



Temperature effect on the internal conversion dynamics following different stimulated absorptions in a conjugated polymer

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ABSTRACT

By applying a femtosecond electric pump pulse to a conjugated polymer, we theoretically study the temperature effect on the internal conversion dynamics following different stimulated absorptions. The simulations are performed within the framework of an extended version of the tight-binding Su-Schrieffer-Heeger model modified to include temperature effect. Firstly, temperature effect on different stimulated absorptions is focused, by which we speculate that the absorption spectra of a single polymer should be nearly temperature independent. However, following stimulated absorptions, the internal conversion (IC) from a higher-lying excited state to the lowest-lying exciton state will be remarkably accelerated by increasing temperature. From this point of view, temperature effect is not favorable for charge separation in polymer solar cells (PSCs), since charge separation from a higher-lying excited state can be effectively suppressed by its IC relaxation. In addition, considering that these IC relaxations are lattice vibration assisted, effects of the vibrational damping and the electron-lattice interaction on them are separately discussed. These findings are crucial for further understanding the primary photovoltaic process in PSCs, especially the role of a higher-lying excited state in charge separation.

1. Introduction

Over the past few decades, polymers solar cells (PSCs), in which the photoactive layers are composed of a blend of polymer donors (D) and fullerene (or non-fullerene) acceptors (A), have attracted considerable attention owing to their advantages in enabling the fabrication of lightweight, large-area, flexible solar panels through low-cost printing technologies [1,2]. Although many efforts have been devoted to improve the performance of PSCs, the power conversion efficiency in large area modules as well as the stability remain to be far away from actual applications [3,4]. As we know, the power conversion efficiency of PSCs reported in laboratory has broken through 13% [5], which value is still much lower than that reported in other photovoltaic devices, such as the rapidly developing perovskite solar cells [6–9] and the conventional silicon-based solar cells. One of the reasons for this situation is that the exciton binding energy in polymers is much larger than that in perovskite or silicon-based systems, typically in the range of 0.2–1.0 eV [10,11]. As a result, it is difficult for polymers to directly produce free charges by light absorption [2,12]. In addition, due to the flexibility and the strong electron-lattice interaction in polymers, the photovoltaic process in PSCs is usually complex and much sensitive to their intrinsic morphologies [2,13–15] and external environments [4].

In actual operation of a PSC, the working temperature is usually high due to continuous illumination and different relaxation processes [2,12,16]. Therefore, temperature effect should play a vital role in the photovoltaic process of a PSC [11,12,17–23]. Up to now, effects of temperature on the optical absorption (i.e. stimulated absorption process) and charge separation in polymers have been investigated with different degrees. As early as in 2009, Kanemoto et al. investigated the temperature effect on the absorption spectra of 16-mer oligothiophene (16T) extremely diluted in polypropylene over a wide temperature range (4–300 K) [16]. They found that the absorption spectra presents a blueshift with increasing temperature, and attributed the result to the decrease of effective conjugation length of polymer chains caused by the thermal conformational changes. In the next years, such a phenomenon was successively reported in different polymers, while the result was attributed to other reasons, such as the decrease of the refractive index of the solvents [18] and the weakening of the intermolecular interactions [24] with temperature increase. In addition, charge separation and its temperature dependence in PSCs have been focused in the past few years. However, such an issue remains controversial due to the complexity of its detection and analysis. On the one hand, some works demonstrated that charge separation in PSCs is temperature independent [25–27]. For instance, by using ultrafast

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transient absorption and microwave photoconductance techniques, Grzegorzczak et al. studied the temperature effect on charge separation yield in P3HT/PCBM blend films [26]. They found that the quantum yield is virtually independent upon temperature effect for timescales up to tens of nanoseconds after photoexcitation. On the other hand, Gao et al. verified that charge separation in PSCs is tightly related to temperature effect by examining the open-circuit voltage in a wide temperature range [20]. They ascribed the reasons to two aspects: one is the temperature dependent charge delocalization, the other is the contribution of entropy to the free energy, which determines whether holes and electrons are free from each other [28,29]. Theoretically, investigations about the temperature effect in polymers are focused on the scattering process between charge carriers and the relaxation process of different excited states, separately addressed by Junior's group [22,30] and An's group [21].

In addition to the above processes, internal conversion (IC) and other relaxation processes inevitably exist in actual operation of a PSC. As we know, by light absorptions of polymers, different higher-lying excited states (i.e. hot excitons) as well as the lowest-lying exciton state can be created with the yields determined by the photoexciting energy and intensity [11,24,31–35]. Compared with the lowest-lying exciton state, a higher-lying excited state is expected to facilitate the electronic delocalization and consequently results in efficient charge separation due to the higher energy, which has been known as the “hot exciton mechanism” [11,31–33]. However, a crucial issue is that the higher-lying excited state will simultaneously relax to the lowest-lying exciton state through ultrafast IC relaxation [11], by which charge separation yield in PSCs can be modified. Considering that the IC relaxation is actually a vibrationally assisted process, it should be sensitive to temperature effect. However, compared with the optical absorption and charge separation processes, the IC relaxation process and its temperature dependence in polymers have been barely investigated. In this paper, we will present a detailed study of the temperature effect on the IC relaxation process following different stimulated absorptions in a polymer. One of the goals is to gain insight into the temperature effect on charge separation in PSCs by examining the timescales of different IC relaxations over a wide temperature range 0–300 K, since it is expected that charge separation should occur on a timescale comparable to or shorter than IC relaxations in high-performing PSCs. The paper is organized as follows. Section 2 describes the model and method, in which temperature effect is included by employing a thermal random force. The results and discussion are presented in Section 3. Finally, in Section 4, a conclusion is given.

