

## Polarization of Triplet Factor Group States

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## Polarization of Triplet Factor Group States\*

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An account of the polarization of triplet factor group, or dimeric, states is given. It is shown that in the presence of a twofold axis the resulting *plus* (symmetric) and *minus* (antisymmetric) states are not generally uniquely polarized along the  $C_2$  and perpendicular to the  $C_2$ , respectively. This arises because of the spin correlation induced by the exciton exchange interactions. The intensities can be reduced to geometric parameters and predictions and comparisons with experiment are made for naphthalene, anthracene, and phenazine crystals.

## I. INTRODUCTION

In recent years the problems associated with triplet states of organic crystals have received considerable attention. One can trace the theoretical development of this field through the contributions by Dexter,<sup>1</sup> Merrifield,<sup>2</sup> Nieman and Robinson,<sup>3</sup> and Jortner and Rice *et al.*<sup>4,5</sup>

Basically it is expected that triplet states will manifest factor group splitting, analogous to the Davydov splitting of singlet states,<sup>6</sup> and that for crystals with two molecules in the unit cell the two factor group states will have different polarization for light traveling perpendicular to the crystal symmetry axis. One of the states will have parallel (usually taken as the *plus* state), and the other will have perpendicular polarization (the *minus* state) for electric dipole transitions.

The purpose of this article is to examine these suppositions regarding the polarization of singlet-triplet transitions. The whole concern is really to question whether there is any fundamental difference between a pair of molecules and a molecule that can be described in terms of two constituent parts. In fact, it is shown that spin-orbit coupling in the dimer or crystal causes a mixing of the *plus* and *minus* states of the factor group—in the presence of intermolecular exchange interactions—and that this effect becomes noticeable when the plus and minus states are split by the intermolecular potential.

## II. THE POLARIZATION OF SINGLET-TRIPLET TRANSITIONS IN AGGREGATES

For convenience we consider a system of two molecules each having two excited states, a triplet state

$^3\phi_r$  ( $r=0, \pm 1$ ), and a singlet state  $^1\phi$  with which the triplet can mix under spin-orbit coupling. The dimer is assumed to have a twofold symmetry axis (**b**) which interchanges the two molecules A and B. The dimer states are given in zero order by

$$^3\Psi_r(\pm) = 2^{-1/2} [^3\phi_r(A)\phi_0(B) \pm \phi_0(A)^3\phi_r(B)], \quad (1)$$

$$^1\Psi(\pm) = 2^{-1/2} [^1\phi(A)\phi_0(B) \pm \phi_0(A)^1\phi(B)]. \quad (2)$$

The dimer coordinate system is labeled as **a**, **b**, **c**, with **b** as  $C_2$ . The  $\pm$  sign refers to symmetry with respect to the twofold axis, that is  $C_2^b\phi(A)$  is defined as  $(+1)\phi(B)$ . For the singlet states, transitions to the *plus* and *minus* states are polarized **b** and  $\perp \mathbf{b}$ , respectively. The ground state of a molecule is written as  $\phi_0$ , and of the dimer as  $\phi_0(A)\phi_0(B) = ^1\Psi_0$ . The triplet states are now coupled to the singlet states by  $H_{s0}$ —the full spin-orbit operator for the dimer. The corrected states are written as  $^3\psi_r(\pm)$  in terms of the above zero-order states:

$$^3\psi_r(\pm) = ^3\Psi_r(\pm) + \sum_g \Delta E_g^{-1} \langle ^1\Psi(g) | H_{s0} | ^3\Psi_r(\pm) \rangle ^1\Psi_g, \quad (3)$$

where  $g$  is first the *plus* then the *minus* state, these being the only singlets;  $\Delta E_g = \{E[^3\Psi_r(\pm)] - E[^1\Psi(g)]\}$ . The transition moments are then given by

$$e \langle ^1\Psi_0 | \mathbf{r} | ^3\psi_r(\pm) \rangle = \mathbf{m}^{(r)}(\pm) = \sum_g \Delta E_g^{-1} \langle ^1\Psi(g) | H_{s0} | ^3\Psi_r(\pm) \rangle \mathbf{m}(g). \quad (4)$$

