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Ultrafast on-chain dissociation of hot excitons in conjugated polymers

V. I. Arkhipov and E. V. Emelianova
Laboratorium voor Halfgeleiderfysica, K. U. Leuven, Celestijnenlaan 200D, B-3001 Heverlee-Leuven, Belgium

S. Barth and H. Bässler
Institut für Physikalische-, Kern- und Makromolekulare Chemie und Zentrum für Materialwissenschaften, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

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A model describing field-assisted on-chain dissociation of hot optical excitations in conjugated polymers is developed. It rests on the notion that excess photon energy is required for the onset of intrinsic charge-carrier photogeneration. Conversion of this energy into excited vibrational modes within a conjugated polymer segment leads to temporal overheating. The vibrational heat bath is considered as the main source of the energy that allows charge carriers to escape from the potential well formed by Coulomb and external electric fields. Although the quantum yield of carrier photogeneration strongly increases with increasing external field, it reveals an anomalously weak temperature dependence in quantitative agreement with experimental data on a ladder-type poly-para-phenylene and on a polyphenylenevinylene derivative.

I. INTRODUCTION

Photogeneration of charge carriers in low-mobility materials is traditionally considered within the framework of the Onsager theory[1,2] as a two step process.[3,4] Initially a Coulombically bound electron-hole (e-h) pair is generated by an absorbed photon. Subsequently, photogenerated pairs undergo Brownian random walk within the potential well formed by a superposition of the binding Coulomb field and an external field. This random walk results either in recombination of the carriers or in their full separation. Therefore, the quantum yield of charge carrier photogeneration, η, must be calculated as the Onsager probability for a given geminate pair to dissociate in the course of its Brownian random walk.

Onsager's theory is capable of accounting for the yield dependencies upon the external field F, the temperature T, and the wavelength of the exciting light λ_{exc}.[2,3] The two former parameters govern the carrier kinetics within the potential well, while the latter is supposed to determine the initial intrapair distance r_0, i.e., the initial Coulomb binding energy of a geminate pair, $E_b^{(0)}$. It is normally supposed that the initial separation increases with increasing exciting photon energy. Within the framework of Onsager's theory, r_0 is the only parameter which is sensitive to the photon energy and, therefore, the dependence of the carrier photogeneration quantum yield upon photon energy is solely determined by the dependence of r_0 upon λ_{exc}. The external electric field bends the shape of the Coulombic potential well and reduces the potential barrier which carriers must cross to become fully separated. Concomitantly, η increases with increasing F. Crossing the potential barrier requires an additional energy that carriers can acquire only from the ambient heat bath. This energy is normally much higher than kT, implying a strong Arrhenius-like temperature dependence of η, especially at weak and moderate external electric fields.

Conjugated polymers consist of arrays of electronically coupled molecular units, i.e., conjugated segments, with random mutual positions and orientations of the units belonging either to the same chain or to different chains. Conjugated segments of the same polymer chain are separated by topological defects. The length of segments ranges from 5 to 10 nm depending on a particular material, and is much longer than the intersegmental distance of typically 0.6 nm. For a segment with the length of 5 nm oriented parallel to an external electric field of 10^6 V/cm, the gain of electrostatic energy is 0.5 eV, i.e., comparable to the binding energy of optical excitations, E_b, in these materials.[4–9] Therefore, two modes of free-carrier photogeneration are possible in conjugated polymers: an optical excitation can dissociate either due to full carrier separation within a single conjugated segment of a polymer chain or as a result of multiple carrier jumps via different segments. The former process might be considered as an example of the one-dimensional (1D) version of the Onsager theory (1DO),[10] while the 3D Onsager theory (3DO) is more relevant to the latter mode. One should emphasize that, within the framework of both the 1 DO and 3DO the field and temperature dependencies of η are inevitably coupled to each other.

