Transient Spectroscopy of Frenkel and Charge Transfer Excitons in α-Sexithienyl Films

G. Lanzani
Istituto di Matematica e Fisica, Università di Sassari, Sassari 07100 Italy and Istituto Nazionale per la Fisica della Materia, Unità di Milano, Milano 20133 Italy

S. V. Frolov, P. A. Lane,* and Z. V. Vardeny
Department of Physics, University of Utah, Salt Lake City, Utah 84112

M. Nisoli and S. De Silvestri
Centro di Elettronica Quantistica e Strumentazione Elettronica Dipartimento di Fisica, Politecnico di Milano, Milano 20133 Italy

(Received 23 December 1996)

Photoexcitations dynamics are investigated in α-sexithienyl nanocrystalline films using transient photomodulation in a spectral range from 0.4 to 2.5 eV and time domain from 200 fs to 50 ms. We identify intrachain and interchain excitations. The former are even parity excitons with ultrafast dynamics, whereas the latter are long-lived charge transfer excitons generated within 300 fs, which separate into uncorrelated polaron pairs in the submicrosecond time domain. [S0031-9007(97)04247-6]

PACS numbers: 78.47.+p, 72.20.Jv, 78.55.Kz, 78.66.Qn

Organic molecular materials based on linear conjugated systems are considered to be good candidates for photovoltaic and optoelectronic applications [1,2]. In particular, thin films of short thiophene oligomers have highly ordered structures [3] with high carrier mobility. Using the six-ring-membered compound, α-sexithienyl (T_6), carrier mobilities as high as 0.075 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ have been measured in T_6 field effect transistors [4]. The interplay between electrical and structural properties in T_6 films has been widely discussed [4]. Despite their fundamental importance, the optical properties and, in particular, charge photogeneration (CPG) process have received much less attention. CPG is a fundamental process in the class of conducting polymers which is directly related to photovoltaic applications and indirectly, as an important nonradiative deactivation path, to electroluminescent devices performance.

T_6 films are molecular solids in which the oligomer units are bound by weak intermolecular interactions. Using above-gap excitation, charges are photogenerated in T_6 with an estimated quantum yield of 10^{-3} [5]. CPG is thus expected to be an indirect process, and the primary excitations in T_6 films are therefore neutral, tightly bound Frenkel type excitons [6]. The details by which CPG occurs, especially at the earliest stages, have not yet been elucidated. In T_6 films, where relatively sharp optical transitions have been associated with the long-lived charged states [5,7], it may be easier to follow the CPG dynamics than in relatively disordered conducting polymer films spun from solutions.

For studying photoexcitation dynamics in T_6 films we have used here a variety of cw and transient optical probes in a time domain from 200 femtosecond (fs) to milliseconds (ms) and spectral range from 0.3 to 2.5 eV. For the first time in the field of conducting polymers we investigate the earliest stages of the CPG process by following the dynamics of the charge transfer (CT) exciton separation into long-lived polarons. A relatively sharp and long-lived photoinduced absorption (PA) band at 1.6 eV is identified as due to CT excitons, which are formed within 300 fs. We have also identified the lowest lying intrachain excitons in T_6 as even parity Frenkel excitons.

T_6 films with thickness of about 1500 Å were evaporated in vacuum (10^{-7} Torr) onto heated quartz substrates at a deposition rate of 0.2–1 Å/s. Structural characterization has shown [8] that such films are polycrystalline. The nanocrystals have a monoclinic lattice with the long axis of the unit cell perpendicular to the substrate [9].

