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Photobleaching and spectral diffusion in disordered media

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The photochemical bleaching of an energetically disordered molecular system is studied theoretically. Spectral diffusion is taken into account, which is marked by downhill energy transfer of excitons between the molecular sites. The resulting redshift in the excited-state occupation gives rise to a relatively stronger bleaching of the lower-lying states, which is observed in the blueshift of both the absorption spectrum and the photoluminescence spectrum of the bleached system. During the photochemical bleaching reaction, quenching sites are formed, at which the excitons decay nonradiatively. These quenching sites modify the excited-state dynamics and thus the bleaching process. The relevance of our model to the photobleaching of poly(*p*-phenylene-vinylene) is pointed out.
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I. INTRODUCTION

The photochemical bleaching of organic dyes, resulting in the fading of colors, is a well-known problem for the textile and graphics industries.[1] The same process poses a fundamental limit to the lifetime of optical devices based on organic materials, such as organic dye lasers[2–4] and polymer light-emitting diodes.[5–8] The photochemical stability of these materials is described by the quantum yield for bleaching γ, which is the probability that a chromophore (optical absorber) is destroyed after a photon is absorbed. In this description, it is implicitly assumed that the destroyed chromophore is identical to the chromophore that absorbed the photon. However, in an energetically disordered system, an excitation may relax in the course of a random walk towards sites of lower energy, a process known as spectral diffusion.[9] This effect causes a relatively stronger bleaching of chromophores with a low excitation energy, as observed in organic dye aggregates.[10] The bleaching of dye aggregates has recently been described by Tomioka and Miyano[11] using a numerical simulation of coherent exciton transport on a two-dimensional lattice with on-site energy disorder.

The present work has been instigated by the observation that photobleaching of poly(*p*-phenylene-vinylene) (PPV) films causes a blueshift of the absorption spectrum.[7,12,13] Experiments suggest that the optical properties of conjugated polymers are well modeled by replacing the polymer chains by a set of chain segments with a distribution of effective conjugation lengths.[14] Upon illumination, on-chain singlet excitons[12,15] are formed that relax in the course of an incoherent random walk between different polymer chain segments.[14] The bleaching of the polymer appears to be due to a photo-oxidation[5] reaction, resulting in a chain scission of the macromolecule.[6,8] The simulation of Ref. 11 is not applicable here, because the system is three dimensional, the lattice structure is absent, and the exciton transport is incoherent.

In this paper, the incoherent migration of excitons in a system with positional and energetic disorder is described analytically using an effective-medium approximation (EMA). This transport formalism is used to calculate the excited-state occupational probability of a given site, which determines its bleaching rate. When the system is then excited by a broadband light source, spectral diffusion leads to a redshift of the excited-state occupational probability and hence to a relatively stronger bleaching of the lower-lying states. In some systems, specifically in PPV,[5] photobleaching not only reduces the absorption of the material, but the photoluminescence (PL) efficiency as well. Apparently, the excitons in these systems are quenched in the presence of a bleached chromophore. In our model, this is accounted for by attributing an additional nonradiative decay channel to excitons on sites that are next to bleached sites. These sites are referred to as ‘‘quenching sites.’’

This paper is organized as follows. The incoherent migration of excitons is described in Sec. II. This formalism is used in Sec. III to model the photochemical bleaching. The influence of quenching sites is described in Sec. IV. In Sec. V, the applicability of the model to photobleaching of PPV is discussed. A short summary of the main results is given in Sec. VI.

II. SPECTRAL DIFFUSION

Consider a system with N localized states, with position $\mathbf{R}_i$ and excited-state energy ε_i, for $i=1,\dots,N$. For low excitation densities, the occupational probability $f_i(t)$ of the site i at time t is described by a linearized master equation

$$\frac{\partial}{\partial t} f_i(t) = -\sum_{j\neq i} W_{ji} f_i(t) + \sum_{j\neq i} W_{ij} f_j(t) - \lambda f_i(t), \qquad (1)$$

where W_{ij} is the transition rate from site j to site i, and λ is the decay rate due to both radiative recombination and nonradiative decay processes, which is assumed to be constant for all sites. For the moment, the effect of photobleaching is not taken into account. At zero temperature, only transitions to sites with lower energy are possible, implying

$$W_{ij}=w(\mathbf{R}_{ij})\,\theta(\varepsilon_j-\varepsilon_i), \tag{2}$$

with $\mathbf{R}_{ij}\equiv\mathbf{R}_i-\mathbf{R}_j$ and $\theta(x)=1$ if $x>0$, $\theta(x)=0$ otherwise. The function $w(\mathbf{R}_{ij})$ depends on the exciton transfer mechanism.