Experimental studies of η in conjugated polymers often reveal dependencies of η upon F, and upon the photon energy similar to what is predicted by the Onsager theory, while an Arrhenius-like temperature dependence is usually observed only at higher temperatures.[11–14] At lower temperatures η turns out to be practically T-independent. The model of disorder-assisted Onsager dissociation of geminate pairs[15,16] attributes the lack of the temperature dependence to carrier separation by tunneling jumps via localized states which belong to the deep tail of the density-of-states distribution. This approach implies a weaker temperature dependence of the yield in hopping systems with stronger energy disorder. However, the anomalously weak T dependence of η is observed both in strongly and weakly disordered conjugated polymers.[17,18] Therefore, there must be another, more fundamental, reason for the vanishing T dependence of η than the disorder. We believe that the clue to this phenomenon is related to the occurrence of extended electronic states in the chain segments, implying that the intrasegmental dissociation can be the dominant mode of carrier separation within a short time domain following the photoionization event.[19] There exists another important experimental observation, namely, that the intrinsic photoconductivity in conjugated polymers commences at the photon energy typically from 0.5 to 1 eV above the $S_1 \leftarrow S_0$ 0-0 transition.[12,13,17,20,21] Remarkably, there is a correlation between the excess photon energy, $E_{\mathrm{exc}} = h\nu - h\nu_0$ (where $h\nu$ is the photon energy of the inducing light, and $h\nu_0$ is the energy of the $S_1 \leftarrow S_0$ 0-0 transition) and the temperature dependence of the photogeneration yield. The higher E_{exc}, the weaker the T dependence of η. For instance, typical values of the excess energy are about 0.5 eV in the PPV-type polymers that reveal some residual temperature dependence of the yield,[13] while the latter is practically T-independent in methyl-substituted ladder-type poly-para-phenylene (MeLPPP) with $E_{\mathrm{exc}} = 1.1$ eV.[17] We shall argue that these notions are a signature of fast intrasegmental dissociation of a hot optical excitation into a pair of separated charge carriers localized on the opposite ends of the segment.[19,22,23]

In the present paper we develop a model of intrasegmental dissociation of hot optical excitations into pairs of free carriers. The model rests on the notion that, after relaxation of a Franck-Condon state through a vibronic progression, the excess photon energy is transferred into intrasegmental vibronic excitations. Before this energy is dissipated into the ambient equilibrium phonon bath, the optical excitation remains within a hot segment that makes it easier to acquire a portion of energy sufficient for carriers to escape from a Coulombic potential well and become completely separated.

Dissociation of optical excitations within hot molecular segments after relaxation of a Franck-Condon state was considered earlier,[23] neglecting the effect of the ambient temperature. This approximation can be justified if the characteristic time of the vibronic energy dissipation into the equilibrium phonon bath is much shorter than the characteristic time of the electron-phonon interaction. Under such conditions the equilibrium phonon bath cannot assist charge-carrier separation within still hot segments and, concomitantly, the photogeneration yield must be literally independent of the ambient temperature as in MeLPPP. However, in many conjugated polymers, e.g., in PPV-type polymers, the yield does depend upon temperature although the observed T dependence is much weaker than predicted by the Onsager theory. The main goal of the present work is to incorporate the effect of ambient temperature into the model of on-chain hot exciton dissociation. The model of hot exciton dissociation is shown to be able to describe quantitatively dependencies on the field, temperature, and photon energy of the intrinsic charge carrier generation in two chemically different conjugated polymers, namely, in a PPV-type polymer (PPV-amine) and in MeLPPP.

II. INTRASEGMENTAL DISSOCIATION OF HOT EXCITONS

Optical excitation into the manifold of vibronic states, built on either the first or higher singlet states, occurs on the premise of the Franck-Condon principle. In π-bonded conjugated polymers, the predominant vibronic coupling involves one or two vibrational modes of the phenyl ring. On a time scale of less than 100 fs the structural skeleton of that part of the chain, where the excitation was initially localized, relaxes into an equilibrium configuration characteristic of the first singlet state, and the excess energy, $E_{\mathrm{exc}} = h\nu - E(S_1)$ will be distributed among the vibrational modes due to vibronic coupling. This generates a vibrational heat bath whose effective temperature T_{eff} exceeds that of the ambient temperature. Dissociation of the relaxed singlet exciton can be accomplished in terms of a Boltzmann-like activation process where kT is replaced by kT_{eff}. In view of the rapidity with which the polymer chain element returns to the ambient temperature T, the excess energy is only effective on an ultrashort time scale, while the thermal energy is available during the whole lifetime of an exciton. Therefore, the total on-chain dissociation probability must be determined as a sum of the probability of fast exciton dissociation, while the segment is still hot and of the probability of a thermally assisted dissociation during the lifetime of the excitation in a segment which is already cooled down to the ambient temperature. The time dependence of the effective temperature in the course of the vibronic energy dissipation can be written as

$$T_{\mathrm{eff}}(t) = T + T_0 \Theta(t), \tag{1}$$

where T_0 is the temperature jump at $t=0$, and the function $\Theta(t)$ describes dissipation of the vibronic energy into the equilibrium phonon bath: $\Theta(0)=1$ and $\Theta(\infty)=0$. It is worth noting that the concept of the effective temperature can be introduced only if the time of excess energy dissipation, i.e., the characteristic time of the $\Theta(t)$ function, is not shorter than the time of the electron-phonon interaction. Otherwise, an excitation, occupying a still hot segment, has no chance to obtain any additional energy from the ambient phonon bath. Under this condition, the ambient phonon bath cannot contribute to the effective temperature of the hot segment, and the first term in the right-hand side of Eq. (1) vanishes, implying a complete lack of the temperature dependence of the dissociation probability.