The  $\mathbf{m}(g)$  are given by

$$\mathbf{m}(\pm) = 2^{-1/2} [\mathbf{u}(A) \pm \mathbf{u}(B)],$$

where  $\mathbf{u}(A)$  and  $\mathbf{u}(B)$  are the electric dipole transition amplitude vectors in Molecules A and B. The intensity observed with light having a unit electric vector  $\hat{\mathbf{f}}$  ( $\hat{\mathbf{f}}$  will always be chosen in the direction of **b** or  $\perp \mathbf{b}$  in which cases it will be written as  $\hat{\mathbf{f}}_+$  or  $\hat{\mathbf{f}}_-$ , respectively) is given by  $|\mathbf{m}^{(r)}(\pm) \cdot \hat{\mathbf{f}}|^2$ . There are four possible manifestations of this intensity, as follows, assuming

\* This work was supported in part by the Advanced Research Projects Agency and by a U.S. Department of Health Grant GM-12 592-03.

† Alfred P. Sloan Foundation Fellow.

<sup>1</sup> D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

<sup>2</sup> R. Merrifield, J. Chem. Phys. **23**, 402 (1955).

<sup>3</sup> G. C. Nieman and G. W. Robinson, J. Chem. Phys. **37**, 2150 (1962); H. Sternlicht, G. C. Nieman, and G. W. Robinson, *ibid.* **38**, 1326 (1963).

<sup>4</sup> J. L. Katz, J. Jortner, S. I. Choi, and S. A. Rice, J. Chem. Phys. **39**, 1897 (1963).

<sup>5</sup> J. Jortner, S. A. Rice, J. L. Katz, and S. I. Choi, J. Chem. Phys. **42**, 309 (1965).

<sup>6</sup> A. S. Davydov, Soviet Phys.—JETP **18**, 210 (1948).

a unit moment for the singlet-singlet transition:

$$|\mathbf{m}^{(r)}(+)\cdot\hat{\xi}_+|^2 \equiv I_+(+) = 2\Delta E_+^{-2} |\langle {}^1\Psi(+) | H_{s0} | {}^3\Psi_r(+) \rangle|^2 \cos^2\theta_b, \quad (5a)$$

$$|\mathbf{m}^{(r)}(+)\cdot\hat{\xi}_-|^2 \equiv I_- (+) = 2\Delta E_-^{-2} |\langle {}^1\Psi(-) | H_{s0} | {}^3\Psi_r(+) \rangle|^2 \cos^2\theta_{\perp b}, \quad (5b)$$

$$|\mathbf{m}^{(r)}(-)\cdot\hat{\xi}_+|^2 \equiv I_+(-) = 2\Delta E_+^{-2} |\langle {}^1\Psi(+) | H_{s0} | {}^3\Psi_r(-) \rangle|^2 \cos^2\theta_b, \quad (5c)$$

$$|\mathbf{m}^{(r)}(-)\cdot\hat{\xi}_-|^2 \equiv I_-(-) = 2\Delta E_-^{-2} |\langle {}^1\Psi(-) | H_{s0} | {}^3\Psi_r(-) \rangle|^2 \cos^2\theta_{\perp b}. \quad (5d)$$

In these formulas  $\theta_b$  and  $\theta_{\perp b}$  are the angles that the transition moment  $\mathbf{y}(A)$  makes with  $\mathbf{b}$  and  $\perp\mathbf{b}$ , respectively.

In Eqs. (5a) and (5d) the spin-orbit operator involved is that component which is invariant to rotations about the  $\mathbf{b}$  axis of the system. In (5b) and (5c) the appropriate components are those that are antisymmetric under rotations about this axis. If the dimer point group were  $C_2$ , the former components would classify as A, and the latter as B, while the *plus* and *minus* states would classify as A and B, respectively. With the addition of inversion symmetry the two operators would classify as  $A_g$  and  $B_g$ , respectively, while the *plus* and *minus* states would be  $A_u$  and  $B_u$ , respectively.

There are two important extremes to consider; namely, the limits of intermolecular coupling strengths in the triplet states.

