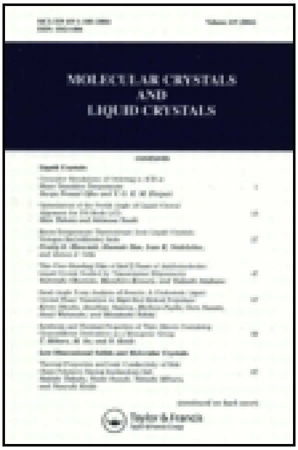

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Intersystem Crossing and Raditive Transitions in Naphthalene Triplet Mini-Excitons

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Intersystem Crossing and Radiative Transitions in Naphthalene Triplet Mini-Excitons

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The relative radiative, intersystem crossing and decay rates for the triplet spin levels of the naphthalene AB pair are calculated. The polarization and radiative transitions results for the zero-field levels justify the neglect of intermolecular spin-orbit coupling compared to intramolecular mechanisms.

1. INTRODUCTION

The study of mini-excitons (or resonance pairs) is rapidly gaining popularity as a simple model of excitonic interactions. Often, the properties of the pair can be written as a function of monomer properties. Thus the triplet zero-field splitting parameters of triplet excitons and mini-excitons were calculated and measured.[1-6] The absorption spectra of dimers was derived by Gianneschi and Kuruscev.[7] Retanapan and Tang calculated the naphthalene dimer self-energy and resonances.[8] Wertheimer and Silbey[9] derived relaxation equations for the rate constants in triplet mini-excitons. Furthermore, the polarization of triplet factor group states as well as electric magnetic field effects were studied by Hochstrasser and co-workers.[10] An estimate of intermolecular spin-orbit coupling (SOC) by Cooper and Fayer[11] led to an insight into the dynamic properties of triplet tetrachlorobenzene pair. Lemaistre and co-workers derived the OMDR, PMDR and phosphorescence line shapes of translationally equivalent and inequivalent pairs.[12] They also calculated the phenazine dimer's triplet radiative rate constants from monomeric values.

The resonance pair concept has also found application in paracyclophanes, where the optical properties and zero-field parameters for triplet cyclophanes were compared to those of the parent monomer.[13] In addition, the triplet decay rates of dimers in photosynthetic bacteria were formulated in terms of monomer rates.[14] This led to an understanding of the relative orientation of monomers in such bacteria.

In this work equations are derived for the relative intersystem crossing ratios to the zero-field levels of mini-excitons as well as the relative radiative rate constants from these levels to the ground state. The equations are applied for the AB pair in naphthalene and qualitative discussion of some cyclophanes is presented. Throughout, the derivations spin-lattice and cross-relaxation effects are neglected.

2. RESONANCE PAIR STATES

Let (ν, ρ) represent the vibrational quantum number in the ρ^{th} normal mode, then $S_{0i}^{\nu,\rho}$, $S_i^{\nu,\rho}$, $T_{i\mu}^{\nu,\rho}$ are the ground state, singlet excited states and triplet excited states of molecule i, with $\mu = B$, A or N being the molecular axes along which the zero-field spin states are quantised (N is perpendicular to the molecular plane). Neglecting to write ν, ρ means the state is in its lowest vibrational level. The triplet state can be written as $T_i^{\nu,\rho}\tau_\mu$, with T_i the orbital part and τ_μ the spin part of wavefunction.

