# Hot Exciton Dissociation in a Conjugated Polymer

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A model has been developed to treat field-assisted ultrafast on-chain dissociation of optical excitations in a conjugated polymer. Conversion of the excess photon energy above the singlet exciton into the vibrational heat bath of a polymer segment is considered as a main source of the energy required for charges to escape from a potential well formed by a superposition of the Coulomb and external electric fields. The calculated yield of carrier photogeneration increases strongly with increasing field but is independent of the temperature in good quantitative agreement with data obtained by Barth *et al.* [Chem. Phys. Lett. **288**, 147 (1998)] on weakly disordered conjugated ladder-type poly-phenylene. [S0031-9007(98)08372-0]

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The strong dependence of the yield of optical charge carrier generation upon external electric field $(F)$ and temperature $(T)$ is a common feature of low-mobility materials such as amorphous semiconductors, molecular crystals, and photosensitive polymers [1–3]. Traditionally, it is interpreted in terms of the classic Onsager theory of geminate recombination [2–5]. It invokes the formation of a geminate $e$-$h$ pair either after thermalization of photoexcited hot carriers (amorphous semiconductors) or after breaking of neutral optical excitation in molecular crystals and photosensitive polymers. While remaining coulombically bound, carriers execute a Brownian random walk within the potential well formed by a superposition of the Coulomb potential and the external electric field $\mathbf{F}$:

$$U(\mathbf{r}) = -(e^2/4\pi\varepsilon_0\varepsilon r) - e\mathbf{F}\cdot\mathbf{r}\,, \qquad (1)$$

where $\mathbf{r}$ is the coordinate, $e$ is the elementary charge, $\varepsilon_0$ is the dielectric permittivity, and $\varepsilon$ is the electric constant. To overcome the potential barrier described by Eq. (1), a carrier has to acquire a sufficient energy from the phonon bath via a temperature driven activated process. Therefore, the Onsager theory predicts strong dependencies of the dissociation probability upon both the external field and the temperature, with both dependencies being inevitably coupled to each other.

However, applicability of the traditional 3D Onsager theory to the analysis of charge carrier photogeneration in conjugated polymers is doubtful for several reasons. This theory rests on the notion that the medium is homogeneous and isotropic. In low-molecular solids, this condition is approximately realized because the intermolecular distance is much shorter than the radius $r_c$ of the Coulombic capture sphere. In that case, a geminate $e$-$h$ pair can escape in the course of a multistep random walk. The situation is different in a conjugated polymer whose electronic building blocks are conjugated, i.e., covalently bonded, segments typically 10 nm long and comprising several repeat units. This implies that (i) the length of the segment may exceed $r_c$ [6], (ii) motion of charges forming an $e$-$h$ pair is highly anisotropic, and (iii) the concept of diffusive escape on a chain [7] becomes inapplicable. As far as off-chain $e$-$h$ pairs are concerned, their binding energy is supposed to be typically 0.7 eV premised upon an average dielectric constant of 3.5 and a mean interchain distance of 0.6 nm. Their dissociation should, therefore, be highly inefficient.

Meanwhile, it has been firmly established that intrinsic photogeneration in conjugated polymers commences around 1 eV above the absorption edge identified as the $S_1 \leftarrow S_0$ 0-0 (excitonic) transition [8–10]. Photogeneration below that intrinsic threshold is believed to originate from localized states of either extrinsic or intrinsic origin [9,10]. The yield $\eta$ increases strongly at higher electric fields while the temperature dependence is weak if not negligible [9–12]. The prototypical example of that phenomenon appears to be a ladder-type poly-phenylene (MeLPPP) in which covalent binding leads to exceptionally weak structural disorder [13]. The yield ranges from $10^{-5}$ to $10^{-2}$ depending on $F$ and photon energy while virtually no temperature dependence is observed [13]. This is in disagreement with Onsager's theory, both its 1D and 3D versions, predicting that $\lim_{F\to\infty}\eta(F,T) = \lim_{T\to\infty}\eta(F,T) = \eta_0$, where $\eta_0$ is the yield of the precursor $e$-$h$ pairs prior to diffusive escape [5,7].