#### A. Case (i) Intermolecular Interactions are Unobservably Small

In this event the *plus* and *minus* states cannot be distinguished, and the total  $\mathbf{b}$  polarized intensity  $I(\mathbf{b})$  is given by the sum of (5a) and (5c):

$$\sum_r I^{(r)}(\mathbf{b}) = 4\Delta E_g^{-2} \cos^2\theta_b \sum_r |\langle {}^1\phi(A) | H_{s0}(A) | {}^3\phi_r(A) \rangle|^2; \quad (6a)$$

similarly

$$\sum_r I^{(r)}(\perp\mathbf{b}) = 4\Delta E_g^{-2} \cos^2\theta_{\perp b} \sum_r |\langle {}^1\phi(A) | H_{s0}(A) | {}^3\phi_r(A) \rangle|^2. \quad (6b)$$

To obtain (6a) and (6b) it was assumed that  $H_{s0}$  is a one-electron (or one-molecule) operator, but it was not assumed that  $H_{s0}$  was specifically  $[H_{s0}(A) + H_{s0}(B)]$  or  $[H_{s0}(A) - H_{s0}(B)]$ . The operator  $H_{s0}(A)$  is the spin-orbit interaction for Molecule A in the dimer coordinate system: the choice of axes for Molecule B is not presumed here. The equations (6a)–(6b) are precisely the results that would be obtained for the sum of the intensities due to two independent absorbers. These results coincide with the case of singlet-singlet transitions whether or not the *plus* and *minus* states are split apart.

#### B. Case (ii) The Plus and Minus States are Independently Observable

This situation would arise if the matrix elements of the electrostatic potential (excitation exchange elements) are larger than the linewidth. The interaction between the states  ${}^3\phi_r(A)\phi_0(B)$  and  $\phi_0(A){}^3\phi_r(B)$  gives rise to two states that can be separately observed.

The spin-orbit operator for Molecule A can be written in terms of components along  $\mathbf{b}$  and perpendicular to  $\mathbf{b}$ . The electronic coordinates for Molecule A will be written as  $x_A, y_A$ , and  $z_A$  with origin at the center of mass of A. There is now a choice for the equivalent coordinates in Molecule B. In accordance with the definitions (1) and (2) and of the directions  $\mathbf{m}(g)$ , these coordinates are chosen such that the set  $\{x_A, y_A, z_A, x_B, y_B, z_B\}$  is invariant under rotations about the  $b$  axis, and both systems are right-handed. In terms of these components the total spin-orbit operator is given by

$$\begin{aligned} H_{s0} = & \{H_{s0}(A_b) + H_{s0}(B_b)\} \\ & + \{H_{s0}(A_c) + H_{s0}(B_c) + H_{s0}(A_a) + H_{s0}(B_a)\} \\ \equiv & h_{s0}^+(\mathbf{b}) + h_{s0}^-(\mathbf{ac}), \end{aligned} \quad (7)$$

where  $H_{s0}(A_b)$  is the  $\mathbf{b}$  component of  $H_{s0}(A)$ . The intensities of transitions to the *plus* state are therefore given by

$$\begin{aligned} I_b^{(r)}(+ ) & = 2\Delta E_+^{-2} \cos^2\theta_b |\langle {}^3\Psi_r(+) | h_{s0}^+(\mathbf{b}) | {}^1\Psi(+) \rangle|^2, \end{aligned} \quad (8)$$

$$\begin{aligned} I_{\perp b}^{(r)}(+ ) & = 2\Delta E_-^{-2} \cos^2\theta_{\perp b} |\langle {}^3\Psi_r(+) | h_{s0}^-(\mathbf{ac}) | {}^1\Psi(-) \rangle|^2, \end{aligned} \quad (9)$$

with comparable relations for the *minus* state. It is therefore seen that in general Eq. (8) gives zero for all but the  $\mathbf{b}$  component, and that (9) gives zero for all but the  $\mathbf{a}$  and  $\mathbf{c}$  components of  $H_{s0}(A)$  or  $H_{s0}(B)$ .

These results are readily extended to crystals containing two molecules per unit cell that are related by a twofold screw axis about  $\mathbf{b}$ . In that case the  $\mathbf{b}$  axis would become the crystallographic  $\mathbf{b}$  axis and the  $\mathbf{a}$  and  $\mathbf{c}'$  crystal directions could correspond to  $\mathbf{a}$  and  $\mathbf{c}$  which are in any case arbitrarily chosen. In general the spin-orbit axis in the molecule will not coincide with a crystal axes, so the intensity sources 5(a)–(d) should all be manifested. This implies that the Davydov

components of a triplet state need not have unique polarizations in the crystal; in general the *plus* states will have both **b** and **ac** polarized intensity, and the *minus* states will have **b** intensity in addition to the normally expected **ac** intensity. We now consider the geometrical considerations associated with the simplification of the matrix elements.