Equation (1) can be solved using a Green-function formalism.[16–18] The Green function $G_{ij}(t)$ is the probability to find a particle at site i at a time t, given that it was at site j at $t=0$, and is a function of all N positions and energies of a given configuration $\{\mathbf{R}_k,\varepsilon_k\}$. To determine the configurational averages of the Green function, we assume that the positions and energies are uncorrelated and denote the density of states (DOS) at energy ε as $\rho(\varepsilon)$. The local Green function, i.e., the average of $G_{jj}(t)$, and the nonlocal Green function, i.e., the average of $G_{ij}(t)$ with $i\neq j$, are given by

$$G_1(\varepsilon_j,t)\equiv\int\left[\prod_{k\neq j}d\mathbf{R}_k d\varepsilon_k\frac{\rho(\varepsilon_k)}{N}\right]G_{jj}(t), \tag{3a}$$

$$G_2(\varepsilon_i,\varepsilon_j,\mathbf{R}_{ij},t)\equiv\int\left[\prod_{k\neq i,j}d\mathbf{R}_k d\varepsilon_k\frac{\rho(\varepsilon_k)}{N}\right]G_{ij}(t). \tag{3b}$$

We calculate the Green functions (3) in the EMA,[16] which allows us to proceed with analytical expressions. Here, the migration from a site is described by a single effective rate, rather than by the sum of all distinct transition rates. This approximation tends to be inaccurate for long times,[16] which is not of importance for this work in view of the finite exciton lifetime. The local Green function is given by

$$G_1(\varepsilon,t)\simeq e^{-\lambda[1+Kn(\varepsilon)]t}, \tag{4}$$

where

$$K=\frac{1}{\lambda}\int d\mathbf{R}\,w(\mathbf{R}), \tag{5}$$

$$n(\varepsilon)=\int_{-\infty}^{\varepsilon}d\varepsilon'\rho(\varepsilon'). \tag{6}$$

The first term in the exponent of Eq. (4) describes the exciton decay, the second the exciton migration. The exact value of K depends on $w(\mathbf{R})$ and thus on the exciton transfer mechanism. For example, when using rates of the Förster type,[16–19] $K=\frac{4}{3}\pi R_0^3\nu_0/\lambda$, with R_0 the nearest-neighbor distance and ν_0 the nearest-neighbor transition rate.

Following Movaghar *et al.*,[16] we found for the Fourier-Laplace transform of the nonlocal Green function (3b) (Refs. 17 and 18)

$$\tilde{G}_2(\varepsilon,\varepsilon',\mathbf{k},p)=\theta(\varepsilon'-\varepsilon)\tilde{G}_1(\varepsilon,p)\tilde{g}(\varepsilon',\mathbf{k},p)\times\exp\left[\int_{\varepsilon}^{\varepsilon'}d\varepsilon''\rho(\varepsilon'')\tilde{g}(\varepsilon'',\mathbf{k},p)\right], \tag{7}$$

where $\tilde{g}(\varepsilon',\mathbf{k},p)$ is the Fourier-Laplace transform of $g(\varepsilon',\mathbf{R},t)$, which is the average probability to jump at time t from the initial site with energy ε' to a site at a distance $\mathbf{R}$ with lower energy. The exponential function results from the summation over all different paths to go from the initial site to the final site and $\tilde{G}_1(\varepsilon,p)$ denotes the probability to remain on the final site. It follows from Eq. (4) that

$$\tilde{G}_1(\varepsilon,p)=\frac{1}{p+\lambda+\lambda Kn(\varepsilon)}. \tag{8}$$

For $\mathbf{k}=\mathbf{0}$, the jump probability reads[16]

$$\tilde{g}(\varepsilon,\mathbf{0},p)=\frac{\lambda K}{p+\lambda+\lambda Kn(\varepsilon)}, \tag{9}$$

which is the product of the local Green function and the transition rate for a jump to a site with lower energy, integrated over all space. Substitution into Eq. (7) yields

$$\tilde{G}_2(\varepsilon,\varepsilon',\mathbf{k}=\mathbf{0},p)=\frac{\theta(\varepsilon'-\varepsilon)\lambda K}{[p+\lambda+\lambda Kn(\varepsilon)]^2}. \tag{10}$$

Equations (8) and (10) constitute the effective medium description of spectral diffusion in an energetically disordered system.

Under constant illumination, sites with energy ε absorb photons at a rate $\alpha(\varepsilon)$. The total absorption rate per unit volume is given by

$$\alpha_{\mathrm{tot}}=\int d\varepsilon\rho(\varepsilon)\alpha(\varepsilon). \tag{11}$$

Using Eqs. (8) and (10), we find for the steady-state occupational probability $f(\varepsilon)$

$$\begin{aligned}f(\varepsilon)&=\alpha(\varepsilon)\tilde{G}_1(\varepsilon,0)+\int d\varepsilon'\rho(\varepsilon')\alpha(\varepsilon')\tilde{G}_2(\varepsilon,\varepsilon',\mathbf{0},0)\\&=\frac{\alpha(\varepsilon)}{\lambda+\lambda Kn(\varepsilon)}+\frac{K\lambda}{[\lambda+\lambda Kn(\varepsilon)]^2}\int_{\varepsilon}^{\infty}d\varepsilon'\rho(\varepsilon')\alpha(\varepsilon').\end{aligned} \tag{12}$$

We note that in the absence of spectral diffusion ($K=0$) the occupational probability is just $\alpha(\varepsilon)/\lambda$. The PL spectrum follows from the occupational probability,

$$L(\varepsilon)=\eta\lambda\rho(\varepsilon)f(\varepsilon), \tag{13}$$

where η is the PL efficiency, i.e., the fraction of excitons that recombine radiatively.

We will consider excitation by a broadband light source, described by

$$\alpha(\varepsilon)=\alpha_0, \tag{14}$$

so that all chromophores have the same excitation rate. Now Eqs. (11) and (12) imply

$$\alpha_{\mathrm{tot}}=\alpha_0 n(\infty), \tag{15}$$

$$f(\varepsilon)=\frac{\alpha_0[1+Kn(\infty)]}{\lambda[1+Kn(\varepsilon)]^2}. \tag{16}$$

The occupation, and hence the PL spectrum, is clearly redshifted with respect to the situation in the absence of spectral diffusion, as $n(\varepsilon)$ increases with increasing energy.

