Spin–orbit coupling in exciton bands of molecular crystals

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The problem of spin–orbit coupling (SOC) of exciton bands in molecular crystals is considered. In addition to the usual intramolecular SOC terms, intermolecular SOC terms are obtained if the exciton Bloch functions are properly antisymmetrized and if finite overlap of nearest neighbor molecular functions is accounted for. The magnitude of the intermolecular terms depends on the exciton wave vector k. Numerical calculations on the first triplet exciton bands of 1,2,4,5-tetrachlorobenzene crystals indicate that intermolecular SOC terms are approximately $2 \times 10^{-3}$ as large as allowed one-center intramolecular terms. This is comparable in magnitude to vibronically induced SOC which is important in many isolated molecules. The effects of triplet exciton intermolecular SOC on intersystem crossing, radiative relaxation, and nonradiative relaxation are discussed for $\pi\pi^*$ triplet exciton bands.

I. INTRODUCTION

The nature of the pathways for populating and depopulating the first excited triplet state of pure molecular crystals (triplet Frenkel excitons) is a problem of considerable importance which has received little attention although the pathways involving triplet excitations localized on guest molecules in host crystals have been studied in detail. Intersystem crossing from excited singlet states and relaxation to the ground singlet state through both radiative and nonradiative channels are processes governed by spin–orbit coupling (SOC) between the singlet and triplet manifolds. Since in general the extent of SOC differs for the three triplet spin sublevels, the intersystem crossing rates and decay rates will also vary among the levels. In most instances the isolated molecules which have been investigated belong to point groups of high symmetry, and differences in the symmetry properties of the spin sublevels have played an important role in determining the SOC routes. Experimentally, the isolated molecule problem has been successfully attacked using optically detected magnetic resonance (ODMR) to obtain the ratio of spin sublevel rate constants for intersystem crossing and radiative relaxation.

The theory of excited state delocalization and transport in molecular crystals is based upon the presence of small intermolecular interactions. Due to these interactions the stationary states of a crystal are not equivalent to the isolated molecule stationary states, but rather are wavelike linear combinations of the isolated molecule eigenstates. Because the crystal excited state wavefunctions are delocalized, the symmetry selection rules which govern their interactions are those of the crystal space group rather than the molecular point group. Thus for a crystal made up of highly symmetric molecules there is a reduction in the symmetry of the excited state in going from the isolated molecule to the crystal, and processes that are symmetry forbidden in isolated molecules may become allowed in the crystal. It is thus necessary to investigate the nature of spin–orbit coupling between delocalized exciton states. The many–molecule nature of the exciton wavefunction permits the existence of intermolecular spin–orbit coupling routes which are not available to the isolated molecule.

Because intramolecular matrix elements involve short–range (one-center) interactions, they are expected to be much larger than intermolecular matrix elements, which involve two-center integrals. But in cases where the intramolecular interactions are forbidden by molecular symmetry, the intermolecular coupling routes must be considered. In aromatic hydrocarbons, for example, the isolated molecule spin–orbit coupling between all low–energy singlets and triplets is either zero by symmetry or involves three–center integrals, as was first pointed out by McClure. Thus intermolecular SOC may be important in pure crystals of aromatic hydrocarbons.

In this paper the theory of intermolecular spin–orbit coupling is developed. It is determined that in the absence of overlap between molecular wavefunctions centered on different lattice sites, the exciton spin–orbit coupling problem reduces to the isolated molecule problem. In the general case where overlap exists, additional intermolecular terms are found. Numerical estimates are made of the intermolecular terms and they are compared to intramolecular matrix elements of representative aromatic molecules. The intermolecular terms are considerably smaller than allowed one-center intramolecular matrix elements, but are comparable in magnitude to vibronically induced spin–orbit matrix elements which are important in $\pi\pi^*$ excited triplet states. Finally, the results are applied to radiative and nonradiative processes in pure molecular crystals.

II. THEORY

Consider a pure molecular crystal composed of molecules with wavefunctions $\theta^s$, where $s$ labels the molecular eigenstate. These wavefunctions are taken to be eigenstates of the entire molecular Hamiltonian excluding the SOC term. The molecular wavefunctions can be used to construct wavefunctions for the entire crystal. The ground state crystal wavefunction $\chi^0$ is the antisymmetrized product of the ground state molecular wavefunctions at every crystal site:
\[ x^o_j = M^{-1/2} \sum_{\nu=1}^M (-1)^\nu \rho_\nu \prod_{n=1}^N \theta^{(0)}_{n\nu}, \]  
where \( \rho_\nu \) is an intermolecular electron permutation operator, subscripted such that \( \nu \) is even for even permutations and odd for odd permutations. There are \( M \) of these permutation operators. The index \( j \) labels a particular molecule within the crystal, and \( N \) is the number of molecules in the crystal.

