

Triplet energy transfer in conjugated polymers. II. A polaron theory description addressing the influence of disorder

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Motivated by experiments monitoring motion of triplet excitations in a conjugated polymer containing Pt-atoms in the main chain (see Paper I), a theoretical formalism for electronic transport has been developed. It considers the interplay between polaronic distortion of the excited chain elements and disorder treated in terms of effective-medium theory. The essential parameters are the electronic coupling J , the polaronic binding energy λ that determines the activation energy of polaron motion E_a , and the variance σ of the density of states distribution controlling the incoherent hopping motion. It turns out that for the weak electronic coupling associated with triplet motion (J a few meV), the transfer is nonadiabatic. For a critical ratio of $\sigma/E_a < 0.3$, Marcus-type multiphonon transport prevails above a certain transition temperature. At lower temperatures, transport is disorder controlled consistent with the Miller-Abrahams formalism. Theoretical results are consistent with triplet transport in the Pt-polymer. Implications for charge and triplet motion in random organic semiconductors in general are discussed.

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I. INTRODUCTION

The success of organic semiconductor materials in device applications depends on our understanding of the excited-state photophysics. At present, there is a particular need to develop our knowledge about the spin triplet excited state, which is used extensively in organic light-emitting diodes (LEDs) and solar cells. In LEDs, triplet states are harvested and employed in sometimes elaborate device architectures for light emission.^{1–5} Similarly an increasing number of solar cells relies on the diffusion of triplet states to the dissociating interface.^{6–9} Both applications benefit from clever use of the triplet state migration. While much research has been dedicated to the spin singlet excited-state transfer that proceeds through dipole-dipole coupling,^{10–13} the mechanism of triplet motion has received less attention.

Triplet migration occurs as a succession of triplet energy-transfer processes. The individual transfer is based on an exchange mechanism (Dexter transfer) that is well understood for an individual donor-acceptor pair.^{14–18} However our insight into the mechanism of triplet transfer in a disordered organic solid is still limited to only a few studies.^{19–24} The transfer of a triplet excitation from a site in a molecular solid to another one involves the correlated exchange of two electrons under conservation of the total spin. The electron that has been excited to the lowest unoccupied molecular orbital (LUMO) is transferred to the previously unexcited acceptor molecule. Simultaneously, an electron of the highest occupied molecular orbital (HOMO) of the previously unexcited molecule is transferred to the singly occupied HOMO of the initially excited molecule. This implies that triplet transfer and charge transfer are related phenomena. Moreover, by studying the triplet transfer, we will also gain information on charge-transfer processes. A full picture of the

physics of charge transport is fundamental to the development of LEDs and transistors.^{25,26}

In some respect, the study of triplet migration can complement the information gained from charge measurements in LEDs and transistors. The transport of charges is determined by two parameters, which are the energetic disorder present in the material (referred to as σ) and the amount of lattice relaxation associated with the charge (the geometric reorganization energy λ). Since triplet motion is based on a double charge transfer, the same parameters will also play a key role in the process of triplet diffusion.^{18,27} However, in contrast to a single charge, a spin singlet or triplet excited state is overall charge neutral. It is therefore less sensitive to polarization effects of the environment that induce energetic disorder. In addition, in a spin triplet excitation, the two electrons are correlated. The resulting small size of the triplet state further reduces its susceptibility to energetic disorder. Thus in contrast to a single charge, the triplet exciton is characterized by a much lower disorder parameter. When we want to know how charge transfer is affected by the relative contributions of energetic disorder compared to polaronic effects, it is often difficult to experimentally access the regime of low disorder in order to study the transport that is predominantly of a polaronic nature. By studying the (double) charge transfer in the triplet motion, however, both the low and the high disorder regime can be probed. This allows us to contribute to a fuller and more complete picture of charge transfer in organic semiconductors.

In our previous paper [Paper I (Ref. 28)], we experimentally studied the temperature dependence of triplet motion in a conjugated polymer and its associated monomer that are characterized by a particularly low disorder of the triplet density of states (DOS). For the polymer we found a ther-

mally activated motion to occur from room temperature down to a transition temperature at 80 K. In this regime we found that, similar to charge transfer, the Dexter-type triplet transfer may also be described by using a Marcus theory model for thermally activated multiphonon hopping.²⁸ Below the transition temperature, triplet motion becomes nearly temperature independent and we attributed this to a tunneling mechanism similar to the one suggested initially by Holstein in his small polaron theory. When analyzing the data in our previous experimentally focused paper, we neglected the contribution from a very small disorder present for the triplet state in this compound and we only considered the polaronic effects, since Marcus theory is a purely polaronic theory.^{29,30} Here we present a full theoretical treatment that explicitly takes into account both polaronic contributions and effects due to the energetic disorder commonly present in disordered molecular or polymeric semiconductors.

