

Ultrafast Spectroscopy of Even-Parity States in π -Conjugated Polymers

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(Received 8 October 1999)

Relaxation dynamics of even parity (A_g) states in poly(*p*-phenylene vinylene) derivatives are studied using a novel fsec transient spectroscopy, in which two different excitation pulses successively generate odd parity (1^1B_u) excitons at 2.2 eV and then reexcite them to higher A_g states. For reexcitation energies $\hbar\omega < 1.1$ eV ultrafast internal conversion back to 1^1B_u takes place in accordance with Vavilov-Kasha's rule. However, for $\hbar\omega > 1.1$ eV the decay occurs in a nonemissive state identified as a polaron pair, showing that the A_g states above 3.3 eV mediate charge transfer.

PACS numbers: 78.30.Jw, 78.47.+p, 78.55.Kz

For the majority of organic materials intramolecular internal conversion (IC) is the fastest relaxation channel, providing efficient nonradiative transfer from higher to lower excited states [1,2]. As a result, molecular fluorescence originates exclusively from the lowest excited state and its quantum yield does not depend on the excitation energy. This observation is referred to as Vavilov-Kasha's rule [1]. Exceptions to this rule are found in media, where other relaxation channels successfully compete with IC. Such an anomaly is observed in azulene molecules [1], in which IC is relatively slow. In larger systems like polymers or molecular crystals, where the IC rate is high, deviations from Vavilov-Kasha's rule are due to ultrafast decay into states other than the lowest fluorescent state. For example, excitons in such media can dissociate into free electrons and holes; in the presence of electric field the competition between IC and exciton dissociation gives rise to photocurrent [2]. Currently, the details of this competition are not well understood.

In this work we study ultrafast relaxation processes in polymer semiconductors and develop a novel spectroscopic tool, which allows us to directly observe the interplay between IC and exciton dissociation. Luminescent π -conjugated polymers, like many other molecular systems, are expected to follow Vavilov-Kasha's rule [3], since IC and vibrational relaxation in these materials occur in ~ 100 fsec [4]. Ultrafast photophysics of π -conjugated polymers in general is determined by the sequence of odd (B_u) and even (A_g) parity exciton states [5], corresponding to one-photon and two-photon transitions, respectively. Excitation into either B_u or A_g states should be followed by IC and rapid nonradiative decay into the lowest singlet exciton (1^1B_u). However, it has been suggested that some excited states may be prone to exciton dissociation and therefore promote carrier photogeneration [6,7]. We use a novel fsec transient spectroscopy to monitor the relaxation dynamics of A_g states generated by successive two-photon absorption in poly(*p*-phenylene vinylene) (PPV) derivative polymer films. Two prominent bands of different A_g

states (m^1A_g at 3.2 eV and k^1A_g at 3.6 eV) are identified by both two-photon absorption and transient photomodulation spectroscopies. We find that whereas m^1A_g obeys Vavilov-Kasha's rule and relaxes back to 1^1B_u via IC within 200 fsec, k^1A_g exhibits anomalous behavior and decays into a long-lived, nonemissive state, attributed to a bound electron-hole polaron pair. This result indicates that k^1A_g belongs to a category of charge transfer states thought to be a prerequisite for carrier generation.

Polymer films (0.5–1 μm thick) are evaporated from chloroform solutions of two different PPV derivatives: dioctyloxy-PPV (DOO-PPV) [8] and dendritic side-chain substituted PPV (PPVD0) [9]. A pump-and-probe technique is used to obtain time-resolved photomodulation (PM) spectra by measuring $\Delta T(t)/T$ vs probe photon energy $\hbar\omega$, where T is the probe transmission, ΔT is the change in T due to the pump pulse, and t is the time delay between the pump and probe pulses. Negative ΔT implies photoinduced absorption (PA), whereas positive ΔT is due to probe-induced stimulated emission (SE). Two synchronized Ti:sapphire mode-locked lasers (Spectra-Physics "Tsunami"), one of which pumps an optical parametric oscillator ("Opal"), are used to produce 100 fsec pump and probe pulses at a repetition rate of 80 MHz. The excitation energy ($\hbar\omega$) can vary from 2.5 to 3.2 eV, whereas the probe $\hbar\omega$ varies from 0.11 to 2.2 eV. Photoexcitation density is below 10^{17} cm^{-3} , so that $\Delta T/T$ never exceeds 3×10^{-4} .