This model leads to an equation describing the dependencies of the on-chain carrier photogeneration quantum yield upon the field F, the temperature, and the excess photon energy as

$$\begin{aligned} \eta(F,T,T_0) = \nu_0 \int_{z_{\min}(F)}^{1} dz \int_0^{\infty} dt \\ \times \mathrm{Bol}\left[\frac{E_b}{kT_{\mathrm{eff}}(t)} - \frac{e}{kT_{\mathrm{eff}}(t)}\left(\frac{eFz}{4\pi\epsilon_0\epsilon}\right)^{1/2}\right] \\ \times \exp\left\{-\frac{t}{\tau_{opt}} - \nu_0 \int_0^t dt' \, \mathrm{Bol}\left[\frac{E_b}{kT_{\mathrm{eff}}(t')} \right.\right. \\ \left.\left. - \frac{e}{kT_{\mathrm{eff}}(t')}\left(\frac{eFz}{4\pi\epsilon_0\epsilon}\right)^{1/2}\right]\right\}, \end{aligned} \tag{2}$$

where τ_{opt} is the lifetime of optical excitations, ν_0 the attempt-to-jump frequency, e the elementary charge, ϵ_0 the permittivity of vacuum, and ϵ the dielectric constant. The functions $\mathrm{Bol}(y)$ and $z_{\min}(F)$ are defined by

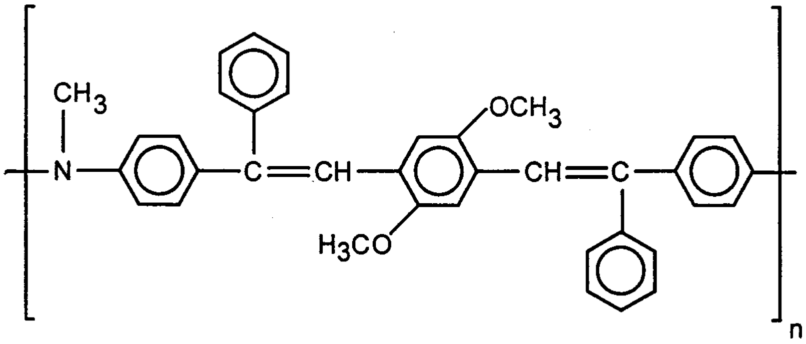
$$\mathrm{Bol}(y)=\begin{cases}1, & y<0\\ \exp(-y), & y>0\end{cases}, \tag{3}$$

$$z_{\min}(F)=\cos\vartheta_{\max}=\frac{e}{4\pi\epsilon_0\epsilon l^2 F}, \tag{4}$$

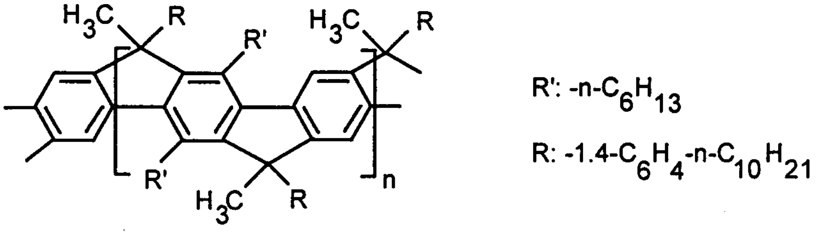
with $\vartheta_{\max}$ being the maximum value of the aperture cone of the dissociating segment, and l the segment length. Derivation of Eq. (2) can be found elsewhere.[23] One should also take into account that in extended π-conjugated polymers the high-frequency dielectric constant is anisotropic. For a fully aligned polydiacetylene a value between 5 and 7 parallel to the chain has been reported.[24]

III. EXPERIMENT

We have performed electric field and temperature-dependent steady-state photoconduction experiments on films of a substituted PPV derivative, poly (methylimino-1,4-phenylene-1-phenyl-1,2-ethenylene-2,5-dimethoxy-1,4-phenylene-2-phenyl-1,2-ethenylene-1,4-phenylene) (PPV-amine),



and (MeLPPP),



The route by which the PPV-amine was synthesized[25] guarantees a high level of purity inaccessible with standard PPV. Therefore, defect-sensitized bulk photocarrier generation is expected to be less important. In the MeLPPP the rigidity of the polymer backbone[26] results in reduced disorder effects compared to the PPV-amine, and the methyl-groups prevent the formation of aggregates possible in ordinary LPPP.