### III. TRANSFORMATION OF THE SPIN-ORBIT OPERATOR

In the **a**, **b**, **c** frame, the spin and orbital parts of the spin-orbit operator for Molecule A are given by

$$\mathbf{L}(A) = L_a(A)\hat{a} + L_b(A)\hat{b} + L_c(A)\hat{c}, \quad (10)$$

$$\mathbf{S}(A) = S_a(A)\hat{a} + S_b(A)\hat{b} + S_c(A)\hat{c}. \quad (11)$$

Thus any one component—say the **a** component—is written as:

$$\{\mathbf{L}(A) \cdot \mathbf{S}(A)\}_a = L_a(A) S_a(A). \quad (12)$$

We assume that taken for each electron in A this form is a good approximation to the one-electron spin-orbit operator for Molecule A.<sup>7</sup> From the straightforward transformation properties of *L* and *S* we find in general for molecule R,

$$L_a(R) = l_{xR}L_{xR} + l_{yR}L_{yR} + l_{zR}L_{zR}, \quad (13)$$

where *l* is the direction cosine of the **a** axis with respect to the molecular framework axes *x*, *y*, and *z*. For example, for Molecule A, *l<sub>yA</sub>* is the cosine of the angle between the molecular axis *y<sub>A</sub>* and the axis **a**. The expression for the **a** component of the spin-orbit operator can now be found by substitution of Eq. (13) into (12). For the present purposes we are considering the spins, decoupled from the molecular axes, in the space-fixed set of coordinates **a**, **b**, **c**. Thus the spin functions are not rotated by the spatial transformations of the dimer framework, and all the symmetry of *H<sub>s0</sub>* comes from the orbital part. We choose **b** as the axis of quantization, thus we have

$$S_b(A) {}^3\sigma_r(A) = r\hbar {}^3\sigma_r(A), \quad (14)$$

where *σ<sub>r</sub>* are the space-fixed triplet spin functions with *r* = 0, ±1; e.g.,

$${}^3\sigma_1(A) \equiv {}^3\sigma_1(1, 2) \equiv \alpha(1)\alpha(2),$$

$${}^3\sigma_1(B) \equiv {}^3\sigma_1(3, 4) \equiv \alpha(3)\alpha(4), \text{ etc.,}$$

where the optical electrons of Molecule A are 1, 2 and those of B are 3, 4.

If we consider only the two optical electrons (*j* = 1, 2) in the triplet state each  $\sum_j L_{\mu j} S_{\nu j}$  term can be written

<sup>7</sup> We are assuming here only that the components of *L* have the transformation properties of an axial vector, like orbital angular momentum. Actually *L* is of the form  $\text{grad}V \times \mathbf{r}$  where  $\text{grad}V$  is the electric field due to all nuclei and electrons.

in the form

$$\sum_j L_{\mu j} S_{\nu j} = \frac{1}{2} \{ (L_{\mu 1} - L_{\mu 2}) (S_{\nu 1} - S_{\nu 2}) + (L_{\mu 1} + L_{\mu 2}) (S_{\nu 1} + S_{\nu 2}) \}. \quad (15)$$

Since only the (*S<sub>ν1</sub>* − *S<sub>ν2</sub>*) terms can mix singlet and triplet states we can obtain an effective spin-orbit operator by excluding the (*S<sub>ν1</sub>* + *S<sub>ν2</sub>*) terms. This effective operator is given below, with *L<sup>−</sup>* and *S<sup>−</sup>* used as abbreviations for the antisymmetric terms in (15), and apart from universal constants,

$$\{H_{s0}(AB)\}_{\text{eff}} = \{L_a^-(A) S_a^-(A) + L_a^-(B) S_a^-(B)\}. \quad (16)$$

There is an effective operator of this type for each components **a**, **b**, and **c**. The operators *S<sub>a</sub><sup>−</sup>*, *S<sub>b</sub><sup>−</sup>*, and *S<sub>c</sub><sup>−</sup>* have the following well-known properties:

$$\begin{aligned} S_a^- {}^3\sigma_r &= - (r\hbar/\sqrt{2}) {}^1\sigma_0, \\ S_c^- {}^3\sigma_r &= (-ir^2\hbar/\sqrt{2}) {}^1\sigma_0, \\ S_b^- {}^3\sigma_r &= (1-r^2)\hbar {}^1\sigma_0, \end{aligned} \quad (17)$$

where it is assumed that **a** and **c** are arbitrarily chosen orthogonal axes in the plane perpendicular to the **b** axis.