Figure 1 shows the absorption spectrum $\alpha(\hbar\omega)$ of a DOO-PPV film up to 6 eV. Three absorption bands marked I, II, and III were identified as π - π^* transitions [10], where bands I and II involve delocalized molecular orbitals (MO) and band III involves both delocalized and localized MO's [11]. Band I marks the 1^1B_u exciton and from its electroabsorption Stark shift we previously determined $E(1^1B_u) = 2.2$ eV [12]. The 1^1A_g states, which are not observable by one-photon absorption, are found from electroabsorption at $E(m^1A_g) \approx 3.1$ eV and $E(k^1A_g) \approx 3.5$ eV [12]. We can also locate these 1^1A_g

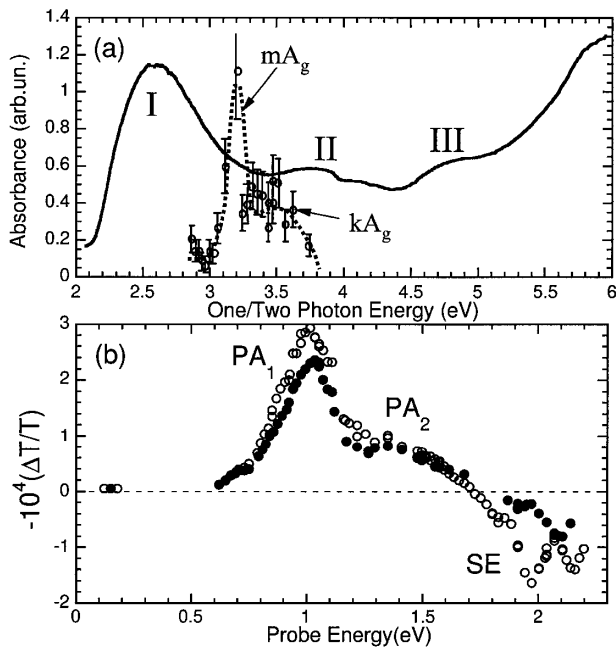


FIG. 1. (a) One-photon (solid line) and two-photon (circles) absorption spectra of DOO-PPV; bands I, II, and III, mA_g and kA_g states are assigned. (b) Transient PM spectra in DOO-PPV (open circles) and PPVD0 (solid circles) films at $t = 2$ ps.

states in DOO-PPV solutions using two-photon absorption spectroscopy [Fig. 1(a)] [13]. Apart from a slight blueshift (~ 0.15 eV), the 1A_g energies extracted from the two-photon absorption spectrum are in good agreement with those obtained from the electrophotoluminescence spectrum. Figure 1(b) shows the transient PM spectra of DOO-PPV and PPVD0 films measured at $t = 2$ ps. The prominent features are assigned to transitions of 1^1B_u excitons: SE at $\hbar\omega > 1.7$ eV and two PA bands at $\hbar\omega < 1.7$ eV (PA₁ and PA₂, attributed to transitions from 1^1B_u to m^1A_g and k^1A_g , respectively) [8]. The exciton lifetime τ measured from the SE decay is about 200 ps (300 ps) for DOO-PPV (PPVD0) films.

In the earlier studies [14] m^1A_g was described as an excited 1^1B_u exciton with energy close to the continuum edge, whereas k^1A_g was assigned to a biexciton. The later assignment, however, has been questioned recently [15]. In order to clarify the nature of the strongly coupled A_g states, we use a three-pulse transient PM technique to monitor the exciton dynamics following optical reexcitation from 1^1B_u to m^1A_g or k^1A_g , as shown in Fig. 2 insets. In this technique a population of 1^1B_u excitons is initially produced by the first pump pulse (1) at $\hbar\omega = E_1 > E(1^1B_u)$ and then reexcited after a delay time t_2 by the second pump pulse (2) at $\hbar\omega = E_2$, tuned to a specific exciton transition (within either PA₁ or PA₂ bands). The resulting exciton PM dynamics are monitored by the probe pulse (3) at $\hbar\omega = E_3$ at a delay time t_3 using either an absolute or a relative measuring mode. In the absolute mode ΔT due to both pump pulses is measured, whereas in the