Both investigated materials were deposited on top of an indium-tin-oxide covered glass slide by spin-coating from a chloroform solution. Before completing the sandwich structure by evaporating a semitransparent Al top electrode of 0.07 cm^2, the samples were kept in a vacuum chamber at a pressure of $\cong 10^{-6}$ mbar at 295 K for 12 h to remove residual solvent. The transmittance of the Al contacts was determined by a Perkin Elmer Lambda 9 UV/VIS/NIR spectrometer using quartz blank samples which were placed directly beside the polymer films during the Al evaporation procedure. The stationary photocurrent measurements were performed in a temperature-controlled cryostat. The devices were irradiated through the semitransparent Al electrode by using a calibrated xenon lamp as a light source and quartz optics. Lock-in techniques were employed for signal detection, and all data were recorded in a pointwise manner. In order to minimize space-charge effects, the samples were shorted after each measurement, irradiated with red light (650 nm) for 10 s, and kept in the dark for another 5 min before the next data point was taken immediately after turning on the light. Dark currents were of the order of 10^{-10} A/cm^2, typically one order of magnitude lower than the lowest photocurrent considered for data evaluation. This rather low value of the dark current testifies as to the purity of our samples.

IV. RESULTS AND DISCUSSION

A. Theory

Not knowing the explicit time dependence of the vibrational energy relaxation, we assume that, to a first-order approximation, the decay of the effective temperature is exponential, i.e.,

$$T_{\mathrm{eff}}(t)=T+T_0\exp\left(-\frac{t}{\tau_{\mathrm{diss}}}\right), \tag{5}$$

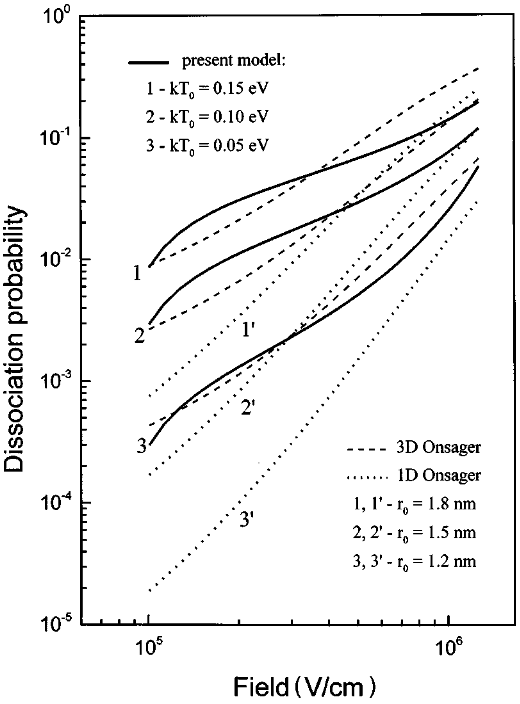


FIG. 1. Field dependence of the dissociation probability calculated from Eq. (2), parametric in the initial excess thermal energy, compared to 1D and 3D Onsager curves parametric in the initial separation. The following set of parameters has been used in Eq. (2): $l=6$ nm, $E_b=0.5$ eV, $\varepsilon=5$, $\tau_{\text{diss}}=10^{-12}$ s, and $\tau_{\text{opt}}=10^{-9}$ s. The ambient temperature is 300 K.

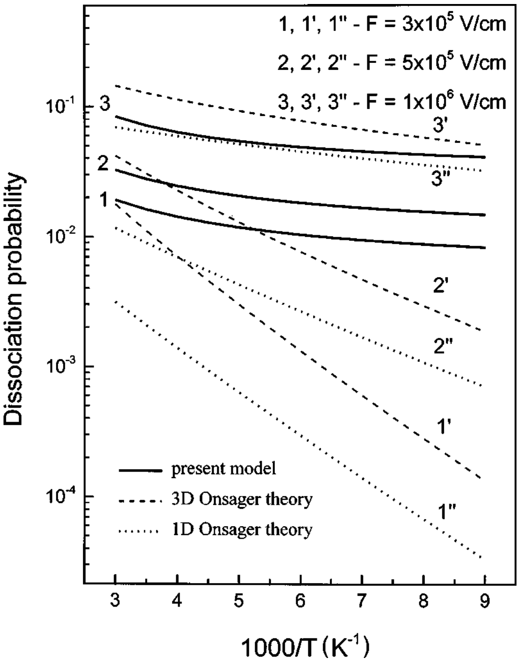


FIG. 2. Temperature dependence of the dissociation probability calculated from Eq. (2), parametric in field strength in comparison with predictions of 1D and 3D versions of the Onsager theory. The initial excess thermal energy and the initial separation of carriers are $kT_0=0.1$ eV and $r_0=1.5$ nm. The set of material parameters is the same as in Fig. 1.

where τ_{diss} is the characteristic time to dissipate the excess intrasegmental vibrational energy into the equilibrium phonon bath.