If the molecule at site \( b \) is in excited state \( s \), the crystal excited state wavefunction is given by
\[ x^s_b = M^{-1/2} \sum_{\nu=1}^M (-1)^\nu \rho_\nu \prod_{n=1}^N \theta^{(s)}_{n\nu} \left| x^0_j \right\rangle. \]

Intermolecular interactions mix the \( N \) degenerate \( x^s_j \) and the resulting crystal wavefunctions are bands of Bloch states \( \phi^S(k) \) characterized by a wave vector \( k \)
\[ \phi^S(k) = N^{-1/2} \sum_j x^s_j e^{i(k \cdot r_j)}, \]
where \( r \) is the position vector of excited lattice site \( j \). These wavefunctions are eigenstates of the static crystal Hamiltonian \( H_0 \) excluding the SOC term.

We wish to examine the spin–orbit matrix element \( S \) which arises from the coupling of pure-singlet and triplet crystal excited states.
\[ S = \left< \phi^S(k) \left| x_{SO} \right| \phi^S(k') \right> \]

The spin–orbit Hamiltonian \( x_{SO} \) is a sum of one-electron operators (neglecting spin–other-orbital coupling) so grouping the electrons by molecules, \( x_{SO} \) can be written as a sum of operators on individual molecules.
\[ x_{SO} = \sum_{i=1}^M x_i. \]

\( x_i \) is itself a sum of the one-electron operators associated with molecule \( i \). Writing \( S \) in terms of the molecular wavefunctions and the single-molecule operators we have
\[ S = N^{-1/2} \sum_j x^s_j e^{i(k \cdot r_j)} \sum_i x_i \left< x^0_j \left| x^0_i \right\rangle x^0_i \left| x^0_j \right\rangle e^{i(k' \cdot r_j)} \right> \]
\[ = N^{-1} \sum_j e^{i(k' \cdot r_j)} \rho_\nu \prod_{n=1}^N \theta^{(s)}_{n\nu} \left< x^0_j \left| x^0_i \right\rangle x^0_i \left| x^0_j \right\rangle e^{i(k' \cdot r_j)} \right> \]
\[ \times \sum_{n=1}^N e^{i(k' \cdot r_j)} M^{-1/2} \sum_{\nu=1}^M (-1)^\nu \rho_\nu \theta^{(0)}_{n\nu} \left| x^0_j \left\rangle \left| x^0_i \right\rangle \right. \left. \right| x^0_j \right\rangle \]

In the lowest level of approximation, the overlap between molecular wavefunctions located on different molecular sites is neglected. This is equivalent to taking the molecular function to be the true orthogonalized site function (Wannier function) when forming the delocalized Bloch states. This is a useful starting place for many types of exact calculations. \(^{11b}\) However, for this problem it will be shown below that neglect of intermolecular overlaps reduces Eq. (6) to intramolecular terms only, and the exciton spin–orbit coupling problem becomes identical to the associated isolated molecule SOC. When intermolecular overlap of molecular wavefunctions is included, additional intermolecular SOC terms are found in Eq. (6). The magnitudes of these terms are estimated in the next section.

Equation (6) involves a sum over the electron permutations \( \nu \) on both the right and left sides of the matrix element. The largest terms will be those where \( \nu = \nu' \), since these will involve no intermolecular integrals. Neglecting all other terms yields
\[ S = N^{-1} \left< x^0 \left| e^{i(k \cdot r_j)} \rho_\nu \prod_{n=1}^N \theta^{(0)}_{n\nu} \right| x^0 \right> \]
\[ \times \sum_{J, \nu} e^{i(k' \cdot r_j)} \rho_\nu \prod_{n=1}^N \theta^{(0)}_{n\nu} \left| x^0 \right\rangle \left| x^0 \right\rangle \]

