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The temperature dependence of the spin relaxation of coupled polaron pairs in organic semiconductors

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ABSTRACT

The coupled polaron pair distributed in adjacent organic molecules has spin relaxation due to molecular vibration. We construct a Hamiltonian with on-site energy fluctuation to investigate its temperature dependence. The relaxation occurs between spin singlet and one of the spin triplet states, but not between spin triplet states. It is found that the polaron pair finally relaxes to a spin state with half probability in spin singlet state and 1/6 probability in each of the spin triplet states, and the relaxation time is inversely proportional to the temperature's square. The connection to the magneto-electroluminescence experiment is also discussed.

Because of their potential applications in electronics and energy industry, the organic semiconductors have attracted much interest, especially on their electrical and optical properties [1,2]. In the optoelectronic or photovoltaic devices, the electronic processes are often comprehensive and comprise of evolution processes of coupled carriers [3–5]. The intermediate states, such as excitons, polaron pairs and charge transfer states (exciplex), can be constructed in close molecules, and are found playing important role[5]. The coupled polaron pair or exciplex in different spin states have different recombination rates and energies, which have been used to explain the magnetic field effect in organic semiconductors (OMEF) at the room temperature [6–13]. The evolution of the exciplex or coupled polaron pair is also important in understanding the organic photovoltaics properties [14]. The intersystem crossing between spin states of the excitons being attained by intramolecular charge transfer is used to improve the efficiency of the organic light-emitting diodes [15,16]. At nonzero temperature, the molecule vibration causes fluctuation of the spin singlet and spin triplet energy levels of polaron pair, and involves the spin relaxation between these levels [17]. More investigation on the temperature's effect on the spin evolution of the intermediate states are necessary for better understanding on the organic electronic and optical processes [18,16]. In this paper, we investigate the temperature dependence of the spin relaxation between spin singlet and spin triplet states in organic semiconductors, and discuss the temperature's effect in the organic magneto electroluminescence.

Let us consider a coupled polaron pair with same or opposite charge spatially close to each other. The polaron pair can reside in same molecule (exciton or bipolaron) or two molecules (coupled polaron pair or exciplex), and the exchange coupling between polarons can not be neglected (Fig. 1(a)). The coupled polarons can be in spin singlet or triplet states. In the presence of magnetic field, the spin levels will split, as illustrated in Fig. 1(b). The spin mixing of the spin states stems from the hydrogen hyperfine interaction and the procession velocity difference. The Hamiltonian for the spin part of the system can be expressed following Ref. [7] as

$$
\begin{aligned}
H &= H_0 + H_{ST}\\
H_0 &= \frac{g_1+g_2}{2}\mu_B(\mathbf{s}_1+\mathbf{s}_2)\cdot\mathbf{B} - J(r)\left(\frac{1}{2}+\frac{2\mathbf{s}_1\cdot\mathbf{s}_2}{\hbar^2}\right) \qquad (1)\\
H_{ST} &= \frac{g_1-g_2}{2}\mu_B(\mathbf{s}_1-\mathbf{s}_2)\cdot\mathbf{B} + (a_1\mathbf{I}_1\cdot\mathbf{s}_1 + a_2\mathbf{I}_2\cdot\mathbf{s}_2)
\end{aligned}
$$

where $\mathbf{s}_{1,2}$ are the spin operators of the polarons 1 and 2 and $g_{1,2}$ are the corresponding g-factors. $\mathbf{I}_{1,2}$ are the effective nuclear spins and $a_{1,2}$ are corresponding hyperfine interaction strength. H_0 has spin singlet and spin triplet states as its eigenstates, while H_{ST} would cause the transition between these spin states (spin mixing). Normally $g_1 - g_2$ are small, therefore the hyperfine interaction (second term of H_{ST}) is the main reason for spin mixing [7,10,12]. $J(r)$ is the exchange interaction strength, and $2J(r)$ is the energy difference between spin singlet and spin triplet states when $B = 0$. For $B \neq 0$, $g\mu_B B$ is the Zeeman energy difference, where $g = (g_1 + g_2)/2$.