III. PHOTOBLEACHING

Under illumination, photochemical reactions may modify the optical properties of chromophores. In the present work, we will follow Tomioka and Miyano[11] in assuming that the chromophore has negligible absorption after photobleaching. Below, we will describe photochemical bleaching using the results of the previous section in combination with a decreasing DOS.

The bleaching of a site is described by a bleaching rate $\beta(\varepsilon,t)$. This rate is proportional to the occupational probability,

$$\beta(\varepsilon,t)=\lambda_b f(\varepsilon,t), \tag{17}$$

where λ_b is the bleaching rate for an excited state. The occupational probability $f(\varepsilon,t)$ is now a function of time, as—due to the continuous bleaching of sites—a steady state cannot be reached. The effect of the bleaching process is modeled by removing the bleached site from the system,

$$\frac{\partial\rho(\varepsilon,t)}{\partial t}=-\beta(\varepsilon,t)\rho(\varepsilon,t). \tag{18}$$

Of experimental interest is the case where bleaching is much slower than exciton decay ($\lambda_b \ll \lambda$). Then the average occupational probability of excited states at a given time t can be obtained using a quasistationary approach,

$$f(\varepsilon,t)=f[\varepsilon,\rho(\varepsilon,t)]. \tag{19}$$

The functional on the right-hand side is given by substituting a time-dependent DOS $\rho(\varepsilon,t)$ for $\rho(\varepsilon)$ in Eq. (12).

The speed at which the system evolves depends on the intensity of the incident light. Hence the total number of absorbed photons per unit volume,

$$A(t)\equiv\int_0^t dt'\,\alpha_{\text{tot}}[\rho(\varepsilon,t')], \tag{20}$$

is a convenient measure of time. [The total absorption rate α_{tot}, cf. Eq. (11), has become a functional of the time-dependent DOS.]

Combining Eqs. (17)–(20) and using A instead of t to measure time, we find that the evolution of the DOS $\rho(\varepsilon,A)$ is described by

$$\frac{\partial\rho(\varepsilon,A)}{\partial A}=-\rho(\varepsilon,A)\frac{\lambda_b f[\varepsilon,\rho(\varepsilon,A)]}{\alpha_{\text{tot}}[\rho(\varepsilon,A)]}. \tag{21}$$

A check on the formalism is performed by substituting the total absorption rate (11) and the occupational probability (12) into Eq. (21) and integrating both sides of this equation over all energies. We then find that the total density of sites $n(A)\equiv n(\infty,A)$ decreases according to

$$\frac{\partial n(A)}{\partial A}=-\frac{\lambda_b}{\lambda}\equiv-\gamma. \tag{22}$$

Here γ is the quantum yield for bleaching, which is constant in time and independent of spectral diffusion. This must hold for any model in which the exciton decay rate is independent of the site energy. The total density of sites decreases linearly with the number of absorbed photons,

$$n(A)=n(0)-\gamma A. \tag{23}$$

Let us now consider the evolution of the DOS, focussing on the energy dependence of the bleaching process. Substituting Eqs. (15) and (16) into Eq. (21) and integrating both sides of this equation up to the energy ε, we find that the evolution of $n(\varepsilon,A)$ is described by

$$\frac{\partial n(\varepsilon,A)}{\partial A}=-\gamma\frac{n(\varepsilon,A)[1+Kn(A)]}{n(A)[1+Kn(\varepsilon,A)]}. \tag{24}$$

Using Eq. (23), we find

$$n(\varepsilon,A)=\mathcal{W}[h(\varepsilon,A)]/K, \tag{25}$$

with Lambert's $\mathcal{W}$ function, which is defined by[20]

$$\mathcal{W}(x)\exp[\mathcal{W}(x)]=x, \tag{26}$$

and

$$h(\varepsilon,A)\equiv Kn(\varepsilon,0)\left[1-\frac{\gamma A}{n(0)}\right]e^{K[n(\varepsilon,0)-\gamma A]}. \tag{27}$$

The density of states $\rho(\varepsilon,A)$ is obtained by taking the derivative of Eq. (25) with respect to ε,

$$\rho(\varepsilon,A)=\rho(\varepsilon,0)\frac{1+1/[Kn(\varepsilon,0)]}{1+1/[Kn(\varepsilon,A)]}. \tag{28}$$

The quasistationary PL spectrum of the system follows from Eq. (13),

$$L(\varepsilon,A)=\eta\lambda\rho(\varepsilon,A)f[\varepsilon,\rho(\varepsilon,A)]. \tag{29}$$

Without spectral diffusion ($K=0$), the DOS and the PL spectrum decrease uniformly:

$$\rho(\varepsilon,A)=\rho(\varepsilon,0)\left[1-\frac{\gamma A}{n(0)}\right], \tag{30a}$$

$$L(\varepsilon,A)=\eta\alpha_0\rho(\varepsilon,A). \tag{30b}$$

In Figs. 1(a) and 1(b), it is shown that, when the spectral diffusion is weak, the DOS decreases almost uniformly and that the PL spectrum is only slightly redshifted with respect to the DOS.