PA spectra were measured at 300 K in the range from 0.7 to 2.5 eV using two ultrafast laser systems: (i) Ti-sapphire chirp pulse amplified system with 1 kHz repetition rate [10]. The excitation was at 3.2 eV with 20 nJ per pulse. The cross correlation time was about 200 fs throughout the entire spectral range (0.82–2.5 eV). (ii) Two dye lasers synchronously pumped by a frequency-doubled mode-locked Nd:YAG laser at a repetition rate of 76 MHz. A NaCl(F2+)H color center laser was also used in place of one of the dye lasers. The pump-probe system had a cross correlation time of about 10 ps and the maximum pump-probe delay time was 3 ns. The PA spectra were obtained at a fixed pump photon excitation of 2.3 eV, in the probe spectral range of 1.2–2.3 eV (dye laser) and 0.74–0.84 eV (color center laser) [11]. The PA related to photoexcitations with lifetime in the μs time domain was obtained by photomodulation spectroscopy at 1 MHz. PA in the ms time range was studied using a standard cw photomodulation apparatus [12]. All PA spectra are given in terms of $-\Delta T/T$, where T is the transmission and ΔT is the induced transmission change at the probe photon energy.

A typical absorption spectrum of T_6 film at 300 K is shown in Fig. 1(a), inset. The vibronic replica at the absorption onset merge into a broad shoulder at 3.2 eV. This is in contrast to the absorption spectrum of isolated T_6 molecules [13], and suggests the existence of dipole forbidden states with "false origin" at the absorption edge and a strong dipole allowed state at 3.2 eV [14]. Importantly, a second optically allowed state is apparent at about 4 eV (Fig. 1, inset).

In Fig. 1(a) we show the fs PA spectrum at pump-probe delays $\Delta t = 0$ and 4 ps, respectively, obtained with initial excitation density, n, of 10^{19} cm^{-3}. The PA spectrum at $\Delta t = 0$ is dominated by a prominent PA band at 1.77 eV (PA_2), which displays a shoulder at 1.55 eV (PA_3). At $\Delta t = 4$ ps PA_2 is considerably reduced, whereas PA_3 is more apparent. Spectral dependent transient PA decay provides a means of separating the slower PA_3 from the dominant PA_2. In Fig. 2 we show PA dynamics at probe energies, $\hbar\omega$, ranging between 1.4 and 1.8 eV; a slower decay around $\hbar\omega = 1.6$ eV is apparent. By plotting the weight of the slow PA component, as obtained from plateau-to-peak ratios of decays such as in Fig. 2, we obtained the data shown as crosses in Fig. 1(a). This procedure, though qualitative, indicates that there is a rather sharp long-lived PA band at about 1.6 eV (PA_3).

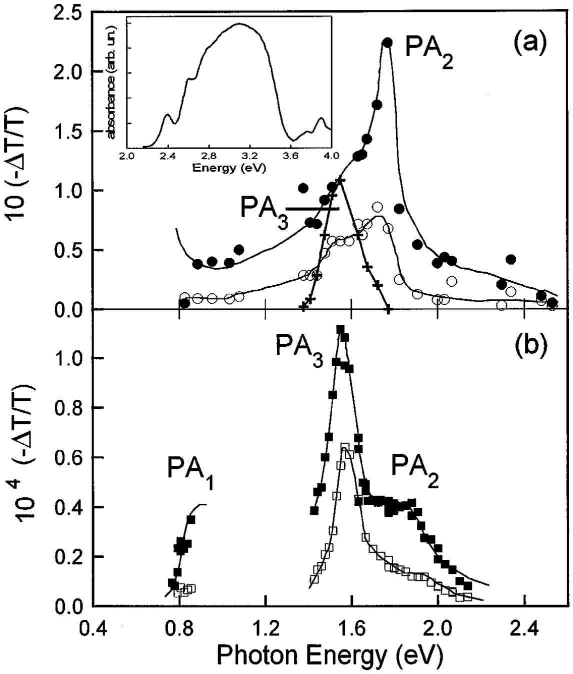

FIG. 1. (a) PA spectra of T_6 nanocrystalline films at pump-probe delay $\Delta t = 0$ (filled circles) and $\Delta t = 4$ ps (open circles). The excitation energy is 3.2 eV and density 10^{19} cm^{-3}. Crosses are obtained as explained in the text. Lines through the data points are guides to the eye. Inset: ground state absorption of T_6 films. (b) PA spectra of T_6 nanocrystalline films obtained using ps excitation at 2.3 eV and density of 10^{16} cm^{-3} at $\Delta t = 0$ ps (filled squares) and $\Delta t = 2$ ns (open squares). Lines through the data points are guides to the eye.

