mathrm{IV}) - \Phi_m(\mathrm{III})\rangle \equiv 2(V_{14} - V_{13}) \\ \Delta E_{\mathbf{ac}} &= 2\langle \Phi_m(\mathrm{I})|V|\Phi_m(\mathrm{IV}) - \Phi_m(\mathrm{II})\rangle \equiv 2(V_{14} - V_{12}) \\ \Delta E_{\mathbf{bc}} &= 2\langle \Phi_m(\mathrm{I})|V|\Phi_m(\mathrm{III}) - \Phi_m(\mathrm{II})\rangle \equiv 2(V_{13} - V_{12}) \end{aligned}\right\} \tag{10}$$

Each of the site functions in (10) is an antisymmetrized product function of one-electron molecular orbitals. The triplet spin functions which are assumed to be integrated out of Eq. (10) have imposed a restriction on the permutation symmetry of the spatial parts such that the interactions V_{ij} reduce to exchange interactions between electrons in atomic orbitals on different molecules.[6] Numerical answers for the V_{ij} have been obtained when the orbitals are exclusively $2p\pi$ carbon type.[8] In the present example a large number of possible interactions are possible due to the proximity of the iodine atoms to each other, and to a variety of carbon and hydrogen atoms. Furthermore the actual hydrogenic type of orbital (or orbitals) of iodine that might be involved in the crucial overlap interactions are not known *a priori*: all that is known from experiment (and this indirectly) is the symmetry of the singlet states from which the $S \rightarrow T$, intensity is obtained.

In summary, if the differences between the V_{ij} are large enough, there should be three energetically distinct factor group states polarized along the mutually perpendicular crystallographic axes $\mathbf{a}(B_{1u})$, $\mathbf{b}(B_{2u})$, and $\mathbf{c}(B_{3u})$. The experimental measurement of each of these three energies should provide values for the differential interaction between each molecule in the cell and two nearest neighbors.

In the foregoing factor group analysis of the $\mathbf{k} = 0$ states of the triplet exciton band the influence of intra and intermolecular spin effects has been ignored. To a first approximation this should be a valid neglect since even with iodine substituents on benzene the spin-orbital coupling does not appreciably influence the spatial eigenfunctions of the pure triplet state. The influence of such effects on the intensities of the factor group components is another matter, and this will be discussed in a later paper.

Experimental

Special precautions were taken to ensure that the crystals were of high purity, as even extremely small concentrations of impurities having a singlet-singlet absorption in the region of the singlet-triplet absorption of *p*-diiodobenzene will seriously complicate the spectra due to the very weak strength of the singlet-triplet transition.

The starting material was Eastman-Kodak 1102 *p*-diiodobenzene which was repeatedly recrystallized from absolute ethanol until colorless. The material was then extensively zone refined in an atmosphere of 2 mm of nitrogen prior to crystal growth under vacuum in a Bridgmann furnace. In initial zone purifications, it was noticed that the molten zones became colored red if exposed to daylight; thus, subsequent zone purifications were performed in the dark. The final single crystals were colorless and stable in air and showed no light sensitivity as did the melt.

The single crystals of *p*-diiodobenzene exhibited a perfect *bc* cleavage (confirmed by X-Ray Counter Diffractometry), and orientation was determined conoscopically (the optic plane is 001). Thin cleaved sections of approximately 0.5 mm thickness were used to determine the *b* and *c* polarized spectra. Thinner sections (~ 0.2 mm) cut and benzene polished parallel to the *ab* face provided the *a* polarized spectrum. The solution spectrum was taken in a 50% ethanol–ether rigid glass at 77° K.

The crystals were mounted on the cold finger of a conventional liquid helium dewar. Experiments performed with samples completely immersed in liquid helium showed no considerable sharpening of the spectra over these taken using the dewar. The spectra were recorded on a $\frac{3}{4}$ meter Czerny-Turner Scanning Spectrometer (Spex-1500). A Bausch and Lomb Deuterium arc lamp provided a convenient continuous light source in the region 3750–3000 Å.