When the spectral diffusion is strong, the DOS decreases at the low-energy side [Fig. 1(c)]. The PL spectrum is narrower than the DOS and redshifted. Upon bleaching, the blueshift of the PL spectrum follows the blueshift of the low-energy flank of the DOS [Fig. 1(d)]. In the limit $K\rightarrow\infty$, all excitons are immediately tranferred towards the sites with the lowest energy. Hence, there is only emission by and bleaching of these lowest-energy sites. The DOS and the PL spectrum are then given by

$$\rho(\varepsilon,A)=\rho(\varepsilon,0)\,\theta[n(\varepsilon,0)-\gamma A], \tag{31a}$$

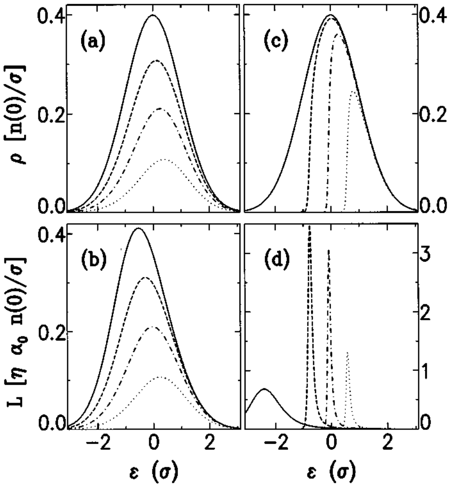

FIG. 1. Evolution of the DOS $\rho(\varepsilon,A)$ [(a) and (c)] and the PL spectrum $L(\varepsilon,A)$ [(b) and (d)] for a medium that is bleached by a broadband light source, as given by Eqs. (28) and (29), respectively. The initial DOS is a Gaussian with standard deviation σ. The plots show $\rho(\varepsilon,A)$ and $L(\varepsilon,A)$ after $A=0.00$, 0.25, 0.50, and $0.75n(0)/\gamma$ photons per unit volume have been absorbed. Plots (a) and (b) show the case of weak spectral diffusion $[Kn(0)=1.0]$, whereas the spectral diffusion is strong $[Kn(0)=100.0]$ in (c) and (d).

$$L(\varepsilon,A)=\eta\alpha_0\rho(\varepsilon,0)n(A)\delta[n(\varepsilon,0)-\gamma A], \tag{31b}$$

where $\delta(x)$ is the Dirac delta function.

With or without spectral diffusion, the decrease of the PL intensity upon bleaching is proportional to the decrease in absorption. This is due to the constant PL efficiency η.

The effect of spectral diffusion on photobleaching can be demonstrated experimentally by monitoring the density of sites in a given energy interval $[\varepsilon_0,\varepsilon_1]$ as a function of time, while the system is bleached by white light. The time evolution of this site density $\Delta n(A)=n(\varepsilon_1,A)-n(\varepsilon_0,A)$ is qualitatively different for weak and for strong spectral diffusion, as shown in Fig. 2. Without spectral diffusion $(K=0)$, the sites in the interval are bleached with an efficiency that is time independent $[\partial\Delta n(A)/\partial A=-\gamma\Delta n(0)/n(0)]$. When spectral diffusion is strong, sites are bleached from the low-energy side. Initially, the bleaching efficiency of sites in the interval is zero, as only lower-energetic sites are bleached. After all sites with energy $\varepsilon<\varepsilon_0$ have been bleached, we have $\partial\Delta n(A)/\partial A=-\gamma$ until all sites in the interval have been bleached.

IV. INFLUENCE OF QUENCHING SITES

In the preceding discussion, it is assumed that the bleached chromophores do not interact with the excited states in the system. However, as shown by, e.g., Yan *et al.*,[5] the PL efficiency in conjugated polymer films decreases drastically upon bleaching. Apparently, the excited states are quenched by the bleached chromophores.

In this section, we study the case where bleached sites induce an additional nonradiative decay channel for excitons on sites within a certain range of the bleached site. We assume a short-range interaction, i.e., only the Z nearest neighbors of the bleached site are affected. The intact (unbleached) sites can now be subdivided into normal sites and quenching sites. A quenching site is a site next to a bleached site, so that an exciton decays at a rate $\lambda+\lambda_q$, where λ_q is the additional quenching rate induced by the bleached site. The density of quenching sites is given by $n^q(A)$, and the DOS by $\rho^q(\varepsilon,A)$. On the normal sites, the exciton decays at a lower rate λ. The density and the DOS of these (nonquenching) sites are denoted as $n^{nq}(A)$ and $\rho^{nq}(\varepsilon,A)$, respectively. The density and DOS of intact sites are given by $n(A)=n^q(A)+n^{nq}(A)$ and $\rho(\varepsilon,A)=\rho^q(\varepsilon,A)+\rho^{nq}(\varepsilon,A)$.

