Photogeneration of charge carriers in a weakly disordered π-conjugated polymer at high photon energies of exciting light

L.V. Lukin *

V.L. Talrose Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences, Semenov Avenue, 1/10, Chernogolovka, Moscow Oblast 142432, Russian Federation

ABSTRACT

Model of photoionization of a weakly disordered conjugated polymer is proposed for high photon energies of exciting light. The vibrational energy of photogenerated excitons is assumed to go into heating of a conjugated segment. This results in an increase of temperature of mobile charges produced by dissociation of excitons. The vibrational heating of the conjugated segment is assumed to be conserved for so long that charge carriers can cross the potential barrier formed by the Coulomb and external electric fields during their diffusion motion along the excited segment with effective temperature T_{eff}. It is shown that the model agrees with experimental data on photocarrier quantum yield in films of a methyl-substituted ladder-type poly-para-phenylene (MeLPPP) obtained by Bath et al. [Chem. Phys. Lett. 288 (1998) 147–154]. The effective temperature $T_{eff} > 1200$ K is estimated in MeLPPP for wavelength 250 nm.

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1. Introduction

Conjugated polymers are attracting great interest as new materials for application in devices of organic electronics, like solar cells, light emitting diodes, and transistors [1–6]. However, many questions on initial stages of charge photogeneration in pristine polymers still remain to be answered.

In recent years, many works have been devoted to study photoionization in a methyl-substituted ladder-type poly-para-phenylene (MeLPPP) in which disorder effects are weaker than in most conjugated polymers of the para-phenylenevinylene family, and the effective conjugation length is 6.5 ± 0.5 nm [7–9]. It has been established that intrinsic one photon generation of charge carriers in a bulk of MeLPPP, as well as in other conjugated polymers [10,11], commences as a photon energy $h\nu$ of exciting light becomes about 1 eV higher than the optical absorption edge identified as the $S_1 \leftarrow S_0$ 0–0 transition [12]. For MeLPPP, the absorption edge $E(S_1) = 2.7$ eV [9,13] and threshold of intrinsic bulk photogeneration $h\nu_0 = 3.85 \pm 0.1$ eV [12] were found (1 eV $= 1.602 \times 10^{-19}$ J). It is believed that photogeneration below $h\nu_0$ originates from localized states of either extrinsic or intrinsic origin [10–12]. As to higher photon energies, the measurements of steady-state photoconductivity in MeLPPP have shown that at $h\nu > h\nu_0$ the quantum yield ϕ of free charge carriers strongly increases with

increasing external electric field strength F but the value of ϕ is practically independent of temperature [12]. The dependence of ϕ on F is super-linear as the external electric field varies between about 5×10^6 and 10^8 V/m [12].

As noted [14–16], experimental results obtained for MeLPPP do not agree with the Onsager model of geminate recombination frequently used to interpret experimental data on photoconductivity in molecular solids [17–19]. According to the model, the next processes are involved in the photogeneration of free charge carriers. Light absorption leads to formation of intrachain excitons, electronically excited neutral states of conjugated segments of polymer chain, which can dissociate into geminate pairs of charges of opposite signs bound by the mutual Coulomb attraction. Theoretical model of Onsager [19] describing Brownian motion of a pair of classic charge particles in the joint Coulomb and external electric field predicts a strong dependence of free charge yield on ambient temperature and external electric field. In the framework of the Onsager model, the probability for charges to escape geminate recombination, found as a function of the external electric field, shows saturation with increasing electric field in fields of 10^8 V/m. This is at variance with super-linear dependence of ϕ on F observed in MeLPPP [12].

To explain the revealed peculiarities of the cw photoconductivity, Arkhipov et al. [14–16] have developed a model of intrasegmental dissociation of hot optical excitations. According to the model, at $h\nu > h\nu_0$ the photon absorption creates the Franck–Condon states above the absorption edge which relax, within time interval $\Delta t_{rel} \approx 0.1$ ps, into their new configuration. The initial

* Tel.: +7 916 680 1645; fax: +7 916 680 3573.
E-mail addresses: lukin@binep.ac.ru, leonid.v.lukin@gmail.com (L.V. Lukin).

excess energy, $h\nu - E(S_1)$, is quickly distributed among other vibrations of the conjugated segment of polymer chain generating a vibrational heat "bath". The average excess energy of the vibrational bath $<E>$ decreases rapidly, within time Δt_{rel}, down to thermal energy. In view of the fact that $<E>$ is more than $k_B T$, this facilitates jumps of an electron–hole pair, generated by dissociation of exciton, across the potential barrier formed by superposition of the Coulomb and strong external electric fields (here, T is an ambient temperature, and k_B is the Boltzmann constant). The key assumption of the model [14–16] is that relaxation time Δt_{rel} during which the initial vibrational energy dissipates into vibrations of the polymer segment is very short (≈ 0.1 ps). However, the following arguments allow us to assume that relaxation time of vibronic degrees of freedom in conjugated segments can be much above 0.1 ps.