In the limit of a large intermolecular potential compared to the zero-field splitting energies, and assuming weak intermolecular vibrational coupling (the molecules can still undergo vibrational motion independently) the mini-exciton states are given by plus and minus combinations of states formed as a product of the excited state of one molecule and the ground state of the other,[1,4,6,11,14] and thus the ground state dimer functions are:

$$S_0^{\nu,\rho}(\pm) = \left(1/\sqrt{2}\right)\left[S_{02}S_{01}^{\nu,\rho} \pm S_{01}S_{02}^{\nu,\rho}\right] \tag{1}$$

Similarly and considering one (π, π^*) and one (σ, π^*) excited singlet:

$$S_{\pm}^{\nu,\rho}(\pi,\pi^*) = \left(1/\sqrt{2}\right)\left[S_{02}S_1^{\nu,\rho}(\pi,\pi^*) \pm S_{01}S_2^{\nu,\rho}(\pi,\pi^*)\right] \tag{2}$$

With a similar expression for $S_{\pm}^{\nu,\rho}(\sigma,\pi^*)$, while the first triplet state (considering π, π^* states only):

$$T_{\pm j}^{\nu,\rho} = \left(1/\sqrt{2}\right)\left[S_{02}T_1^{\nu,\rho}\tau_j^*(1) \pm S_{01}T_2^{\nu,\rho}\tau_j^*(2)\right] \tag{3}$$

The index j stands for resonance pair triplet spin axes x^*, y^* and z^* with $\tau_j^*(i)$ of molecule i given by[10d]:

$$\tau_j^*(i) = \sum_{\mu} t_{j\mu}(i)\tau_{\mu}(i) \tag{4}$$

$t_{j\mu}(i)$ are the direction cosines between the molecular spin axis μ (A, B or N) and the pair axis j. Equation (4) can be substituted in (3), whenever needed.

3. RADIATIVE PROPERTIES OF TRIPLET RESONANCE PAIRS

In the Herzberg–Teller expansion[15] the total hamiltonian is:

$$H = H^0 + H_{s0} + \sum_{\rho}\left(\frac{\partial H^0}{\partial Q_\rho}\right)_0 Q_\rho + \sum_{\rho}\left(\frac{\partial H}{\partial Q_\rho}\right)_0 Q_\rho \tag{5}$$

Where H^0 is the zeroth order Born-Oppenheimer hamiltonian of the equilibrium position 0. Q_ρ is the coordinate of the ρ^{th} normal mode. H_{s0} is the spin-orbit coupling term. The third term is the spin-orbit vibronic term (H_1), while the fourth is the spin-vibronic term (H_2). Thus one may consider the perturbation which is responsible for mixing singlet character into the triplet spin levels (and hence for their emissive properties) as:

$$H_r = H_{s0} + H_1 + H_2 \tag{6}$$

In (π,π^*) triplets, H_{s0} mixes τ_B and/or τ_A by strong one-centre terms to $S(\sigma,\pi^*)$ and τ_N to $S(\pi,\pi^*)$ via weak three-centre terms.[16] In 0-0 phosphorescence this causes τ_B and/or τ_A to be more emissive than τ_N. The same trend also occurs for emission to a vibrationally excited ground state level. However, the mechanism for this latter behaviour is governed by H_1 and H_2.[17]

As far as the resonance pair states are concerned the perturbation can be written as the sum of the molecular ones. This means that no new SOC or vibronic channels are opened due to the intermolecular interactions. In fact intermolecular SOC has been shown to be too small compared to the molecular coupling scheme.[18] Furthermore, the molecules are assumed to still undergo their vibrational motion independently. Thus:

$$H_r' = H_r(1) + H_r(2) \tag{7}$$

The new triplets to first order become:

$$T^{\nu,\rho}_{\pm j'} = T^{\nu,\rho}_{\pm j} + \sum_n \frac{\langle S_n | H_r' | T^{\nu,\rho}_{\pm j} \rangle}{E_n - E_j} \cdot S_n \tag{8}$$

