

Linear and Nonlinear Photoexcitation Dynamics in π -Conjugated Polymers

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Linear and nonlinear recombination kinetics with various lifetime distributions were identified for long-lived photoexcitations in a series of π -conjugated polymer films using modulation frequency and excitation intensity dependencies of the photoinduced absorption. This includes monomolecular, bimolecular, and defect-limited recombination processes that lead to saturation. Using generalized kinetics parameters, we found characteristic plots for all recombination processes. Specifically, the bimolecular recombination process shows superlinear intensity dependence away from the steady state; on the contrary, dispersive bimolecular recombination leads to sublinear dependence.

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The nature of long-lived photoexcitations and their decay kinetics in films of π -conjugated polymers (PCP) and hydrogenated amorphous silicon (*a*-Si:H) have been a matter of controversy for almost two decades. In both classes of materials, there is an ongoing debate with regard to the role of geminate recombination of photo-generated charged excitations. This is of utmost importance for potential optoelectronic applications such as photodetectors (PD) and photovoltaic (PV) cells. However, there is a lack of sufficient theoretical and experimental tools for analyzing the recombination kinetics of the photogenerated charged excitations. The reason for this is the intricate behavior of the nonlinear recombination dynamics, as well as the dispersive recombination caused by the disorder in these materials.

Photoinduced absorption (PIA) measurements performed with a modulated cw laser excitation have been used for many years to probe the long-lived photoexcitations in such materials [1–6]. PIA dependencies on the modulation frequency ω and excitation intensity I have usually been utilized to determine the photoexcitation lifetime τ and the recombination mechanism. In particular, the monomolecular recombination (MR) [linear] and bimolecular recombination (BR) [quadratic] processes may unravel the generation mechanism of the photoexcitation species. Carrier MR kinetics in PCP hint to a possible geminate generation process, where the hole and electron polarons (P^\pm) come from a common excitation parent. Carrier BR kinetics, on the other hand, indicate the dominance of distant pair recombination dynamics. This is especially relevant in light of the recent optically detected magnetic resonance studies of spin 1/2 polarons in PCPs [7], in connection with the maximum electroluminescence yield in organic light emitting diode devices.

When disorder in the film is not severe, then the PIA dynamics are clear: near the steady state, where $\omega\tau < 1$, the PIA magnitude gently decreases with increasing ω ,

whereas for frequencies above $\omega\tau \approx 1$, the signal decrease with ω is more apparent [8]. In addition, the PIA scales linearly with I for MR kinetics, whereas a \sqrt{I} is expected for BR kinetics near steady state. This simple approach, however, does not work out in reality because of complications related to the disorder and inhomogeneity known to exist in most PCP films. First, the long-lived photoexcitations may be associated with deep traps in the film; in this case, the traps might be partially saturated at high I showing sublinear dependence on I , where, in fact, the kinetics may still be due to MR [9]. Second, there may be a broad distribution of recombination rates (RR); its influence on the BR dynamics has not been studied yet in detail. In addition, steady state conditions may not be reached and this precludes the use of the above intensity dependence criterion.

In this Letter we analyze in detail the dominant recombination kinetics thought to exist in PCP films. These processes are a MR (BR) mechanism, for which the RR of the photoexcited species is linear (quadratic) with the photoexcitation density, and the associated “defect limited” mechanisms for which either the generation or recombination channels may partially be inhibited by defects. We find two generalized kinetic parameters that unify the recombination dynamics, with which the PIA dependencies on ω and I may be treated on equal footing. Using these generalized parameters, we show that when the inhomogeneity in the sample is not severe, all the above processes show similar dependence leading to a *universal* plot with a characteristic knee. A superlinear I dependence is predicted for the BR process away from the steady state. The universal plot is analyzed at various degrees of disorder, and we found that the characteristic knee in the plot gradually disappears when the RR distribution becomes dispersive leading to sublinear I dependence for BR kinetics in the entire dynamic range.