At nonzero temperature there are both intermolecular and intramolecular vibrations, or both the intermolecular and

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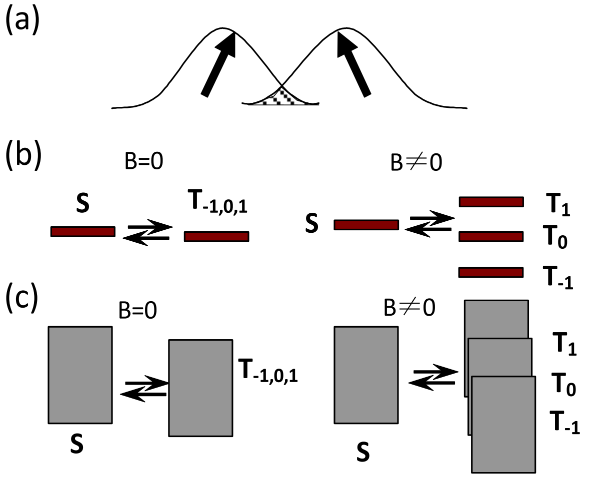

Fig. 1. Illustration of the molecular vibration effect on the polaron pair or exciplex. (a) Our model: a (coupled) polaron pair or an exciplex. The shadow area is the wavefunction overlap. The spin related energy levels are shown when there is no vibration (b) and there is vibration (c).

intramolecular vibration phonon modes are excited. Nevertheless, the first-principle calculations of naphthalene crystal have shown that at room temperature the main excited modes are intermolecular vibration [19]. In addition, at same temperature the intermolecular vibration amplitudes is larger than intramolecular counterpart because of their weak coupling strength. The vibration amplitude of a naphthalene molecule is estimated to be around 0.03 nm at temperature $T = 300$ K based on the results in Ref. [19]. As shown in Fig. 1(a), the polaron pair or exciplex distributes in neighbor molecules, and their exchange interaction depends on the vibration. The exchange interaction $J(r)$ is a function of r, the wave package distance, and can be expressed as $J(r) = J_0 e^{-\lambda r}$, where λ and J_0 are two parameters related to specific molecular structure [20]. With the increase of temperature, more phonons are excited and the vibration is more severe. Therefore, we assume that only the intermolecular vibration takes effect, and the exchange interaction $J(r)$ in Eq. (1) depends on the vibration so as on the temperature. As in Ref. [17], we assume that the molecular vibration induces the oscillation of $J(r)$, described by a stochastic process, and the oscillation strength of $J(r)$ is proportional to $k_B T$ [20]. In this case the oscillation strength reflects the temperature's effect in the Hamiltonian, and this is all the temperature dependence comes from. Consequently, in the basis of spin singlet and spin triplet states, the Hamiltonian can be written in the form of a 4 × 4 matrix, with fluctuation in the diagonal elements.

$$H = \begin{bmatrix} \epsilon_1 + \xi(t)/2 & s_1 & s_2 & s_2 \\ s_1 & \epsilon_2 - \xi(t)/2 & s_3 & s_3 \\ s_2 & s_3 & \epsilon_3 - \xi(t)/2 & s_4 \\ s_2 & s_3 & s_4 & \epsilon_4 - \xi(t)/2 \end{bmatrix}, \tag{2}$$

where $\epsilon_{1,2,3,4} \pm \xi(t)/2$ are the energies of the four spin states and $\xi(t)$ is stochastic process describing the temperature's effect; $s_{1,2,3,4}$ are the coupling between different spin states. Based on Eq. (1), these couplings s_i stem mainly from hyperfine interaction. Here the couplings are chosen as constants because the nuclear spins evolve very slow, and assume to be vibration independent. In the following calculation, the energy of four states are set as $\epsilon_1 = 0$, $\epsilon_2 = -2J_0$, $\epsilon_{3,4} = -2J_0 \pm g\mu_B B$, where J_0 is the coupling strength at $T = 0$ K. Here we have set the energy difference between spin singlet state and T_0 spin triplet state as $2J(r) = 2J_0 + \xi$, and the energy difference between spin triplet states is Zeeman splitting without any fluctuation since the only fluctuation term is $J(r)$. For the polaron pair distributes in different molecules, $\xi(t) \neq 0$, while for an exciton situating on one molecule, there are no fluctuating part of exchange interaction, $\xi(t) = 0$ is satisfied. Normally a stationary process is used to describe the effect of temperature [21], which has a zero average, $\langle \xi(t) \rangle = 0$.