Because different molecular wavefunctions on the same site are orthogonal, (7) will be zero unless the excited state is on the same site on the right and left of the matrix element, which forces \( j = m \), and \( r = r' \). Also \( x_i \) must couple \( \theta^{(0)}_{n\nu} \) and \( \theta_\nu \). This coupling will be strongest when \( \nu = \nu' \) because of the short range nature of the SOC Hamiltonian. Thus (7) simplifies to
\[ S = N^{-1} \left< x^0 \left| e^{i(k \cdot r_j)} \rho_\nu \prod_{n=1}^N \theta^{(0)}_{n\nu} \right| x^0 \right> \]
\[ \times \left< x^0 \left| e^{i(k' \cdot r_j)} \rho_\nu \prod_{n=1}^N \theta^{(0)}_{n\nu} \right| x^0 \right\rangle \]

Each of the matrix elements in the sum in (8) is identical, so the sum over the exponential factor will be zero unless \( k = k' \). This eliminates the exponential factor, and performing the summation yields
\[ S = \left< \rho_\nu \prod_{n=1}^N \theta^{(0)}_{n\nu} \left| x_i \right\rangle \left| x_i \right\rangle \rho_\nu \prod_{n=1}^N \theta^{(0)}_{n\nu} \right> \]

Integration over all coordinates except those on site \( j \) yields
\[ S = \left< \rho_\nu \prod_{n=1}^N \theta^{(0)}_{n\nu} \left| x_i \right\rangle \left| x_i \right\rangle \right> \]

This is equivalent to the isolated molecule case. The approximations that have been made in arriving at this expression are the neglect of intermolecular exchange terms and the neglect of terms arising from the coupling of excited singlets and triplets on a common site by an operator centered on another site. These approximations retain all the one-center integrals while eliminating most of the terms in Eq. (6).

For compounds where the intramolecular SOC is orbitally allowed, the terms of Eq. (10) will be dominant and the SOC characteristics of the crystal will not differ from those of the isolated molecule. But frequently intramolecular SOC to particular states, such as those responsible for intersystem crossing, is orbitally forbidden. For example this is the case for \( \pi \pi^* \) states of aromatic hydrocarbons. For these compounds the terms in Eq. (10) are small and it is important to consider other terms in (6). To simplify notation, we shall consider the case where the intermolecular interactions are one dimensional. Physically this arises in crystals where the molecular stacking is much more compact along one crystal axis than the other two. Experimentally studied crystals which have basically one-dimensional intermolecular interactions include 1,4-dibromo-
naphthalene and 1, 2, 4, 5-tetrachlorobenzene. Extension to the three-dimensional case is straightforward.

The intermolecular SOC exchange terms arise when \( \nu \neq \nu' \) in (6). The largest of these terms are those for which \( \nu = \nu' \) differ by the exchange of one pair of electrons between adjacent molecules along the one-dimensional axis of the crystal. Let \( S' \) denote all such exchange terms in (6). If each \( \theta_j^f \) is considered in the optical electron approximation it is a two-electron wavefunction. Then for each permutation \( \nu \) in (6) there are four permutations \( \nu' \) which exchange a pair of optical electrons with the adjacent site on each side of the excited site in \( \chi_j^f \). For clarity we explicitly label the exchanged electron coordinates with Roman numerals. For a one-dimensional system \( r = \sigma j \), where \( \sigma \) is the lattice spacing. With these substitutions we have

\[
S' = -4 \sum_{\nu=1}^{M} \sum_{\nu=1}^{N} N^{-1} M^{-1} \left( \frac{1}{\nu} \right) \frac{1}{\nu} \prod_{\nu, \nu} \theta_j^f \left( \frac{1}{\nu} \right) \frac{1}{\nu} \prod_{\nu, \nu} \theta_j^f \ 
\]

Performing the summation over \( \nu \) and extracting the exponential yields

\[
S' = -4N^{-1} \sum_{j} e^{i\theta_j^f} \left( \frac{1}{\nu} \right) \frac{1}{\nu} \prod_{\nu, \nu} \theta_j^f \left( \frac{1}{\nu} \right) \frac{1}{\nu} \prod_{\nu, \nu} \theta_j^f 
\]

The summation over \( j \) forces \( k = k' \), and thus

\[
S' = -4e^{i\theta_j^f} \left( \frac{1}{\nu} \right) \frac{1}{\nu} \prod_{\nu, \nu} \theta_j^f \prod_{\nu, \nu} \theta_j^f 
\]