Complementary to Onsager's theory, the present model is aimed at describing the dependencies of the carrier photogeneration quantum yield upon the field, temperature, and photon energy. The most important difference between the two approaches is the role of the excess photon energy. According to Onsager's theory, this parameter determines the initial separation of carriers within a geminate pair r_0, while the effect of the dissipated excess photon energy on the local temperature is neglected. The probability for the carriers to cross the potential barrier in the course of subsequent Brownian random walk increases with increasing r_0, and, therefore, the quantum yield rises with increasing photon energy. The present model is based on the assumption that carriers are delocalized within a conjugated segment, preventing diffusive intrasegmental motion of carriers. Under these conditions, the concept of the initial carrier separation becomes also irrelevant. Instead, the effect of the excess photon energy is attributed to local and temporal heating of the excited segment after relaxation of a Franck-Condon state. The effect of the excess photon energy on the field dependence of the yield is illustrated in Fig. 1 in comparison with results of 1DO and 3DO theories. The η vs F curves calculated from Eqs. (2)–(4) are parametric in the initial excess temperature, T_0, while 1DO and 3DO curves are plotted for different values of r_0.

The dependence of the quantum yield upon the ambient temperature is illustrated in Fig. 2 together with 1DO and 3DO curves parametric in the electric field. The 1DO quantum yield was calculated by averaging the dissociation probability over all possible directions of segments. While both 1DO and 3DO predict Arrhenius-like $\eta(T)$ dependencies, the present model leads to a much weaker T dependence of the yield with the latter remaining nonzero at $T\rightarrow 0$ due to a finite probability of charge carrier separation in a hot segment even at zero ambient temperature. Comparing η vs T curves calculated from the model of hot exciton dissociation with those obtained from 1DO proves that, even at the room temperature, carrier separation within a short time while excited segments are still hot gives the main contribution to the total dissociation probability.

The dependence of the quantum yield upon the initial excess thermal energy is illustrated in Fig. 3 by η vs T_0 curves plotted for different electric fields. These curves approach straight lines in the $\eta^{1/2}$ vs T_0 axis at sufficiently high values of T_0, implying an almost quadratic dependence of the yield upon the excess photon energy, in good agreement with existing experimental data.[12,17] Another important parameter of the model is the exciton binding energy E_b. Together with the external field this parameter determines the relative height of the potential barrier carriers must cross to become free. At variance with the excess photon energy this is a material sensitive parameter which is affected neither by the field nor by the photon energy. In Fig. 4 the temperature dependence of the yield is presented as parametric in the exciton binding energy. Although the dissociation probability increases with decreasing binding energy, all the η vs $1/T$ curves are practically parallel to each other, implying that slopes of such curves yield no information on the binding energy of the optical excitation.

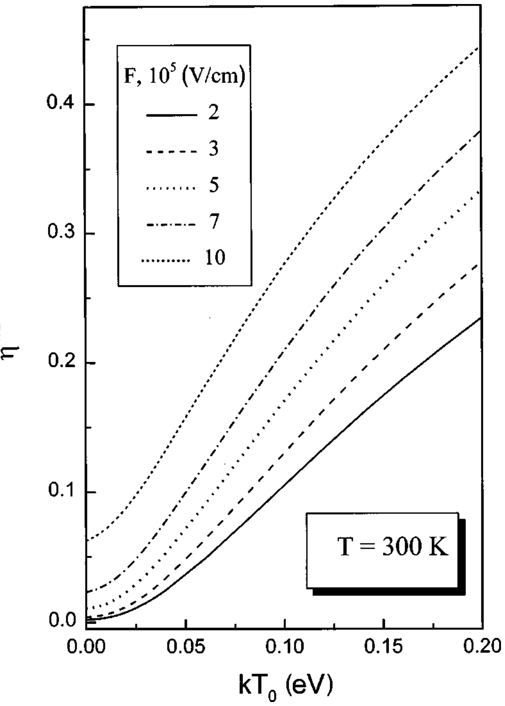


FIG. 3. Dependence of the dissociation probability η upon the initial excess thermal energy parametric in the field strength. The set of material parameters is the same as in Fig. 1.