Results and Discussion

A primary problem in obtaining undistorted singlet-triplet absorption spectra of aromatic compounds is to separate the $S \rightarrow T$ absorption from the background absorption arising from the long wavelength tail of the normal singlet absorption. In the case of *p*-diiodobenzene this is particularly difficult as the spectra are very broad and the background absorption is very strong even at low temperatures.[4] This is illustrated in Fig. 2 which shows a plot of optical density of a solution of *p*-diiodobenzene in a rigid glass of 50% EtOH-Et_2O at 77° K. The dashed lines are extrapolations

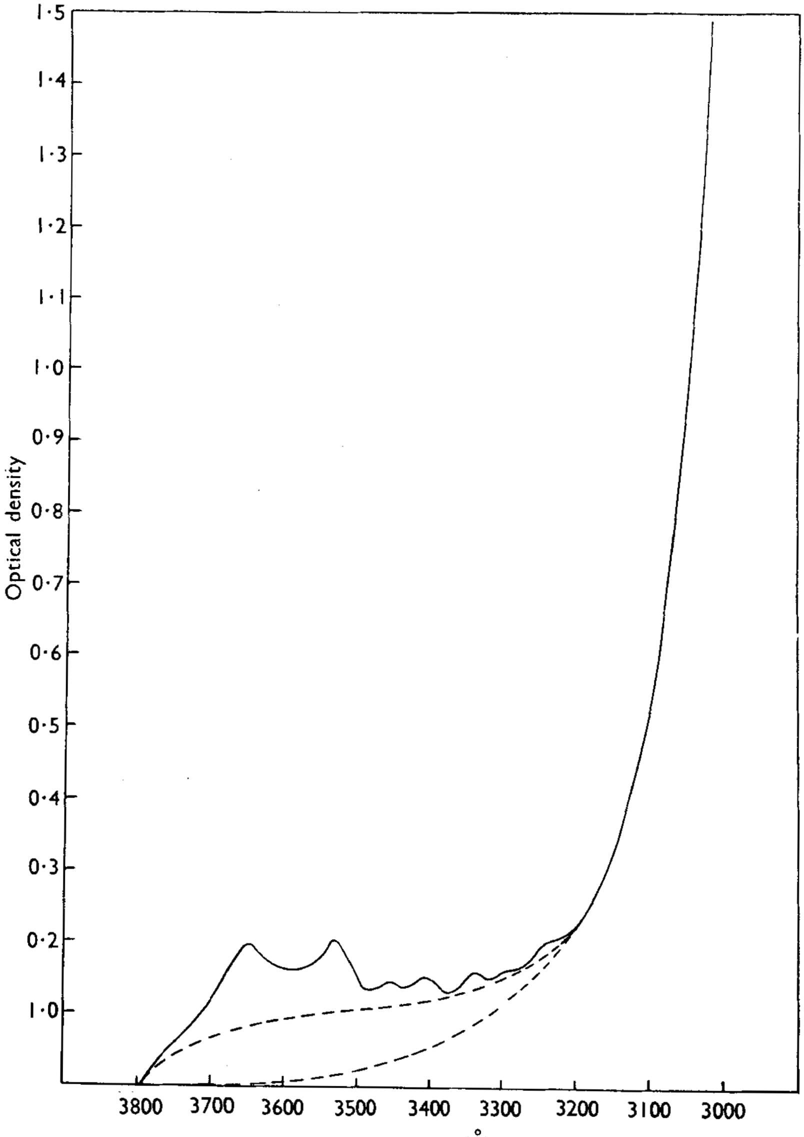


Figure 2. Near UV absorption of *p*-diiodobenzene. In 50% EtOH-Et_2O at 77°K, c = 0.146 M, l = 1.3 cm.

which represent maximum and minimum estimates of the normal absorption in the region of the $S \rightarrow T$ absorption. The lower dashed line represents the Gaussian type of extrapolation more commonly employed. However, it is our opinion that the upper dashed line more nearly represents the true shape of the background absorption even though the shape is non-Gaussian.