In Fig. 1(b) we show the PA spectra obtained using the ps setup with initial $n \approx 10^{16}$ cm^{-3} for pump-probe delays of 0 (i.e., within 10 ps of the excitation pulse) and 2 ns, respectively. The ps spectrum now consists of three PA bands: a steep rise at 0.8 eV, a sharp PA band at 1.6 eV, and a shoulder at 1.85 eV. The correspondence of the 1.6 eV PA band to PA_3 cannot be fortuitous, and we conclude that these two PA bands are due to the same photoexcited species. Moreover, in both fs and ps spectra we see a PA band at higher energy with faster dynamics. We therefore associate the shoulder at 1.85 eV in Fig. 1(b) with PA_2 in Fig. 1(a). The steep rise at 0.8 eV indicates a third PA band (PA_1) which is probably quite sharp. Figure 3 shows that PA_1 and PA_2 display the same dynamics up to 2 ns indicating that they are correlated, and we conjecture that they are due to the same photoexcitation.

In order to account for the three observed PA bands we assume, as a crude approximation, that T_6 films are ensembles of noninteracting molecules. In this case the photoexcited state is just a sum of the isolated molecule excited states. However, measurements of ps PA in T_6 molecules dissolved in solution [15,16] are not consistent with our results, indicating that the *collective* nature of the excited state (molecular exciton) has to be taken into account.

We first discuss the long-lived PA_3 band at 1.6 eV. A possible assignment could be optical transitions of isolated molecules within the disordered regions of the film. Two observations, however, contradict this conclusion: (i) Radiative recombination is highly efficient in isolated T_6 molecules (about 40%) [17], while it is very

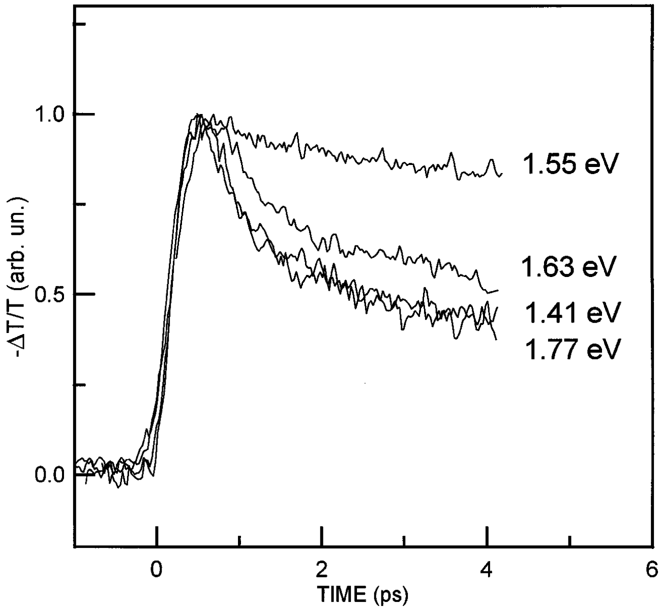

FIG. 2. PA dynamics in T_6 nanocrystalline films at different probe photon energies. Excitation conditions are the same as for Fig. 1(a).

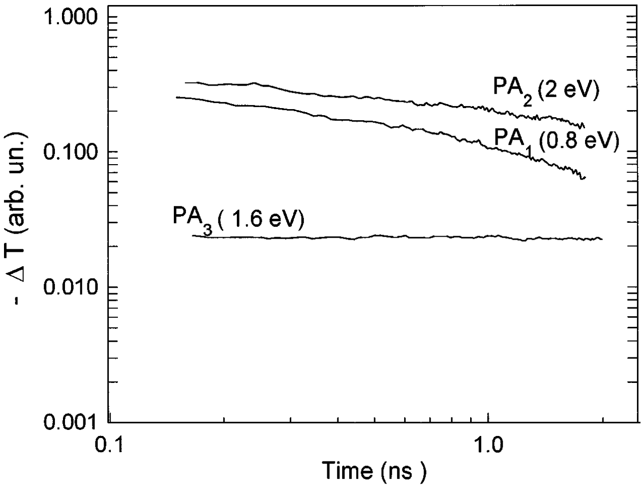

FIG. 3. PA and PL dynamics in T_6 nanocrystalline films. Excitation conditions are the same as for Fig. 1(b).