When \( \theta_j^f \) and \( \theta_j^f \) are the same parity (inversion symmetry) the two matrix elements are equal, and using \( e^{i\theta_j^f} + e^{-i\theta_j^f} = 2 \cos k a \) results in

\[
S' = -8 \cos k a \left( \frac{1}{\nu} \right) \frac{1}{\nu} \prod_{\nu, \nu} \theta_j^f \prod_{\nu, \nu} \theta_j^f 
\]

If \( \theta_j^f \) and \( \theta_j^f \) are of different parity the two matrix elements in (13) will be the negative of each other, and using \( e^{i\theta_j^f} - e^{-i\theta_j^f} = 2 \sin k a \) gives

\[
S' = -8 \sin k a \left( \frac{1}{\nu} \right) \frac{1}{\nu} \prod_{\nu, \nu} \theta_j^f \prod_{\nu, \nu} \theta_j^f 
\]

These expressions can be simplified by considering only the \( f + 1 \) term in \( \chi_j^f \), which will dominate the coupling. Making this substitution and integrating over all nonexchanged electrons yields

\[
S' = -8 \cos k a \omega_j^f \left( \frac{1}{\nu} \right) \frac{1}{\nu} \prod_{\nu, \nu} \theta_j^f \prod_{\nu, \nu} \theta_j^f 
\]

Equation (16) is the intermolecular SOC interaction due to electron exchange. It is important to note that \( S' \) is \( k \) dependent. The SOC matrix element in (16) involves two-center integrals that can be estimated in a straightforward manner. The intermolecular overlap factor can also be computed. In the next section the magnitudes of these brackets are discussed.

In addition to the intermolecular exchange SOC there is another intermolecular SOC pathway arising from terms in Eq. (6) in which the excitations represented by the right and left sides of the matrix elements are on the same site but the SOC operator is centered on an adjacent site. This results in two-center integrals such as \( \left( \chi_j^f \chi_j^f \chi_j^f \right) \). This type of coupling term does not involve electron exchange and thus there is no intermolecular overlap factor as in (16) to scale down the interaction. However, due to screening effects this type of two-center integral may be much smaller than the one arising from exchange terms. This intermolecular SOC coupling term must be kept in mind as a possible contribution to SOC in pure crystals, but because of the computational difficulties associated with screening effects, we will restrict our attention to the intermolecular exchange SOC.

III. NUMERICAL ESTIMATES

In this section the magnitude of the intermolecular SOC factor, \( S' \) of Eq. (16), will be estimated. In a later
section these values will be employed to discuss the possibility of observable effects due to the intermolecular SOC interaction. 1, 2, 4, 5-tetrachlorobenzene (TCB) will be used as a model system for this estimate. The TCB triplet state has been extensively studied in both mixed and pure crystals and the pure crystal intermolecular interactions are basically one dimensional. In TCB the molecular stacking is very compact, with only 3.3 Å separating adjacent molecular planes.11 This small interplane separation is comparable to that of many molecular crystals of planar aromatic compounds, and results in relatively large intermolecular overlap and intermolecular SOC factors.

The TCB intermolecular overlap factor \( \langle \phi_{\ell} | \xi_{\tau,\kappa} \rangle \) can be approximated by the overlap of two benzene \( \pi \) MO's spatially oriented as in the TCB crystal. The \( \pi \) MO's employed are linear combinations of carbon \( 2p_x \) AO's with coefficients on each carbon normalized for all intra-molecular overlaps. This gives the overlap of the MO's located on adjacent molecules as the sum of 36 terms consisting of overlaps of atomic orbitals at various distances and orientations. These can be evaluated using Mulliken's tables of atomic orbital overlaps.12 The atomic orbital wavefunctions used were the three-term Slater orbitals as given by Mulliken. This procedure yields a value of 0.10 for the overlap of a pair of lowest energy \( \pi \) MO's. The MO that must actually be considered is the ground state MO of the optical electrons, which is the highest occupied MO. A simple Hückel calculation (including Cl substituents) predicts that the HOMO is of \( B_{1g} \) symmetry, with a node passing through the two unsubstituted carbons. This node reduces the overlap somewhat, and the resulting value of \( \langle \phi_{\ell} | \xi_{\tau,\kappa} \rangle \) is 0.05. Although delocalization of the \( \pi \) electrons onto the Cl atoms will add additional terms and increase the overlap slightly, we will use 0.05 as an estimate of the intermolecular overlap term.