The summation over all singlets (for our purposes only one σ, π^* and one π, π^* is considered). Restricting ourselves to 0-0 emission we only use direct spin-orbit coupling. The integrals in (8) are expanded using (2), (3) and (4), and bearing in mind τ_A and τ_B couple only to $S(\sigma, \pi^*)$, while τ_N couples to $S(\pi, \pi^*)$:

$$\begin{aligned} T'_{\pm j} = T_{\pm j} + \frac{1}{2} \Bigg[& \langle S_1(\pi, \pi^*) | H_{s0}(1) | T_1 \tau_N \rangle \\ & \times \left\{ \left(t_{jN}(1) \pm t_{jN}(2) \right) \frac{S_+(\pi, \pi^*)}{E_\pi - E_T} \right. \\ & \qquad \left. + \left(t_{jN}(1) \mp t_{jN}(2) \right) \frac{S_-(\pi, \pi^*)}{E_\pi - E_T} \right\} \\ & + \frac{\langle S_1(\sigma, \pi^*) | H_{s0}(1) | T_1 \tau_A \rangle}{E_\sigma - E_T} \\ & \times \left\{ \left(t_{jA}(1) \pm t_{jA}(2) \right) S_+(\sigma, \pi^*) \right. \\ & \qquad \left. + \left(t_{jA}(1) \mp t_{jA}(2) \right) S_-(\sigma, \pi^*) \right\} \\ & + \frac{\langle S_1(\sigma, \pi^*) | H_{s0}(1) | T_1 \tau_B \rangle}{E_\sigma - E_T} \\ & \times \left\{ \left(t_{jB}(1) \pm t_{jB}(2) \right) S_+(\sigma, \pi^*) \right. \\ & \qquad \left. + \left(t_{jB}(1) \mp t_{jB}(2) \right) S_-(\sigma, \pi^*) \right\} \Bigg] \end{aligned} \tag{9}$$

In equation (9) the molecular singlet-triplet gap is assumed to be the same as for the dimer (a reasonable assumption for naphthalene).

The radiative rate constant in (0-0) is now written as:

$$k^r_{\pm j'} \propto |\langle T_{\pm j'}|e \cdot r|S_{01}S_{02}\rangle|^2 \tag{10}$$

The expansion of (10) by substituting (9) is a direct matter. If the polarization along the z^* (which coincides with the b-axis for the naphthalene crystal) is considered one obtains.

$$\begin{aligned} k^r_{\pm j'}(b) = \tfrac{1}{8}\Big[&\big(t_{jN}(1)\cos\gamma_{jN}(1) \pm t_{jN}(2)\cos\gamma_{jN}(2)\big)\big(k^r_N\big)^{1/2} \\ &+\big(t_{jA}(1)\cos\gamma_{jA}(1) \pm t_{jA}(2)\cos\gamma_{jA}(2)\big)\big(k^r_A\big)^{1/2} \\ &+\big(t_{jB}(1)\cos\gamma_{jB}(1) \pm t_{jB}(2)\cos\gamma_{jB}(2)\big)\big(k^r_B\big)^{1/2}\Big]^2 \end{aligned} \tag{11}$$

$\cos\gamma_{j\mu}$ is the projection of the polarization of k^r_μ onto the dimer axis z^*. A similar expression for the polarization in the $x^*y^*(ac)$ plane can be obtained. The molecular radiative rate constants were substituted using:

$$k^r_N = C\left\{\frac{\langle S_1(\pi,\pi^*)|H_{s0}(1)|T_1\tau_N\rangle\langle S_1(\pi,\pi^*)|e\cdot r|S_{01}\rangle}{E_\pi - E_T}\right\}^2 \tag{12}$$

C is a constant, while k^r_B and k^r_A could similarly be defined using $S_1(\sigma,\pi^*)$ instead of $S_1(\pi,\pi^*)$.