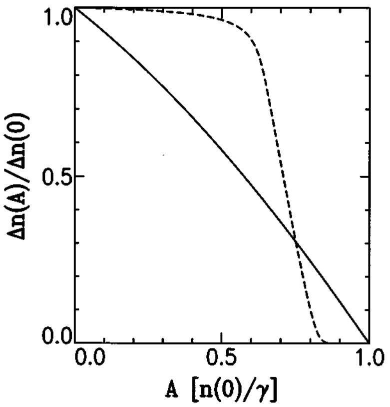

FIG. 2. Evolution of the total density of sites $\Delta n(A)=n(\varepsilon_1,A)-n(\varepsilon_0,A)$ in an energy interval $[\varepsilon_0,\varepsilon_1]$, as given by Eq. (25). The system is bleached by a broadband light source. The initial densities are $n(\varepsilon_0,0)=0.6n(0)$ and $n(\varepsilon_1,0)=0.8n(0)$. The full line shows the case of weak spectral diffusion $[Kn(0)=1.0]$, whereas the case of strong spectral diffusion $[Kn(0)=100.0]$ is given by the dashed line. The results are independent of the form of the DOS.

Let us first consider the exciton dynamics *without photobleaching* in a system that contains both normal sites and quenching sites, analogous to Sec. II. We can use the model we have developed in Ref. 17 for field-induced PL quenching in conjugated polymers. There are two distinct local Green functions, depending on which kind of site the exciton is located,

$$\tilde{G}_1^q(\varepsilon,p)=\frac{1}{p+\lambda+\lambda_q+\lambda Kn(\varepsilon)}, \tag{32a}$$

$$\tilde{G}_1^{nq}(\varepsilon,p)=\frac{1}{p+\lambda+\lambda Kn(\varepsilon)}. \tag{32b}$$

The same holds for the jump probabilities [cf. Eq. (9)] from either a quenching site or a normal site,

$$\tilde{g}^q(\varepsilon,\mathbf{0},p)=\frac{\lambda K}{p+\lambda+\lambda_q+\lambda Kn(\varepsilon)}, \tag{33a}$$

$$\tilde{g}^{nq}(\varepsilon,\mathbf{0},p)=\frac{\lambda K}{p+\lambda+\lambda Kn(\varepsilon)}. \tag{33b}$$

There are four distinct nonlocal Green functions, as both the initial site and the final site may be a quenching site or not,

$$\tilde{G}_2^{a,b}(\varepsilon,\varepsilon',\mathbf{k},p)=\theta(\varepsilon'-\varepsilon)\tilde{G}_1^{a}(\varepsilon,p)\tilde{g}^{b}(\varepsilon',\mathbf{k},p)\times\exp\left[\int_{\varepsilon}^{\varepsilon'}d\varepsilon''\rho(\varepsilon'')\tilde{g}(\varepsilon'',\mathbf{k},p)\right].\tag{34}$$

Here, $a=q,nq$ indicates the type of the final site and $b=q,nq$ that of the initial site. The function $\tilde{g}(\varepsilon,\mathbf{k},p)$ is the average probability to jump away from any site

$$\tilde{g}(\varepsilon,\mathbf{k},p)=\frac{\rho^{q}(\varepsilon)}{\rho(\varepsilon)}\tilde{g}^{q}(\varepsilon,\mathbf{k},p)+\frac{\rho^{nq}(\varepsilon)}{\rho(\varepsilon)}\tilde{g}^{nq}(\varepsilon,\mathbf{k},p).\tag{35}$$

Unlike in Sec. II, there is no simple $\mathbf{k}=\mathbf{0}$ expression for the nonlocal Green function. The integral in the exponent of Eq. (34) can only be evaluated numerically, due to the fact that $\tilde{g}(\varepsilon,\mathbf{0},p)$ is explicitly energy dependent according to Eq. (35).

Let us again study the situation of constant illumination. We assume an equal absorption rate $\alpha(\varepsilon)$ for normal sites as well as quenching sites. The steady-state occupational probabilities $f^{nq}(\varepsilon)$ for normal sites and $f^{q}(\varepsilon)$ for quenching sites are given by

$$\begin{aligned}f^{a}(\varepsilon)&=\alpha(\varepsilon)\tilde{G}_1^{a}(\varepsilon,0)+\int d\varepsilon'\alpha(\varepsilon')\sum_{b=q,nq}\rho^{b}(\varepsilon')\tilde{G}_2^{a,b}(\varepsilon,\varepsilon',\mathbf{0},0)\\&=\tilde{G}_1^{a}(\varepsilon,0)\left\{\alpha(\varepsilon)+\int_{\varepsilon}^{\infty}d\varepsilon'\rho(\varepsilon')\alpha(\varepsilon')\tilde{g}(\varepsilon',\mathbf{0},0)\times\exp\left[\int_{\varepsilon}^{\varepsilon'}d\varepsilon''\rho(\varepsilon'')\tilde{g}(\varepsilon'',\mathbf{0},0)\right]\right\}.\end{aligned}\tag{36}$$

The average occupational probability reads

$$f(\varepsilon)=\frac{\rho^{q}(\varepsilon)}{\rho(\varepsilon)}f^{q}(\varepsilon)+\frac{\rho^{nq}(\varepsilon)}{\rho(\varepsilon)}f^{nq}(\varepsilon).\tag{37}$$

