

## Ultrafast Spectroscopy of Even-Parity States in $\pi$ -Conjugated Polymers

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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.

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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  $\pi$ -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  $\sim 100$  fsec [4]. Ultrafast photophysics of  $\pi$ -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  $\mu\text{m}$  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,  $\Delta T$  is the change in  $T$  due to the pump pulse, and  $t$  is the time delay between the pump and probe pulses. Negative  $\Delta T$  implies photoinduced absorption (PA), whereas positive  $\Delta T$  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  $10^{17}$   $\text{cm}^{-3}$ , so that  $\Delta T/T$  never exceeds  $3 \times 10^{-4}$ .

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  $\pi$ - $\pi^*$  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  $^1A_g$  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  $^1A_g$

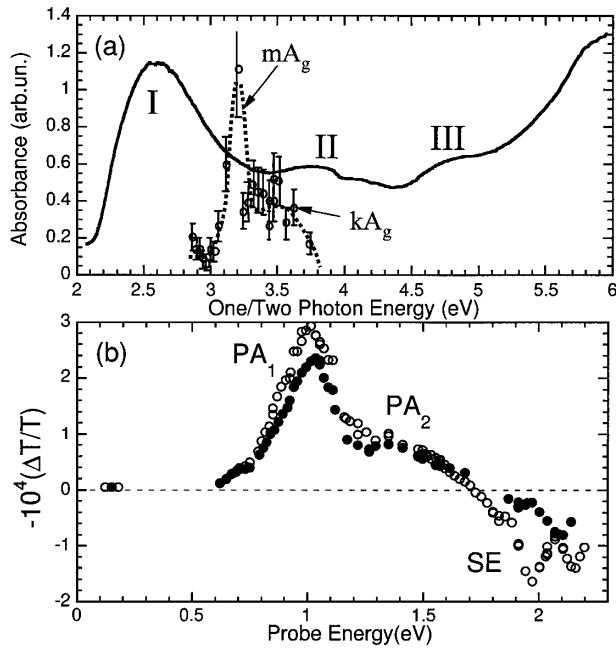


FIG. 1. (a) One-photon (solid line) and two-photon (circles) absorption spectra of DOO-PPV; bands I, II, and III,  $m^1A_g$  and  $k^1A_g$  states are assigned. (b) Transient PM spectra in DOO-PPV (open circles) and PPVD0 (solid circles) films at  $t = 2$  ps.

states in DOO-PPV solutions using two-photon absorption spectroscopy [Fig. 1(a)] [13]. Apart from a slight blueshift ( $\sim 0.15$  eV), the  $^1A_g$  energies extracted from the two-photon absorption spectrum are in good agreement with those obtained from the electrobroadening 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 (PA<sub>1</sub> and PA<sub>2</sub>, attributed to transitions from  $1^1B_u$  to  $m^1A_g$  and  $k^1A_g$ , respectively) [8]. The exciton lifetime  $\tau$  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 PA<sub>1</sub> or PA<sub>2</sub> 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  $\Delta T$  due to both pump pulses is measured, whereas in the

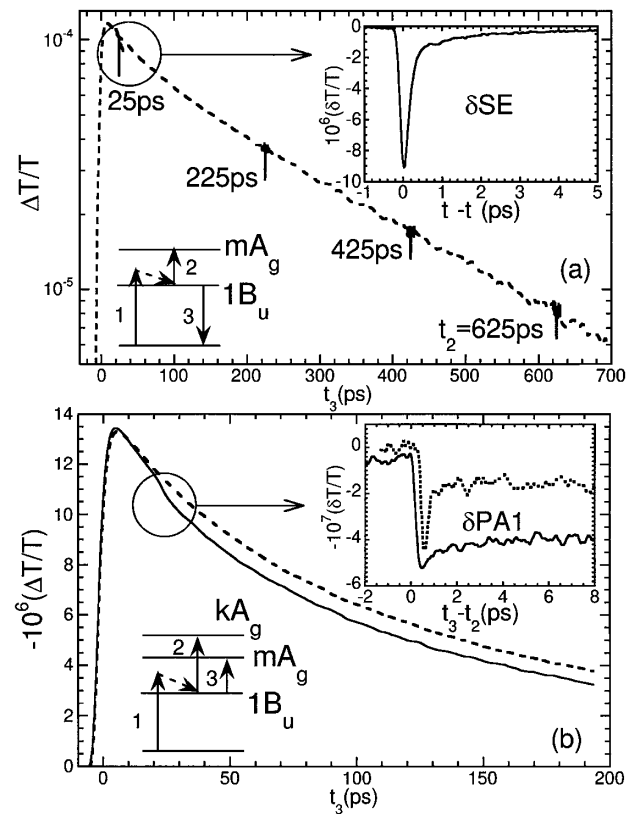


FIG. 2. (a)  $\Delta T/T$  decay at  $E_3 = 2.0$  eV without (broken line) and with (solid lines) the second pump pulse at  $E_2 = 1.0$  eV, for four different  $t_2$  in PPVD0 films; the upper inset shows the corresponding  $\delta T/T$  decay. (b)  $\Delta T/T$  decays at  $E_2 = 0.6$  eV without (broken 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,  $\delta T$ , due to the second pump pulse is detected using the double-frequency modulation (DM) technique [16]. The second pump switching efficiency,  $\eta$ , 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 PA<sub>1</sub>) and four different  $t_2$ . The resulting transient  $1^1B_u$  population is monitored by SE decay ( $\delta$ SE) at  $E_3 = 2.0$  eV, as shown in Fig. 2(a) for the PPVD0 film. We note that  $\eta$  is independent of  $t_2$ , indicating that only  $1^1B_u$  excitons are involved in the reexcitation process. Also,  $\delta$ SE 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