Expression (11) can be expanded differently by squaring the A, B and N terms first and then adding. This largely depends on the nature of the emitting state. If the state is coherent (which is the case for the naphthalene pair[1a]) then expression (11) is valid.[1a,14,19]

4. INTERSYSTEM CROSSING (ISC)

The ISC process from the triplet resonance pair to the ground state has already been discussed by Bowman and Norris.[14e] Their results for the decay rates are:

$$\begin{aligned} k_{\pm j'} = \tfrac{1}{2}\Big[&\big(t_{jN}(1) \pm t_{jN}(2)\big)k_N^{1/2} + \big(t_{jA}(1) \pm t_{jA}(2)\big)k_A^{1/2} \\ &+\big(t_{jB}(1) \pm t_{jB}(2)\big)k_B^{1/2}\Big]^2 \end{aligned} \tag{13}$$

There remains the task of deriving the population rates of the triplet dimer levels. Normally, levels τ_A and τ_B are populated from the lowest vibrational level of the lowest singlet via spin-vibronic and/or vibronic spin-orbit coupling to a (σ, π^*) singlet. τ_N, however, is populated via direct SOC to $S_1(\pi, \pi^*)$. The τ_A and τ_B coupling scheme may occur by vibrational coupling between singlet (π, π^*) and singlet (σ, π^*) states with SOC to the triplet in question. Alternatively, vibrational coupling could be assumed in the triplet manifold. The former scheme will be adopted, but the results should be the same in either scheme. By including the full coupling perturbation one obtains:

$$\begin{aligned} T^{\nu,\rho}_{\pm j'} = T^{\nu,\rho}_{\pm j} &+ \Bigg\{ \frac{\langle S_+(\pi,\pi^*)|H_{s0}|T^{\nu,\rho}_{\pm j}\rangle}{E_\pi - E_T} \\ &+ \sum_{r=+,-} \frac{\langle S_+(\pi,\pi^*)|H_{vs0}(1,2)|S_r(\sigma,\pi^*)\rangle}{E_\sigma - E_\pi} \\ &\times \frac{\langle S_r(\sigma,\pi^*)|H_{s0}(1,2)|T^{\nu,\rho}_{\pm j}\rangle}{E_\sigma - E_T} \Bigg\} \cdot S_+(\pi,\pi^*) \\ &+ \Bigg\{ \frac{\langle S_-(\pi,\pi^*)|H_{s0}(1,2)|T^{\nu,\rho}_{\pm j}\rangle}{E_\pi - E_T} \\ &+ \sum_{r=+,-} \frac{\langle S_-(\pi,\pi^*)|H_{vs0}(1,2)|S_r(\sigma,\pi^*)\rangle}{E_\sigma - E_\pi} \\ &\times \frac{\langle S_r(\sigma,\pi^*)|H_{s0}(1,2)|T^{\nu,\rho}_{\pm j}\rangle}{E_\sigma - E_T} \Bigg\} \cdot S_-(\pi,\pi^*) \end{aligned} \qquad (14)$$

Where H_{vs0} is the sum of molecular spin-vibronic terms. The populating rates $K_\pm(j', \pm)$ from either state $S_\pm(\pi, \pi^*)$ to any of the six triplet zero-field levels of the pair can be written (again using singlet triplet energy gaps). For example,

$$K_\pm(j', \pm) = \sum_{\nu,\rho} |\langle S_\pm(\pi,\pi^*)|T^{\nu,\rho}_{\pm j'}\rangle|^2 \frac{2\pi}{\hbar} \delta(E_\pi - E_T) \qquad (15)$$

The bracketed $(\pm)$ refers to the singlet combination. Substituting (14) into (15) and expanding $T^{\nu,\rho}_{\pm j'}$ into the molecular states (Eq. (3) and (4)) one gets after considering only the terms that survive for each level (τ_A and τ_B and τ_N)