weak in polycrystalline films. Moreover, comparing PA$_3$ decay to the photoluminescence (PL) decay (Ref. [11]) we find that the two decays are *not* correlated in the ps-ns time domain. (ii) The PA spectrum for isolated molecules in solution shows a single band [assigned to $S_1(B_u) \rightarrow S_n(A_g)$ transitions] at 1.39 eV [15] in disagreement with PA$_3$ at 1.6 eV. A triplet-triplet transition can also be ruled out because PA$_3$ is formed in less than a ps, whereas the intersystem crossing time is estimated to be within a few hundred ps [10]. Optical transitions of uncorrelated charged polarons can also be disregarded because PA$_3$ does not match the PA bands of charged T_6 molecules, observed at 0.8 and 1.54 eV, respectively [5,7]. *We therefore assign PA$_3$ in T_6 nanocrystals to optical transitions of correlated polaron pairs* [18,19], *i.e., a charge transfer (CT) state* [20].

We now discuss the CT formation mechanism. The comparison between the ps and fs PA data is instructive because of the very different excitation conditions. Bimolecular generation via exciton-exciton annihilation may in principle take place at the high excitation density used with the fs laser system ($n \approx 10^{19}$ cm^{-3}) [21], but it is probably insignificant for the ps excitation density ($n \approx 10^{16}$ cm^{-3}). We note that the CT exciton is generated with similar relative probability with both ps (at 2.3 eV) and fs (at 3.2 eV) excitation. Since the optical cross sections for CT and intrachain excitons are comparable in strength [20], we can estimate from the ps PA data the quantum efficiency for CT generation of about 10%. We then speculate that the CT excitons are produced via the lowest lying excited state, in contrast to hot excited state branching. Furthermore, our results indicate that the CT state is formed within 300 fs, which is approximately the initial decay time of PA$_2$. Based on these observations, we propose the following CT generation process. We assume that delocalized Frenkel excitons interact with nearest-neighbor CT states with a strength that is inversely proportional to the energy difference between these states [6]; this energy difference may be small in T_6 because of the low ionization potential and the small nearest-neighbor distance of about 4.9 Å. The coupling between Frenkel and CT states gives rise to an hybridization which allows the CT state to become quickly populated [22]. The PA at 1.6 eV is due to the internal optical transitions related to the ion pair composing the CT state; it may correspond to the 1.54 eV transition (P_2) of isolated polarons [shown in Fig. 4(a)], whereas the second polaron transition (P_1) is pushed to lower energies and may be outside of our experimental spectral range [19].

The CT excitons either recombine (mostly nonradiatively) to the ground state or separate into uncorrelated, isolated charged polarons. These are long-lived species, which can be observed in the ms time domain [5,7]. The long-lived PA spectrum of T_6 at 140 K is shown in Fig. 4(a) for a pump modulation frequency of 200 Hz. There are two PA bands at 0.8 (P_1) and 1.55 eV (P_2). P_1 and P_2 correspond to the respective absorption bands of polarons in doping induced absorption measurements [23], and also based on their spin-1/2 signature in PADMR spectroscopy [7] they can be readily assigned to photogenerated charged polarons. Photoexcitations at μsec times were detected by photomodulation measurements