We now make the assumption that only one component of *L* will be effective in mixing molecular singlet and triplet states, say *L<sub>z</sub>*. Then substitution of the results (13) and (16) into Eqs. (8) and (9), as well as into the corresponding relations for the *minus* state, yields the following results:

$$\begin{aligned} I_b^{(0)}(+) &= 2\hbar^2 \Delta E^{-2} \langle L_z^- \rangle^2 \cos^2 \theta_b m_z^2, \\ I_b^{(\pm 1)}(+) &= 0, \\ I_{\perp b}^{(0)}(+) &= 0, \\ I_{\perp b}^{(\pm 1)}(+) &= \hbar^2 \Delta E^{-2} \langle L_z^- \rangle^2 \cos^2 \theta_{\perp b} (1 - m_z^2), \\ I_b^{(0)}(-) &= 0, \\ I_b^{(\pm 1)}(-) &= \hbar^2 \Delta E^{-2} \langle L_z^- \rangle^2 \cos^2 \theta_b (1 - m_z^2), \\ I_{\perp b}^{(0)}(-) &= 2\hbar^2 \Delta E^{-2} \langle L_z^- \rangle^2 \cos^2 \theta_{\perp b} m_z^2, \\ I_{\perp b}^{(\pm 1)}(-) &= 0. \end{aligned} \quad (18)$$

The only crucial step in the development of these expressions is to remember that *l<sub>zA</sub>*, *m<sub>zA</sub>*, and *n<sub>zA</sub>* are equal to −*l<sub>zB</sub>*, *m<sub>zB</sub>*, and −*n<sub>zB</sub>*, respectively. These being the projections of the molecular *z* axes onto the frame axes **a**, **b**, and **c**. These relations are obtained on the assumption that Δ*E<sub>+</sub>* and Δ*E<sub>−</sub>* are equal, which should be a very good approximation for almost all situations. The spatial parts of the spin-orbit matrix elements are

$$\begin{aligned} \langle L_z^- \rangle &= \langle {}^1\phi(A) | L_z^-(A) | {}^3\phi(A) \rangle \\ &= \langle {}^1\phi(B) | L_z^-(B) | {}^3\phi(B) \rangle. \end{aligned}$$

TABLE I. Squared direction cosines for naphthalene.

	<i>L</i>	<i>M</i>	<i>N</i>
<i>a</i>	0.193	0.103	0.705
<i>b</i>	0.044	0.760	0.196
<i>c'</i>	0.764	0.137	0.099

The ratios of any two of these intensities is subject to direct experimental test by Zeeman measurements with **b** as the axis of quantization. However, even in the absence of magnetic fields the **a** and **b** intensity in each factor group component can be analyzed, for example the total **b** intensity in the *plus* and *minus* states is given by

$$I_b(+)=I_b^{(0)}(+)+2I_b^{(\pm 1)}(+)$$

$$=2\hbar^2\Delta E^{-2}\langle L_z^- \rangle^2 \cos^2\theta_b m_z^2, \quad (19)$$

$$I_b(-)=I_b^{(0)}(-)+2I_b^{(\pm 1)}(-)$$

$$=2\hbar^2\Delta E^{-2}\langle L_z^- \rangle^2 \cos^2\theta_b (1-m_z^2). \quad (20)$$

The ratio of these two quantities is directly measurable:

$$I_b(+)/I_b(-)=m_z^2/(1-m_z^2). \quad (21)$$

This result implies that if factor group splitting is observed in a triplet state the spin-orbit activity in the molecule can be immediately discovered by a measurement of the relative intensity of the **b** intensity in each line. Previously the spin-orbit route could only be discovered by observing the intensities of transitions to the 0 and  $\pm 1$  states, as in the electronic Zeeman effect.<sup>8</sup>

The polarization ratio with light at the frequency of one of the factor group components is given by (say for the *plus* state)

$$I_b(+)/I_{\mathbf{b}}(+)=\cos^2\theta_b m_z^2/[\cos^2\theta_{\mathbf{b}}(1-m_z^2)]. \quad (22)$$

If the polarization of the transition is known—and it is, since the total **b** intensity and the total **a** intensity from both factor group states gives the oriented gas ratio—the ratio in Eq. (22) can also provide the spin-orbit route.