We can now take into account the influence of quenching sites on the bleaching process. Two processes take place simultaneously: normal and quenching sites are destroyed (albeit with different bleaching efficiencies) and normal sites are transformed into quenching sites when a neighboring site is bleached. Equation (21), which describes the time evolution of the DOS, is now replaced by two coupled equations,

$$\frac{\partial\rho^{q}(\varepsilon,A)}{\partial A}=-\frac{\lambda_b f^{q}}{\alpha_{\text{tot}}}\rho^{q}(\varepsilon,A)+\frac{Z\gamma(A)}{n(0)}\rho^{nq}(\varepsilon,A),\tag{38a}$$

$$\frac{\partial\rho^{nq}(\varepsilon,A)}{\partial A}=-\frac{\lambda_b f^{nq}}{\alpha_{\text{tot}}}\rho^{nq}(\varepsilon,A)-\frac{Z\gamma(A)}{n(0)}\rho^{nq}(\varepsilon,A),\tag{38b}$$

where the first term on the right-hand side describes the bleaching process and the second term describes the transformation of normal sites into quenching sites. We have again used the quasistationary approach, i.e., the occupational probabilities and the total absorption rate are functionals $f^{q}[\varepsilon,\rho^{q}(\varepsilon,A),\rho^{nq}(\varepsilon,A)]$, $f^{nq}[\varepsilon,\rho^{q}(\varepsilon,A),\rho^{nq}(\varepsilon,A)]$, and $\alpha_{\text{tot}}[\rho(\varepsilon,A)]$. The absorption rate $\alpha_{\text{tot}}[\rho(\varepsilon,A)]$ is only a functional of the total DOS, as we have taken identical absorption rates for both types of intact sites. For brevity, we have omitted these functional dependencies in the notation of Eqs. (38). The quantum yield for bleaching $\gamma(A)$, which is no longer constant in time, is given by

$$\gamma(A)\equiv-\frac{\partial n(A)}{\partial A}=\frac{\lambda_b\int d\varepsilon'\rho(\varepsilon',A)f[\varepsilon',\rho^{q}(\varepsilon,A),\rho^{nq}(\varepsilon,A)]}{\alpha_{\text{tot}}[\rho(\varepsilon,A)]}.\tag{39}$$

The transformation of normal sites into quenching sites has been modeled as follows. When a photon is absorbed, it has a probability $\gamma(A)$ of bleaching a site. For a further unbleached system, such a bleached site has Z nearest neighbors on which the excited states can be quenched. This implies that, for a partially bleached system, a fraction $n^{nq}(A)/n(0)$ of these Z nearest neighbors will be transformed from normal sites into quenching sites. There is no effect on bleached sites or on sites that already are quenching sites, which form the remaining fraction of the Z nearest neighbors. As the site energies are uncorrelated, there are $Z\rho^{nq}(\varepsilon,A)/n(0)$ nearest neighbors with energy ε that are transformed into quenching sites. Thus, per photon that is absorbed, $Z\gamma(A)\rho^{nq}(\varepsilon,A)/n(0)$ nonquenching sites with energy ε are transformed into quenching sites [see Eqs. (38)].

The evolution of the system is completely defined by Eqs. (32)–(39) for given initial conditions $\rho^{q}(\varepsilon,0)$ and $\rho^{nq}(\varepsilon,0)$. In the following, the properties of this system are discussed according to a typical example. We take a Gaussian DOS with, initially, no quenching sites. The system is bleached by a broadband light source $[\alpha(\varepsilon)=\alpha_0]$. The spectral diffusion is strong $[Kn(0)=100.0]$ and exciton quenching takes place at a high rate, comparable to the fastest transition rates $[\lambda_q=\lambda Kn(0)]$, such that an escape from a quenching site is unlikely. A bleached site can induce exciton quenching on one neighboring site $(Z=1.0)$.

Figure 3 shows the evolution of the total density of sites $n(A)$, the density of quenching sites $n^{q}(A)$, and the bleaching efficiency $\gamma(A)$ as a function of the number of absorbed photons A. Initially, $n(A)$ decreases with a quantum yield for bleaching $\gamma(0)=\lambda_b/\lambda$. Without quenching, the system would then be fully bleached at $A=n(0)/\gamma(0)$. When quenching sites are formed, the quantum yield for bleaching rapidly decreases. In the long-time limit, the value $\gamma(\infty)=\lambda_b/(\lambda+\lambda_q)$ is reached, which is the quantum yield for bleaching on a quenching site.

The evolution of the DOS of the system is shown in Fig. 4. Indeed, we observe that the DOS of the normal sites decreases faster than that of all the sites. The difference is, of course, due to the formation of quenching sites. As the number of quenching sites increases, the migration of excitons gets suppressed. As a result, the evolution of $\rho(\varepsilon,A)$ resembles that of Fig. 1(c) in the beginning, where spectral diffusion is strong, and that of Fig. 1(a) later on, where spectral diffusion is weak.

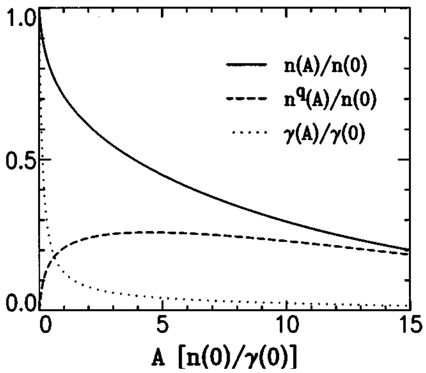

FIG. 3. Evolution of the total density of sites $n(A)$, the density of quenching sites $n^q(A)$, and the quantum yield for bleaching $\gamma(A)$ with the number of absorbed photons per unit volume A. The system is bleached by a broadband light source. The bleached sites induce exciton quenching on neighboring sites. Parameters are given in the text.

