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Effects of Lattice Relaxation on Photoinduced Electron Transfer in Molecularly Doped Conjugated Polymers

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Abstract

The effect of polaron formation on the photoinduced electron transfer from a conjugated polymer to a dopant molecule is studied by the Bogoliubov-de Gennes formalism in the electron-hole representation. Depending on the relative strength of electron-phonon coupling and electron-hole attraction, we found that the initial neutral and final CT excitations of the conjugated polymer/dopant composite can be in a localized self-trapped or delocalized scattering state. Within the lattice relaxation theory, we found the rate of electron transfer is sensitive to the relative position between the LUMO's energy of dopant molecule and the exciton energy of the conjugated polymers. The forward transition rate from the polymer's exciton state to the CT final state is larger than to the CT continuum by two orders of magnitude.

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The photoinduced electron transfer in the conjugated polymers/dopant composites has attracted much attention both experimentally and theoretically since the discovery of the enhanced photoconductivity of C_{60} doped poly(phenylene vinylene) [1,2]. Recent theoretical works on this phenomenon have mainly concentrated on the purely electronic mechanism and can also give a correct estimate of the time scales by using suitably chosen parameters. [3] In these theoretical studies the lattice relaxation of the conjugated polymer/dopant composite is neglected. We believe that a microscopic theory based on pure electronic coupling is insufficient and may lead to incorrect prediction in the limit of high concentration.

It is well known that the lattice reorganization energy plays an important role for the electron transfer rate in small molecules. While in one dimensional conducting polymers, the interactions between various elementary excitations are usually strong. For instance, the final state interaction between the hole left behind on the conjugated polymer and the phonon leads to a hole-polaron formation by radiationless multiphonon excitation. Similarly, depending on the strength of electron-phonon ($e - p$) coupling of dopant molecules, the electron may also induce a displacement in the certain vibration modes. Both of these two types of lattice relaxation could affect the electron transfer rate.

We present in this letter a microscopic theory for the photoinduced electron-transfer between a conjugated polymer and a dopant based on the lattice relaxation theory (LRT) developed by Huang and Rhys originally for describing the absorption and luminescence of a defect in an ionic crystal [4]. In the LRT, the multiphonon processes exhibited in the absorption and luminescence of a defect in an ionic crystal are due to a difference in a specific lattice configuration coordinates Q . The LRT has been successfully generalized by Su and Yu to the radiative and nonradiative decay processes in conducting polymers and fullerenes [5–8]. Using LRT formalism, we will show that the initial state is a self-trapped exciton by solving the nonlinear gap equations with electron-hole ($e - h$) interaction included, and the final states consist of a hole-polaron for the lowest bound CT-exciton and a continuous delocalized CT band. The electron transfer rates are then calculated through the first-order perturbation theory on the weak perturbations that describe the single-particle hopping

and charge-fluctuation charge-transfer processes. The calculated time scale for the electron transfer is in good agreement with experiments. Here we consider only photoinduced electron transfer in an isolated polymer/dopant composite and postpone all possible solid state effect such as exciton migration for future studies.

In order to consider the effect of lattice relaxation, we introduce the site-offdiagonal $e - p$ coupling to the electron and hole hopping terms. Hence, the effective Hamiltonian for describing the molecularly doped conjugated polymers [3] can be expressed as $H = H_0 + V$ with

$$\begin{aligned}
H_0 = & \sum_{n\sigma} \epsilon [a_{n\sigma}^+ a_{n\sigma} + b_{n\sigma}^+ b_{n\sigma}] + \sum_{n\sigma} (t + \alpha(x_n - x_{n+1})) [a_{n\sigma}^+ a_{n+1\sigma} + b_{n\sigma}^+ b_{n+1\sigma} + h.c.] \\
& + \sum_{nm\sigma\sigma'} U_{nm} a_{n\sigma}^+ a_{n\sigma} b_{m\sigma'}^+ b_{m\sigma'} - \sum_{n\sigma s} V(i - n) d_{i\sigma}^+ d_{i\sigma} a_{n\sigma}^+ a_{n+1s} \\
& + \Delta \sum_{\sigma} d_{i\sigma}^+ d_{i\sigma} + \frac{1}{2} \sum_n K(x_n - x_{n+1})^2 \quad (1)
\end{aligned}$$