The paper is organized as follows: In Sec. II, the theoretical approach is developed. We will first consider whether charge carriers move adiabatically or nonadiabatically in order to derive a formalism for triplet transport following earlier work by Emin and co-workers^{31–34} on charge transfer. This then serves as a basis to develop expressions that describe the triplet transport using an effective-medium approximation (EMA). The pioneering work by Emin and co-workers considers only isolated energetic sites while the effective-medium approximation takes the many-body character of the solid into account. In Sec. III, the resulting expressions are first compared to the experimental data before using them to explore how the triplet transfer characteristics depend on the relative weight of polaronic relaxation versus energetic disorder. The implications of our findings are discussed in Sec. IV.

II. THEORETIC FORMULATION

Triplet transfer consists of a double charge transfer.^{18,27} The theoretical approach we take is therefore based on the same formalism that has already been employed to describe charge transfer,³⁵ yet certain terms will have a slightly different interpretation as outlined below.³⁶ We have recently considered the influence of disorder on charge transfer using an analytical theory based on the effective-medium approach.³⁵ Here we will use a similar approach. As a starting point, we need to consider whether triplet transfer occurs in an adiabatic or nonadiabatic transport regime.

A. Adiabatic versus nonadiabatic polaron transport regime

Polaron transfer between different molecular sites is generally considered in two different limits, adiabatic or nonadiabatic, depending on material parameters.^{34,37–39} The difference between the two regimes is illustrated in Fig. 1. Let us consider a two-site system. For a charge carrier on a molecular site, the local change in the equilibrium position of the associated atoms can be described by means of two corresponding configuration coordinates (Fig. 1, curves $E_{(+)}$ and $E_{(-)}$), which intersect at some point.^{16,17} If the resonance electron coupling integral J between neighboring sites is not

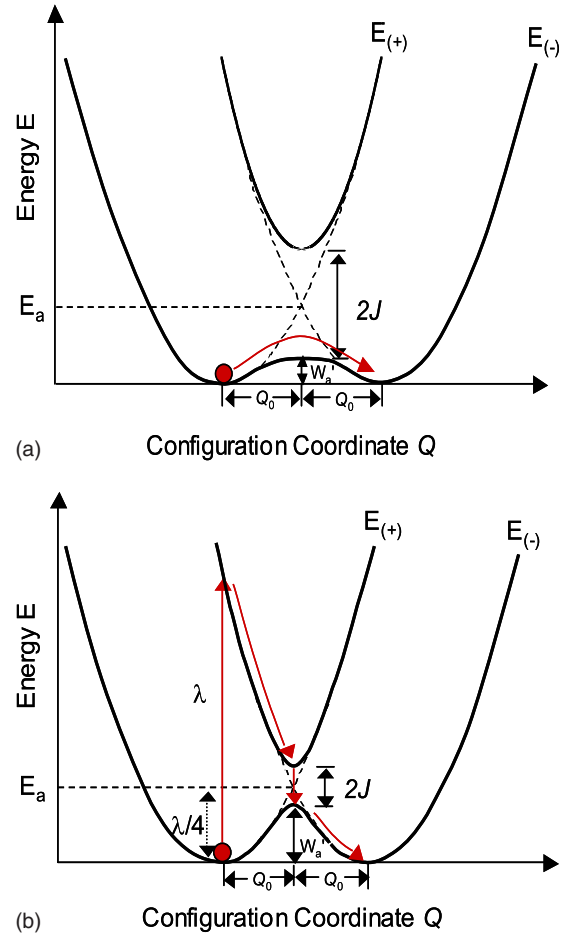


FIG. 1. (Color online) Schematic representation of (a) adiabatic and (b) nonadiabatic motions in the configurational coordinates for a two-site system. The arrow indicates the path of the excited state.

zero, the degeneracy at the intersection point is eliminated giving rise to a gap ΔE with $\Delta E = 2J$ between two resulting generalized (collective) coordinates shown by upper and lower solid curves in Fig. 1. The energy barrier E_a that separates the two equilibrium positions is reduced by the coupling to a modified barrier height,

$$W'_a = E_a - J. \quad (1)$$

In the case of adiabatic motion a carrier is able to instantaneously follow the positions of the atoms and the system remains on the same lower-energy surface [Fig. 1(a)]. This is possible for a large electron coupling integral, i.e., large J . However, if J is small, the carrier cannot adapt to vibrations of atoms. This is the case of nonadiabatic motion. Here, the carrier jumps from the lower to upper energetic surface at the first site and relaxes then to an energy minimum at the second site [Fig. 1(b)]. In a perfect crystalline solid in the absence of scattering events, adiabatic or nonadiabatic motion would give rise to a coherent or noncoherent way of propagation, respectively.