In the Letter, we develop a theory to account for photogeneration in a conjugated polymer as a function of electric field, temperature, and photon energy. It rests on the idea that photon absorption creates a Franck-Condon state above the $S_1 \leftarrow S_0$ 0-0 transition. Within 100 fs, the chain skeleton relaxes into its new configuration associated with either the electronic $S_1$ state or, possibly, a higher electronic state. The excess energy, $\hbar\omega - E(S_1)$, is distributed among vibrations of the chain segment thus generating a vibrational heat bath whose actual temperature is above ambient temperature. The bound parent $e$-$h$ pair can subsequently escape from the Coulombic well in terms of a Boltzmann process in which $kT$ is replaced by the momentary average energy $\langle E\rangle$ of the vibrational heat bath of the chain. Pair escape must compete with the dissipation of the excess energy into intermolecular vibrational and phonon modes. Conceptually, the $e$-$h$ yield must increase with field because it lowers the Coulombic barrier and with the excess photon energy because it raises the local chain temperature. Since dissipation of the vibronic energy is a fast process, only few excitations can dissociate before the segment is cooled down to the ambient temperature and the occurrence of two or more sequential jumps of carriers is almost impossible. Being once separated, carriers have no time to cross the barrier again and to recombine while still hot. After cooling the segment, the probability to cross the barrier again and to recombine is much lower such that separated charges will mostly make jumps onto other segments and contribute to photoconductivity. Therefore, the quantum yield of ultrafast on-chain dissociation, $\eta$, can be evaluated as the probability for carriers to cross the potential barrier and to form an on-chain geminate pair neglecting the possibility of geminate recombination.

For times shorter than both the decay time of neutral optical excitations and the time of intersegmental carrier jumps, a pair of charge carriers within an excited segment may be considered as a system having two metastable states separated by a potential barrier. The first state is a neutral optical excitation identified as the exciton of the binding energy $E_b$. This energy is practically independent of the external electric field. The second state is formed by a dissociated geminate pair of carriers localized at opposite ends of the segment. The energy of this state, $E_s$, depends upon the external field as determined by Eq. (1):

$$E_s = -(e^2/4\pi\varepsilon_0\varepsilon l) - elFz\,, \tag{2}$$

where $l$ is the length of the segment, and $z = \cos\varphi$, where $\varphi$ is the angle between the direction of a segment and the external electric field. In a segment of the length $l$ oriented along the angle $\varphi$, the state of separated twins is metastable (i.e., it is separated by a potential barrier from the state of a neutral excitation) if the external field is sufficiently strong:

$$F > e/4\pi\varepsilon_0\varepsilon l^2 z\,. \tag{3}$$

The height of the potential barrier, $E_{\max}$, separating the two metastable states is also field dependent as described by Eq. (1):

$$E_{\max} = -e\sqrt{eFz/\pi\varepsilon_0\varepsilon}\,. \tag{4}$$

We assume that the excess photon energy, $\hbar\omega - E(S_1)$, establishes an average excess energy of the vibrational "bath" of $\langle E_0\rangle$. Since the time dependence of the cooling process is not known exactly, we further assume a constant energy-dissipation rate $\beta$:

$$\langle E\rangle = \langle E_0\rangle - \beta t\,, \tag{5}$$

We also presume that the probability for a charge carrier to get energy sufficient to cross the potential barrier, $w(\langle E\rangle, E_{\max})$, can be described by the Boltzmann distribution,

$$w(\langle E\rangle, E_{\max}) = \mathrm{Bol}\left(\frac{E_b - |E_{\max}|}{\langle E\rangle}\right), \tag{6}$$

with the temperature replaced by the average vibronic energy. The function $\mathrm{Bol}(x)$ is introduced as

$$\mathrm{Bol}(x) = \begin{cases} \exp(-x), & x > 0\,, \\ 1, & x < 0\,. \end{cases} \tag{7}$$