Modern theory of the nonradiative decay of high lying electronically excited states in polyatomic molecules takes into account complex transitions between intramolecular vibrations [20], and the theory rests on advancements in the femto- and picosecond spectroscopy. As noted [20], one of the important recent experimental results was the discovery of the spatially resolved transfer of vibrational energy for long distances within large molecules. It has been established that in polyatomic molecules the vibrational excitation is not evenly distributed among a large number of intramolecular vibrations, but it is transferred, for example, through a chain consisting of 12–26 CH_2 units [21,22] and between moieties linked by 4–8 conjugated bonds [23]. Using the method of the two-dimensional (2D) infrared spectroscopy [23], Lin et al. have shown that transport of the intramolecular vibration energy in the polyethylene glycol (PEG) oligomers of different length, having 4, 8, and 12 repeating units [24], and in perfluoroalkane oligomers with various chain lengths [25] occurs in a ballistic energy transport regime. In the ballistic regime the energy is transferred by vibrational states delocalized over the whole transport region [24]. The energy transport speed was found to be 450 m/s for the PEG oligomers in CCl_4 [24] and 1150 m/s for perfluoroalkane oligomers in chloroform [25]. These values are close to a speed of propagation (950 m/s) of the heat burst in a monolayer of long-chain hydrocarbon molecules anchored to metal substrates that was measured by using the method of the sum-frequency generation spectroscopy [21]. The energy transport time increases with increasing the chain length and reaches about 15 ps at the chain length of 6 nm [24].

Relying on such experimental results, one can concede that the relaxation time Δt_{rel} of excess energy of the vibrational heat "bath" in MeLPPP, having the conjugated segments with lengths of 6–7 nm, is of the order of 10 ps. It may be even longer when it is considered that the theory [20,26] predicts the recurrence cycles. At $\Delta t_{rel} > 1$ ps, the electron–hole pair can cross the potential barrier during the diffusion motion with effective temperature $T_{eff} > T$ provided that the intra-chain mobility of holes and electrons is sufficiently large.

In the recent years, the charge transport along the chain of a conjugated polymer has been studied by the time resolved electrodeless methods of measurements [27]. For MeLPPP, the intrachain hole mobility of 30 $cm^2 V^{-1} s^{-1}$ [28] and about 1 $cm^2 V^{-1} s^{-1}$ [29] were reported. So, it is of interest to consider a diffusion mechanism for the initial stages of the charge separation using the experimental estimates of the intrachain charge mobility.

The goal of the present article is to answer the question of whether the excess vibrational energy of photogenerated excitons is transferred through conjugated segments of the polymer chain. If the excess vibrational energy is conserved within an excited conjugated segment for sufficiently long time, this can result in enhanced effective temperature for intrachain motion of geminate electron–hole pairs and in an increase of the photoionization

quantum yield. In the present article, we propose a simple diffusion model of one-dimensional (1D) motion of holes along a conjugated segment which allows us to relate parameters of the intrachain transport of holes to the photocarrier quantum yield. Analysis of experimental data [12] on the cw photoconductivity in MeLPPP made below shows that effective temperature of conjugated segment is greater than 1200 K at high photon energies of exciting light. In addition, from a comparison between predictions of the model developed and the experimental dependence $\phi(F)$ observed in MeLPPP [12] it is concluded that the rate of the primary charge generation due to exciton dissociation depends on an external electric field as opposed to the traditional Onsager model.

2. Model

We consider the initial stages of generation of charges following the absorption of photons with $h\nu > h\nu_0$ in polymer matrix consisting of the array of the conjugated segments with length of $b \approx 6$–7 nm. The light absorption with $h\nu > h\nu_0$ produces the vibrationally hot excitons S_1 and higher optically allowed vibrationally hot excitons S_n which are the intra-chain states (Fig. 1). For MeLPPP, the difference in energy $E(S_n) - E(S_1)$ of the vibrationally relaxed states is about 1.5 eV [30]. (The S_n state is not shown in Fig. 1 because of the high rate 1.7×10^{13} 1/s of the internal conversion for the transition $S_n \rightarrow S_1$ via vibrational modes [30].) According to the idea of Arkhipov et al. [14–16], a part ΔE_{vibr} of the initial vibrational energy of the S_1 state goes into heating of the conjugated segment. The electron–hole pair is produced as a result of the electron transfer from an intermediate vibrationally hot S_1^* state to electron acceptor species [31]. The acceptor species can be either moieties within the same conjugated segments, or impurities, or a neighboring conjugated segment different from that of the site of the initially photogenerated exciton [32]. Generation of the electron–hole pair due to dissociation of the exciton state S_1^* competes with a nonradiative decay of S_1^* to the vibrationally relaxed (cold) state. In the present article, we do not consider formation of charges due to dissociation of the vibrationally cold S_1 state that takes place at $h\nu < h\nu_0$ [33]. The dissociation of the long-lived vibrationally cold S_1 state of excitons
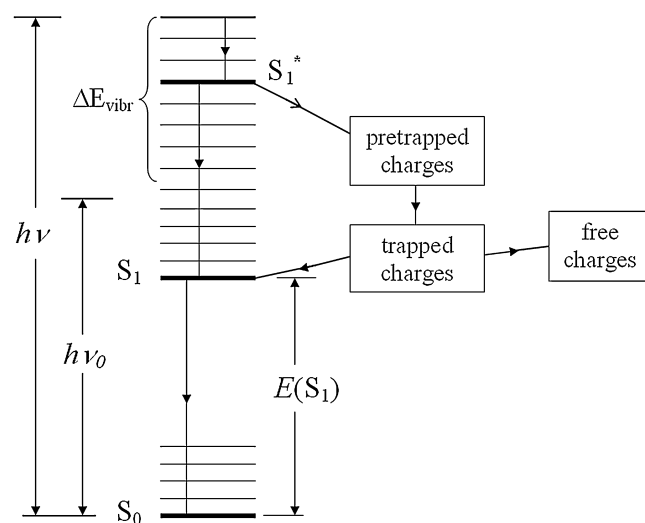

Fig. 1. The energy-level diagram of the photogenerated excitons and scheme of the processes and transitions used in the model. Name "free charges" denotes those charge carriers which escape geminate recombination and contribute to a steady-state photoconduction.