in the electron-hole representation. Here $b_{n\sigma}^+$ ($a_{n\sigma}^+$) is fermion operators, which creates an electron (a hole) with spin polarization σ in a conduction (valence) band Wannier function $w_{nc}^*(r)$ ($w_{nc}(r)$) located at the n th unit cell of the polymer. The first two terms of Eq.1 describe the electrons and holes in the conduction and valence bands of the conducting polymer but without interaction among themselves. β characterizes the strength of the $e - p$ coupling. The third term of H_0 describes the effective attractive Coulomb interaction between an electron and a hole on a polymer; while the fourth term is the interaction of a hole on the polymer and an electron in the acceptor level of the dopant. The effective $e - h$ interaction potentials are taken to be $U_{nm} = U/\sqrt{r_{nm}^2}$ and $V_{ni} = V[(n - i)^2 + B]^{-1/2}$, where U , V , and B are positive constants. Δ is the energy for putting an electron in the acceptor level of the dopant molecule relative to the center of energy band of the polymer. The last term is the lattice elastic energy. Note that the exciton migration term is ignored, there is no distinction between the singlet and triplet state. However, it is straightforward to include this terms in the present formalism which will enable us to handle the triplet state electron-transfer problem. [9] About the weak perturbation V , we will consider the two major coupling mechanism between polymer and dopant in the Rice and Garstein's model,

[3,9]: the single particle hopping, $V_1 = t_0 \sum_{\sigma} (d_{i\sigma}^{\dagger} b_{i\sigma} + h.c.)$, and the charge-fluctuation charge transfer, $V_2 = \sum_{\sigma} v(n-i)(d_{i\sigma}^{\dagger} a_{ns}^{\dagger} a_{ns} b_{i\sigma} + h.c.)$, which can lead to the transition from the initial exciton state to final CT excitation. The charge-fluctuation charge transfer can be visualized as a collision between an electron and a hole, in which the hole scatters the electron from the polymer to the dopant molecule.

Upon initial photoexcitation in the photoinduced electron transfer, an $e-h$ pair is created. Then through multiphonon emission, the lattice will quickly relax. As we will show later this relax structure is a self-trapped intermediate exciton state along the conjugated polymer. It is a Frenkel exciton in the sense that it is localized on a single big molecule, however a Wannier exciton along the chain. Note that the initial STE corresponds to a one dimensional positronium molecule in a deformable lattice. Under the Born-Oppenheimer approximation, the vibronic wavefunction is given by $\Phi_i = |\Phi^{Ex}(q_e; \mathbf{x}_0^i)\rangle |\chi_i(\mathbf{x})\rangle$ with $\Phi^{Ex} = \frac{1}{\sqrt{2N}} \sum_{nm\sigma} \Phi_{nm} e_{n\sigma}^{\dagger} h_{m-\sigma}^{\dagger} |HF\rangle$. Hence, the amplitude, Φ_{nm} , to find of the electron and hole located at n and m respectively is the solution of a difference equation that corresponds to the equation $H(\mathbf{x}^i)\Phi^{Ex} = E_{Ex}\Phi^{Ex}$. To determine the fully relaxed structure of STE, a self-consistent procedure is employed. Taking advantage that the order of the energy derivative with respect to electronic and nuclear degrees of freedom at equilibrium does not matter, we can set $\partial E(\mathbf{u})/\partial u_i = 0$ with $u_i = x_{i+1} - x_i$ to obtained the gap equation for the $e-h$ amplitude

$$K\Delta u_{i,ex} = -\frac{1}{N} \sum_{n,m=1}^N \frac{\partial U_{nm}}{\partial \Delta u_{i,ex}} |\Phi_{nm}|^2 - \frac{2\beta}{N} \sum_{m=1}^N (\Phi_{im}\Phi_{i+1,m} + \Phi_{mi}\Phi_{m,i+1}) \quad (2)$$

The equilibrium nuclear configuration determined self-consistently in this way is similar to the BdG formalism used in the standard conjugated polymers. To obtain the rate for the electron transfer, we still need the nuclear part of vibronic wavefunction. We perform a normal mode analysis in Cartesian coordinate by numerically compute the Hessian matrix after the equilibrium configuration for the exciton state is found.