The intermolecular SOC integral \( \langle \phi_{\ell} | \xi_{\tau,\kappa} | \xi_{\tau,\kappa} \rangle \) is more difficult to calculate, but a numerical integration for a representative pair of carbon \( 2p_x \) orbitals gives a crude estimate of its size. This is equivalent to considering the entire MO to be concentrated on one atomic center. The one-electron SOC Hamiltonian is

\[
\xi_{SO} = \frac{1}{\gamma} \frac{\partial U(\gamma)}{\partial \gamma} \mathcal{L}_{x,y,z} \tag{17}
\]

Where \( U(\gamma) \) is the electrostatic potential due to a nuclear charge, and \( \mathcal{L}_{x,y,z} \) is the \( x, y, \) or \( z \) component of orbital angular momentum about that nucleus. If \( U(\gamma) \) is Coulombic, then \( \partial U(\gamma)/\partial \gamma \propto \gamma^{-3} \), and \( \xi_{SO} \propto \gamma^{-3} \mathcal{L}_{x,y,z} \). \( \mathcal{L}_{x,y,z} \) has no radial component, and acts on \( p \) orbitals by extinguishing them or rotating them by 90°. Here we only want to consider the effect of the intermolecular separation between \( \ell \) and \( \ell' \), and so the angular part of \( \xi_{SO} \) can be neglected for a suitably chosen pair of orbitals. Thus we approximate \( \xi_{SO} \propto \gamma^{-3} \) and the effect of the intermolecular separation will be estimated by comparing the one-center integral \( \langle 2p_x | \gamma_{2p_x}^1 | 2p_x \rangle \) to the two-center integral \( \langle 2p_x | \gamma_{2p_x}^1 | 2p_x \rangle \), where \( \gamma_1 \) is the distance from center 1. The orbital \( 2p_x \) is translated along the orbital axis by 3.5 Å. This is the optimal angular orientation for this integral, and results in an algebraically simple form. The atomic orbitals used were the three-term Slater orbitals given by Mulliken. The integrations were computed numerically, and the accuracy was checked by comparing the numerical result for the one-center integral to the analytical result. The ratio of the two-center integral to the one-center integral is 0.005. The actual intermolecular SOC factor for a pair of TCB MO's could be larger or smaller than this for several reasons. Most of the SOC terms resulting from an interaction between a pair of LCAO MO's will be smaller than that considered here because of unfavorable orientations. But the large number of atomic orbital pair terms (36) will in part compensate for this. Also delocalization of the \( \pi \) electrons onto the chlorines will lead to terms involving chlorine atoms. \( \xi_{SO} \) increases rapidly with increasing nuclear charge (the heavy atom effect) and SOC is 20 times stronger for a \( 3p \) Cl orbital than a \( 2p \) C orbital. Thus a favorable intermolecular SOC interaction with the Cl substituents could dramatically enhance intermolecular SOC. As discussed in detail below, the magnitude of the intermolecular spin–orbit interaction is comparable to vibronically induced spin–orbit coupling. Vibronic coupling matrix elements have been calculated for benzene and naphthalene. Since we wish to compare the results obtained here to the vibronic calculations which do not include heavy atom substituents, we have restricted our attention to the carbon–carbon interactions in the TCB system. Because of these factors 0.005 must be considered an order-of-magnitude estimate of the intermolecular SOC factor.

Putting the intermolecular overlap factor and the intermolecular SOC factor together with the factor of 8 (for the number of exchange terms) we have a rough estimate of \( 2 \times 10^{-4} \) for the ratio of the intermolecular exchange SOC matrix element in TCB to the matrix element for an allowed one-center SOC interaction.

IV. DISCUSSION

From the discussions in the last two sections, it is clear that intermolecular spin–orbit coupling can occur in triplet exciton systems and that the extent of this coupling is small relative to allowed intramolecular spin–orbit coupling. In this section the possible influence of intermolecular spin–orbit coupling on three processes associated with the lowest triplet state of molecular exciton systems will be discussed. These processes are: (A) intersystem crossing to \( T_1 \), (B) radiative relaxation from \( T_1 \) to the ground singlet state, \( S_0 \), and (C) radiationless relaxation from \( T_1 \) to \( S_0 \).