Under these conditions, the rate of over-barrier dissociation jumps of carriers is determined by the following equation:

$$\begin{aligned} \frac{df_s(t)}{dt} &= \nu_0[1 - f_s(t)]\,\mathrm{Bol}\left(\frac{E_b - |E_{\max}|}{\langle E(t)\rangle}\right), \\ f_s(0) &= 0\,, \end{aligned} \tag{8}$$

where $f_s$ is the probability for carriers to be separated at the time $t$; $\nu_0$ is the constant describing the electron-phonon coupling within a segment similar to the "attempt-to-jump frequency" which normally accounts for the electron-phonon coupling in solids. Since the time and the average excess energy are related to each other by Eq. (5), one can also consider the separation probability $f_s$ as a function of the excess energy, $\varphi_s(\langle E\rangle)$. By the use of Eq. (5), one may then rewrite Eq. (8) using $\langle E\rangle$ as an independent variable:

$$\begin{aligned} \frac{d\varphi_s(\langle E\rangle)}{d\langle E\rangle} &= -\frac{\nu_0}{\beta}[1 - \varphi_s(\langle E\rangle)]\,\mathrm{Bol}\left(\frac{E_b - |E_{\max}|}{\langle E\rangle}\right), \\ \varphi_s(\langle E_0\rangle) &= 0\,. \end{aligned} \tag{9}$$

Solving Eq. (9) yields

$$\varphi_s(\langle E\rangle) = 1 - \exp\left[-\frac{\nu_0}{\beta}\int_{\langle E\rangle}^{\langle E_0\rangle} d\langle E'\rangle \times \mathrm{Bol}\left(\frac{E_b - |E_{\max}|}{\langle E'\rangle}\right)\right], \tag{10}$$

Since the rate of dissociation jumps sharply decreases with decreasing average vibronic energy, most dissociation jumps occur while the excess vibronic energy is still close to its initial value as shown in Fig. 1, and a separated $e$-$h$ pair will find itself occupying a segment which is already cooled down. This allows neglecting backward recombination jumps of carriers and evaluating the probability of the on-chain charge separation within a given

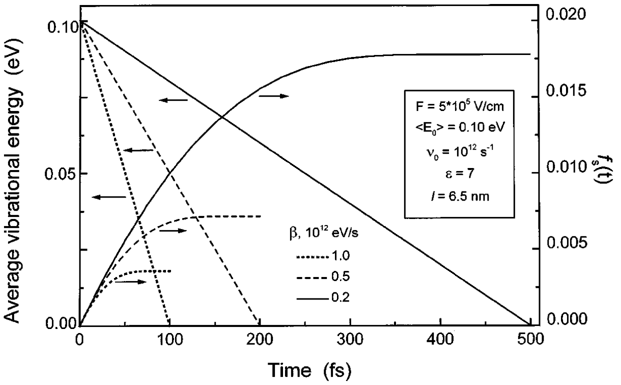

FIG. 1. Time dependencies of the dissociation probability and of the average vibrational energy parametric in the energy-dissipation rate.

segment, $w_d(F, \langle E_0 \rangle, z)$, as the occupational probability for the dissociation state after complete relaxation of the excess energy:

$$w_d(F, \langle E_0 \rangle, z) = \varphi_s(\langle E \rangle = 0) = 1 - \exp\left[ -\frac{\nu_0}{\beta} \int_0^{\langle E_0 \rangle} d\langle E \rangle \times \mathrm{Bol}\left( \frac{E_b}{\langle E \rangle} - \frac{e}{\langle E \rangle} \sqrt{\frac{eFz}{\pi \varepsilon_0 \varepsilon}} \right) \right]. \qquad (11)$$