B. Experiment

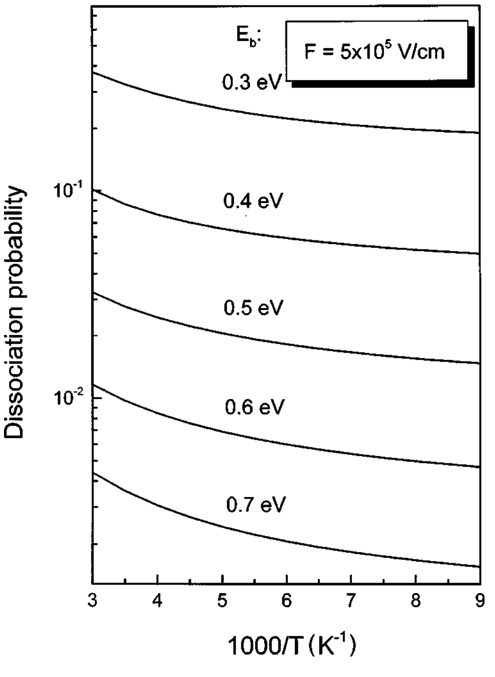


FIG. 4. Temperature dependence of the dissociation probability parametric in the exciton binding energy. The set of material parameters is the same as in Fig. 1, and the field is 5×10^5 V/cm.

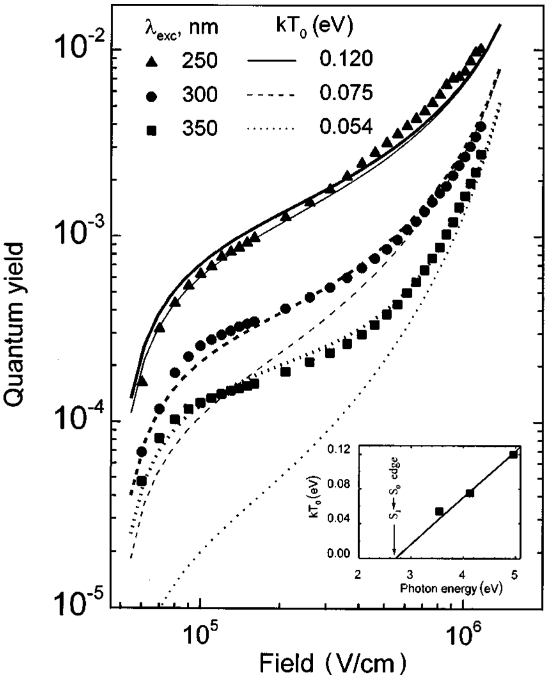


FIG. 5. Field dependence of the photocarrier generation yield in MeLPPP measured at variable photon energies (dots) and calculated (solid, dashed, and dotted lines) from Eq. (2) for different values of the initial excess thermal energy and for the following set of material parameters: $l=6.5$ nm, $E_b=0.35$ eV, $\varepsilon=7$, $\tau_{\rm diss}=3.5\times10^{-14}$ s, and $\tau_{\rm opt}=10^{-9}$ s. The inset shows the correlation between the photon energies and excess thermal energies kT_0 used to fit the experimental data.

First we consider photogeneration in π-conjugated MeLPPP, which has been characterized spectroscopically in detail. It is known to be the least disordered material, though still amorphous, as evidenced by the unusually small inhomogeneous width of the well-resolved vibronic bands.[27] Virtually no temperature dependence of the photocurrent is observed while the field dependence is strong, as shown in Fig. 5. Those data have been analyzed in terms of the present theoretical approach. It turns out that at a photon energy of 4.9 eV (i.e., $\lambda_{\rm exc}=250$ nm) the field dependence as well as the absolute value of the photogeneration efficiency η are in excellent agreement, assuming an exciton binding energy of 0.35 eV, and a dissipation time $\tau_{\rm diss}=3.5\times10^{-14}$ s. The $\tau_{\rm diss}$ should be identified as the time within which the excess energy $[E_{\rm exc}=h\nu-E(S_0)]$, confined to a chain element comparable to the size of the exciton, i.e., ~1.4 nm, and equivalent to three phenylene rings, is spread out in the adjacent chain segments.

Discrepancies between theory and experiment as far as the $\eta(F)$ dependence is concerned are noted at $F\leqslant3\times10^5$ V/cm. They may be a signature of extrinsic interior photogeneration. An optical excitation generated in a segment next to an extrinsic electron scavenger may dissociate into a geminate pair, with one of the carriers being captured by the deep trap. The released energy may facilitate crossing the intrasegmental potential barrier by the other carrier.