A. Intersystem crossing

At low temperatures, intersystem crossing usually takes place from the lowest vibrational level of the first excited singlet state into the triplet manifold. If there are no triplet states with energy in the interval between \( T_1 \) and \( S_0 \), intersystem crossing will occur directly into the vibrational manifold of \( T_1 \). This requires admixture of the \( T_1 \) and \( T_1 \) electronic states via the spin–orbit interaction.
Determination of the extent of $S_1 - T_1$ coupling in isolated molecules is a complex problem which must be treated on a molecule by molecule basis. However, certain generalizations can be made. For example, molecules with $\pi^* T_1$ states may have $\pi^* S_1$ states. In this situation, El-Sayed\textsuperscript{15} pointed out that direct SOC between $T_1$ and $S_1$ is orbitally allowed, and the matrix elements involved are intramolecular one-center integrals. Thus the coupling can be substantial. In contrast, isolated molecules with $\pi^* T_1$ and $S_1$ states, such as naphthalene, do not have direct strong coupling between $S_1$ and $T_1$. In naphthalene and similar planar molecules, two of the triplet spin sublevels (in-plane) can couple to $S_1$ only by an indirect vibronic coupling route\textsuperscript{6} and the third $T_1$ sublevel (out-of-plane) can couple only via very small terms involving three-center integrals.\textsuperscript{4} When considering spin-orbit coupling in triplet exciton bands of pure molecular crystals, the nature of SOC in the isolated molecule which forms the crystal is of primary importance. As pointed out in Sec. II in connection with Eqs. (6) and (10), if allowed intramolecular SOC exists, these terms will dominate the intermolecular terms and the exciton SOC will be virtually identical to the isolated molecule case.

From the above considerations, intermolecular spin-orbit coupling should have little effect on intersystem crossing in $\pi^* T_1$ exciton systems if $S_1$ is $\pi^*$ in character. However, since $\pi^*$ systems have weak intramolecular coupling between $T_1$ and $S_1$, it is necessary to consider the relative size of the intermolecular and intramolecular terms in more detail. The primary $\pi^*$ intramolecular pathway involves direct SOC of $T_1$ to high lying $\sigma^*$ singlet states $S_\mu$, and vibronic mixing of $S_1$ and the $S_\nu$ (or similar pathways involving high lying triplet states). This indirectly results in an admixture of $S_1$ and the in-plane sublevels of $T_1$. The first attempt to estimate the magnitude of the vibronic coupling was by Siebrand \textit{et al.},\textsuperscript{5(a)} who attributed the vibronic coupling to non-Born–Oppenheimer terms in the molecular Hamiltonian. Siebrand reported that the resulting second-order SOC interaction in naphthalene is $5 \times 10^{-4}$ as large as a one-center interaction. More recently, Siebrand and Zgierski\textsuperscript{5(b)} employed another approach to estimate the intramolecular SOC matrix element in benzene which was found to be on the order of $1.5 \times 10^{-5}$ as large as an orbitally allowed interaction. Metz and co-workers attributed the vibronic coupling solely to adiabatic Hertzberg–Teller coupling and building on Siebrand’s early work arrived at a vibronically mediated SOC matrix element for naphthalene only $1.2 \times 10^{-4}$ down from a one-center interaction.\textsuperscript{5(c)} Most recently, Fujimura and co-workers obtained a SOC matrix element for benzene $8 \times 10^{-4}$ down from an allowed SOC interaction.\textsuperscript{5(d)}

The numbers cited above are comparable in magnitude to the intermolecular spin-orbit coupling matrix elements calculated in Sec. III for the $1, 2, 4, 5$-tetra-chlorobenzene triplet exciton system. The intermolecular terms permit direct coupling between the TCB $T_1$ and $S_1$ states due to the reduction in symmetry resulting from the extended nature of the excited states. For the two in-plane spin sublevels which utilize vibronic coupling in the isolated molecule as part of the $T_1 - S_1$ coupling mechanism, it is possible that in a given crystal the intermolecular terms will enhance the $T_1 - S_1$ interaction and therefore increase the intersystem crossing rate. The out-of-plane spin sublevel, which in the isolated molecule couples only to $\pi^*$ singlet states via very small three-center terms has additional SOC pathways opened in $\pi^*$ exciton systems. The intermolecular terms couple this spin sublevel to high lying $\sigma^*$ states, which in turn must be vibronically coupled to $S_1$ to produce the necessary coupling between $T_1$ and $S_1$. Again we have been assuming that there is no other triplet state $T_2$ lying in the energy interval between $T_1$ and $S_1$. The vibronic–intramolecular coupling between $T_1$ and $S_1$ will be on the order of $10^{-6}$ of allowed one-center intramolecular coupling matrix elements. The vibronic–intermolecular terms are probably smaller than the intramolecular three-center terms and therefore should have little effect on intersystem crossing into the out-of-plane sublevel.