Based on Eq. (2) Liouville equation for density matrix $\rho(t)$ would be solved to give the probability of system in spin singlet $|S\rangle$ and spin triplet states $|T_{0,\pm 1}\rangle$,

$$i\hbar \frac{d\rho(t)}{dt} = [H, \rho(t)]. \tag{3}$$

This equation is actually 4 coupled ordinary differential equations with stochastic processes involved, or stochastic differential equations [22]. The numerical analysis of these equations differs significantly from that of ordinary differential equations [21,22]. It is worth stressing that we are only interested in the probability of the system being in the four states, the ensemble average has to be applied to give valuable results. In real organic devices, each polaron spin has half probability in both spin-up state and spin-down state. For the coupled polaron pair, statistically the probability of being in each of the four spin states is 1/4. Therefore we assume that the spin state of the system evolves from a pure state, $|\psi(0)\rangle = (|S\rangle + |T_1\rangle + |T_{-1}\rangle + |T_0\rangle)/2$, and all the matrix elements of density matrix are initially $\rho_{ij}(0) = 1/4$, and evolve according to Eq. (3).

Eq. (3) can be solved analytically in two cases, at zero temperature $T = 0$ K or for the case that the electron–hole pair distributes in same molecule (exciton). In both cases $\xi(t) = 0$, and the equations reduce to normal coupled differential equations without stochastic process. The related results and discussions for the 2 × 2 case have been shown in Ref. [17]. Here we only give the numerical results for $\xi \neq 0$.

In the calculation, we assume that the coupling between molecules at $T = 0$ K, $J_0(r)$, is small and omitted. Therefore $\epsilon_1 = 0 = \epsilon_2$, $\epsilon_{3,4} = \pm g\mu_B B$. In organic semiconductors the hyperfine and the spin–orbit coupling accounting for the spin mixing are small [23]. In our numerical simulation, for simplicity we assume that $s_{1,2,3,4}$ have same value s, and $s = 5 \times 10^{-3}$ meV (Fig. 2) and $s = 4 \times 10^{-4}$ meV are used. The stochastic process $\xi(t)$ is chosen to be a stationary Gaussian white noise (corresponding time integrals are Wiener Processes), with zero average and $\langle \xi(t)\xi(t+\tau) \rangle = \sigma^2 \delta(\tau)$, where σ depicts the strength of disorder. In our model the disorder stems from temperature T, hence the strength of disorder is set as $\sigma \propto k_B T$. Taking into the consideration of the dimensionality, $\sigma = k_B T \sqrt{\hbar/2s}$ is chosen in the numerical simulation [24]. Furthermore, the presence of *white noise* process in Schrödinger equation will induce the violation of the conservation of probability using normal discretization methods, $\langle \Psi(t+\delta t) | \Psi(t+\delta t) \rangle \neq \langle \Psi(t) | \Psi(t) \rangle$, because of the unique property of white noise process $\int_t^{t+\delta t} \int_t^{t+\delta t} \langle \xi(t_1)\xi(t_2) \rangle dt_1 dt_2 = \delta t$. To avoid this, we may artificially add another term $-i\hbar\sigma^2\rho/2$ to the right side of Eq. (3) to give the so-called Schrödinger–Langevin equation [22]. All numerical calculations are based on this new rate equation [17].

The numerical results for the spin state relaxation at $B = 0$ are shown in Fig. 2. At each nonzero temperature, there is spin relaxation, and finally the system will relax to a mixed state that 1/2 probability in spin singlet state and 1/6 probability in each of the three spin triplet states. This can be explained because the direct relaxation only happened between spin singlet state and one of the spin triplet states, but not between two spin triplet states [17]. As shown in Ref. [17], a two-level system comprising of the spin singlet state and one of the spin triplet state will relax to the final state having 1/2 probability in singlet and 1/2 in triplet state, implying the symmetry of the levels in the relaxation of