In order to emphasize the main issues described above, we use, as an example, a characteristic simple case for

which the photoexcitation density $N(t)$ is governed by a single rate equation:

$$dN/dt = G(t)S(N_0) - U(N), \quad (1)$$

where $G(t)$ is the generation rate term which, for experiments using the photomodulation spectroscopy technique, is given by $G(t) = g(1 + \cos\omega t)$, where g is proportional to I . Equation (1) includes, through the function $S(N_0)$, defect-limited cases in which, due to trap filling, N tends to saturate at high I . N_0 is the trap density and U specifies the recombination mechanism. Defect-limited MR and BR processes are given, respectively, by the following U and $S(N_0)$ terms:

$$\begin{aligned} \text{DMR : } U &= N/\tau; & S &= (1 + g\tau/N_0)^{-1}, \\ \text{DBR : } U &= bN^2; & S &= [1 + (g\tau_{\text{BR}}/N_0)^2]^{-1}, \end{aligned} \quad (2)$$

where τ^{-1} is the MR characteristic RR, and $\tau_{\text{BR}}^{-1} = \sqrt{gb}$ is the BR effective, generation rate dependent, RR. Note that the familiar MR and BR processes are specific cases of the DMR and DBR processes, respectively, in the limit $N_0 = \infty$ in Eq. (2).

Experimentally, the PIA ($\propto N$, see below) is studied using an excitation intensity modulated phase sensitive technique measuring both the in-phase (N_I) and quadrature (N_Q) components: $N_{I,Q} = (2\pi/\omega) \int_{\text{period}} N(t) \times \cos(\omega t - \phi_{I,Q}) dt$, ($\phi_I = 0$, $\phi_Q = \pi/2$). This technique is particularly suitable for photoexcitations undergoing relatively slow recombination processes ($\tau = 0.1 \mu\text{s} - 10 \text{ ms}$). For the DMR process, we find

$$N_I(\omega) = g^* \tau / (1 + \omega^2 \tau^2), \quad N_Q(\omega) = \omega \tau N_I, \quad (3)$$

where $g^* = gS$. Replacing τ by $\tau_{\text{BR}} = (gb)^{-1/2}$ in Eq. (3), we get for the DBR process a modulation frequency dependence that is very close to the one found by numerically solving Eqs. (1) and (2).

In order to treat the various recombination processes on equal footing, we define a dynamic phase, $\phi = \tan^{-1}(N_Q/N_I)$. For the MR process $\phi = \omega\tau$, whereas for the BR process we take $\phi = \omega\tau_{\text{BR}}$. Moreover, in order to treat the dependencies of the PIA on I and ω on equal footing, we define two generalized coordinates, μ and χ :

$$\mu = N/g\omega\tau_{\text{eff}}^2, \quad \chi = 1/(\omega\tau_{\text{eff}})^2, \quad (4)$$

where τ_{eff} is either τ (for MR and DMR) or τ_{BR} (for BR and DBR). The two components of μ , namely, μ_I and μ_Q , are plotted in Fig. 1(a) vs χ . It is seen that for each μ component there exists a *universal* curve, which is approximately given by $\mu_I = \chi^{3/2}/(1 + \chi)$, $\mu_Q = \chi/(1 + \chi)$, that *uniformly* describes MR, BR, and the associated defect-limited processes, in the limit of a “moderate” saturation, i.e., $g\tau_{\text{eff}}/N_0 < 1$ [10]. The importance of this plot lies in that it clearly distinguishes the various dynamic regimes: $\chi > 1$, i.e., close to steady state, and $\chi < 1$, away from steady state. For the BR process, for instance, in this latter regime the excitation intensity dependence is superlinear ($\propto I^{3/2}$) and is achieved either at high ω and/or low I . This feature is demonstrated in