B. Radiative transition probability

Phosphorescent emission from the first triplet state of aromatic molecules to the ground singlet state is dependent on the SOC admixture of singlet states into $T_1$ to remove the $T_1 - S_0$ spin orthogonality.\textsuperscript{2(b)} The radiative transition probability is determined both by the extent of spin–orbit coupling between $T_1$ and the various singlet states $S_\mu$ and by the $S_1 - S_0$ oscillator strengths.

To illustrate the role of intermolecular spin–orbit interactions we will again discuss molecules such as naphthalene whose low lying excited states are $\pi^*$ in nature. In the isolated molecule, the two in-plane $T_1$ spin sublevels can couple directly to high lying $\sigma^*$ states. Thus there is a reasonably large admixture of these states into $T_1$. However theoretical results indicate that the $\sigma^*$ singlet states are very weakly radiative, and experimental attempts to observe these states have been unsuccessful.\textsuperscript{16} The out-of-plane triplet spin sublevel in the isolated molecule couples to low lying $\pi^*$ singlet states. However, this coupling is so weak that there is insufficient admixture of the highly radiative $\pi^*$ singlets to give significant radiative character to this spin sublevel. Thus for an isolated molecule such as TCB, two of the spin sublevels are moderately radiative while the third level is weakly radiative.

In triplet exciton systems the intermolecular spin–orbit terms provide an additional mechanism for inducing oscillator strength into the $T_1$ state. As discussed in the previous section, intermolecular spin–orbit interactions in $\pi^*$ triplet exciton states induce direct coupling between the in-plane sublevels and low lying $\pi^*$ singlet states. These coupling matrix elements are approximately three orders of magnitude down from the allowed one-center intramolecular $\pi^*$ matrix elements. This difference is somewhat offset by the smaller energy denominator associated with the coupling between $T_1$ and the closely adjacent $\pi^*$ singlet states. However, the intermolecular spin-orbit terms will only contribute significantly to the overall radiative transition
probability if the oscillator strengths of the σπ* singlet states are two or more orders of magnitude weaker than the singlet ππ* oscillator strengths. If this is the case, the intermolecular terms may enhance the radiative transition probabilities of the in-plane sublevels.

A much more sensitive indicator of the SOC route which induces oscillator strength into T1 is polarization of the phosphorescent emission relative to the molecular plane. Coupling of T1 to σπ* states will produce phosphorescence polarized perpendicular to the molecular plane, and for molecules isolated in mixed crystals this is the observed polarization. But coupling of T1 to ππ* singlet states results in phosphorescence polarized parallel to the molecular plane. Thus the emission induced by intermolecular SOC is in principle experimentally distinguishable from emission caused by intramolecular SOC, and might be detectable even if the intramolecular coupling dominates, provided crystal depolarization effects and other experimental problems are not too severe.

The out-of-plane triplet spin sublevel is coupled via the intermolecular spin-orbit interaction to σπ* singlet states, whereas in the isolated molecule it is only coupled to ππ* singlet states via very small three-center terms. Judging from the small amount of intersystem crossing to the out-of-plane sublevel in aromatic hydrocarbons, these three-center terms are smaller than the vibronically mediated SOC matrix elements that coupled S1 to the in-plane sublevels of T1. This implies that the three-center intramolecular SOC matrix elements are more than three orders of magnitude smaller than an allowed SOC matrix element, and thus the out-of-plane spin sublevel intramolecular coupling to ππ* states is probably smaller than its intermolecular SOC to σπ* singlet states. If the oscillator strength of the σπ* singlet states is not much smaller than that of the ππ* singlets then the out-of-plane sublevel will have enhanced radiative activity due to the intermolecular terms. Note that the condition for increased out-of-plane spin sublevel oscillator strength is the opposite of that for increased in-plane oscillator strength. Thus in general the intermolecular SOC will have an effect on the relative radiative strengths of the three spin sublevels. If the σπ* singlets' oscillator strengths are approximately equal to those of the ππ* singlets, the out-of-plane sublevels' radiative transition probability will be greatly enhanced. In contrast, if the σπ* singlets' oscillator strengths are several orders of magnitude weaker than those associated with ππ* singlet states, the in-plane T1 spin sublevels will have enhanced radiative transition probability.