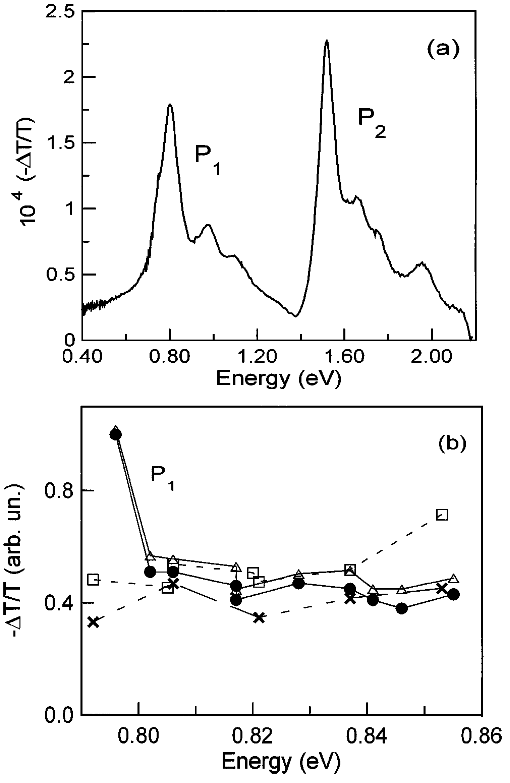

FIG. 4. (a) PA spectrum in T_6 nanocrystalline films at T = 140 K in the ms time domain. (b) PA in T_6 nanocrystalline films in the near infrared region and different time domains: 10 ps (squares); 2 ns (crosses); 250 ns (circles); 10 μs (triangles).

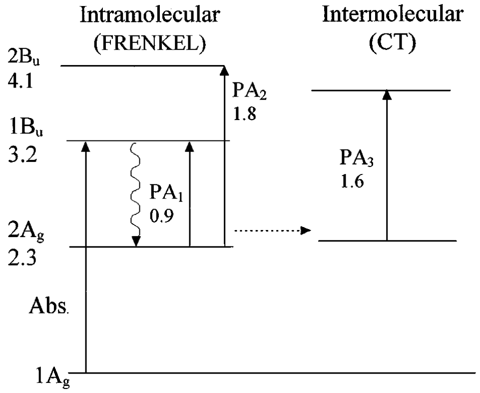

FIG. 5. Electronic energy levels and corresponding optical transitions given in eV in T_6 nanocrystalline films. Wavy and dashed lines show nonradiative transitions.

where the modulation frequency (f_{CH}) was swept from 1 MHz to below 100 kHz. In this case only photoexcitations with formation times and lifetimes $\tau \approx 1/f_{\mathrm{CH}}$ (i.e., $1 < \tau < 10$ μs) can be observed. Figure 4(b) compares ps, ns, and μs data, and it shows that *a PA band in the spectral range at about 0.8 eV, which corresponds to P_1 of polarons, appears in the ns time domain.* This result indicates that the separation of CT excitons into uncorrelated charge polarons occurs in time between 2 ns and 1 μs following pulsed excitation.

We now turn our attention to the photoexcitations related to PA_1 and PA_2 in Fig. 1. The strong reduction of PL efficiency in T_6 nanocrystals may be explained as a result of a lowest lying even parity state ($2A_g$) [14,24] with forbidden direct emission. PL is, however, weakly allowed from X traps located below the even exciton band [25]. Indeed, PL efficiency measured in T_6 films by two photon excitation has located an even parity state at 2.3 eV [26], at the onset of the absorption (Fig. 1, inset). We conjecture that the lowest lying Frenkel exciton in T_6 nanocrystals is of even parity, i.e., an A_g state ($2A_g$), and this may explain PA_1 and PA_2 as due to intrachain exciton transitions, as summarized in Fig. 5. The $2A_g$ state is populated following excitation and subsequent ultrafast thermalization. Then dipole allowed optical transitions to higher lying electronic states of odd parity (B_u) may be observed. We thus identify PA_1 and PA_2 at 0.9 and 1.8 eV, respectively, as transitions from $2A_g$ at 2.3 eV to $1B_u$ and $2B_u$ states at 3.2 and 4.1 eV, respectively (Fig. 5). These latter B_u states can be observed in the linear absorption (Fig. 1, inset), since optical transitions from $1A_g$ to these two states are also dipole allowed. Because of their energy overlap, CT excitons are quickly formed from $2A_g$. Then the CT transition PA_3, which is equivalent to P_2 of isolated polarons, is observed (Fig. 5). Subsequently, some of the CT excitons may dissociate on a sub-μs time scale into isolated polarons with PA bands P_1 and P_2 at 0.8 and 1.5 eV, respectively.