2. Model and method

Here, we choose a poly (*p*-phenylene vinylene) (PPV) molecule as the model system. To highlight its strong electron-lattice interaction, an extended version of the well-known Su-Schrieffer-Heeger (SSH) model is employed, which is originally proposed to describe a long trans-polyacetylene chain [36]. In such a framework, a PPV molecule can be modeled as a one-dimensional chain by a renormalization treatment, as sketched in Fig. 1(a). Considering the periodic structure of a PPV monomer, the electron transfer integral $t_{n,n+1}$ between the nearest-neighbor sites n and $n+1$ can be expressed as follows

$$t_{n,n+1} = t_0 - \alpha(u_{n+1} - u_n) - t_1 \cos n\pi + t_2 \cos\left(\frac{n+1}{3}\pi\right) \cdot \delta\left(\frac{n+1}{3}, \text{int}\right). \quad (1)$$

$\delta\left(\frac{n+1}{3}, \text{int}\right) = 1$, if $\frac{n+1}{3} = \text{int}$; and $\delta\left(\frac{n+1}{3}, \text{int}\right) = 0$, if $\frac{n+1}{3} \neq \text{int}$. “int” indicates an integer. t_0 represents the nearest-neighbor electron transfer integral of a uniform bond structure, α is the electron-lattice interaction constant, and u_n describes the lattice displacement of site n . t_1 and t_2 are symmetry-breaking parameters introduced to reflect the lattice feature of a PPV monomer. In fact, by such a treatment to the

PPV monomer, its six-periodic bond structure is well described by

$$t_{1,2} = t_0 - \alpha(u_2 - u_1) + t_1, \quad t_{2,3} = t_0 - \alpha(u_3 - u_2) - t_1 - t_2,$$

$$t_{3,4} = t_0 - \alpha(u_4 - u_3) + t_1, \quad t_{4,5} = t_0 - \alpha(u_5 - u_4) - t_1,$$

$$t_{5,6} = t_0 - \alpha(u_6 - u_5) + t_1 + t_2, \quad t_{6,1} = t_0 - \alpha(u_1 - u_6) - t_1.$$

Thus, the Hamiltonian of a PPV molecule can be written as

$$H = - \sum_n t_{n,n+1} (C_{n+1}^+ C_n + C_n^+ C_{n+1}) + \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2 + \frac{1}{2} M \sum_n \dot{u}_n^2. \quad (2)$$

The first term shows the electron hopping between the nearest-neighbor sites of the molecule with spin index omitted for clarity. C_n^+ (C_n) is the operator that creates (annihilates) an electron at site n . The second term and the third one separately describes the classical treatment to the elastic energy and kinetic energy of all sites. K is the elastic constant and M the mass of a site.

To describe an incident photon of the PPV molecule, we employ a femtosecond electric pump pulse $E(t)$, which is chosen as a Gaussian form with the pulse width t_w centered at time t_c ,

$$E(t) = E_0 \exp\{-(t - t_c)/t_w\} \cos(\omega t). \quad (3)$$

E_0 and ω separately shows the pulse intensity and frequency. Here, contribution of the pump pulse to the Hamiltonian can be written as

$$H_E = \sum_n e E(t) (na + u_n) (C_n^+ C_n - 1). \quad (4)$$

e indicates the electronic charge and a lattice constant.

After applying such a pump pulse to the PPV molecule, the molecule will experience an evolution, during which we employ a nonadiabatic evolution method. The lattice displacement u_n (i.e. nuclear motion) is classically described by the Newtonian equation of motion,

$$M\ddot{u}_n = -K(2u_n - u_{n+1} - u_{n-1}) + 2\alpha[\rho_{n,n+1}(t) - \rho_{n-1,n}(t)] + eE(t)[\rho_{n,n}(t) - 1] - \lambda M\dot{u}_n + f_n(t). \quad (5)$$

$\rho_{n,n'}(t)$ is the density matrix, defined as

$$\rho_{n,n'}(t) = \sum_v \Phi_{v,n}^*(t) g_v \Phi_{v,n'}(t). \quad (6)$$

g_v ($=0,1,2$) is the time-independent distribution function and determined by the initial occupation of the electronic state $|\Phi_v(t)\rangle$. $|\Phi_{v,n}(t)\rangle$ is the projection of the electronic state $|\Phi_v(t)\rangle$ on the wannier state of site n [i.e. $\Phi_{v,n}(t) = n|\Phi_v(t)\rangle$]. The evolution of an electronic state $|\Phi_v(t)\rangle$ depends on the time-dependent Schrodinger equation

$$i\hbar \frac{\partial}{\partial t} |\Phi_v(t)\rangle = (H_e + H_E) |\Phi_v(t)\rangle. \quad (7)$$

In Eq. (5), a damping term $-\lambda M\dot{u}_n$ is introduced to describe the damping force applying on site n during its motion, in which λ is the damping coefficient and the value determined by the external environment [37]. Especially, temperature effect is also included in Eq. (5), where we employ a thermal random force $f_n(t)$. It is characterized by the statistical properties and satisfies the statistical laws:

$$f_n(t) = 0,$$

$$f_n(t)f_{n'}(t') = 2k_B T M \gamma \delta_{n,n'} \delta(t - t').$$

k_B is the Boltzmann constant, T is the temperature, and γ is a coefficient related to the lattice vibration. Distribution of the random force $f_n(t)$ along the PPV molecule can be represented by presetting a set of random numbers in every time step Δt of our dynamic simulations, and the strength of $f_n(t)$ is determined by temperature. Here, a discrete time step $\Delta t = 1$ fs is employed, by which the thermal random forces $f_n(t)$ is taken to be unchanged in each femtosecond.

It is important to note from Eqs. (5) and (7) that the nuclear motions

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