In the present work, we have chosen the parameter set to be $a_0 = 6.5\text{\AA}$, $\alpha = 3.5\text{eV}$, $t^{\circ} = -1\text{eV}$, $m_1 = m_N = 103.14 \text{ g/mol}$, $m_i = 102.1356 \text{ g/mol}$ when $i = 1, 2, \dots, N-1$ the

mass C_8H_7 for the chain ends and chain C_8H_6 . To study the effect of competition between $e - e$ and $e - p$ coupling on the lattice relaxation and electron transfer rate, we study by systematically varying the relative magnitudes of U , V , β . The energy gaps for a chain with $N = 30$ sites using this parameter set together with $U = -2$, $U/(V/a_0) = 2 \sim 4$ and $\beta = 0 \sim 0.1$ are about 2.00 \sim 3.00 eV. The exciton binding energy is around 0.2 \sim 0.5 eV and the lattice relaxation energy 0.01 \sim 0.03 eV. Examining the wavefunction of the STE, we found that the e-h amplitude is concentrated around the center of the chain with a width that depends on the β . But the typical size of the envelop function is about 14 unit cells when $\beta = 0.1$. These results are compatible with the previous results. Since we consider only the $e - h$ attraction and no exciton migration is allowed, so there is no singlet-triplet splitting. The importance of the exciton migration will be discussed in another publication.

After the electron is transferred to the dopant molecule due the the weak perturbation V , the imbalance between the hole and lattice will cause the remaining hole on the polymer to relax to a new stable configuration. This final state is a CT exciton consisted of a hole on the conjugated polymer chain and an electron on the dopant molecule. Similar to the initial neutral exciton state, the CT exciton wavefunction can be written as $\Phi_f = |\Psi^{CT}(\mathbf{x}_0^f)\rangle|\chi_f\rangle$. The structure of polaron has to satisfy a similar equilibrium condition. Hence, with some straightforward manipulation, the corresponding hole BdG equation for the CT state is given by

$$K(2u_{i,ct} - u_{i+1,ct} - u_{i-1,ct}) = -\frac{\partial V_{ji}}{\partial u_{i,ct}}|\phi_i|^2 - 2\beta(\phi_{i-1}\phi_i - \phi_i\phi_{i+1}). \quad (3)$$

In the case that electron electron interactions are independent of the geometry such as the Hubbard ($U(n - m) = U\delta_{nm}$) and the extended Hubbard model ($U(n - m) = V\delta_{n,\pm 1}$), the Eq.(3) can be simplified to a form which is similar to the bond-order-bond-length relation in the standard Hückel theory. The equilibrium geometry for the charge-transfer state very efficiently by using the self-consistent relation Eq. (3). In the more general situation, Eq. (3) can only be determined through numerical situation.

As expected, the lowest energy level for the CT states is found to be a bound state consists

of a localized hole polaron on the polymer and an electron on the acceptor level of dopant molecule. The energy for the lowest CT-exciton is about 1.00 eV and the binding energy is around 0.30 eV. It varies with different strength of $e-e$ and $e-p$ coupling. Interestingly, the lattice relaxations for the bound CT-state and the scattering states in the CT-continuum are quite different. Generally speaking, there is a significant lattice distortion when the e-h amplitude of CT-state is localized; while the lattice distortion become negligible when the final state is in the CT-continuum. Later, we will see this has a significant effect on the transition rate.