#### IV. APPLICATIONS TO KNOWN STRUCTURES

##### A. Naphthalene

The direction cosines for the *L*, *M*, and *N* axes of naphthalene in the crystal are given in Table I according to Cruickshank.<sup>9</sup> The crystal contains two molecules per unit cell and is monoclinic *P2<sub>1</sub>/a*. The first

<sup>8</sup> G. Castro and R. M. Hochstrasser, Solid State Commun. **3**, 425 (1965).

<sup>9</sup> D. W. J. Cruickshank, Acta Cryst. **10**, 504 (1957).

singlet-triplet transition of naphthalene is mainly out-of-plane polarized (*N*) and a factor group splitting has both been measured<sup>10</sup> and agrees fairly well with the previously calculated<sup>6</sup> value. Theory would predict the spatial symmetry of this triplet as <sup>3</sup>*B<sub>2u</sub>* [transforming like a short axis (*M*) vector].<sup>11</sup> The active spin-orbit route therefore most probably uses the *L* component of the spin-orbit operator. It follows that

$$I_b(+)/I_b(-)=0.064; \quad I_a(+)/I_b(+)=78.2.$$

The results imply that, if the approach to the assignment of the triplet is correct, the theoretically calculated *minus* state of the crystal should be almost entirely **b** polarized. The *plus* state should be stronger by a factor of 3.55 and be predominantly **a** polarized.

##### B. Phenazine

This example is chosen because the crystal structure is *P2<sub>1</sub>/a* with two molecules per unit cell,<sup>12</sup> because the lowest triplet state is the analog of that in anthracene, and primarily because there are some measurements available on this triplet state in single crystals of phenazine.<sup>13</sup>

As in anthracene, the lowest triplet state is assumed to be <sup>3</sup>*B<sub>2u</sub>*, and the polarization of the transition is normal to the molecular plane. The spin-orbit route should again be through the *L* component. The orientation of a molecule, deduced from the data of Herbstein and Schmidt,<sup>12</sup> is given in Table II. The 0,0 band is found to be split into two states, the lower energy component being stronger than the higher by 1:0.95. Both states are at least 5 times stronger along **b** than along **c**. This ratio is quite close to the oriented gas ratio for *N*-polarized transitions (8:1). The calculation gives

$$I_b(+)/I_b(-)=0.48/0.52=0.92.$$

The calculated ratio is in excellent agreement with experiment, suggesting that the *minus* state lies lowest in energy.

TABLE II. Squared direction cosines for phenazine.

	<i>L</i>	<i>M</i>	<i>N</i>
<i>a'</i>	0.333	0.172	0.495
<i>b</i>	0.480	0.041	0.479
<i>c</i>	0.187	0.787	0.026

<sup>10</sup> D. M. Hanson and G. W. Robinson, J. Chem. Phys. **43**, 4174 (1965).

<sup>11</sup> R. Pariser, J. Chem. Phys. **24**, 250 (1956).

<sup>12</sup> F. H. Herbstein and G. M. J. Schmidt, Acta Cryst. **8**, 399 (1955).

<sup>13</sup> I should point out that it was these measurements,<sup>12</sup> done by R. H. Clarke of this laboratory, which raised the issues discussed in this paper.

### C. Anthracene

Again the crystal structure is  $P2_1/a$  with two molecules per cell. The orientation of the molecules are given in Table III as calculated from the 95°K data of Mason.<sup>14</sup> The lowest triplet state is again calculated as  $^3B_{2u}$ ,<sup>10</sup> and if polarized normal to the plane would require an  $L$ -axis spin-orbit route. Thus we would expect

$$I_b(-)/I_b(+) = (1 - m_L^2)/m_L^2 = 57.82.$$

Furthermore, the total **a** polarization should be 3.62 times stronger than the **b**. Thus two almost uniquely polarized lines should be observed; the *plus* state should be **a** polarized, and the *minus* state should be **b** polarized. Jortner, Rice, Katz, and Choi<sup>5</sup> calculate a splitting of 34.9 cm<sup>-1</sup> (from electron-exchange contributions only) with the *minus* state at lowest energy. What is observed is a doublet with a separation of 21 cm<sup>-1</sup> (0,0 band only) with the lowest energy component of the doublet about 4 times stronger than the higher energy component.<sup>15</sup> Thus we could conclude that the lower energy state is the *plus* state, and that it should be **a** polarized.

