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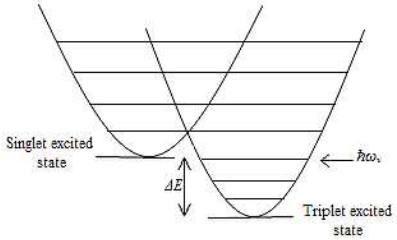
Intersystem crossing rate from singlet excited state to triplet excited state of an organic molecule has been derived using exciton-spin-orbit-molecular vibration interaction as a perturbation operator. Incorporation of heavy metal atom enhances the spin-orbit interaction and hence the intersystem crossing rate because it depends on the square of the heaviest atomic number. We found that in the presence of heavy atom the singlet-triplet energy difference still plays an influential role in the intersystem crossing process. The derived exciton-spin-orbit- molecular vibration interaction operator flips the spin of the singlet exciton to triplet exciton after photoexcitaion from the singlet ground state with the assistance of molecular vibrational energy. From this operator an expression for the intersystem crossing rate is derived and calculated in some organic solids.



Displaced potential energy surfaces of the singlet and triplet excited states.

1 Introduction The use of organic materials in organic optoelectronic devices such as organic light emitting diodes (OLEDs), organic transistors, organic solar cells (OSCs) and organic-hybrid solar cells is an area of increasing research interest [1]. The advantages of using organic materials are reduced cost of fabrication, easy processing, large scale production and compatibility with flexible substrates[2-4].

Direct conversion of sun light into electrical energy in OSC involves four electronic processes: i) exciton generation after photon absorption, ii) exciton diffusion to the donor acceptor (D-A) interface, iii) dissociation of excitons at the D-A interface, and iv) charge carriers transport to the electrodes [5]. Excitons excited in organic semiconductors can be in singlet (*S*) and triplet (*T*) spin configurations and as a consequence, both singlet and triplet excitons can be excited in OSCs. In organic materials the selection rules for the electronic dipole transitions allow generation of only singlet excitons by exciting an electron from the singlet ground state. To excite triplet excitons, one needs to flip the spin to triplet configuration in the excited state, which is achieved through the strong exciton-spin-orbit interaction (ESOI) [6, 7]. This is how ESOI also helps in creating triplet excitons via intersystem crossing (ISC). In organic solids, the triplet exciton state usually lies below the singlet exciton state and their vibronic states overlap in energy. In this case, first a singlet exciton is excited by photon absorption to a higher vibronic energy level which is isoenergetic with the vibronic level of the triplet state. As a result, if the ESOI is strong it flips the spin of the excited electron to triplet and it crosses to the triplet exciton state [8]. As ESOI is proportional to the atomic number (Z_n) [7], it is expected to be weak in organic materials which are composed mainly of carbon and hydrogen [9]. To enhance ESOI, therefore, one needs to incorporate heavy metal atoms in organic solids and polymers.

The incorporation of iridium (Ir) and platinum (Pt) into the active layer of OSCs results in the phosphorescent

sensitizer, fac-tris(2-phenylpyridine) iridium [Ir(ppy)3] [1, 10] and platinum-acetylide [p-PtTh][11] and has been found to increase the power conversion efficiency (PCE) [8, 10] of OSCs. Although this improvement has been attributed to the increase in the triplet exciton concentration with higher diffusion length [1, 10, 12], the mechanism of such a process has never been fully understood.

In this paper, our objective is to study the effect of spin- orbit interaction on the mechanism of ISC in organic semiconductors and polymers. It is known that the spin-orbit coupling flips the singlet spin configuration to triplet and vice versa and hence facilitates ISC [6, 8, 13]. ISC from a singlet excited state to a triplet excited state has been studied theoretically [14-16] and as well as experimentally [11,12]. Theoretical models have so far been limited to either numerical calculation of ISC rates [14-16] or estimation of the spin-orbit interaction transition matrix element [17]. To the best of the authors' knowledge no attempt has yet been made to derive the transition matrix element due to the spin-orbit interaction in calculating the ISC rates. Here, an exciton-spin-orbit-molecular vibration interaction operator suitable for ISC in organic solids is derived. Using this operator, an expression for ISC rate is derived and calculated in some organic solids. The effects of incorporation of heavy atom on the ISC rate are explored and the results are compared with their experimental values.