Now consider the electron-transfer rate between the conjugated polymer and the dopant. Using the Fermi-Golden Rule: $W = \frac{2\pi}{\hbar} \sum_{i,f} \rho_i |\langle \Phi_f | V | \Phi_i \rangle|^2 \delta(E_i - E_f)$ where Φ_i and Φ_f are the initial and final wavefunction for the conjugated polymer/dopant composite respectively, $\rho_i = e^{-\beta E_i} / \sum_i e^{-\beta E_i}$, $\beta = 1/k_B T$ and V is the operator for the electron hopping. The δ -functional guarantees the conservation of energy. Within Born-Oppenheimer approximation, the hopping matrix element becomes $M_{if} = |\langle \chi_v(\mathbf{Q}) | \hat{M}_{IF}^e | \chi_{v'}(\mathbf{Q}) \rangle|^2$ where $\hat{M}_{IF}^e(\mathbf{Q}) = \langle \phi_F | V | \phi_I \rangle$ is still an operator in the Hilbert space spanned by the nuclear wavefunctions. Applying Condon approximation, i.e. M_{IF}^e is independent of nuclear coordinates. Then the the electronic and nuclear parts can be factored out :

$$W = \frac{2\pi}{\hbar} |M_{IF}^e|^2 \sum_{v,v'} \rho_v |\langle \chi_v | \chi_{v'} \rangle|^2 \delta(E_v - E_{v'}). \quad (4)$$

Using V_1 and V_2 and the electronic wavefunction of conjugated polymer in the presence of exciton and hole polaron, we can explicitly write down the electronic matrix elements for these two mechanisms: $M_1 = \frac{\hbar_0}{\sqrt{N}} \frac{1}{\sqrt{N}} \sum_{n=1}^N \phi_{nu} (\Phi_{N/2,i} + \Phi_{N/2+1,n})$ and $M_2 = v_0 / \sqrt{N} (\phi\Phi + \phi\bar{\Phi})$.

The nuclear wavefunctions for the conjugated polymer/dopant composite can written in the product form if we go to the normal mode coordinate. $|\chi_i\rangle = \prod_k |\chi_k^i\rangle$ and $|\chi_f\rangle = \prod_k |\chi_k^f\rangle$ where χ_k^i the k th normal mode for the i th electronic state.

$$\langle \chi_i | \chi_f \rangle = \prod_k e^{\Delta_k^2/4} L_{m_k}(\Delta_k^2/2) \quad (5)$$

where $\Delta_k \equiv (M\omega_k/\hbar)^{1/2}\delta_k$ and L_k is the Laguerre polynomial of the m_k th degree. Δ_k is the displacement of each normal modes.

$$W = \frac{2\pi}{\hbar^2} \sum_n |\langle \Psi_{ct,n} | V_1 + V_2 | \Psi_{ex} \rangle|^2 \sum_{v_{n_1}} \sum_{v_{n_2}} \dots \sum_{v_{n_k}} \left(\prod_{i=1}^k \frac{S^{v_{n_i}}}{v_{n_i}!} e^{-S_{n_i}} \right) \delta(\omega_{ct} - \omega_{ex} + \sum_{i=1}^k v_{n_i} \omega_i) \quad (6)$$

The total energy difference is $\omega_{ct} - \omega_{ex} + \sum_{i=1}^k v_{n_i} \omega_i$. Using short time approximation in the strong coupling limit, we obtain the rate expression in the current work:

$$W = \frac{1}{\hbar^2} \sum_n |\langle \Psi_{CT,n} | V | \Psi_{ex} \rangle|^2 \sqrt{\frac{2\pi}{\sum S_{n_i} \omega_i^2}} \exp \left[-\frac{(\omega - \omega + \sum S_{n_i} \omega_i)^2}{2 \sum S \omega} \right]. \quad (7)$$

We have calculated the relative contributions of the V_1 and V_2 mechanisms by the pure electronic coupling without the lattice relaxation, the result is in agreement with Rice and Garstein's work. However, direct irreversible transition to CT-bound state is not possible in the Rice and Garstein's model. When the effect of the lattice relaxation is included, it becomes possible for electron to hop directly to CT-bound state since the extra energy can be absorbed by the lattice through multiphonon excitation in the direction of most important configuration coordinate.