### V. CONCLUSIONS

It has been shown that the polarization criteria associated with factor group states deriving from singlets are not upheld for triplet states. The extent of agreement between the intensities calculated herein and those observed will depend on a number of criteria such as crystal field mixing, intermolecular spin-orbit coupling, and the presence of intensity due to higher multipole radiation.

The physical nature of the two different polarizations for dimer or crystal singlet states is caused by the indistinguishability of the molecules. Once we specify a

direction for the transition amplitude in Molecule A (arbitrary) the direction of the amplitude in B can be *plus* or *minus* the equivalent direction of A. This gives electric dipole intensity both parallel and perpendicular to the symmetry axis. However if the electric dipole in A is  $\langle H_{s0}(A) \rangle \mathbf{u}(A)$  then the choice of the *plus* combination may lead to  $|\langle H_{s0} \rangle| \{ \mathbf{u}(A) - \mathbf{u}(B) \}$  for the transition amplitude of the system, since the same symmetry conditions (i.e., a  $C_2$  axis) may demand that for certain components  $\langle H_{s0}(A) \rangle = -\langle H_{s0}(B) \rangle$ . Thus the non-observable  $\langle H_{s0} \rangle$  is imposing an "extra" phase condition on the transition amplitudes due to alignment of the spins.

The exchange integrals that contribute to the factor group splittings are of the form

$$\langle \bar{a}(1)\bar{b}(1) | 1/r_{12} | a'(2)b'(2) \rangle,$$

where  $a$ ,  $b$  and  $a'$ ,  $b'$  are the highest occupied and lowest unoccupied  $\pi$  orbitals of two molecules ( $a$  and  $b$ ). These interactions, if manifested, should force a correlation of spins in the "optical" orbitals of the two molecules. Thus if the factor group splitting is observable, and if this is much larger than the zero-field splitting, then the spin orientations in the two molecules will be controlled by the exchange coupling. In this event the spin-orbit coupling should be treated as if the optical electrons were common to both molecules, such as is done herein; this procedure, for example, would normally be carried out for a diatomic molecule wherein one-center spin-orbit coupling terms at each atom may add or cancel depending on the wavefunctions of the triplet and mixing singlet states. In the limit of exchange coupling dominating the zero-field splitting, only the individual magnetic substates can normally display uniquely polarized factor group components analogous to singlet exciton spectra, but the total intensity will not be uniquely polarized as is evident from Eqs. (18).<sup>16</sup>

In this presentation no formal justification is given for taking a dimer problem having a  $C_2$  over into a crystal problem where there is no  $C_2$ , but only a twofold screw axis. As long as one admits cyclic boundary conditions it is possible to show that the dimer results are identical with those in the crystal at  $\mathbf{k}=0$ . This will be dealt with in a forthcoming article.

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<sup>14</sup> R. Mason, Acta Cryst. **17**, 547 (1964).

<sup>15</sup> R. Clarke, unpublished results from this laboratory. The 0,0 band of the anthracene crystal singlet-triplet system at 14 742 cm<sup>-1</sup> is split into two bands. The **a** polarized origin band lies at 22 cm<sup>-1</sup> to lower energy than the **b** polarized band, the former being at least 4 to 5 times stronger. The **a** polarized band splits into two bands (transitions to  $m_s = \pm 1$ ) with the crystal in a magnetic field down the **b** axis. The **b** component appears to give only wing lines in the Zeeman pattern. These results are in agreement with the predictions of Eq. (18).

<sup>16</sup> An exception is an orthorhombic structure such as the benzene crystal. All four factor group states can be observed in electric dipole radiation; one of the states ( $A_u$ ) should appear polarized along all three crystal directions; the other three states are each polarized along only two crystal axes.