The evolution of the PL spectrum $L(\varepsilon,A)$ can be calculated according to Eqs. (29) and (37), and is depicted in Fig. 5. Unlike in Fig. 1, the PL intensity decreases faster than the total absorption. This reduction of the PL *efficiency* is due to the formation of quenching sites. The PL efficiency can be calculated using Eqs. (29) and (39),

$$\eta[\rho^q(\varepsilon,A),\rho^{nq}(\varepsilon,A)]\equiv\frac{\int d\varepsilon L(\varepsilon,A)}{\alpha_{\rm tot}[\rho(\varepsilon,A)]}=\frac{\eta\lambda}{\lambda_b}\gamma(A), \tag{40}$$

and appears to be proportional to the quantum yield for bleaching, shown in Fig. 3. Furthermore, one can observe in Fig. 5 that the PL peak is broadened after long bleaching times. This is due to the transition from strong towards weak spectral diffusion.

Due to the energy distribution of quenching sites, the PL efficiency of excitons is strongly dependent on their initial energy. This energy dependence can be probed in a photoluminescence excitation (PLE) experiment. In such an experiment the system is excited site selectively, i.e., at a specific energy. This can be modeled by an excitation rate of the form

$$\alpha(\varepsilon)=\alpha_0\delta(\varepsilon-\varepsilon_0). \tag{41}$$

Substituting this excitation rate in Eq. (37), we find, analogous to Eq. (40), the PLE efficiency $\eta_{\rm PLE}[\varepsilon_0,\rho^q(\varepsilon,A),\rho^{nq}(\varepsilon,A)]$, plotted in Fig. 6 for the same system as in Figs. 3–5. We stress that the site-selective ex-

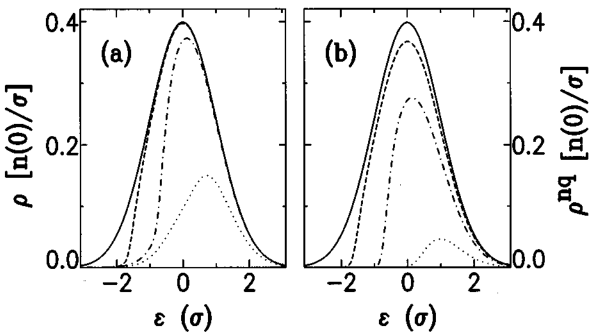

FIG. 4. Evolution of the total DOS $\rho(\varepsilon,A)$ (a) and the DOS $\rho^{nq}(\varepsilon,A)$ for the normal sites (b) with the number of absorbed photons per unit volume A. Initially, the DOS is a Gaussian (with standard deviation σ) without quenching sites. The system is bleached by a broadband light source. The bleached sites induce exciton quenching on neighboring sites. Both $\rho(\varepsilon,A)$ and $\rho^{nq}(\varepsilon,A)$ are shown after $A=0.00$, 0.10, 1.00, and $10.0n(0)/\gamma(0)$ photons per unit volume have been absorbed. Parameters are given in the text.

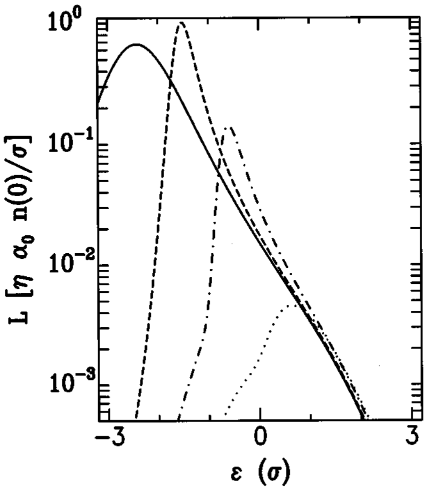

FIG. 5. Evolution of the PL spectrum $L(\varepsilon,A)$ with the number of absorbed photons per unit volume A. The system is bleached by a broadband light source. The bleached sites induce quenching of excitons on the intact sites. The PL spectrum is shown after $A=0.00$, 0.10, 1.00, and $10.0n(0)/\gamma(0)$ photons per unit volume have been absorbed. Parameters are given in the text.

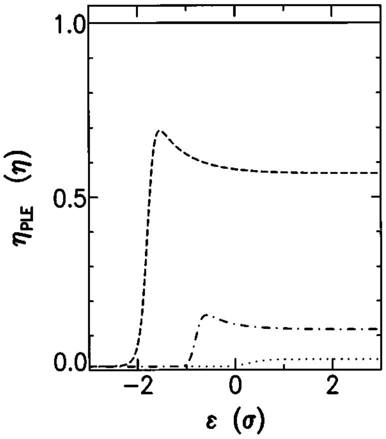

FIG. 6. The PLE efficiency $\eta_{\rm PLE}$ as a function of the excitation energy ε. The system is bleached by a broadband light source. The bleached sites induce quenching of excitons on the intact sites. The PLE efficiency is shown after $A=0.00$, 0.10, 1.00, and $10.0n(0)/\gamma(0)$ photons per unit volume have been absorbed. Parameters are given in the text.

citation is only used to measure the PLE spectrum of the system; the bleaching of the system is still performed through the broad-band light source [Eq. (14)].