We shall now assess which limit applies to the motion of triplet excitation in organic semiconductors. The rate W_{ij} for the transfer of a polaron from site i to site j in the adiabatic

limit for a disorder-free system is given by:¹⁷

$$W_{ij} = \omega_0 \exp\left(-\frac{W'_a}{k_B T}\right), \quad (2)$$

where ω_0 is a characteristic frequency of optical or acoustic phonons such as the high-energy modes observed in the vibrational progression of absorption and emission spectra or low-energy torsional or librational modes. If the electron coupling integral J is large enough (for instance, at small enough spacing between localized states) it will become comparable to the energy barrier E_a separating the two equilibrium positions. Now, if $J \approx E_a$, then $W'_a \approx 0$ so that the transfer rate W_{ij} indeed depends weakly on T . This is the case when the coupling integral exceeds a critical value $J > J_{\text{cr}}$.

Let us estimate the critical electron coupling integral J_{cr} at which the change in transport regime occurs. The critical value J_{cr} is given by the following expression:¹⁷

$$J_{\text{cr}} = (E_a - J)^{1/4} \left(\frac{2k_B T}{\pi}\right)^{1/4} \left(\frac{\hbar\omega_0}{\pi}\right)^{1/2}. \quad (3)$$

In Paper I,²⁸ we considered a platinum-containing polymer and we derived an activation energy and electronic coupling integral of $E_a = 60$ meV and $J = 0.14$ cm⁻¹ = 0.0174 meV. For the lowest temperature used in the experiment ($T = 10$ K) (Ref. 28) and choosing $\omega_0 = 6.5 \times 10^{13}$ s⁻¹ (the frequency of the dominant carbon-carbon triple bond stretching vibration at 2100 cm⁻¹), Eq. (3) yields a critical value J_{cr} of 8.84 meV. Thus, for this material one obtains $J \ll J_{\text{cr}}$ for the considered temperature range. This implies that *only nonadiabatic* triplet exciton transport takes place in this material in the whole range of temperatures used in experiment. We note that this still holds when only the acoustic phonons with energies around 100 cm⁻¹ are considered.

We note that if the energetic disorder is completely absent then one could expect a band-type triplet exciton transport at low temperature. However, even in a very weakly energetically disordered system (in the present case $\sigma = 0.003$ eV) one has $\sigma/J \approx 170 \gg 1$. Therefore the material should be still considered as energetically disordered and, in the low-temperature regime, transport can only occur via single phonon hopping.^{40,41}

B. Theoretic formalism for nonadiabatic triplet transport

The nonadiabatic motion of a carrier has been described by Emin and co-workers.^{31,32} In the general case of multiphonon transitions, the jump rate W_{ij} for hopping transport of a carrier between sites with energies ε_i and ε_j is given as

$$\begin{aligned} W_{ij} &= \left(\frac{J_{ij}}{\hbar}\right)^2 \left(\frac{2\pi}{\omega_0}\right) \exp(-2S) \exp\left(-\frac{\varepsilon_j - \varepsilon_i}{2k_B T}\right) \\ &\times \sum_{n=-\infty}^{\infty} \{I_b[(4E_a/\hbar\omega_0)A_n \cosh(\hbar\omega_0/2k_B T)] \\ &\times \cos(b\phi_n) - \delta_{b,0}\}, \end{aligned} \quad (4)$$

where

$$A_n \cong 1 - \frac{(2\pi)^2}{8} \left(\frac{\omega_b}{\omega_0}\right)^2 n^2, \quad S = \frac{2E_a}{\hbar\omega_0} \cot g\left(\frac{\hbar\omega_0}{2k_B T}\right), \quad (5)$$

and $b = (\varepsilon_j - \varepsilon_i)/\hbar\omega_0$. E_a is the polaron activation energy, $J_{ij} = J_0 \exp(-r_{ij}/L)$ is the electron coupling integral, r_{ij} is distance between molecular sites i and j , and L is the charge-carrier localization radius. Frequencies ω_0 and ω_b determine optical-phonon dispersion $\omega_{\mathbf{q}} = \omega_0 + \omega_b(\cos q_x + \cos q_y + \cos q_z)$ and ϕ_n is the lattice-relaxation phase shift.

When considering triplet motion, some parameters take on a different interpretation. For example, E_a no longer denotes the activation energy for a polaronic charge carrier but instead it represents the activation energy for triplet transfer. Note that E_a relates to the polaron binding energy E_p as $E_a = E_p/2$ and to the geometric reorganization energy λ as $E_a = \lambda/4$ for triplet transfer.^{26,28} Similarly, L here corresponds to a parameter characterizing “effective” localization radii of the charge carriers involved in the triplet transfer. The fact that two charge carriers are exchanged is included implicitly through the different magnitude of the coupling integral J .