2 Exciton-spin-orbit-molecular vibration interaction operator

The stationary part of the spin-orbit interaction for an exciton in a molecule consisting of N atoms can be written as [6]

$$H_{so} = -\frac{e^2 gk}{2\mu_x^2 c^2}\sum_{n}^{N}\left(\frac{Z_n}{r_{en}^3}\mathbf{s}_{\mathrm{e}}\bullet\mathbf{l}_{\mathrm{en}}+\frac{Z_n}{r_{hn}^3}\mathbf{s}_{\mathrm{h}}\bullet\mathbf{l}_{\mathrm{hn}}\right), \tag{1}$$

where e is the electron charge, $g=2$ is the gyromagnetic ratio, $k=1/4\pi\varepsilon_o$ is the Coulomb constant, $\mu_x^{-1}=m_e^{-1}+m_h^{-1}$ is the reduced mass of exciton, c is the speed of light, $\mathbf{s}_e(\mathbf{s}_h)$ is the electron (hole) spin, $\mathbf{l}_{en}=\mathbf{r}_{en}\times\mathbf{p}_e$ is electron angular momentum and $\mathbf{r}_{en}(\mathbf{p}_e)$ is the position vector (orbital momentum) of the electron from the nth nucleus. Similarly, $\mathbf{l}_{hn}=\mathbf{r}_{hn}\times\mathbf{p}_h$ is the hole angular momentum and $\mathbf{r}_{hn}(\mathbf{p}_h)$ is the position vector (orbital momentum) of the hole from the nth nucleus. For a non-rigid structure, Eq. (1), can be expanded in Taylor series about the equilibrium positions of molecules. Terminating the expansion at the first order, we get:

$$H_{so}=H_{so}^0+H_{sov}, \tag{2}$$

where H_{so}^0 is the zeroth order term and represents the interaction in a rigid structure and H_{sov} is the first order term which gives the interaction between exciton-spin-orbit interactions and molecular vibrations and it is obtained as:

$$H_{sov} = -\frac{3e^2 gkZ}{2\mu_x^2 c^2}\sum_{n,v}\left(\frac{\mathbf{s}_e\bullet\mathbf{l}_e}{r_e^4}R_{nv}+\frac{\mathbf{s}_h\bullet\mathbf{l}_h}{r_h^4}R_{nv}\right), \tag{3}$$

where R_{nv} is the molecular displacement from the equilibrium position due to the intramolecular vibrations . The quantity within parentheses in Eq. (3) depends on r_{en}^{-4} and r_{hn}^{-4} thus the nearest nuclei to the electron and hole is expected to play the dominant influence and as such the presence of other nuclei may be neglected as an approximation. This approximation helps in reducing the summation to only one nucleus for each electron and hole. In carrying out the Taylor series expansion, it is further assumed that the distances r_{en} and r_{hn} of the electron and hole with reference to the individual nuclei of a molecule can be replaced by their distances r_e and r_h, respectively, with reference to the equilibrium position of the individual molecules. This approximation may be regarded to be quite justified within the Born-Oppenheimer approximation regime.

In second quantization R_{nv} can be expressed as [2]:

$$R_{nv}=(q_{vo}-q_{oo})(b_{nv}^{+}+b_{nv}), \tag{4}$$

where $b_{nv}^{+}(b_{nv})$ is the vibrational creation (annihilation) operator in vibrational mode v .

For expressing the operator in Eq. (3) in second quantisation, we can write the field operator for an electron in the LUMO and that of a hole in the HOMO, respectively, as:

$$\hat{\psi}_e=\sum_{\sigma_e}\varphi_{LUMO}a_L(\sigma_e), \tag{5a}$$

$$\hat{\psi}_h=\sum_{\sigma_h}\varphi_{HOMO}d_H(\sigma_h), \qquad d_H(\sigma_h)=a_H^{+}(-\sigma_h), \tag{5a}$$

where φ_{LUMO} and φ_{HOMO} are the wavefunctions of the electron in the LUMO and hole in the HOMO, respectively. It may be clarified here that we are dealing with molecules, hence, the valence and conduction bands wavefunctions are those of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. Using Eq. (5) the interaction operator in Eq. (3) can be expressed in second quantization as:

$$\hat{H}_I \approx -\frac{24e^2 gkZ}{\mu_x^2 c^2 r_x^4}\sum_{v,\sigma_e,\sigma_h}(q_{vo}-q_{oo})a_L(\sigma_e)d_H(\sigma_h)\delta_{\sigma_e,\sigma_h}\times(\mathbf{s}_e\bullet\mathbf{l}_e+\mathbf{s}_h\bullet\mathbf{l}_h)(b_{nv}^{+}+b_{nv}), \tag{6}$$

where r_x is the average separation between the electron and hole in the exciton and it is approximated as:

$$\langle\varphi_{HOMO}\|r_{en}^{-4}\|\varphi_{LUMO}\rangle\approx\langle\varphi_{HOMO}\|r_{hn}^{-4}\|\varphi_{LUMO}\rangle\approx\left(r_x/2\right)^{-4}$$