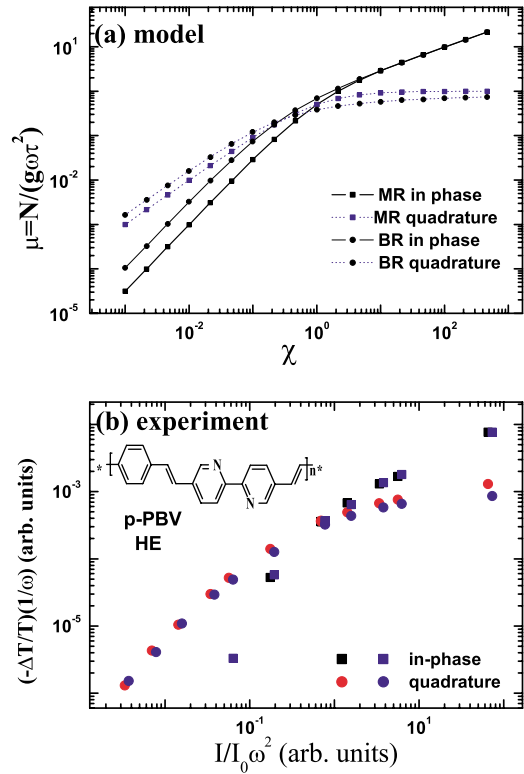


FIG. 1 (color online). (a) MR and BR kinetics plotted as μ vs χ (see text). The in-phase (quadrature) component shows $\chi^{3/2}$ (χ^1) and $\chi^{1/2}$ (χ^0) dependencies at low and high values of χ , respectively. (b) PIA dynamics for the HE band in p -PBV plotted as $(-\Delta T/T\omega)$ vs $I/I_0\omega^2$, where I_0 is a normalizing parameter. Inset: Chemical structure of p -PBV.

Fig. 2(a), where the superlinear intensity dependence for the BR process is apparent away from the steady state. Inclusion of RR distributions results in a broader transition range of $\mu(\chi)$ around $\chi \approx 1$ compared to that in Fig. 1(a).

An experimental demonstration of this general behavior of the recombination kinetics can be obtained using modulated PIA studies of various long-lived photoexcited species, such as P^\pm , triplet and interchain excitons in a variety of PCP films. For these experiments we used an Ar^+ laser beam modulated in the frequency range $10 - 10^5$ Hz. The transmission T of a probe light extracted from a tungsten lamp and its pump related modulation ΔT for both in-phase and quadrature components were measured by phase sensitive techniques, using a variety of solid state detectors. The PIA signal, $-\Delta T/T (= N\sigma d)$, where σ is the optical cross section and d is the sample thickness), is proportional to N . Thus, the two N components in Eq. (1) are simply measured by detecting the two PIA components using a lock-in amplifier. I was varied by placing neutral density filters in front of the laser beam to reduce its intensity in a controlled manner. Note that for BR, for instance, the experimentally measured quantities $(-\Delta T/T)/\omega$ and I/ω^2 are proportional to μ and χ , respectively [Eq. (4)].

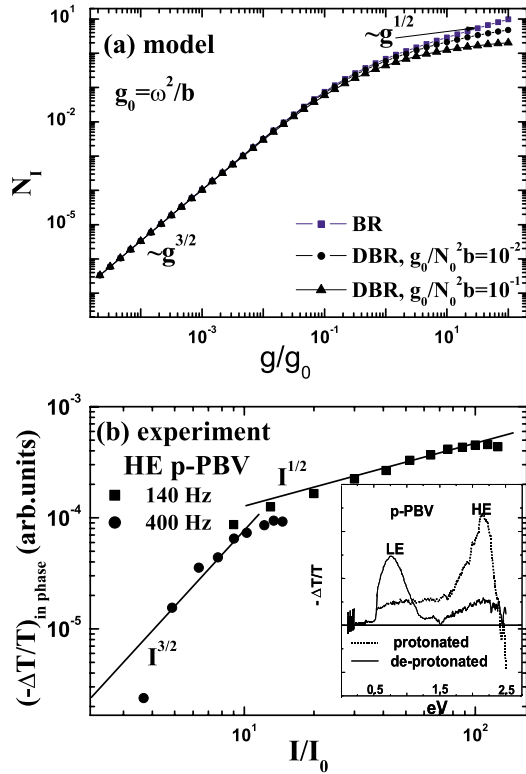


FIG. 2 (color online). (a) N_I vs g calculated for BR and DBR kinetics. $N_I \propto g^{3/2}$ away from the steady state. Near steady state $N_I \propto g^\gamma$ where $\gamma = 1/2$ for BR and $\gamma < 1/2$ for DBR. (b) Experimental in-phase component of the PIA vs I for the HE band in p -PBV. The straight lines, marked $I^{1/2}$ and $I^{3/2}$, signify the two dynamic regions indicating BR. Inset: PIA spectra of p -PBV for acid saturated and free base forms [6].