It is important and most useful to consider the Eq. (4) for two limiting cases of high and low temperatures.³¹ (i) For the high-temperature regime ($T \gg \hbar\omega_0/k_B$) the Eq. (4) reduces to

$$W_{ij} \cong \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{4E_a k_B T}} \exp\left[-\frac{E_a}{k_B T} - \frac{\varepsilon_j - \varepsilon_i}{2k_B T} - \frac{(\varepsilon_j - \varepsilon_i)^2}{16E_a k_B T}\right]. \quad (6)$$

As one can note, Eq. (6) is basically a Marcus expression (cf. Ref. 28), which accounts for multiphonon hopping transitions of triplet excitons. (ii) For low-temperature regime ($T \ll \hbar\omega_0/k_B$) the Eq. (4) gives

$$W_{ij} = \nu_{ij} \exp\left[-\frac{|\varepsilon_j - \varepsilon_i| + (\varepsilon_j - \varepsilon_i)}{2k_B T}\right], \quad (7)$$

where

$$\begin{aligned} \nu_{ij} &\cong J_{ij}^2 \left(\frac{\omega_0}{2\pi}\right) \left[\frac{2\pi \exp(-2E_a/\hbar\omega_0)}{\hbar\omega_0}\right]^2 \frac{(4E_a/\hbar\omega_0)^{|\varepsilon_j - \varepsilon_i|/\hbar\omega_0}}{(|\varepsilon_j - \varepsilon_i|/\hbar\omega_0)!} \\ &\times \sum_{n=-\infty}^{\infty} (A_n)^{|\varepsilon_j - \varepsilon_i|/\hbar\omega_0} \cos\left(\frac{|\varepsilon_j - \varepsilon_i|}{\hbar\omega_0} \phi_n\right). \end{aligned} \quad (8)$$

We should note that prefactor ν_{ij} does not depend on temperature.

In Eqs. (6) and (7) the electron coupling integral is given by $J_{ij} = J_0 \exp(-r_{ij}/L)$, where L is the effective triplet localization radius. The exponential term in Eq. (7) is responsible for a functional dependence on $\varepsilon_j - \varepsilon_i$ because all the terms in the expression for ν_{ij} [Eq. (8)] depend much weaker on $\varepsilon_j - \varepsilon_i$ compared to the exponential term in Eq. (7). Therefore the Eqs. (6) and (7) for the triplet transfer rate can eventually be presented in the following form for the high-temperature and low-temperature regimes, respectively:

$$W_{ij} = \frac{J_0^2}{\hbar} \sqrt{\frac{\pi}{4E_a k_B T}} \exp\left(-2\frac{r_{ji}}{L}\right) \times \exp\left[-\frac{E_a}{k_B T} - \frac{\varepsilon_j - \varepsilon_i}{2k_B T} - \frac{(\varepsilon_j - \varepsilon_i)^2}{16E_a k_B T}\right], \quad (9)$$

and

$$W_{ij} = \nu_0 \exp\left(-2\frac{r_{ji}}{L}\right) \exp\left[-\frac{|\varepsilon_j - \varepsilon_i| + (\varepsilon_j - \varepsilon_i)}{2k_B T}\right]. \quad (10)$$

As one can see, the Eq. (10) is basically the same as predicted by the Miller-Abrahams model.⁴⁰ In the Miller-Abrahams model, the triplet transfer involves a single phonon tunneling process between the energetic sites ε_i and ε_j , where ε_j is larger than ε_i . The role of the phonon is to provide the energy corresponding to the site energy difference. This is in contrast to the Marcus model, where several phonons are involved to overcome not only the difference between the site energies but also the energy barrier separating them.³⁰ We note that Eqs. (9) and (10) formally correspond to Eqs. (4) and (3), respectively, in Ref. 35.

It should be noted that the Eqs. (9) and (10) can be obtained also for charge-carrier coupling to acoustic phonons $\omega_q = \omega_D q / q_D$ as demonstrated in Refs. 32, 35, and 40. However, for charge carriers Eq. (9) is valid when $T \gg T_D / 2$ ($T_D = \hbar \omega_D / k_B$, where ω_D and q_D are the Debye frequency and Debye wave vector, respectively) and, correspondingly, Eq. (10) is valid for $T \ll T_D / 2$.

C. Effective-medium approximation theory of nonadiabatic triplet transport

It should be noted that in all previous works we cited, the authors used the approximation of just two-site transitions in the presence of energetic disorder. In our theory we consider effective values that are more closely related to experiment and amenable to experimental evaluation. This naturally requires developing an appropriate approach (the effective-medium approach has been used in this work).^{25,42} In order to compare the theoretical results with experimental data, one has to calculate the *effective energy-transfer rate* for a general case of a disordered hopping system.

First, let us consider the high-temperature regime. We will use Eq. (9) and an EMA method to derive an expression for the effective triplet energy-transfer rate W_e . Drawing on the expressions developed in Ref. 35, we obtain

$$W_e = \frac{J_0^2}{\hbar} \sqrt{\frac{\pi}{4E_a k_B T}} \exp\left(-2\frac{a}{L}\right) \frac{1}{q} \exp\left[-\frac{E_a}{k_B T} - \frac{1}{8q^2} \left(\frac{\sigma}{k_B T}\right)^2\right], \quad (11)$$

where $q = \sqrt{1 - (\sigma/E_a)(\sigma/k_B T)/8}$, a is an average distance between neighboring localized states, and σ is the width of the Gaussian DOS distribution of localized states. At moderate energetic disorder and relatively large temperatures when $(\sigma/E_a)(\sigma/k_B T)/8 \ll 1$, one obtains $q \cong 1$. The Eq. (11) then reduces to

$$W_e = \frac{J_0^2}{\hbar} \sqrt{\frac{\pi}{4E_a k_B T}} \exp\left(-2\frac{a}{L}\right) \exp\left[-\frac{E_a}{k_B T} - \frac{1}{8} \left(\frac{\sigma}{k_B T}\right)^2\right]. \quad (12)$$