PA<sub>2</sub>), we observe completely different  $\delta T$  dynamics. Figure 2(b) shows the  $1^1B_u$  population decay probed at  $E_3 = 0.6$  eV (within PA<sub>1</sub>) 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  $\delta T$  dynamics obtained with  $E_2 = 1.35$  eV (dashed line); in this case an intermediate behavior is observed where both ultrafast and long-lived  $\delta T$  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  $\delta T$  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  $\delta T$  decay consists of two parts: an ultrafast  $\delta PA$  component lasting 1 ps and a slow  $\delta PA$  ( $\delta SE$ ) component for  $E_3 = 1.6$  eV (1.8 eV). We attribute the ultrafast  $\delta PA$  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  $\delta SE$ ,  $\delta PA_1$ , and  $\delta PA_2$  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 ( $\delta PL$ ) in cw photoluminescence (PL) from the first pump pulse, which are induced by the second pump pulse.  $\delta PL$  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,  $\eta_{PLQ}$ , 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,  $\eta_{PLQ}$  abruptly increases at

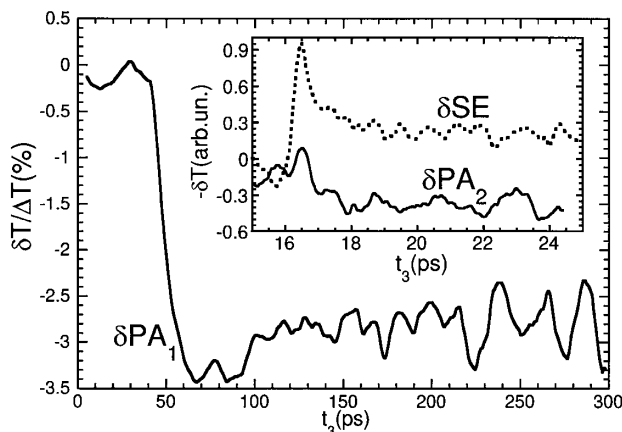


FIG. 3. Normalized  $\delta T/\Delta T$  decay in DOO-PPV films at  $E_3 = 0.6$  eV with the second pump pulse at  $E_2 = 1.6$  eV and  $t_2 = 25$  ps. The inset shows two  $\delta T$  decays with the second pump pulse at  $E_2 = 1.5$  eV probed, respectively, at  $E_3 = 1.6$  eV (solid line) and 1.8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

$E_2^* \approx 1.1$  eV, which corresponds to the onset of PA<sub>2</sub>. 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<sub>T</sub>) peaking at 1.45 eV [8]. We find, however, that as a result

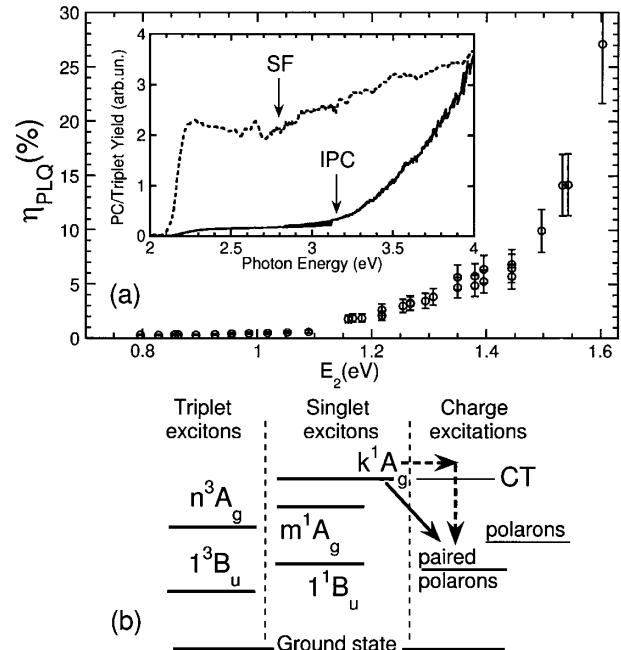


FIG. 4. (a) PL quenching efficiency ( $\eta_{PLQ}$ ) spectrum in DOO-PPV films. The inset shows triplet exciton (dashed line) and PC (solid line) excitation spectra; arrows indicate the onset of singlet fission (SF) and intrinsic photoconductivity (IPC). (b) Energy level diagram (without vibronic sidebands) 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  $\eta_{PLQ}$ ), 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  $\delta T$  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  $\delta T$ ). Yet, these measurements do not reveal long-lived  $\delta PA$  at  $\sim 0.6$  eV and  $\sim 0.15$  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  $\pi$ -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.

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