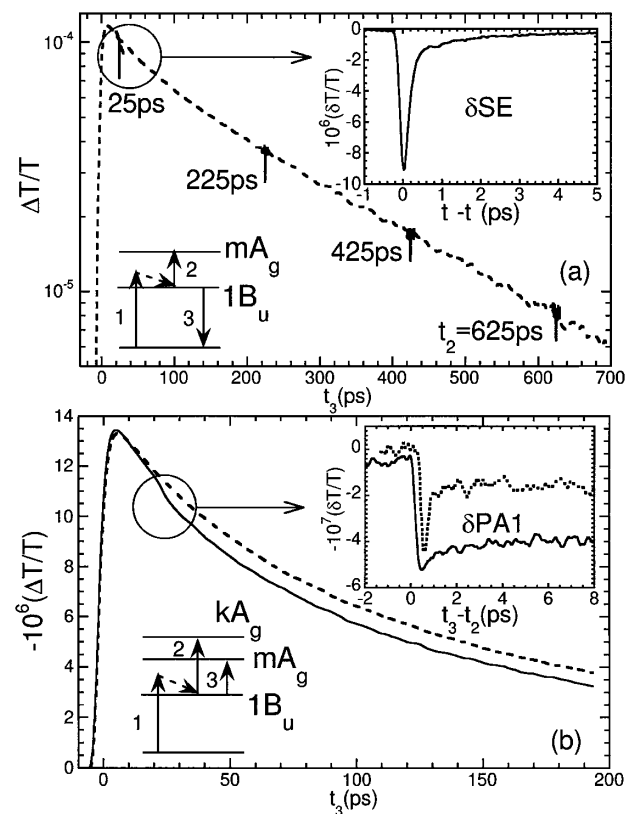


FIG. 2. (a) $\Delta T/T$ decay at $E_3 = 2.0$ eV without (broken line) and with (solid lines) the second pump pulse at $E_2 = 1.0$ eV, for four different t_2 in PPVD0 films; the upper inset shows the corresponding $\delta T/T$ decay. (b) $\Delta T/T$ decays at $E_2 = 0.6$ eV without (broken line) and with (solid line) the second pump pulse at 1.6 eV and $t_2 = 25$ ps in DOO-PPV films; the upper inset shows the corresponding $\delta T/T$ decays for $E_2 = 1.6$ eV (solid line) and $E_2 = 1.35$ eV (dashed line). The lower insets show schematically the respective optical transitions involved in each measurement: 1—excitation by the first pump; 2—reexcitation by the second pump; and 3—absorption or emission induced by the probe pulses.

relative mode only the change, δT , due to the second pump pulse is detected using the double-frequency modulation (DM) technique [16]. The second pump switching efficiency, η , is thus equal to $|\delta T/\Delta T|$. The A_g relaxation dynamics described below are virtually the same for both DOO-PPV and PPVD0 films.

The m^1A_g relaxation dynamics are measured after 1^1B_u reexcitation at $E_2 = 1.0$ eV (within PA₁) and four different t_2 . The resulting transient 1^1B_u population is monitored by SE decay (δSE) at $E_3 = 2.0$ eV, as shown in Fig. 2(a) for the PPVD0 film. We note that η is independent of t_2 , indicating that only 1^1B_u excitons are involved in the reexcitation process. Also, δSE decays [Fig. 2(a), inset] are the same for four different t_2 values. We find that m^1A_g quickly relaxes back to 1^1B_u via IC with a time constant of about 200 fsec; over 99% of m^1A_g excitons recover back to 1^1B_u within 10 ps after reexcitation. Upon increasing E_2 to 1.6 eV (within

PA₂), we observe completely different δT dynamics. Figure 2(b) shows the 1^1B_u population decay probed at $E_3 = 0.6$ eV (within PA₁) with and without the second pump pulse at $t_2 = 25$ ps. The Fig. 2(b) inset (solid line) indicates that within 1 ps only limited relaxation occurs from k^1A_g back to 1^1B_u . In the same inset we plot δT dynamics obtained with $E_2 = 1.35$ eV (dashed line); in this case an intermediate behavior is observed where both ultrafast and long-lived δT components are present. Figure 3 shows the normalized $\delta T/\Delta T$ decay up to 300 ps for $E_2 = 1.6$ eV, illustrating that within the 1^1B_u exciton lifetime only a small fraction of k^1A_g relaxes to 1^1B_u .