Trap-assisted dissociation requires carrier jumps from excited segments into those localized states. The localization radius for such jumps is normally much shorter than that for carrier jumps within a segment. Therefore, only relatively short jumps are possible within the lifetime of optical excitations, with the typical jump distance being much shorter than the length of conjugated segments. Under these circumstances one may still consider trap-assisted dissociation as a 1D process. From the mathematical point of view this problem is very similar to the above-described model. The differ-

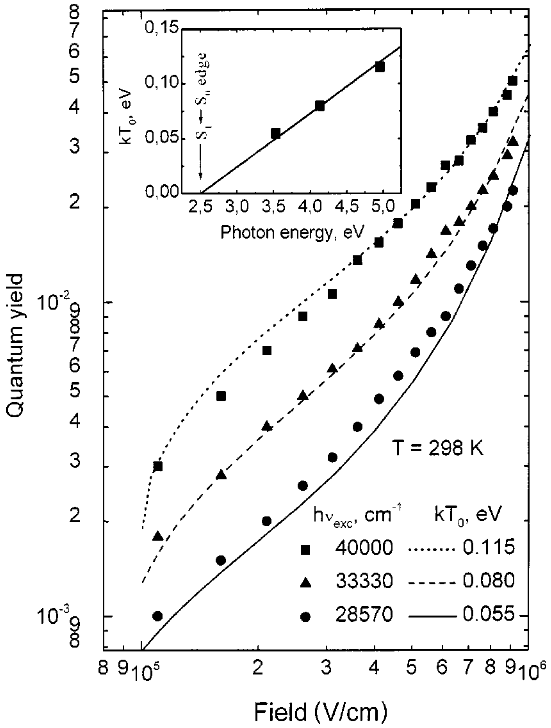


FIG. 6. Field dependence of the quantum yield η for intrinsic carrier photogeneration in a 100-nm-thick PPV-amine film parametric in the photon energy (dots), taking into account a built-in voltage of 0.6 V due to the difference in work functions of Al and ITO. The excitation was through a semitransparent positively biased Al electrode at ambient temperature. Lines are calculated from Eq. (2) for different values of kT_0. The inset illustrates the correlation between the initial excess thermal energy and the excess photon energy. The following set of material parameters was used for calculations: $l = 6$ nm, $E_b = 0.42$ eV, $\varepsilon = 5$, $\tau_{\text{diss}} = 2.0 \times 10^{-13}$ s, $\tau_{\text{opt}} = 10^{-9}$ s, and $\nu_0 = 10^{12}$ s^{-1}.

ence are that (i) only a few segments have deep traps as nearby neighbors, and only those few segments are available for the trap-assisted dissociation of optical excitations; and (ii) the amount of the excess energy does not depend upon the photon excess energy, implying the occurrence of trap-assisted dissociation at the absorption edge already.[17] The contribution of the trap-assisted dissociation can, therefore, be calculated from Eq. (2) by adding the relative density of the trap-related charge transfer centers, δ, to the integrand on the right-hand side of this equation. The contribution of trap-assisted dissociation to the total photogeneration yield is shown by thick lines in Fig. 5. Accounting for this effect provides a much better fit of experimental data at weak fields and low excess photon energies. The inset of Fig. 5 shows the variation of T_0 with the photon energy. The comparison between theory and experiment indicates that $T_{\text{eff}}(0) = T_0$, implying that the ambient heat bath does not contribute to the exciton dissociation. The experimental evidence for this is the lack of an appreciable temperature dependence, although the field dependence is strong. Conceptually, this is a result of the fast dissipation of the excess energy (see Sec. II) relative to the coupling between the mostly low-energy intermolecular mode comprising the ambient heat bath and the intrachain modes which promote dissociation. Although data are sparse, T_0 varies smoothly with E_{exc}. This argues against any threshold effect invoking, for instance, the second excited singlet state at $h\nu \geqslant 4.3$ eV. It is worth noting that for $h\nu < 4.3$ eV the initially generated excited state is a Franck-Condon state of S_1 parentage. Therefore, it is vibrationally hot already once the chain skeleton has relaxed into its new configuration.

Figure 6 shows the quantum yield η of intrinsic charge carrier generation in PPV-amine as a function of the electric field at 298 K and variable excitation wavelength, while in Fig. 7 the temperature dependence at constant field (3.25×10^5 V/cm) is plotted. The inset to Fig. 6 illustrates an almost linear dependence of T_0 upon the excess photon energy and shows the photoconductivity action spectrum. At low excess photon energies the quantum yield remains practically independent of the wavelength of exciting light that can be explained by trap-assisted dissociation of excitons as discussed above. This extrinsic contribution to the yield is subtracted from the data shown in Figs. 6 and 7. Both the field and temperature dependences of the yield can be rationalized in terms of the parameter set $E_b = 0.42$ eV, $\tau_{\text{diss}} = 2.0 \times 10^{-13}$ s, segment length $l = 6$ nm, a dielectric constant of 5, and a lifetime of the excitation of 10^{-9} s. This implies that in order to achieve satisfactory data fitting one has to invoke a heat dissipation time by a factor of 6 larger than in MeLPPP. At the moment one can only speculate on the reason why both systems differ in this respect. One obvious suspicion relates to the disorder as evidenced from the inhomogeneous broadening of the absorption. While in MeLPPP the $S_1 \leftarrow S_0$ $0-0$ transitions feature a full width at half maximum of 70 meV, the PPV-amine spectrum is structureless, implying an inhomogeneous broadening in excess of the vibronic spacing, i.e., $\cong$ 0.18 eV. Considering its magnitude τ_{diss} is likely to be an intrachain property. Therefore it is plausible that dissipation of the excess vibrational energy is impeded by intrachain disorder,which is reflected by the statistics of the conjugation length. Estimating the number of intra-segmental excited vibrational modes n_{vib}, that can share the excess photon energy in MeLPPP and PPV-amine yields $n_{vib} \approx 21$ for both materials.