The background absorption for the crystal spectra taken at 4.2° K is considerably reduced over the solution spectrum at 77° K for light polarized parallel to the **b** and **c** crystal directions, but is still very strong in the **a** direction. Thus there is no problem in obtaining the true **b** and **c** polarized $S-T_1$ crystal spectra, but the strong **a** polarized background has prevented us from obtaining the $S-T_1$ spectrum for wavelengths less than 3500 Å, even for the thinnest crystals we have been able to obtain (0.2 mm) with faces perpendicular to the *bc* cleavage face.

The magnitudes of the background absorption (optical densities) for light polarized parallel to the **a b** and **c** crystal direction are in the ratios $a:b:c$ of 2.4 : 1 : 1.1 taken at the center of the $S-T_1$ band ($\sim$3500 Å).

The corrected $S-T_1$ solution spectrum is given in Fig. 3. The spectrum was taken for a solution whose concentration was 0.146 M (corrected for solvent contraction at 77° K) and for a pathlength of 1.3 cm. The total integrated intensity yields an oscillator strength, $4.31 \times 10^{-9} \int \epsilon d\nu$, of 4.3×10^{-6}. The first two bands of the spectrum contain 81% of the total intensity. (*Note:* By assuming a background absorption as in the lower dashed curve in Fig. 2, the percentage of the total intensity residing in the first two bands is still 75%.)

The solution spectrum is much too broad to obtain the excited state vibrational frequencies, and these are obtained from the **c** polarized spectrum, and by analogy with the differences in excited triplet and ground state frequencies of *p*-dibromobenzene. The pertinent frequencies are collected in Table 4.

Using the frequencies in Table 4, a vibrational analysis of the solution spectrum is presented in Table 5.