To evaluate the spin and orbital angular momentum operators in the interaction operator Eq. (6), we can use [18]

$$s \bullet l = \frac{J^2 - l^2 - s^2}{2} \quad , \tag{7}$$

where J is the total angular momentum. Equation (7) can be re-arranged as:

$$J^2 = l^2 + s^2 + 2(s_x l_x + s_y l_y + s_z l_z) \, , \tag{8}$$

Defining s_i and l_i ($i = x, y$) in Eq. (8) in terms of orbital angular momentum raising (lowering) operator as $L_+ = l_x + il_y$ ($L_- = l_x - il_y$) and spin angular momentum raising (lowering) operator as $S_+ = s_x + is_y$ ($S_- = s_x - is_y$), respectively, we get

$$J^2 = l^2 + s^2 + 2\left(\frac{S_+L_+ + S_-L_+ + S_+L_- + S_-L_-}{4}\right) - 2\left(\frac{S_+L_+ - S_-L_+ - S_+L_- + S_-L_-}{4}\right) + 2s_z l_z \, , \tag{9}$$

Using Eq. (8) in Eq. (6) we obtain

$$s \bullet l = s_z l_z + \frac{S_-L_+}{2} + \frac{S_+L_-}{2} \, , \tag{10}$$

It is this term in the interaction operator Eq. (6) that flips the spin of the exciton from the singlet to triplet configuration. Using Eq. (10) in Eq. (6) we get:

$$\hat{H}_I \approx \frac{12\hbar^2 gkZe^2}{\mu_x^2 c^2 r_x^4} \sum_{v,\sigma_e,\sigma_h} (q_{vo} - q_{oo}) \times a_L(\sigma_e) d_H(\sigma_h) \delta_{\sigma_e,\sigma_h} (b_{nv}^+ + b_{nv}) \, , \tag{11}$$

here we assume $l_{ez} \approx l_{hz} = l_z = \hbar$, which is the angular momentum associated with first excited state with the magnetic quantum number 1.

3 Intersystem crossing rate Assuming that the initial state $|i\rangle$ consists of an exciton in the singlet spin configuration and molecular vibrations and the final state $|f\rangle$ consists of a triplet exciton and molecular vibrations. Using occupation number representation the initial state can be written as:

$$|i\rangle = \frac{N^{-3/2}}{\sqrt{2}} \sum_{n_1,m_1,v_1} \sum_{\sigma_e,\sigma_h} [a_{n_1L_1}^+(+\sigma_e) d_{m_1H_1}^+(-\sigma_h) + a_{n_1L_1}^+(-\sigma_e) d_{m_1H_1}^+(+\sigma_h)] b_{n_1v_1}^+ |0\rangle |v_1\rangle \, , \tag{12}$$

where the electron is created in the LUMO at site n_1 and a hole in the HOMO at site m_1, $|0\rangle$ represents the electronic vacuum state and $|v_1\rangle$ is the initial molecular vibrational occupation state. Likewise, the final state can be expressed as:

$$|f\rangle = \frac{N^{-3/2}}{\sqrt{2}} \sum_{n_2,m_2,v_2} \sum_{\sigma_e^I,\sigma_h^I} [a_{n_2L_2}^+(+\sigma_e^I) d_{m_2H_2}^+(-\sigma_h^I) - a_{n_2L_2}^+(-\sigma_e^I) d_{m_2H_2}^+(+\sigma_h^I)] |0\rangle |v_2\rangle \, , \tag{13}$$

where the electron is located in the LUMO at site n_2 and a hole in the HOMO at site m_2, and $|v_2\rangle$ is the final molecular vibrational occupation state after the spin flip into the triplet excited state.

Using the usual anticommutation relation for fermions and commutation relations for boson operators, the transition matrix element is obtained from Eqs. (11)-(13) as

$$\left\langle f \middle| \hat{H}_I \middle| i \right\rangle = -\frac{12gkZe^2\hbar^2 n_v}{\mu_x^2 c^2 r_x^4} (q_{vo} - q_{oo}) \, , \tag{14}$$

where n_v is the effective number of vibrational levels taking part in the transition process.

Using Fermi's golden rule then the rate of intersystem crossing k_{isc} can be written as:

$$k_{isc} = \frac{2\pi}{\hbar} \left| \left\langle f \middle\| \hat{H}_I \middle\| i \right\rangle \right|^2 \delta(E_f - E_i) \, , \tag{15}$$

Here $E_f = E_T + n_1\hbar\omega_v$ is the final triplet state energy and $E_i = E_S + n_2\hbar\omega_v$ is the initial singlet state energy including the energy of corresponding vibrational energies. E_S and E_T are the singlet and triplet exciton energies, respectively.