We thank R. Zamboni, M. Ibrahim, and A. J. Frank for supplying T_6 films used in this study. R. Tubino and C. Taliani are acknowledged for fruitful discussion. We also thank W. Gellermann for technical assistance. This work was partially supported by the National Research Council and by INFM. The research at the University of Utah was supported in part by DOE 96ER45490.

---

*Current address: Physics Department, University of Sheffield, Sheffield, UK.

[1] L. F. Lindoy, Nature (London) **364**, 17 (1993).
[2] A. Dodabalapur, L. Torsi, and H. E. Katz, Science **268**, 270 (1995); P. Ostoja *et al.,* Synth. Met. **54**, 447 (1993).
[3] K. Hamano, T. Kurata, S. Kubota, and H. Koezuka, Jpn. J. Appl. Phys. **33**, 1031 (1994).
[4] G. Horowitz *et al.,* Adv. Mater. **8**, 52 (1996).
[5] G. Lanzani *et al.,* Chem. Phys. Lett. **226**, 547 (1994).
[6] M. Pope and C. E. Swenberg, in *Electronic Processes in Organic Crystals* (Clarendon Press, Oxford, 1982).
[7] P. A. Lane *et al.,* Chem. Phys. **210**, 229 (1996).
[8] F. Biscarini *et al.,* Phys. Rev. B **52**, 14 868 (1995).
[9] W. Porzio, S. Destri, M. Mascherpa, and S. Bruckner, Acta Polymer **44**, 266 (1993).
[10] G. Lanzani *et al.,* Phys. Rev. B **53**, 4453 (1996).
[11] S. V. Frolov, Ph.D. thesis, University of Utah, 1996 (unpublished); S. V. Frolov *et al.,* in *Optical Probes of Conjugated Polymers,* SPIE Proceedings Vol. 3145 (SPIE–International Society for Optical Engineering, Bellingham, WA, 1997).
[12] X. Wei, Ph.D. thesis, University of Utah, 1992 (unpublished).
[13] A. Yassar *et al.,* J. Phys. Chem. **99**, 9155 (1995).
[14] F. Garnier *et al.,* in *Optical Probes of Conjugated Polymers,* SPIE'97 Proceedings (Ref. [11]).
[15] F. Charra, D. Fichou, J.-M. Nunzi, and N. Pfeffer, Chem. Phys. Lett. **192**, 566 (1992).
[16] H. Chosrovian *et al.,* Synth. Met. **60**, 23 (1993).
[17] R. S. Becker *et al.,* Pure Appl. Chem. **67**, 9 (1996).
[18] M. Yan *et al.,* Phys. Rev. Lett. **72**, 1104 (1994).
[19] P. Lane, X. Wei, and Z. V. Vardeny, Phys. Rev. B (to be published).
[20] H. A. Mizes and E. M. Conwell, Phys. Rev. B **50**, 11 243 (1994).
[21] G. Lanzani, M. Nisoli, F. Abbate, and S. De Silvestri, Chem. Phys. Lett. **264**, 667 (1997).
[22] J. Kalinowski, W. Stampor, P. Di Marco, and V. Fattori, Chem. Phys. **182**, 341 (1994); C. Taliani and L. M. Blinou, Adv. Mater. **8**, 353 (1996).
[23] D. Fichou, G. Horowitz, B. Xu, and F. Garnier, Synth. Met. **39**, 243 (1990).
[24] M. Muccini *et al.,* Synth. Met. **84**, 863 (1997); Chem. Phys. Lett. (to be published).
[25] M. Muccini *et al.,* Synth. Met. **84**, 599 (1997).
[26] N. Periasamy *et al.,* Phys. Rev. Lett. **68**, 919 (1992).