$$\begin{aligned}K_{\pm}(j',+) = \frac{1}{4}\sum_{\nu,\rho}\frac{2\pi}{\hbar}\delta(E_\pi - E_T)\Big|\big(t_{jN}(1) \pm t_{jN}(2)\big)\\ \times \frac{\langle S_1(\pi,\pi^*)|H_{s0}(1)|T_1^{\nu,\rho}\tau_N\rangle}{E_\pi - E_T}\\ + \frac{\langle S_1(\pi,\pi^*)|H_{vs0}(1)|S_1(\sigma,\pi^*)\rangle}{(E_\sigma - E_\pi)(E_\pi - E_T)}\\ \times\Big\{\big(t_{jA}(1) \pm t_{jA}(2)\big)\langle S_1(\sigma,\pi^*)|H_{s0}(1)|T_1^{\nu,\rho}\tau_A\rangle\\ + \big(t_{jB}(1) \pm t_{jB}(2)\big)\langle S_1(\sigma,\pi^*)|H_{s0}(1)|T_1^{\nu,\rho}\tau_B\rangle\Big\}\Big|^2\end{aligned} \tag{16}$$

As in the radiative rate constants Eq. (16) can be written in terms of the molecular populating rates constants:

$$\begin{aligned}K_{\pm}(j',+) = \tfrac{1}{4}\Big|\big(t_{jN}(1) \pm t_{jN}(2)\big)K_N^{1/2} + \big(t_{jA}(1) \pm t_{jA}(2)\big)K_A^{1/2}\\ + \big(t_{jB}(1) \pm t_{jB}(2)\big)K_B^{1/2}\Big|^2\end{aligned} \tag{17}$$

The expression for $K_{\pm}(j',-)$ interchanges the ($\pm$) sign in (17) to ($\mp$). Again the validity of Eq. (17) depends on the coherence of the pair states. Another factor that must be considered is the speed of ISC compared to the triplet energy exchange process. If ISC is faster then the delocalised singlet will decay into a localised triplet. This case is not considered in this work.

5. THE NAPHTHALENE RESONANCE PAIR

In the naphthalene resonance pair, the b crystal axis coincides with the z^* dimer spin axis. The x^*y^* plane lies in the ac crystal plane. A counterclockwise rotation[1a,3,21a,21] of 22.43° relates the x^*, y^* spin axes into the a, c crystal axes. The AB pair (translationally inequivalent) possess a C_2 screw rotation symmetry around the b-axis. Thus Tables (I) and (II) give the direction cosines between the molecular spin axis (A, B, N) and the crystal axes (a, b, c) as well as those between (A, B, N) and the dimer spin axes (x^*, y^*, z^*) (an excellent diagram showing the relationships of these axes is found in ref. 1a).

TABLE I

Direction Cosines between Molecular and Crystal Axes

	B	A	N
a	-0.4379	-0.3207	0.8399
b	-0.2103	-0.8718	-0.4425
c	0.8741	-0.3704	0.3143

TABLE II

Direction Cosines between Molecular and Dimer Zero-field Axes

	B	A	N
X^*	-0.7383	-0.1551	0.6564
Y^*	0.6409	-0.4647	0.6110
Z^*	-0.2103	-0.8718	-0.4425

TABLE III

Naphthalene Triplet Dynamics

k_B^r	100 (out of plane polarised)	K_B	0.64	k_B	0.85 sec^{-1}
k_A^r	3	K_A	0.25	k_A	0.5 sec^{-1}
k_N^r	5	K_N	0.11	k_N	0.07 sec^{-1}

Table (III) gives the molecular rate constants.[17,22] In the calculation only τ_B is considered emissive with an out-of-plane polarization (parallel to N).[22d,e] Table (IV) gives the results for the dimer. k_j^r and K_j are given in ratio form.