The same fundamentals, overtones and combinations assumed

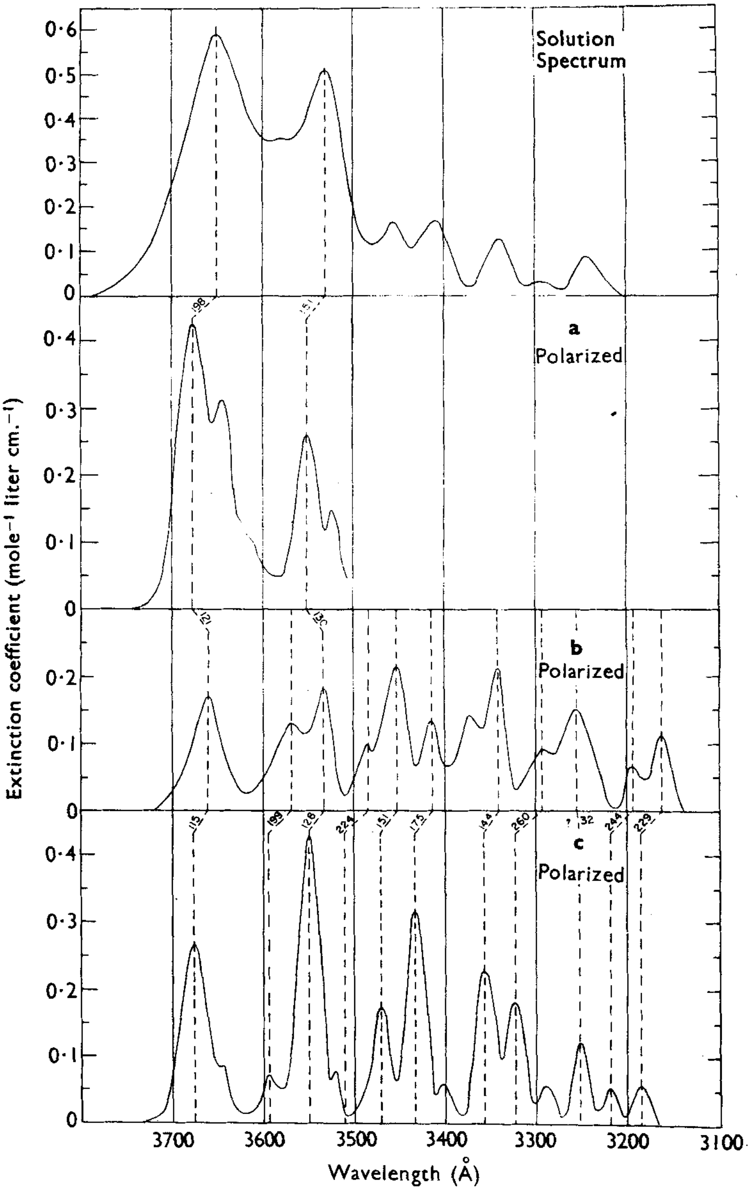


Figure 3. Singlet-triplet absorption in *p*-diiodobenzene. Upper, solution spectrum at 77°K. Lower, **a**, **b**, and **c** polarized crystal spectra at 4.2°K [$\epsilon = (OD)/(3cl)$].

TABLE 4

	p-Dibromobenzene			p-Diiodobenzene (from c polarized spectrum)		
	Ground state[13]	Excited state[14]	% diff.	Ground state[13]	Excited state	% diff.
ν_4 a_g	708 cm^{-1}	644	9.4	680	639	6.0
ν_5 a_g	1067	981	8.1	1044	968	7.2
ν_{10} b_{2g}	271	257	−5.2[a]	241	244	−1.2[1]

[1] In all probability this frequency does not change from the ground to the excited state, and the differences just represent experimental error.

in the vibrational analysis in Table 5 are exactly those which appear as the strongest bands in the corresponding sharp spectrum of p-dibromobenzene: furthermore the relative intensities are the same.[14]

TABLE 5 Vibrational Analysis of Solution Spectrum

% of total intensity	Å	cm^{-1}	Interpretation	Error (cm^{-1})
57.5	3651	27390	0, 0	
?	3580	27933	639	−96
23.5	3531	28320	968	−38
4.8	3455	28943	968 + 639	−54
5.7	3408	29343	2 × 96	+17
3.5	3337.6	29962	2 × 968 + 639	− 3
0.9	3293.2	30366	3 × 968	+72
2.7	3241.9	30846	3 × 968 + 639	−87

The a polarized crystal spectrum is shown in Fig. 3. As mentioned before, the spectrum below 3500 Å could not be obtained due to the intense, steeply rising background absorption. Another difficulty involved in obtaining the spectrum in the short wavelength region may very well be that the **a** polarized spectrum has the same Franck-Condon envelope as the solution spectrum with almost all of the intensity residing in the first two major bands; thus, one would only expect a very weak **a** polarized spectrum at wavelengths shorter than 3500 Å. The first two major bands of the **a** polarized spectrum have the same Franck-Condon envelope as the solution spectrum which is a very different situation than for the **b** or **c** polarized spectra. The vibrational analysis for the **a** polarized spectrum thus far obtained is given in Table 6.

TABLE 6

	Å	cm^{-1}	Interpretation	Error (cm^{-1})
VS	3677.5	27192	0, 0	
M	3645.0	27435	244	− 1
S	3552.0	28153	968	− 7
M	3524.5	28373	968 + 244	−31

The **b** and **c** polarized crystal spectra and the factor group splitting of the different vibronic states are presented in Fig. 3. The vibrational analysis of the **b** and **c** polarized spectra are given in Table 8.

For the **c** direction the error in the vibrational analysis is very small considering the diffuseness of the spectrum. The observed vibrational frequencies for the **c** polarized spectrum agree very well with those that would be expected by analogy with *p*-dibromobenzene (see Table 4), and are assumed to be the same as for the free molecule. The frequencies also agree within experimental error with these found in the **a** polarized spectrum.