C. Radiationless relaxation

The effect of intermolecular spin–orbit coupling on radiationless relaxation from a ππ* T1 state to a high lying vibrational level of the ground electronic state S0 is analogous to the effect on intersystem crossing discussed in Sec. IV.A. Electronic coupling between T1 and S0 is required. The dominant routes in the isolated molecule involve vibronic coupling of S0 to an excited singlet state S1 which directly spin–orbit couples to T1,2 In exciton ππ* systems intermolecular terms couple T1 and S0 directly. Following the same line of reasoning used in Sec. IV.A. One can conclude for the two in-plane sublevels that the intramolecular terms are comparable to the intermolecular terms, and therefore in some ππ* triplet exciton systems radiationless relaxation may be enhanced. For the out-of-plane exciton spin sublevel which is very weakly coupled in the isolated molecule, intermolecular spin–orbit interactions will not substantially increase the T1-S0 coupling.

D. Observables

In the previous sections the effects of intermolecular spin–orbit interactions on the electronic coupling between states involved in the various processes associated with the lowest triplet state were discussed. Direct experimental comparison of the role that SOC plays in isolated molecular systems and in exciton systems is difficult for several reasons. First, in all the processes discussed above, in addition to electronic coupling, vibrational overlaps (Franck–Condon factors) are important. There is no reason to assume that delocalized exciton states and localized isolated molecular states will have identical Franck–Condon factors. Therefore, if, for example, intersystem crossing rates are measured for both a triplet exciton system and for the triplet state of the corresponding isolated molecule, observed differences could not be uniquely attributed to intermolecular spin–orbit interactions. Second, for the isolated molecular systems which have been studied, it is not possible to measure the absolute size of parameters such as intersystem crossing rate constants or radiative rate constants for the individual spin sublevels. Rather, ratios of the parameters associated with each of the three triplet spin sublevels are determined. Finally, a molecule in a host lattice is not really isolated. The host lattice can cause significant perturbations of the guest molecule, e.g., the external heavy atom effect or lattice induced molecular distortions.

However, it should still be possible to experimentally investigate the importance of intermolecular SOC in triplet exciton systems. When the ratio of rate constants is determined, the effect of Franck–Condon factors divides out since the same Franck–Condon factor is associated with each of the triplet spin sublevels of a particular triplet state. Therefore comparison of solated molecule ratios with the corresponding triplet exciton ratios can be used to gauge the importance of intermolecular spin–orbit coupling in triplet exciton systems, provided care is taken in choosing the host crystal to avoid severe perturbations of the guest molecules. In addition, under appropriate experimental conditions, phosphorescence polarization studies can also be a sensitive probe of intermolecular spin–orbit coupling.

V. CONCLUSIONS

Spin–orbit coupling among the delocalized exciton states of pure molecular crystals has been considered. It is determined that intermolecular spin–orbit matrix
elements occur in the exciton problem in addition to the usual intramolecular terms present in the isolated molecular case. The magnitudes of the intermolecular terms depend both on the extent of overlap of the ground state nearest neighbor molecular wavefunctions and on the strength of the intermolecular spin–orbit interaction. Numerical calculations of these quantities for the one-dimensional triplet exciton system in 1, 2, 4, 5-tetra- chlorobenzene crystals indicate that the intermolecular spin–orbit coupling terms are approximately $2 \times 10^{-3}$ smaller than allowed intramolecular coupling terms. This is comparable in magnitude to vibronically induced spin–orbit coupling which is important in isolated molecules in situations where molecular symmetry considerations cause allowed intramolecular coupling terms to vanish. Since the intermolecular terms are governed by the lattice symmetry rather than the molecular point group symmetry, intermolecular spin–orbit interactions provide additional coupling pathways.

As an example, a ππ$^*$ first triplet exciton band was examined. The effect of intermolecular spin–orbit coupling on intersystem crossing to the three $T_1$ spin sublevel exciton bands, radiative relaxation from the three exciton spin sublevels, and nonradiative relaxation from the exciton spin sublevels was considered. It was found that the intermolecular terms can affect each of these processes and in systems with appropriate physical properties the effects can be significant. Finally, experimental observables associated with the intermolecular spin–orbit coupling problem were briefly discussed.

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