In Fig. 1(b) we show the PIA kinetics of the high energy (HE) band in poly(p -phenylene-bipyridine-vinylene) (p -PBV) [see insets in Figs. 1(b) and 2(b) for the chemical structure and the PIA spectra, respectively [6,11]] plotted as $(-\Delta T/T)/\omega$ vs $(I/I_0)/\omega^2$, where I_0 is a normalizing parameter. Comparing Figs. 1(a) and 1(b) we see that the general universal behavior discussed above is clearly present for both $\chi < 1$ and $\chi > 1$. We can get more insight into the recombination process by plotting directly the PIA vs I for both near steady state conditions ($\omega\tau_{\text{eff}} \ll 1$) and away from the steady state ($\omega\tau_{\text{eff}} \gg 1$). In Fig. 2(a) we show the calculated dependencies of $N_I(g, \omega)$ for various recombination mechanisms. The most striking feature of this plot is the superlinear dependence ($N_I \propto g^{3/2}$) for the BR process away from steady state, while a linear dependence is seen for the MR process. Such a superlinear dependence was predicted previously [12], but never observed experimentally. Here we report the first observation of such superlinear behavior. In Fig. 2(b) we show the in-phase PIA component of the HE band of p -PBV vs the normalized pump intensity for low and high ω . The superlinear dependence at 400 Hz is clearly seen, while the overall similarity with Fig. 2(a) for the BR process strongly in-

dicates that the recombination process in this case is basically BR.

The distinct BR superlinear behavior may be masked due to a radical RR distribution, such as “dispersive recombination” [6]. One of the key signatures of the latter mechanism is the gentle high frequency fall off of the PIA: $\propto \omega^{-\alpha}$ ($\alpha < 1$), compared with $N_I \propto \omega^{-2}$ for the uniform RR case, Eq. (3). In many PCP the modulated PIA shows such behavior [5,6,8,13–15]. We therefore extend the “generalized coordinates” approach in order to separate the various kinetics in this case as well. Following the previous analysis [6], we write the photoexcitation density, $N(g, \omega)$, as

$$N(\omega) = gS\tau_0/[1 + (i\omega\tau_0)^\alpha], \quad (5)$$

where g and S are defined in Eqs. (1) and (2), $\alpha < 1$, τ_0^{-1} is a “mean” RR, whose distribution can be obtained explicitly, and $N_I = \text{Re}(N)$, $N_Q = \text{Im}(N)$ [6]. For the MR process τ_0 is independent of the excitation intensity, while for BR we assume the typical excitation intensity dependence $\tau_0^{-1} = \sqrt{gb_0}$, where b_0 is a mean bimolecular RR.

We define the generalized coordinates μ and χ as above, with τ_0 replacing τ_{eff} in Eq. (4). Using Eq. (5) we plot μ_I and μ_Q vs χ in Fig. 3(a) (for $\alpha = 0.6$). We note that for $\omega\tau_{\text{eff}} > 1$, both N_I and N_Q behave similarly, with an α dependent sublinear χ dependence, for both MR and BR processes. This sublinear dependence contradicts the superlinear $\chi^{3/2}$ dependence for nondispersive recombination processes discussed above [Fig. 1(a)].

In Fig. 3(b) we show the PIA experimental I dependence of the low energy (LE) band of p -PBV [Fig. 2(b)], which was shown previously to have a dispersive recombination kinetics [6]. Note the similarity of the in-phase and quadrature components away from the steady state. The overall similarity of Figs. 3(a) and 3(b) demonstrates the usefulness of the plot. We also note that by plotting the experimental data in these generalized coordinates, one can distinguish between dispersive mechanisms (for which the RR distribution is broad and is of special shape) and “regular” mechanisms (i.e., none or narrow distribution).

Examining the PIA I dependence, we observe some interesting features for the dispersive BR case, as shown in Fig. 4(a). In the higher g regime (where g/ω^2 is large, i.e., near steady state), $N_I \propto \sqrt{g}$ (as for the regular nondispersive BR process) and $N_Q \propto g^{1/2(1-\alpha)}$ (i.e., weak dependence, similar to the nondispersive case). In the lower g regime (where g/ω^2 is small, away from steady state), $N_Q \propto g^{(1+\alpha)/2}$, whereas N_I behaves similarly (for α not too close to 1). The striking superlinear dependence ($N_I \propto g^{3/2}$), obtained for the regular BR process away from the steady state, is totally masked away.