Strong-Vibronic Coupling with 4 Molecules/Unit Cell

The purely electronic factor group wavefunctions are the Ψ_{jm}^{α} given in (8) with $\alpha = B_{1u}$, B_{2u}, B_{3u} and A_u. The associated vibrational functions $V^{\epsilon}_{\alpha r;}$ corresponding to the A_g site state and a

TABLE 8

	c Polarized					b Polarized				
	Å	cm^{-1}	Error	Interpretation		Å	cm^{-1}	$\Delta\nu$	E_b-E_c	E_b-E_c $-\Delta\nu$
S	3676.7	27198		0, 0	*M*	3661.2	27313	0	+115	+115
VW	3644	27442	0	244		Absent				
VW	3594.1	27823	−14	639	*W*	3568.6	28022	+ 70	+199	+129
VS	3549.8	28171	+ 5	968	*M*	3533.7	28299	+ 18	+128	+110
VW	3520	28409	− 1	968 + 244		Absent				
VVW?	3511.4	28479	+ 3	2 × 639	*VW*	3484	28703	+112	+227	+112
M	3470.0	28818	+ 1	968 + 639	*M*	3452.0	28969	+ 49	+151	+102
S	3433.4	29126	− 8	2 × 968	*W*	3412.9	29301	+ 52	+175	+123
W	3402	29394	+16	2 × 968 + 244		Absent				
	Absent			968 + 2 × 639	*W*	3372.7	29650	− 91		
S	3557.0	29789	−14	2 × 968 + 639	*M*	3340.8	29933	+ 45	+144	+ 99
M	3322.5	30098	− 3	3 × 968	*W*	3294	30358	+141	+260	+119
W	3290	30395	+17	2 × 968 + 2 × 639		Absent				
M	3251.6	30754	−13	3 × 968 + 639	*M*	3255	30722	−134	− 32	+102
W	3218	31075	+ 4	4 × 968	*W*	3193	31319	+134	+244	+110
W	3185	31397	−17	3 × 968 + 2 × 639	*M*	3162	31626	+131	+229	+ 98

gerade vibration of type r, are given by the same linear combinations as in (8). The vibronic exciton states are given by:

$$\mathscr{H}_{mr}(\alpha, \epsilon) = \Psi_{jm}^{\alpha} V_{\alpha r}^{\epsilon} \tag{11}$$

where $\epsilon = a_g$, b_{1g}, b_{2g}, b_{3g}, namely the four vibronic factor group representations that derive from an a_g site vibrational state. The signs in the factor group functions do not depend on the inversion symmetry. Including mechanical coupling between the vibrations the following result can be obtained for the energy of the crystal states derived from electronic state α and vibrational factor group state ϵ:

$$E_{mr}(\alpha, \epsilon) = \langle \Psi_m^\alpha | \mathscr{H}_e | \Psi_m^\alpha \rangle + \langle V_{\alpha r}^\epsilon | \mathscr{H}_v | V_{\alpha r}^\epsilon \rangle + \langle V_{\alpha r}^\epsilon | V | V_{\alpha r}^\epsilon \rangle \tag{12}$$

Transitions to vibronic states (α, ϵ) can only occur to the first approximation if ϵ is a totally symmetric factor group vibration. The complete Hamiltonian in this case is separable into an electronic part ($\mathscr{H}_e$), a vibrational part ($\mathscr{H}_v$), and the internuclear potential energy (V). The matrix element $\langle V_{\alpha r}^\epsilon | \mathscr{H}_v | V_{\alpha r}^\epsilon \rangle$ is v_r^α the energy of the ϵth factor group component of the rth vibrational mode in the αth factor group electronic state. The difference in energy between, say, the **b** and **c** polarized crystal vibronic states belonging to the same vibrational quantum number of the species r is:

$$\Delta E_{\mathbf{bc}} = \tfrac{1}{2}(V_{13} - V_{12}) + (\nu_r^{(\mathbf{b})} - \nu_r^{(\mathbf{c})}) \tag{13}$$