In Fig. 6, it is shown that, without quenching sites, the PLE efficiency is η, independent of energy. When quenching sites are formed, the PLE efficiency is lowered and has a pronounced energy dependence. Starting at high energies, the PLE efficiency increases when the excitation energy is lowered. This is due to the lower mobility of lower-energetic excitons, which gives rise to a decreased probability to encounter a quenching site. In the low-energy tail of the spectrum, all sites are quenching sites, as follows from Fig. 4. Thus the PLE efficiency of excitons created at these energies is low, $\eta_{\mathrm{PLE}} = \eta\lambda/(\lambda+\lambda_q)$.

V. PHOTOBLEACHING OF PPV

In Sec. III, it is described how spectral diffusion in a system with energetic disorder gives rise to a stronger bleaching at lower energies. In Sec. IV, it is shown that bleaching in combination with exciton quenching, besides the obvious drop in the PL efficiency, leads to a crossover from strong to weak spectral diffusion and a nontrivial energy dependence of the PLE efficiency. These effects have been observed in bleaching experiments on PPV and its derivatives.[5,7,12,13]

The following reaction mechanism for the photobleaching of PPV and its derivatives has been suggested.[6,8] Upon illumination, singlet excited states are formed in PPV that relax energetically through spectral diffusion. These singlet excited states can form triplet excited states through an intersystem crossing. Then the energy of the PPV triplet state can be used to excite molecular oxygen from its triplet ground state to its singlet excited state. The excited oxygen reacts with the vinyl double bond in the PPV backbone, which results in a scission of the polymer chain and the creation of two carbonyl groups ($C=O$ bonds). Experiments on solutions of a PPV derivative show that part of the reaction is self-sensitized, i.e., the oxidation occurs at the initially excited PPV chain segment, and that the remainder is diffusion controlled, i.e., the reaction occurs at a random (ground state) PPV chain segment to which the singlet oxygen has diffused.[8] The branching ratio of these two reaction paths varies for different solvents; it is unknown for solid PPV films. The diffusion-controlled reaction can be suppressed by adding a singlet oxygen quencher to the system.[8]

In our model, we have combined the singlet excited-state dynamics with a self-sensitized bleaching reaction of the molecular sites. Bleaching through the oxygen diffusion-controlled reaction may be taken into account by adding [in Eq. (17)] a bleaching rate that is independent of the site occupation. However, we do not expect the diffusion-controlled reaction to be the dominant mechanism, as it would lead to a uniform decrease of the DOS instead of the experimentally observed blueshift. The dynamics of triplet excitons in PPV may be included as well. Although this would make the description of the excited-state dynamics more complex, we do not expect that this would lead to qualitative changes in our results.

The quenching of the PL efficiency in bleached PPV has been ascribed to the creation of carbonyl groups.[5] It is believed that, due to the high electron affinity of the carbonyls, immediate ($\leqslant 200$ fs) charge transfer takes place between an intact segment of the polymer and an oxidated segment, thereby dissociating the exciton and quenching the PL.[5,7,12,21] This reaction is well described by the fast, short-range quenching mechanism used in our model.

The recent experiments of Harrison *et al.*[12] show an energy independent PLE efficiency in unbleached PPV, which indicates the absence of quenching sites in the initial material. In photo-oxidized PPV, the PLE efficiency is lower and has a pronounced energy dependence: starting at the low-energy flank of the absorption spectrum, the PLE efficiency decreases until a saturation value is reached at high energies. This behavior is reminiscent of our results shown in Fig. 6. Harrison *et al.*[12] ascribe this effect to the fact that the measurements have been performed on a thick layer that was not uniformly oxidized. Due to the blueshift of the bleached absorption spectrum, the response of the PLE measurement at low energies is mainly from deeper, less oxidized parts of the sample, which have a higher PL efficiency.[12] Our calculations show that this energy dependence of the PLE efficiency is inherent to oxidized PPV and that it should be present in uniformly oxidized layers as well. To describe the experiments on thicker layers, our theory should be combined with the approach of Kaminow *et al.*[2] or more recent extensions of this approach.[3,4,22]

VI. CONCLUSION

The influence of spectral diffusion on the photobleaching of an energetically disordered system in the low-temperature regime has been described using an analytical effective-medium theory. Due to spectral diffusion, the excited states are transferred towards chromophores with lower excitation energies, which results in a relatively stronger bleaching of these chromophores. As a consequence, both the absorption spectrum and the PL spectrum are blueshifted in the course of the bleaching process.

When the excited states are quenched on sites that are next to a bleached site, the reduced lifetime of the excitons gives rise to a decrease of the PL efficiency. Furthermore, the reduction of the exciton lifetime results in increasingly less spectral diffusion, which is reflected in the bleaching behavior and the broadening of the PL spectrum. Finally, excitons that are created on the sites with higher excitation energies have a lower PL efficiency, as these excitons are more mobile and have a higher probability to encounter a quenching site. This, in combination with the time dependent DOS of the quenching sites, gives rise to a pronounced energy dependence of the PLE efficiency.

The effects described above have all been observed in photobleaching experiments on PPV and its derivatives. At present, however, the exact nature of both the excited-state dynamics and the photochemical bleaching reaction in PPV is still under debate. Consequently, as experimental information on many system parameters is lacking, a quantitative microscopic modeling of these photobleaching experiments would be unrealistic. However, we believe that our model contains the essential physics. More experiments are clearly needed. An ideal experiment would be on a thin layer of PPV that is uniformly bleached at low temperatures. After different bleaching times, all relevant spectra, such as the absorption spectrum, the PL spectrum, and the PLE spectrum, should be measured for the same sample.

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