Furthermore let us consider the low-temperature regime. When the temperature decreases, the activated multiphonon energy-transfer mechanism changes to single phonon hopping (phonon-activated tunneling) between two states. In the latter case the triplet energy-transfer rate (jump of two charge carriers) is described by the Miller-Abrahams (M-A) model given in Eq. (10). In this case the effective triplet transfer rate W_e as calculated within the EMA theory can be described by the following expression:³⁵

$$W_e = \nu_0 \exp\left(-2\frac{a}{L}\right) \exp\left[-\frac{1}{2} \left(\frac{\sigma}{k_B T}\right)^2\right]. \quad (13)$$

We will use further Eqs. (12) and (13) to describe triplet exciton transport in an energetically disordered system. We note their formal similarity to Eqs. (19) and (10) in Ref. 35, which describe the charge-carrier mobility at zero electrical field.

III. RESULTS

We shall first see whether Eqs. (12) and (13) are suitable to describe the experimental data presented in Paper I.²⁸ There we displayed the temperature dependence of phosphorescence decay rates along with a fit based on a simple Marcus theory expression that is valid in the high-temperature regime to derive an activation energy of $E_a = 60$ meV and an electronic coupling integral $J = 0.14$ cm⁻¹ = 0.0174 meV. The phosphorescence decay rate contains both a temperature-dependent component that arises from the diffusion to quenching sites and an intrinsic temperature-independent component that can be derived from the decay rate extrapolated to 1 K and that takes the value of 2×10^{-2} μs^{-1} for the Pt-polymer. In order to fit the triplet diffusion rate quantitatively in the high-temperature and low-temperature regime, we first subtracted this constant offset from the experimental phosphorescence decay rates. The resulting triplet diffusion rates are displayed in Fig. 2 (symbols) along with fits (solid lines) according to Eqs. (12) and (13). The fitting parameters employed to get an agreement with the experimental data are the energetic disorder σ and the ratio a/L between the average site distance and the effective localization radius of the exciton.

Let us comment on the parameters used for our calculation. The activation energy E_a of 60 meV and the coupling J of 0.0174 meV derived in our earlier paper²⁸ were used as input parameters for both equations. Within the hopping mechanism expressed by Eq. (12), J is represented as $J = J_0 \exp(-2a/L)$ while one also has $\nu = \nu_0 \exp(-2a/L)$ in Eq. (13). For the parameter ν_0 we take a frequency typical for acoustic phonons, namely, $\nu_0 = 3 \times 10^{12}$ s⁻¹ (≈ 100 cm⁻¹). Using ν as fitting parameter to get an agreement with experimental data, then gives the ratio a/L , from which the parameter J_0 can be derived. The values we obtain are $\sigma = 3 \pm 1$ meV and $a/L = 9.6$, which yields $J_0 = 257$ meV.

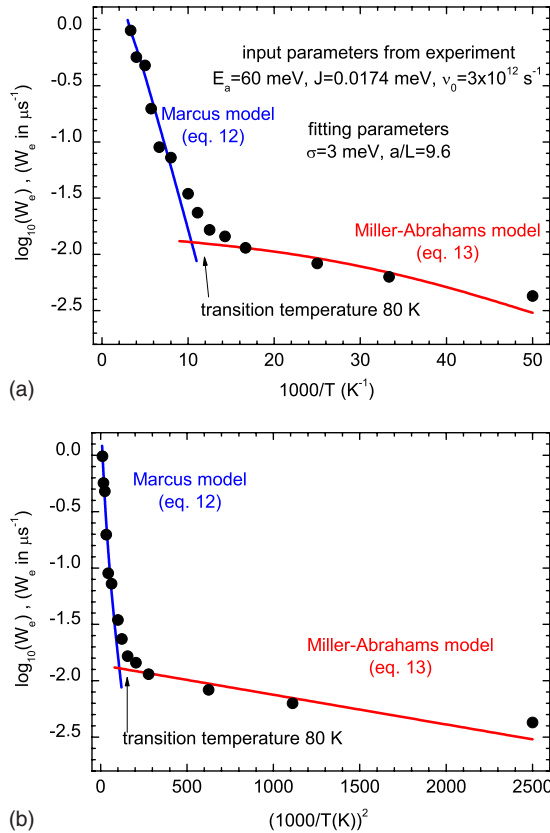


FIG. 2. (Color online) The triplet transfer rate as a function of temperature plotted (a) on Arrhenius coordinates (b) against T^{-2} . The closed circles represent the experimental data as described in the text. The lines indicate fits according to Eqs. (12) and (13) using the parameters listed in (a).