We can directly probe k^1A_g relaxation by monitoring transient PA originating from k^1A_g at $E_3 = 1.6$ – 1.8 eV. The Fig. 3 inset shows δT decays in DOO-PPV at $E_3 = 1.6$ eV and $E_3 = 1.8$ eV, obtained following reexcitation at $E_2 = 1.5$ eV ($t_2 \approx 16$ ps). In this case δT decay consists of two parts: an ultrafast δPA component lasting 1 ps and a slow δPA (δSE) component for $E_3 = 1.6$ eV (1.8 eV). We attribute the ultrafast δPA component to the formation and relaxation (within 350 fsec) of k^1A_g . However, k^1A_g does not relax into 1^1B_u , since δSE , δPA_1 , and δPA_2 last much longer (>250 ps, Fig. 3). We therefore conclude that k^1A_g decays with high quantum yield into a relatively long-lived state, *other than* 1^1B_u . In order to verify that the new state is nonemissive, we study changes (δPL) in cw photoluminescence (PL) from the first pump pulse, which are induced by the second pump pulse. δPL is measured at various E_2 using the DM technique; a pronounced PL quenching (PLQ) is found at $E_2 > 1.1$ eV. Figure 4(a) shows the spectrum of PLQ efficiency, η_{PLQ} , defined as N_A/N_B , where N_A is the number of dissociated k^1A_g excitons that recombine nonradiatively and N_B is the number of reexcited 1^1B_u excitons. PLQ is inefficient at $E_2 < 1.1$ eV and may be mediated by defects in this spectral range. However, η_{PLQ} abruptly increases at

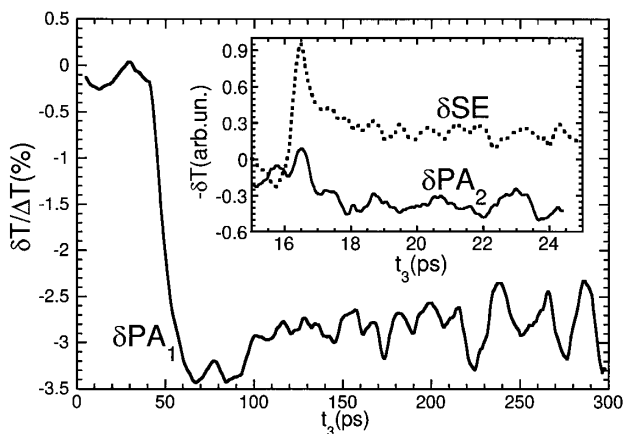


FIG. 3. Normalized $\delta T/\Delta T$ decay in DOO-PPV films at $E_3 = 0.6$ eV with the second pump pulse at $E_2 = 1.6$ eV and $t_2 = 25$ ps. The inset shows two δT decays with the second pump pulse at $E_2 = 1.5$ eV probed, respectively, at $E_3 = 1.6$ eV (solid line) and 1.8 eV (dotted line).

$E_2^* \approx 1.1$ eV, which corresponds to the onset of PA₂. We emphasize that the PLQ at $E_2 > 1.3$ eV is highly efficient [Fig. 4(a)], suggesting a dramatically different relaxation pathway of k^1A_g states compared to those of m^1A_g and other 1^1B_u states.

Two relaxation routes with very different by-products can be envisioned for k^1A_g : (I) singlet fission, when one k^1A_g singlet decomposes into two 1^3B_u triplets, and (II) autoionization, i.e., exciton dissociation into free charges (or polarons). The latter process is possibly mediated by intermediate charge-transfer (CT) states [6,7]. To determine which excitation manifold [see Fig. 4(b)] takes part in k^1A_g relaxation, we measure the triplet exciton and photoconductivity (PC) excitation spectra in DOO-PPV films [Fig. 4(a), inset]. Triplets are mainly produced via intersystem crossing, as indicated by the steplike triplet yield with an onset at $E(1^1B_u)$. There is an additional rise in the triplet yield at $E_{SF} \equiv 2E[1^3B_u] = 2.8$ eV due to singlet fission ($1^1B_u \rightarrow 1^3B_u + 1^3B_u$), which does not correlate with the PLQ spectrum. The latter, on the other hand, closely resembles the PC spectrum, indicating that PLQ should be associated with exciton dissociation rather than singlet fission. Indeed, the onset of intrinsic PC occurs at $E_{IPC} = 3.2$ eV [17], which is in agreement with the onset of the PLQ at $E_2^* + E(1^1B_u) \approx 3.3$ eV. Furthermore, triplets are characterized by a PA band (PA_T) peaking at 1.45 eV [8]. We find, however, that as a result