Substituting Eq.(14) into Eq.(15), we get k_{isc} as:

$$k_{isc} = \left(\frac{12g\varepsilon^4 kZe^2\hbar^2 n_v}{\mu_x^2 c^2 a_x^4} (q_{vo} - q_{oo}) \right)^2 \delta(-\Delta E + n_v\hbar\omega_v) \, , \tag{16}$$

where $r_x = \frac{a_x}{\varepsilon}$ is used to express the rate in terms of the excitonic Bohr radius a_x and ε is the dielectric constant. Expressing $E_f - E_i = -\Delta E + n_v\hbar\omega_v$, where $\Delta E = E_S - E_T$, $n_v = n_2 - n_1$ and the square of the molecular displacement due to excitation as: $(q_{vo} - q_{oo})^2 = \frac{8\pi r_x^2}{3}$ [2], k_{isc} is obtained as:

$$k_{isc} = \frac{3072\pi^2\varepsilon^6 k^2 Z^2 e^4 \hbar^3}{\mu_x^4 c^4 a_x^6 (\hbar\omega_v)^3} (\Delta E)^2 \, , \tag{17}$$

4 Results and discussions The rate derived in Eq. (17) depends on excitonic Bohr radius, molecular vibrational energy, the atomic number of the heaviest atom and ΔE, the exchange energy between the singlet and triplet excited states. Although ISC is very well known process, the interaction operator derived here in Eq. (6) is the first one known to the best of our knowledge. The above derivation also clarifies how the phenomenon of ISC occurs. An exciton is first excited to the singlet exciton state which is higher in energy than the triplet state. The higher energy of the singlet excited state provides the required exciton-spin-orbit-molecular vibration interaction energy to flip the spin to triplet state before the transfer can take place. This

is the reason that k_{isc} in Eq. (17) vanishes when ΔE is equal to zero.

The rate in Eq. (17) is calculated in several known molecules used in the fabrication of organic solar cells and listed in Table 1, along with material parameters used in the calculation.

Table 1 The calculated intersystem crossing rate (k_{isc}) from Eq. (17) and experimental rates $(k_{isc}^{\exp})$, for some OSC materials along with their highest atomic number (Z) and singlet-triplet energy difference (ΔE). For these calculations we have used $\varepsilon = 3$, $a_x = 4.352nm$, and $\omega_v = 8\times10^{14}\,s^{-1}$.

Organic material	z	$\Delta E(eV)$	$k_{isc}(s^{-1})$	$k_{isc}^{\exp}(s^{-1})$	Ref.
NPD (Ir doped)	77	0.90 [10]	$1.1\text{x}10^{11}$		
CBP (Ir doped)	77	0.90 [10]	$1.1\text{x}10^{11}$		
P3HT	16	0.80 [12]	$3.7\text{x}10^{9}$		
SubPc	9	0.71	$9.2\text{ x}10^{8}$	$9.1\text{ x}10^{8}$	[19]
F8BT	16	0.70	$2.8\text{ x}10^{9}$	$1.2\text{ x}10^{7}$	[20]
Toluene	6	0.70	$4.0\text{ x}10^{8}$	$8.5\text{ x }10^{6}$	[21]
Naphthalene	6	1.47	$1.8\text{ x }10^{9}$	$5.0\text{ x }10^{6}$	[22]
1-Bromo-naphthalene	35	1.30	$4.7\text{ x }10^{10}$	$\approx \text{x }10^{9}$	[23]
Benzophenon	16	0.30	$5.2\text{ x }10^{8}$	$\approx \text{x }10^{10}$	[22]
Platinum-acetylide	78	0.80	$8.8\text{ x }10^{10}$	$>\text{x }10^{11}$	[11]

where;

NPD=N,N'-bis (naphthalen-1-yl)-N, N'-bis(phenyl)-benzidine

CBP= 4,4'-bis(9-carbazolyl)-1,1'-biphenyl

P3HT = poly(3-hexylthiophene)

SubPc= boron subphthalocyanine chloride

F8BT = poly(9,9-dioctylfluorene-cobenzothiadiazole)

According to Table 1, the calculated rates are found to be in reasonable agreement with experimental results and the minor discrepancies may be attributed to the approximations used in deriving Eq. (17). The rate in Eq. (17) can be applied to calculate the ISC rate in any molecular solid. It is therefore expected that the results of this paper will provide a simple way to study ISC in any organic device.

5 Conclusions In summary, we have derived an expression for the exciton-spin-orbit-molecular vibration interaction operator which has been used to calculate the rate of ISC from singlet excited state to triplet excited state in organic molecules. The rate is sensitive to spin-orbit coupling and the singlet-triplet energy difference. This study may help in designing OSCs with enhanced triplet exciton concentration.

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