The obtained value for a/L is quite realistic,⁴³ and we think this additionally supports the hopping character of the transport. In contrast, the disorder parameter is extraordinary low as compared to the inhomogeneous linewidth of the $S_1 \leftarrow S_0$ 0–0 transition in a random organic solid (≈ 50 meV).⁴⁴ Nevertheless, it is in qualitative agreement with (i) the narrow linewidth of the $T_1 \rightarrow S_0$ 0–0 phosphorescence transition and (ii) its weak bathochromic shift at low temperature.²⁸ Recall that random walk theory predicts relaxation of the mean energy of an ensemble of hopping elements, in the present case triplet excitations, to a mean energy $-\sigma^2/kT$ below the center of the DOS distribution from where they can recombine radiatively.⁴⁵ Between 300 and 10 K, the measured bathochromic shift amounts to 20 meV only.²⁸

The data in Fig. 2 are displayed in two representations to allow for comparison of the fits with the experimental data. Equation (12) reduces to a Marcus-type expression showing a simply activated behavior in the case of vanishing disorder. The presence of energetic disorder then results in a deviation from the straight line (see Fig. 3). In fact the larger the disorder σ becomes the more curvature occurs in the temperature dependence of the transfer rate. For our material, the disorder is weak, and this manifests itself in a nearly linear dependence when plotted on Arrhenius coordinates as shown in Fig. 2(a). On the other hand, the Miller-Abrahams-type expression of Eq. (13) gives a straight line when the triplet

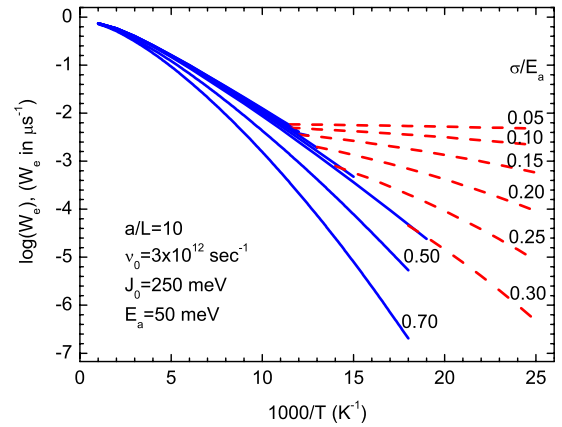


FIG. 3. (Color online) The dependence of the triplet energy-transfer rate on temperature as a function of the ratio σ/E_a . The transfer rates in the high-temperature range (solid lines) are calculated using Eq. (12) (multiphonon hopping) and those in the low-temperature range (dashed lines) are derived from Eq. (13) (single phonon hopping). The values used for σ/E_a are indicated in the figure.

transfer rate is plotted logarithmically against $1/T^2$, in agreement with the low-temperature data shown in Fig. 2(b). From results presented in Fig. 2, one can observe that a change in the nature of the triplet exciton transport occurs at a critical temperature $T_{cr}=80$ K. If triplet excitons couple to acoustic phonons, one can conclude that $T_D=2T_{cr}$ implying that the Debye temperature in the present material is $T_D=160$ K and the Debye frequency is $\omega_D=2.1 \times 10^{13}$ s⁻¹.

Having confirmed that our theoretical approach is suited to describe the experimental results, we next consider how the triplet energy transfer depends on the relative magnitude of disorder effects and polaronic contributions. The influence of disorder is expressed by the width of the Gaussian density of states, σ . Polaronic site relaxation is manifested in the geometric reorganization energy, λ , and it is considered in the model through the activation energy $E_a=\lambda/4$. Figure 3 therefore presents the effective triplet energy-transfer rate W_e as a function of temperature calculated using Eqs. (12) and (13) parametric in the σ/E_a ratio. The material parameters used for the calculation are kept similar to the ones found for the Pt-polymer considered in Fig. 2. The geometric distortion energy λ is fixed to be 200 meV (corresponding to $E_a=50$ meV), and the disorder parameter is varied from $\sigma=2.5$ to 35 meV.

From Fig. 3 it is evident that the two temperature regimes differ in their sensitivity to the σ/E_a ratio. The energy-transfer rate W_e as a function of temperature calculated from Eq. (12) is plotted as solid line. Increasing the energetic disorder results in just a weak change in the temperature dependence of the energy-transfer rate for $\sigma/E_a \leq 0.3$ (i.e., $\sigma \leq 15$ meV). Above this value, increasing the disorder causes a stronger change in the triplet transfer rate with temperature and concomitantly a deviation from simple Arrhenius behavior. In contrast to the high-energy branch, the temperature dependence of W_e calculated within the M-A model for lower temperatures varies strongly with energetic disorder. The underlying concept is a phonon-assisted tunneling