Fig. and show the photoinduced electron-transfer rate from the initial bound exciton to final CT states as a function of Δ . Surprisingly the order of magnitude for the direct transition to the CT-continuum is about two order of magnitudes smaller than the to CT-bound state. The direct transition to the CT-bound exciton seems to be much more efficient. This is because that in order to have an efficient electron transition it is better have a good overlap in both electronic and nuclear parts. Since the initial STE is spatially localized in a region less than ten unit cells, the scattering states in the CT-continuum are delocalized states with little overlaps with initial state. Therefore the electronic contribution is smaller compare with the transition to the bound CT-exciton. About the nuclear factor, we have calculated the lattice displacement between initial and final state along each normal coordinate, in the present study, the Duschinsky rotation is negligible. The result of the normal mode analysis shows that only the symmetric vibration give nonvanishing Huang-Rhys factors and the most important configuration coordinate is the vibration with the longest wavelength. Due

to the mismatch of the lattice distortion of initial STE and the final scattering states in the CT-band, the Franck-Condon factors for nuclear part is unfavorable again.

In conclusion, we have demonstrated the importance of lattice relaxation on the photoinduced electron transfer in a molecularly doped conducting polymer. Using parameters which generate the optical gaps for the conjugated polymers are consistent with observed values. We have shown that the LRT approach combined with BdG formalism is suitable in describing the lattice relaxation structures of the neutral and CT excitons. Moreover the photoinduced electron transfer in the molecularly doped conjugated polymers has been successfully studied using this formalism. Due to the better overlap between the initial and final states both in the electronic and nuclear wavefunctions, the electron-transfer to the bound CT state is more effective than to the CT-continuum. The result of current work suggest that the electron transfer rate can be tuned by controlling the Δ between dopant molecules and polymers, which may be achieved by changing the side group of conjugated polymers. The results of the current work enable us to further investigate the enhancement of photocurrent in the polymer/nanoparticle composites. Works on this subject are currently in progress.

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REFERENCES

- [1] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl. *Science*, 258:1474–1476, 1992.
- [2] René A. J. Janssen *et al.* Photoinduced electron transfer reactions in mixed films of π -conjugated polymers and a homologous series of tetracyano-p-quinodimethane derivatives. *J. Chem. Phys.*, 103(20):8840, 1995.
- [3] M. J. Rice and Yu. N. Garstein. Theory of photoinduced charge transfer in a molecularly doped polymer. *Phys. Rev. B*, 53(16):10764, 1996.
- [4] K. Huang and A. Rhys. Theory of light absorption and non-radiative transitions in F-centres. *Proc. Roy. Soc. London, Ser. A*, 204:406, 1951.
- [5] Z.-B. Su and L. Yu. Theory of soliton generation and lattice relaxation in polyacetylene (i) general formalism. *Commun. in Theor. Phys. (Beijing, China)*, 2(4):1203–1218, 1983.
- [6] Z.-B. Su and L. Yu. Theory of soliton generation and lattice relaxation in polyacetylene (iii) radiative transitions. *Commun. in Theor. Phys. (Beijing)*, 2(5):1341–1356, 1983.
- [7] Z.-B. Su and L. Yu. Soliton pair generation in polyacetylene: A lattice relaxation approach. *Phys. Rev. B*, 27:5199, 1983.
- [8] Wen-Zheng, Chui-Lin Wang, Zhao-Bin Su, and Lu Yu. Lattice relaxation study on self-trapped exciton and biexciton in neutral and charged fullerenes. *Phys. Rev. Lett.*, 72(22):3550, 1994.
- [9] D. S. Yang. Lattice relaxation theory of photoinduced charge transfer in molecularly doped conjugated polymers. Master's thesis, National Taiwan University, 1999.

FIGURES

FIG. 1 The comparison of the lattice relaxation structure of the neutral exciton and CT-bound states at four different d values. Here $K=2.5$, and $(\beta, U, U/(V/a_0))$ equals $(0.01, -2, 2)$ (Upper left), $(0.1, -2, 2)$ (Upper right), $(0.01, -0.5, 4)$ (middle left), $(0.1, -0.5, 4)$ (middle right), $(0.1, -2, 2)$ (lower left), $(0.1, -1, 2)$ (lower right).

FIG. 2 Photoinduced electron transfer rate as a function of dopant energy, $\beta = 0.4$, $U = -1$, $U/(V/a_0) = 2$, $d = 5$, $K = 2.5$

FIG. 3 Photoinduced electron transfer rate from the exciton state to the CT-continuum