The total quantum yield of the on-chain charge carrier photogeneration, $\eta(F, \langle E_0 \rangle)$, can be calculated by averaging Eq. (11) over different possible segment orientations as

$$\eta(F, \langle E_0 \rangle) = \int_0^1 dz \, w_d(F, \langle E_0 \rangle, z) . \qquad (12)$$

Since, within the framework of the present model, dissociation jumps are due to the photon excess energy the rate of such jumps and the dissociation probability does not depend upon the sample temperature. Field dependencies of the quantum yield are illustrated in Fig. 2 parametric in the initial energy $\langle E_0 \rangle$ together with experimental data obtained on MeLPPP [13]. At weak fields, no segment may have a metastable dissociation state—see Eq. (3). Concomitantly, the yield remains zero at such fields and sharply increases when the field reaches the value sufficient to form dissociation states in segments oriented along the field. This increase is mostly due to the increasing number of segments available for dissociation. At moderate and strong fields practically all segments have dissociation states, and further increase of the yield occurs mainly due to decreasing height of the barrier separating the metastable states.

Theoretical curves are in good quantitative agreement with experimental data. Guided by an experimental estimate [14] of the on-chain high frequency dielectric constant in polydiacetylenes $\varepsilon = 7$ has been used for the electric constant along the chain direction to fit experimental data instead of the bulk electric constant $\varepsilon = 3.5$ typical for conjugated polymers. Experimental data shown in Fig. 2 are obtained for different photon energies, whereas theoretical curves are parametric in the initial value of the vibrational energy implying correlation between these two parameters with the rate of energy dissipation, $\beta$, being independent of the excess photon energy. This correlation is illustrated in Fig. 3. The set of thinner curves in Fig. 2 is calculated from Eqs. (11) and (12). These curves fit experimental data quite well at strong fields. However, noticeable deviations from experimental data occur at weaker electric fields and lower photon energies of the exciting light. These deviations can be explained by the contribution of the *extrinsic* bulk photogeneration. Occurrence of this effect in MeLPPP is revealed by a steep increase of the bulk photocurrent at the optical absorption edge [13]. Some photoexcited segments may have deep traps for charge carriers as near neighbors and serve as charge-transfer centers. If one of the carriers is captured by such a deep trap, the released energy may facilitate crossing the potential barrier within the segment by the other carrier of the geminate pair. The density of deep traps is normally

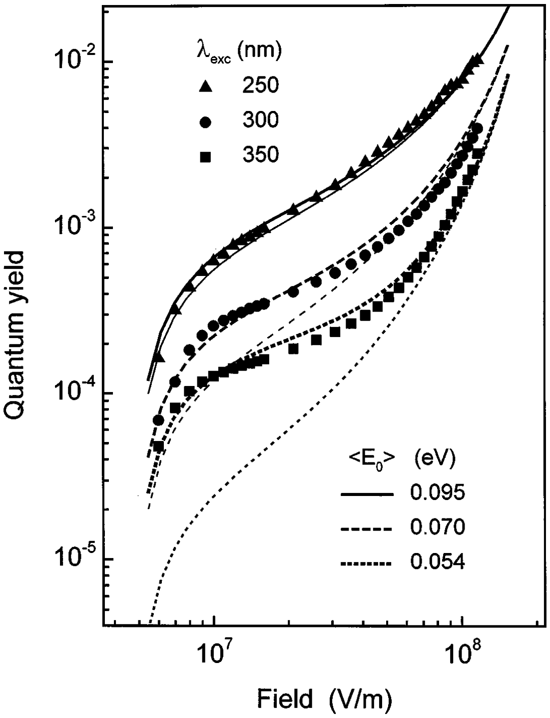

FIG. 2. Field dependence of the carrier photogeneration quantum yield. Experimental data are taken from [13]. Theoretical curves are parametric in the initial excess energy while experimental data are obtained for different photon energies. The following set of material parameters was used in calculations: $E_b = 0.35$ eV, $\nu_0/\beta = 0.9$ eV$^{-1}$, $l = 6.5$ nm, $\varepsilon = 7$, $\delta = 2 \times 10^{-4}$.