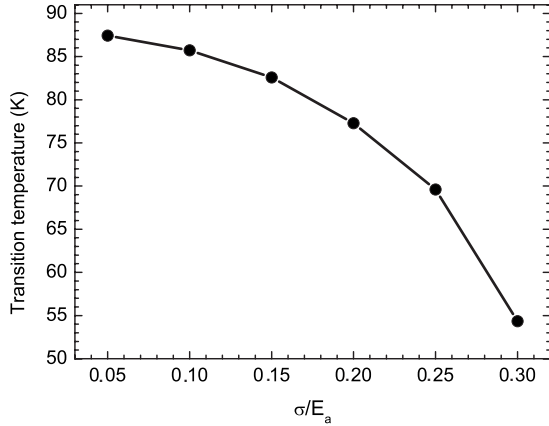


FIG. 4. The critical temperature T_{cr} characterizing the transition from nonpolaronic to polaronic transport as a function of the ratio between the disorder parameter σ and the activation energy E_a .

process. Consequently the triplet motion is almost nonactivated when the disorder is low, yet it acquires a growing temperature dependence with increasing disorder. At $\sigma/E_a = 0.3$ the disorder is sufficiently large that the two regimes can no longer be distinguished and for $\sigma/E_a > 0.3$, the triplet motion is dominated by disorder controlled single phonon-assisted hopping within the entire temperature range.

The intersections of the above curves imply a crossover from the activated polaron motion (multiphonon hopping) to the low-temperature M-A-type motion. The transition temperature (critical temperature T_{cr}) versus the degree of the energetic disorder is shown in Fig. 4 for the σ/E_a range employed in Fig. 3. The highest transition temperature is reached for low disorder with about $T_{cr} = 90$ K. With increasing disorder the transition temperature falls in a seemingly parabolic way.

IV. DISCUSSION

In this work we have employed an effective-medium approach to describe the motion of a triplet excited state. For the limiting cases of high temperature and low temperature, it was possible to develop a formalism that leads to two separate equations. In the high-temperature regime, triplet transfer occurs as a multiphonon hopping process that is of polaronic nature. The associated equation [Eq. (12)] is also known as a Marcus-type equation. In contrast, a nonpolaronic tunneling process (also referred to as single phonon hopping) controls transport in the low-temperature regime. The associated equation is referred to as Miller-Abrahams equation [Eq. (13)]. These equations were tested on the data obtained from a material with very little disorder in the triplet state and they were found to reproduce the experimental results with realistic fit parameters. There are some interesting features to be noted on the experimental data and the theoretical model presented in Paper I (Ref. 28) and in this paper.

First, in the experimental paper, a transition from polaronic Marcus-type transport to nonpolaronic Miller-Abrahams-type tunneling was observed experimentally

through spectroscopic measurements.²⁸ We are not aware that experimental evidence for this transition has been reported before for organic semiconductors. Its observation is a result of the fact that the energetic disorder associated with a triplet state of the experimental test system is very low. Therefore, the intrinsic physical processes are not obscured by disorder effects.

Second, the theoretical model includes both energetic disorder and polaronic effects explicitly through the parameters σ and λ or equivalently through E_a (since $\lambda = 4E_a$). In the model, it is therefore possible to introduce disorder gradually and so to examine the associated change in physical processes. The theory shows us that when disorder increases (i) the Arrhenius-type Marcus theory charge transfer changes to a non-Arrhenius behavior, (ii) the “tunneling”-type Miller-Abrahams branch becomes temperature activated.

For the parameters used here, the two regimes can no longer be distinguished when $\sigma/E_a > 0.3$, i.e., when the variance of the Gaussian DOS distribution becomes larger than approximately a tenth of the geometric reorganization energy λ . From considerations regarding the contribution of the polaronic component to the activation energy for charge-carrier motion, a similar value can be anticipated.⁴³ We consider that the critical value of σ/E_a for the disappearance of the transition is only weakly parameter dependent, yet a quantitative assessment requires a separate theoretical study.

Third, the approach taken in the previous paper and this one allows for the determination of the parameters σ and λ that characterize the respective contribution of disorder and polaronic effects from purely optical measurements. Note that in the case of charges the polaron binding energy and the width of the DOS are not amenable to direct experimental probing and, thus, they have to be inferred from the temperature dependence of the charge-carrier mobility.⁴³ The reason is that the transient absorption spectrum of a charge-carrier monitors the electronic transition between the electronic ground state of the charge, i.e., the radical cation/anion and the first electronically excited state rather than the structural relaxation energy upon adding or removing a charge.⁴⁶ The only source of independent information on λ turns out to be quantum chemical calculation.^{26,36} In the case of spectroscopically monitored triplet motion, however, the λ values can be inferred from the vibronic progression of the phosphorescence spectrum quantified in terms of the Huang-Rhys factor and the σ values can be estimated from bathochromic shift of the emission spectrum due to spectral diffusion.