This result is essentially the same as the one quoted by McClure[15] for a dimer. It follows that the difference between the vibronic energies in the two polarizations should be equal to a constant: this constant, $\tfrac{1}{2}(V_{13} - V_{12})$ for $\Delta E_{\mathbf{bc}}$, is the purely electronic factor group splitting. Such a result is the same for all totally symmetric vibrations (factor group) in the spectrum. Equation (13) is in effect *a diagnostic test for strong coupling of molecular vibronic states.*

The factor group splittings ($E_b - E_c$) indicated in Fig. 3 do not vary in the same way as the vibronic intensities in the solution spectrum, as would be predicted by a weak coupling model.[17] In fact the crystal spectra show some other manifestations of strong coupling, and it was found to be convenient to use this formalism to interpret the spectrum even though the strong coupling criterion that the splitting be larger than the vibrational interval is not manifested. If one assumes that the free molecule vibrational frequencies are retained in the **c** polarized spectrum, then the error ($\Delta\nu$) in the vibrational analysis of the **b** polarized spectrum based on these same frequencies yields the change in frequency of the **b** component states from the free molecule frequencies. Neglecting the effects of the vibrational coupling energy, the change in frequency, $\Delta\nu$, when subtracted from the vibronic factor group splitting, $E_b - E_c$, should yield the purely electronic splitting, $E_b - E_c - \Delta\nu$, cf. Eq. (13). Values of this splitting are given in the last column of Table 8 and are found to be constant within experimental error.

The fact that the frequencies are larger than those in the free molecule are consistent with strong coupling, and in fact the totally symmetric vibration at 709 cm^{-1} (639 + 70) in the **b** polarized spectrum is close to the ground state frequency of 680 cm^{-1} (within experimental error) indicating extreme delocalization of excitation, or strong coupling.

Since the spectrum so clearly represents an approach to strong coupling, and since the strong coupling criteria (18) are not satisfied by the observed factor group components, we conclude that the A_u component of the factor group is removed from the three observed components by at least *ca.* 855 cm^{-1}. This would mean that the energy span of the factor group states is actually about 970 cm^{-1}, which would represent an approach to strong coupling in a band system whose intensity was mainly in vibrations of 968 cm^{-1}. In terms of the matrix elements V_{ij} the difference in energy between the A_u state and the other states is from Eq. (9):

$$E(A_u) - E(B_{1u}) = 2(V_{12} + V_{13})$$

$$E(A_u) - E(B_{2u}) = 2(V_{12} + V_{14})$$

$$E(A_u) - E(B_{3u}) = 2(V_{13} + V_{14})$$

If all the V_{ij} are positive, as previously assumed (9), their values will be in the range of 900 cm^{-1}.

The fact that the observed vibronic intensities (except possibly those in the **a**-direction) are different from those in the solution spectrum, represents a serious derivation from the simple strong coupling model outlined above. However, this model must only be regarded as a first approximation since it excludes the possibility of vibrational–electronic coupling between the various exciton states. This effect will lead to intensity rearrangements amongst the exciton states. The method of Fulton and Gouterman[18] automatically takes into account such interactions, and although their method applies only to dimers it is interesting to note the gross similarities between our spectra, and the computer simulated spectra of strongly coupled dimers, especially in regard to the retention of free molecule frequencies in the lowest energy exciton state.

The Polarization Direction

In a later paper we will present experimental evidence that the zero-field splitting of the triplet magnetic substates is less than $0.5\ \mathrm{cm}^{-1}$ in the case of dibromobenzene.[14] On this basis we extrapolate that the zero-field splitting in diiodobenzene is much smaller than the bandwidths of the $S \rightarrow T_1$ absorption, and also smaller than the crystal splittings. It follows that we may treat the three substrates of each vibronic level of the triplet state as though each behaved similarly in the crystal field, i.e., the spatial character of the wavefunction of T_1 is dominant. Thus the triply degenerate vibronic levels of T_1 are split by the crystal forces into four triply degenerate crystal states ($\mathbf{k}=0$). Since the state T_1 is mixed with higher singlet states S_i, and since as many as three different singlet state symmetries may be involved in T_1, it is clear that the intensity distribution amongst the numerous vibronic levels in each factor group state may be quite complex. For the present problem we assume that the spin-orbit coupling operator introduces short (M) normal (N) and long-axis (L) polarized intensity into the electronic transition $S \rightarrow T_1$. If only a single unit cell is considered, the state function corresponding to site (I) may be written as:

$$\begin{aligned} {}^3\Phi'_m(\mathrm{I}) &= {}^3\psi'_m(\mathrm{I})\,{}^1\psi_0(\mathrm{II})\,{}^1\psi_0(\mathrm{III})\,{}^1\psi_0(\mathrm{IV}) \\ &= \left\{{}^3\Phi_m(\mathrm{I}) + \sum_i \alpha_{im}\,{}^1\psi_i(\mathrm{I})\right\}{}^1\psi_0(\mathrm{II})\,{}^1\psi_0(\mathrm{III})\,{}^1\psi_0(\mathrm{IV}) \end{aligned} \tag{14}$$

where $\alpha_{im} = (E_m - E_i)^{-1}\langle {}^3\psi_m | H_{SO} | {}^1\psi_i \rangle$, with m labelling the triplet state in question, i labelling the perturbing singlet, and H_{SO} representing the molecular spin-orbit interaction operator. The transition moments $\vec{M}_m$ to the three dipole allowed combinations of site states are given by:

$$\vec{M}_m \begin{bmatrix} B_{1u} \\ B_{2u} \\ B_{3u} \end{bmatrix} = \tfrac{1}{2} \sum_i \alpha_{im} \left[\vec{p}_i(\mathrm{I}) \overset{-}{\underset{+}{-}} \vec{p}_i(\mathrm{II}) \overset{-}{\underset{-}{+}} \vec{p}_i(\mathrm{III}) \overset{+}{\underset{-}{-}} \vec{p}_i(\mathrm{IV}) \right] \tag{15}$$

If the sum over the singlet states, i, is carried out three possible directions $\vec{p}_i(\mathrm{I})$ can in principle be obtained. We may number the states according to their polarization in the transition $S_0 \rightarrow S_i$, by introducing the symbol i_ζ where i runs from zero to infinity and ζ labels the polarization L, M or N, thus:

$$\vec{M}_m \begin{bmatrix} B_{1u} \\ B_{2u} \\ B_{3u} \end{bmatrix} = \tfrac{1}{2} \sum_{i_\zeta} \alpha_{i_\zeta m} |m_{i_\zeta}| \left\{ \hat{\zeta}_1 \overset{-}{\underset{+}{-}} \hat{\zeta}_2 \overset{-}{\underset{-}{+}} \hat{\zeta}_3 \overset{+}{\underset{-}{-}} \hat{\zeta}_4 \right\} \tag{16}$$

where $|\vec{m}_{i_\zeta}|$ is the magnitude of the intensity of the ζ polarized transition $S_0 \rightarrow S_i$. The linear combinations of unit vectors in (16) are each just a unit vector along either **a**, **b** or **c** (in general, **t**) multiplied by 4 cos $\theta_{\zeta,\mathbf{t}}$, where $\theta_{\zeta,t}$ is the angle that the ζ axis of molecule I makes with the **t** crystal axis. The relative intensity of light absorption for an electromagnetic wave with electric field vector $\vec{\epsilon}_t (= \epsilon_0 \hat{t})$ is given by:

$$|\vec{\epsilon}_\mathbf{t} \cdot \vec{M}_m|^2 = \epsilon_0^2 \left\{ 2 \sum_t \sum_{i_\zeta} \alpha_{i_\zeta} |\vec{m}_{i_\zeta}| \cos\theta_{\zeta t} \right\}^2 \tag{17}$$

As an example pertinent to the present study we choose a transition that is polarized along the molecular direction $\alpha_L \hat{L}_1 + \alpha_M \hat{M}_1 + \alpha_N \hat{N}_1$: then the relative intensities along **a**, **b** and **c** are given by:

$$I_t = \{\alpha_L \cos\theta_{Lt} + \alpha_M \cos\theta_{Mt} + \alpha_N \cos\theta_{Nt}\}^2 \tag{18}$$