6. DISCUSSION

The results obtained in this work for the radiative rate constants (in 0-0) as well the polarization (b vs. ac) are consistent with the polarization obtained by Hochstrasser[23] and Pee *et al.*[24] The success of the model employed in this work strongly indicates that geometric factors predominate the relative distribution of the molecular triplet spin levels emissive strength over the new resonance pair states. Cooper and Fayer have shown that intermolecular SOC is strong enough to actually modify the radiative strength of the pair triplet levels.[11] More recently, intermolecular SOC has been shown to be

TABLE IV

Dynamic Properties of Naphthalene Triplet Resonance Pair

A. Radiative Properties:			
^3A_u (plus combination):		*b*-polarised	*ac*-polarised
$k^r_{+x^*}$	B_u	0	1.75
$k^r_{+z^*}$	A_u	0.035	0
$k^r_{+y^*}$	B_u	0	1.32
^3B_u (minus combination):			
$k^r_{-x^*}$	A_u	0.44	0
$k^r_{-z^*}$	B_u	0	0.14
$k^r_{-y^*}$	A_u	0.32	0
B. ISC ($S \rightarrow T$):			
		$S_-(B_u) \rightarrow T(\tau_j^*)$	$S_+(A_u) \rightarrow T(\tau_j^*)$
K_{+x^*}	B_u	1.0	0
K_{+z^*}	A_u	0	2.77
K_{+y^*}	B_u	1.15	0
K_{-x^*}	A_u	0	1.0
K_{-z^*}	B_u	2.77	0
K_{-y^*}	A_u	0	1.15
C. Decay Rates to the Ground State:			
k_{+x^*}	0	k_{-x^*}	0.61 sec^{-1}
k_{+z^*}	1.72 sec^{-1}	k_{-z^*}	0
k_{+y^*}	0	k_{-y^*}	0.36 sec^{-1}

negligible compared to intramolecular effects.[18] The present results strongly favour an intramolecular mechanism modified by geometric factors (direction cosines).

Botter *et al.*[1] have estimated the lifetime for the plus state of the naphthalene pair to be of the order of 10^{-11} s. This is in conflict with the values for k_+ obtained in Table (IV). However, the values for k_- (with an average of 0.45 sec^{-1}) is more consistent with the decay rate of 0.42 sec^{-1} they obtained for the minus state. An explanation for the inconsistency in the plus state lifetime, may lie in the inherent assumptions made in this model. Spin-lattice relaxation (SLR) and cross-relaxation (CR) effects were totally neglected in the calculation of the decay rates to the ground state. The exchange process between the two molecules and its effect on the lifetime of the pair states has also been overlooked. Botter *et al.*[1a] have shown that the triplet state in the naphthalene pair is a coherent state with the lower minus state being occupied for most of the time. Thus the overlooked processes (and in particular the exchange process) seem to affect most the calculation (in this work) for the plus state. There are no experimental results for K_j (S_1 to T_1 ISC). The three effects mentioned above may hamper any experimental measurements. Low temperature PMDR and OMDR, under conditions where SLR and CR are negligible, coupled with high optical resolution (to resolve dimer states) are needed. In another type of work geometric relationships between the monomers of photosynthetic bacteria dimers were derived from the monomer and dimer decay rates.[14] Excessive care must be exercised in the interpretation of these results in view of the type of problems arising from the exchange, SLR and CR processes.

The model used here is successful in interpreting optical properties and zero-field splittings of paracyclophanes. In particular Schweitzer *et al.*[13a,b] compared the radiative, ISC and decay rates for triplet 2.2-(1,4)-naphthaleneophane and 2.2-(2,6)-naphthalenophane with those of the corresponding monomers from which they were derived (1,4-dimethylnaphthalene and 2,6-dimethylnaphthalene respectively). The same trends for the radiative and ISC rate constants are observed for monomer and cyclophane. There is also a shortening of the triplet cyclophane lifetimes. If the two monomer portions of the cyclophanes are roughly parallel then Schweitzer's results are consistent with the present model. Calculations of this nature can shed more light on the nature of excitation in paracyclophanes (whether we have a triplet on one monomer exchanging excitation with the opposite π-moiety or a triplet delocalised on the whole cyclophane molecule). The nature of SOC in such molecules can also be better understood (in particular is there such a thing as intermonomer SOC). Unfortunately to the best of the author's knowledge no structural data an direction cosines are available for the two naphthalenophanes mentioned above.

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