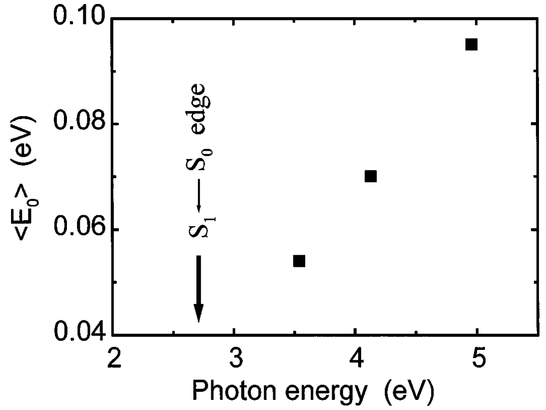

FIG. 3. Correlation between the photon energies and the excess thermal energies used to fit experimental data in Fig. 2.

much less than the concentration of segments, and their effect on the yield can be accounted for by adding the relative density of such specific charge transfer centers, $\delta$, to the right-hand side of Eq. (11). The results are illustrated in Fig. 2 by thicker curves which do provide a much better fit of the experimental data at weak fields and low excess photon energies.

An important parameter of the model is the binding energy of neutral optical excitations. The value of this parameter must be different for different electronic states of an excited molecule. Recent quantum chemical calculations prove that both electrons and holes are localized in the lowest $S_1$ excited state while higher excited states allow for carrier delocalization within an excited segment [15]. Within the framework of the present model, both $S_1$ and higher excited states can dissociate into on-chain geminate pairs if the vibrational relaxation is not yet completed. However, the present consideration is restricted to the assumption that the binding energy remains constant during the vibrational relaxation. This assumption can be justified by the notion that the biggest contribution to the on-chain dissociation probability is realized at short times when the excess energy is still close to its maximum value. However, after relaxation of the excess energy thermally assisted dissociation of $S_1$ excitations should become important. Since the lifetime of a $S_1$ state is much longer than the time scale of the vibrational relaxation, the contribution of conventional thermally assisted 1D Onsager dissociation can be dominant at higher temperatures as normally observed in conjugated polymers [9–12]. A remarkable experimental correlation should be mentioned between the excess energy required for the onset of charge photogeneration and the temperature dependence of the quantum yield. For instance, MeLPPP reveals the excess energy of 1.6 eV, and no $T$ dependence of the intrinsic quantum yield is observed in this material up to the room temperature [13]. For phenylene-vinylene derivatives (PPV-ether and PPV-amine) the intrinsic photoconductivity commences at the excess energy of 0.8 eV, and the yield weakly depends upon the temperature only below 220 K while an Arrhenius $T$ dependence is observed at higher temperatures [10]. Within the framework of the present model, this correlation is quite natural. The probability of the ultrafast $T$-independent dissociation is not affected by the sample temperature while the probability of the slow thermally assisted dissociation increases with increasing temperature. Therefore, the latter must exceed the former at some temperature $T_0$, and the value of $T_0$ must increase with increasing excess energy. The interplay between the ultrafast temperature-independent dissociation and the thermally assisted separation of carriers will be considered in the future work of the authors.

In summary, a model of temperature-independent photogeneration of charge carriers in conjugation polymers is suggested. The model is based on the concept of the on-chain dissociation of unrelaxed higher optical excitations. The dissociation probability is determined by the interplay of the rate of carrier dissociation jumps and the rate of the excess energy relaxation and is virtually independent of the sample temperature. Calculated dependencies of the quantum yield of carrier photogeneration upon the field and the photon energy are in good quantitative agreement with experimental data obtained on weakly disordered conjugated polymers.

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