The three unknowns α_L, α_M and α_N can be obtained from the relative values of I_a, I_b and I_c; in Eq. (18) we put $I_a + I_b + I_c = 1$. Since the band systems are approaching strong coupling the intensities in (18) must refer to the integrated band intensities which are $I_b = I_c \approx I_a$. It is clear from the spectra that some significant vibronic interactions, leading to redistributions of intensity are occurring in the crystal. With only three values of I_t observable it is inherently impossible to deduce a unique set α_L, α_M, α_N from the experimental results (there are four possible answers). However if we assume that the transition contains only N and L intensity a unique molecular polarization vector $\hat{\mu}$ can be found:

$$|\hat{\mu}| = |0.811\,\hat{L} + 0.585\,\hat{N}|$$

This result corresponds to a spin-orbital coupling situation in which 34.2% of the $S \rightarrow T_1$ intensity derives from N-polarized singlets and the remainder from L-polarized states. It should be remarked that a unique molecular polarization direction cannot be obtained from experimental polarized intensities unless the possible answers are restricted by other considerations such as an appeal to theory (e.g., as is usually done for allowed transitions in symmetrical molecules).

Conclusions

The $S \rightarrow T_1$ absorption spectrum of *p*-diiodobenzene has been interpreted on the basis of a strong coupling of molecular states in the crystal. The electric dipole allowed components of the factor group have been observed in light polarized parallel to the three crystal axes. The A_u factor group state was conjectured to lie at least 855 cm^{-1} to higher energies than the allowed group of states. It is surprising that we do not observe transition to the A_u state since this is only forbidden in the absence of crystal field mixing of vibronic states, and in the region of $\mathbf{k} = 0$.

REFERENCES

1. McClure, D. S., *Solid State Physics* **8**, 1 (1959).
2. Craig, D. P. and Walmsley, S. H. in *Physics and Chemistry of the Organic Solid State*, ed. by M. M. Labes, D. Fox and A. Weissberger (John Wiley and Sons, Inc., New York, 1963), Vol. 1, p. 585.
3. Schnepp, O., *An. Rev. Phys. Chem.* **14**, 35 (1963).
4. McClure, D. S., Blake, N. W., and Hanst, P. L., *J. Chem. Phys.* **22**, 255 (1954).
5. Dexter, D. L., *J. Chem. Phys.* **21**, 836 (1953).
6. Merrifield, R. E., *J. Chem. Phys.* **23**, 402 (1955).
7. Nieman, G. C. and Robinson, G. W., *J. Chem. Phys.* **37**, 2150 (1962); *J. Chem. Phys.* **39**, 1298 (1963).
8. Jortner, J., Rice, S. A., Katz, J. L., and Choi, S., *J. Chem. Phys.* **42**, 309 (1965).
9. Castro, G. and Hochstrasser, R. M., *J. Chem. Phys.* **44**, 000 (1966).
10. Dun-choi, L. and Struchkov, Yu T., *Izvest. Akad. Nauk SSSR, OKhN* **12**, 2095 (1959).
11. Craig, D. P. and Walsh, J. R., *J. Chem. Soc.* 1613 (1958).
12. Fox, D. and Schnepp, O., *J. Chem. Phys.* **23**, 767 (1955).
13. Stojiljkovic, A. and Whiffen, D. H., *Spectrochimica Acta* **12**, 47 (1958).
14. Castro, G. and Hochstrasser, R. M., in course of publication.
15. McClure, D. S., *Can. J. Chem.* **36**, 59 (1958).
16. Craig, D. P. and Hobbins, P. C., *J. Chem. Soc.* 2309 (1955).
17. Simpson, W. T. and Peterson, D. L., *J. Chem. Phys.* **26**, 588 (1957).
18. Fulton, R. G. and Gouterman, M., *J. Chem. Phys.* **41**, 2280 (1963).