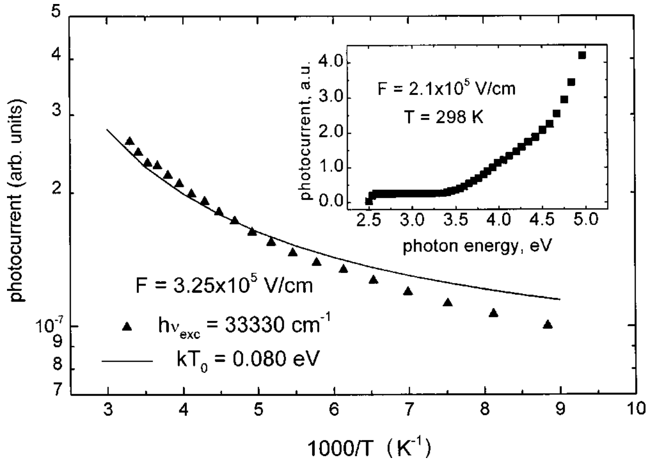


FIG. 7. Temperature dependence of the intrinsic photogeneration yield η in a 80-nm-thick PPV-amine film for different excitation wavelengths (dots). Lines are determined from Eq. (2) for different values of the initial excess thermal energy kT_0. The set of material parameters is the same as in Fig. 6. The inset shows the action spectrum of photoconductivity.

V. CONCLUSIONS

A model to treat field-assisted ultrafast on-chain dissociation of optical excitations in conjugated polymers is suggested. The excess photon energy above the $S_1 \leftarrow S_0$ 0-0 transition is considered to be transferred into intrasegmental vibronic energy and establishes, while dissipating, an important additional source of energy required for carriers to cross the potential barrier and to separate within the segment. Similar to Onsager's theory, the external electric field lowers the potential barrier for carrier separation and, thus, assists the dissociation of optical excitations. Different from Onsager's treatment, the rate determining step is of the intrachain type, not involving diffusive motion inside the Coulombic potential. Predictions of the model are compared with experimental data on the field and temperature dependencies of the intrinsic carrier photogeneration quantum yield a PPV-type polymer as well as weakly disordered MeLPPP.

The essential system parameters are the exciton binding energy E_b, the excess temperature T_0 of the chain element occupied by the excitation, the dissipation time $\tau_{\rm diss}$ of the average excess vibration energy kT_0, and the length l of a chain segment comparable with if not identical to the conjugation length of the excitation. For PPV-amine and MeLPPP, E_b turns out to be 0.42 and 0.35 eV, respectively. It is comparable with previous estimates on noncrystalline as well as crystalline polydiacetylene, and confirms a recent measurement in similar compounds employing scanning tunneling microscopy.[9] Importantly, E_b is not given by the threshold photon energy above which photoconduction increases rapidly.[20] Data fitting requires kT_0 to be in the order of $(3-4)kT$ at room temperature. It is given by anharmonic coupling between that (those) vibrational mode(s) which control(s) optical absorption and the modes which establish the excess vibrational heat bath of an excited chain element needed for dissociation. Further theoretical reasoning in this respect, as well as in the mechanism of dissociation of excess vibrational energy, is beyond the scope of the present paper. Suffice it to say that disorder appears to increase the dissipation time and, concomitantly, renders dissociation more efficient.

The process of photogeneration must become more complicated if the length of a segment of a conjugated polymer decreases, for instance due to excessive disorder or by poor π overlap among the repeat units. In this case a metastable electron-hole pair at the ends of a segment is no longer established. Instead, dissociation must involve interchain coupling inside the Coulombic well. Asymptotically, the classic Onsager treatment should be obeyed in the case of a dense array of small molecules. Dissociation due to the excess energy of optical excitation is also involved in that case, but the thermalization process is completed before the geminate pair escapes from this mutual Coulombic potential. Onsager-type photogeneration and hot exciton dissociation in an elongated conjugated polymer are, thus, complementary limiting processes depending upon the size of the uninterrupted π system. Real materials will often fall into an intermediate range and escape rigorous analytical description.

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