Let us now quantitatively compare the parameters for polaronic and disorder contribution that can be obtained for triplet transfer on one hand and charge transfer on the other hand. Representative examples of a corresponding analysis of charge mobility data is given in the work of Fishchuk *et al.*³⁵ on polysilanes and that of Bradley and co-workers^{47,48} on polyfluorene-type polymers. In view of the singly bonded silicon chain in polysilanes the polaron aspect is expected to be important. Fitting the experimental data yields the parameter sets listed in Table I. Also listed are the values derived in our earlier paper from fitting the triplet data. From the analysis (summarized in Table I) of hole transport as compared to triplet transport the following conclusions can be drawn: (i) In all cases of hole transport, σ/E_a exceeds the critical value

TABLE I. Characteristic parameters for charges and triplet excitations.

Material	Electronic coupling J (meV)	Variance of the density of states, σ (meV)	Activation energy E_a (meV)	σ/E_a
PMPSi ^a	8	89	145	0.61
PBPSi ^a	16	96	220	0.43
Polyfluorene ^{b,c}		63 ± 12	150 ± 40	0.60 ± 0.16
Pt-polymer ^d	0.02	2	60	0.03

^aReference 35.^bReference 47.^cReference 48.^dReference 28.

of 0.3. Therefore, both the turn over between polaronic and nonpolaronic transport vanishes and the entire temperature dependence of the hole mobility is largely controlled by disorder rather than by polaron effects. As a result, the dependence of the hole mobility μ on the temperature T basically features a $\ln \mu \propto T^{-2}$ dependence. In other words, disorder effects dominate the $\mu(T)$ dependence although σ/E_a is only about 0.5. The reason for this is that under quasiequilibrium condition charge carriers are localized in the tail states of the DOS distribution. Therefore their thermal excitation toward the transport energy requires a multiple of σ . (ii) Although the J values for charge transport refer to interchain hopping while in the Pt-polymer a triplet exciton moves along the chain the former are three orders of magnitude higher. We attribute this to the fact that in case of triplet motion two charges have to be exchanged instead of a single charge transfer. This is well documented for the molecular crystal of anthracene.²⁶ The electronic coupling parameter J is amenable from the Davydov splitting of the polarized (weak) absorption spectrum for the transition from the singlet ground state to the lowest triplet exciton state. The $S_0 \rightarrow T_1$ absorption can be measured in the form of an excitation spectrum for delayed fluorescence due to the annihilation of two triplet excitons. Employing this technique, Avakian and Merrifield⁴⁹ determined the matrix element for triplet exciton transfer between two inequivalent anthracene molecules within the crystallographic ab plane and derived $J \approx 0.2$ meV. This is two orders of magnitude less than the value of $J \approx 20$ meV calculated for hole transfer.²⁶ For correlated exchange of two charges involved in the triplet motion, the triplet transfer-matrix element should be, by and large, the square of the matrix element for single charge transfer.

As outlined above, the transfer of a triplet excitation may occur in an adiabatic or nonadiabatic fashion, depending on the magnitude of the electronic coupling parameter J . For

our Pt-polymer, triplet motion clearly occurs in the nonadiabatic regime. Let us briefly consider which regime applies in other organic semiconductors. A simple estimate for the critical value J_{cr} according to Eq. (3) for the triplet in anthracene, using $J=0.2$ meV and $E_a=100$ meV, and for ω_0 an acoustic frequency around 100 cm^{-1} yields $J_{cr}=2.4-4$ meV for temperatures from 10 to 100 K. So $J < J_{cr}$, and thus, the triplet transfer also occurs in a nonadiabatic way for an anthracene crystal. The parameters with similar orders of magnitude apply for many π -conjugated molecules and conjugated polymers. Therefore our approach appears to be valid for triplet motion in many systems.

V. CONCLUSION

Taken together the earlier theoretical work on charge transport,³⁵ the previous experimentally focused paper,²⁸ and the present paper set up a consistent formalism to describe the transport of charge carriers and triplet excitations that couple to a polaronic distortion in the presence of disorder. The model allows us to distinguish between polaron and disorder effects that control the transport in different temperature regimes. By comparing the predictions of the model with experimentally derived parameters, we conclude that in the case of charge carriers the disorder contribution is dominant. It implies that the polaron contribution should manifest itself in a modification of the $\ln \mu \propto T^{-2}$ dependence of the charge-carrier mobility and that a transition from multiphonon to single phonon hopping does not usually occur under common experimental conditions. This is indeed what is observed in experiments on charge mobility.³⁵ However for triplet motion exceptionally weak disorder can be realized and that renders such transition from polaronic to non-polaronic transport observable.

Finally we note that the current effective-medium approach to triplet transfer is a time-independent treatment. Therefore it is applicable to random organic systems, in which disorder is weak enough that spectral diffusion of the initially created triplet excitations is completed before transport enters the regime of temperature-dependent quasiequilibrium transport. A quantitative assessment of the critical disorder parameter, above which dispersive transport becomes important, is beyond the range of the current theoretical approach.

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