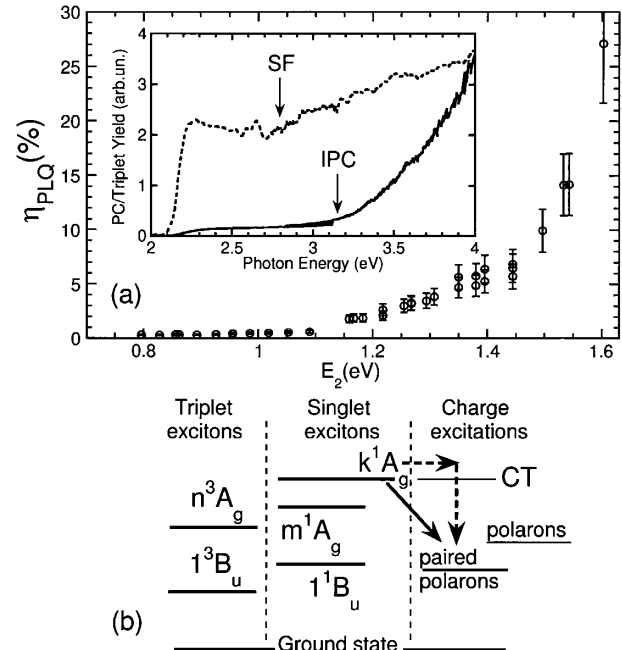


FIG. 4. (a) PL quenching efficiency (η_{PLQ}) spectrum in DOO-PPV films. The inset shows triplet exciton (dashed line) and PC (solid line) excitation spectra; arrows indicate the onset of singlet fission (SF) and intrinsic photoconductivity (IPC). (b) Energy level diagram (without vibronic sidebands) of singlet and triplet excitons, and charged excitations; arrows show two possible relaxation routes from k^1A_g .

of reexcitation to k^1A_g , PA_T is also quenched (with efficiency roughly equal to η_{PLQ}), which indicates that the singlet fission is not the primary relaxation channel for k^1A_g . We measure PA_T quenching at $E_2 = 1.4\text{--}1.6$ eV and $t_3 = -100$ ps, so that only steady state δT accumulated from several pairs of pump pulses is monitored. Similar measurements at $E_2 = 1.65\text{--}1.75$ eV show that after reexcitation to k^1A_g the long-lived PA in this spectral range slightly increases (negative δT). Yet, these measurements do not reveal long-lived δPA at ~ 0.6 eV and ~ 0.15 eV [18,19], which would indicate the presence of free polarons [20]. We conclude that kA_g does not relax into either triplets or free polarons.

An apparent correlation between the PLQ and PC spectra suggests that k^1A_g relaxation may involve a CT state, which in the presence of an electric field dissociates into free carriers. Without the field, these carriers remain bound in pairs by Coulomb attraction. Local microscopic field (due to defects, inhomogeneity, photodoping, etc.) may stabilize the formation of bound polaron pairs [Fig. 4(b)]; this type of excitations has, in fact, been previously observed in C_{60} -doped [21,22] and pristine PPV films [23]. Although it has been shown [15] that both m^1A_g and k^1A_g have a charge transfer character, it appears that only k^1A_g assists exciton dissociation. The k^1A_g state, unlike m^1A_g , contains contributions from localized MO's similar to band III in Fig. 1(a) [15], which in turn assist electron-hole separation [6,7]. Arguably, k^1A_g may possess similar properties and also assist charge transfer. Alternatively, k^1A_g may relax into an intermediate CT state easing polaron pair formation. Earlier theoretical work indicated the existence of a dipole-forbidden state near band II [Fig. 1(a)], produced by an antisymmetric combination of delocalized and localized MO's involved in the formation of band III [10,11]. This state cannot be accessed directly from the ground state via B_u -type excitations; however, it may couple to k^1A_g , providing an efficient route for exciton dissociation.

In summary, we develop a three-beam transient spectroscopy to study the ultrafast relaxation of excited states, which cannot be observed by other means. We use this spectroscopy to study A_g states in π -conjugated polymers and show their role in the ultrafast photophysics. We distinguish two classes of A_g states: one class (m^1A_g) quickly relaxes to the lowest singlet exciton (1^1B_u) via IC, the other (k^1A_g) undergoes a different relaxation pathway and dissociates into long-lived polaron pairs. This result is particularly interesting in view of the fact that direct excitation

into 1^1B_u states at similar photon energies does not result in significant exciton dissociation (consequently, PC yield is low). We therefore argue that A_g states above 3.3 eV mediate carrier photogeneration and suppress IC. Our study is applicable to other organic semiconductors, in which PC spectra show a pronounced increase at much higher energies than the optical gap.

We thank R. Meyer, M. C. DeLong, and G. Levina for the absorption spectra of DOO-PPV. The work at Utah was supported in part by the NSF, DMR-9732820.

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