The I dependence of the PIA bands of triplet excitons (TE) and P^\pm in polyfluorene (PFO) is displayed in Fig. 4(b). The approximate behavior $I^{0.9}$ (low I , both

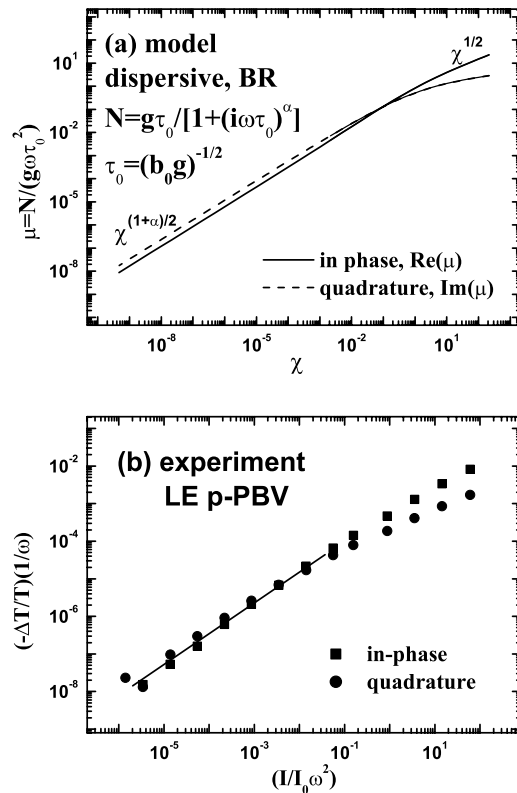


FIG. 3. (a) As in Fig. 1 but for dispersive BR process. (b) PIA measurements of the LE band in *p*-PBV plotted using the generalized coordinates. The solid line corresponds to dispersive BR with $\alpha = 0.5$.

components) and $I^{0.5}$ (high I , in-phase component) agree quite well with the prediction given in Fig. 4(a). We thus conclude that the recombination process of TE and P^\pm in PFO is a *dispersive* BR mechanism. We have also found similar dispersive BR for P^\pm and TE in poly(phenylenevinylene) and *p*-PBV.

In summary, we have suggested a unique way to characterize the kinetics and type of the recombination processes of photoexcitations in PCP; our models can be applied as well to other disordered semiconductors. The determination of the recombination mechanism is especially important for the ultimate quantum yield of optoelectronic devices. In the case that MR dominates the long time photoexcitation dynamics, it may be safely concluded that geminate recombination prevails. Thus, there is less hope to improve the quantum efficiency of PD and PV cells.

We have introduced generalized coordinates by which the dispersive kinetics can unambiguously be distinguished from the “usual” cases where the RR distribution is relatively narrow. In addition, the dependence of the PIA on I , both near steady state and away from steady state, both for the nondispersive, regular cases and for dispersive recombination, is a powerful tool by which BR can be identified. We have provided the first experimental analysis for both of these cases in PCP.

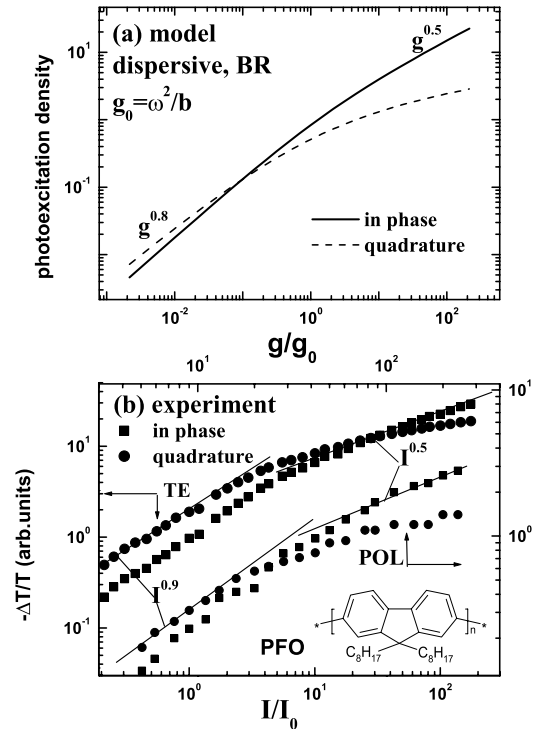


FIG. 4. (a) As in Fig. 2 but for dispersive BR process with $\alpha = 0.6$. Note the sublinear g dependence. (b) The PIA bands of TE and P^\pm in PFO vs I . The approximate $I^{0.9}$ ($I^{0.5}$) dependence at low (high) I corresponds to dispersive BR with $\alpha \approx 0.8$. Inset: Chemical structure of PFO.

Saturation phenomena characteristic to defect-limited recombination processes is most likely to be observed at or near steady state; the effect of saturation away from steady state is minimal [see, for instance, Fig. 2(a)].

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