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Phys. Rev. Lett. **124**, 017401 — Published 8 January 2020

DOI: [10.1103/PhysRevLett.124.017401](https://doi.org/10.1103/PhysRevLett.124.017401)

# Ultrafast Transient Spectroscopy of Trans-polyacetylene in the Mid-infrared Spectral Range

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## Abstract

Trans-polyacetylene, ( $t-(CH)_x$ ) possesses two-fold ground state degeneracy. Using the SSH Hamiltonian it was predicted that charged solitons are the primary photoexcitations in  $t-(CH)_x$ ; this, however has led to sharp debate. To resolve this saga we have used sub-picosecond transient photomodulation spectroscopy in the mid-IR spectral range (0.1-1.5 eV) in neat  $t-(CH)_x$  thin films. We show that odd parity singlet *excitons* are the primary photoexcitations in  $t-(CH)_x$ , similar to many other non-degenerate  $\pi$ -conjugated polymers. The exciton transitions are characterized by two photoinduced absorption (PA) bands at 0.38 eV and 0.6 eV, and associated photoluminescence band at  $\sim 1.5$  eV having similar polarization memory. The primary excitons undergo internal conversion within  $\sim 100$  fs to an even-parity (dark) singlet excitons with PA band at  $\sim 1.4$  eV. We have also found ultrafast photogeneration of charge *polarons* when pumping deep into the polymer continuum band, which are characterized by two other PA bands in the mid-IR and associated photoinduced IR vibrational modes.

Trans-polyacetylene ( $t\text{-(CH)}_x$ ) is the simplest but also the most special  $\pi$ -conjugated polymer since it has two-fold degenerate ground state (DGS), namely ‘A phase’ and ‘B phase’, as shown in Supplemental Materials (S.I.) [1], Fig.S1(a) [2, 3]. The synthesis and following studies of this prototype  $\pi$ -conjugated polymer initiated the field of semiconducting polymers [4, 5]. The misfit between phase A and phase B in the polymer chain forms a domain wall, a nonlinear shape-preserving excitation that is described by Su, Schrieffer and Heeger (SSH) model as soliton, which may be either neutral  $S^0$  [1] (S.I., Fig.S1(b)) or charged  $S^\pm$  (S.I., Fig. S1(c)) [3]. Interestingly the neutral soliton has a single electron, and hence spin  $1/2$ ; whereas the positively and negatively charge soliton has zero or two electrons, respectively, and hence spinless. This leads to the so called ‘reverse spin-charge relationship’, in which the charge species is spinless, whereas the neutral species carries spin  $1/2$ . In particular, this model, which includes electron-phonon (e-p) interaction but neglects electron-electron (e-e) interaction, predicts that upon photon absorption the photoexcited electron and hole pair is unstable, thereby relax within 100 fs to charge soliton-antisoliton ( $S^+S^-$ ) pair with a state in the middle of the optical gap [6]. Therefore, it is expected that in the sub-picosecond (ps) time domain a photoinduced absorption (PA) band is formed, namely from either HOMO to  $S^+$  or  $S^-$  to LUMO as schematized shown in S.I., Fig.S1(d).

Over the years the SSH model has attracted substantive attention, where both experimentalists and theoreticians have tried to prove or disprove the photogenerated  $S^+S^-$  prediction. With time, however other  $\pi$ -conjugated polymers have been synthesized, in which the photophysics is dominated by singlet and triplet excitons [7-10], regardless whether or not their ground state is degenerate. In typical  $\pi$ -conjugated polymers such as polyfluorene, disubstituted polyacetylene and poly(p-phenylene-vinylene) derivatives, it has been shown that the binding energy of the lowest singlet exciton, the  $1B_u$  is of the order of 0.5 eV [11, 12]. The excitons primary photoexcitation species in these polymers indicate that the SSH model is not suitable to describe the photophysics of most  $\pi$ -conjugated polymers. Even in  $t\text{-(CH)}_x$  during the last three decades the study of photoexcitations has revealed several unexpected phenomena, including photogenerated of a neutral excitation, which were not predicted by the SSH model [13-15]. This indicates that the nature of the primary photoexcitations in  $t\text{-(CH)}_x$  may be very different from the  $S^+S^-$  pair predicted by the SSH model. However a decisive experiment that elucidates the

primary photoexcitations in this polymer has not been reported yet.

In this work we have studied the primary photoexcitations in  $t-(CH)_x$  thin films using femtosecond (fs) transient and steady state (cw) photomodulation (PM) spectroscopy in order to resolve the controversy in the literatures. Importantly, since  $t-(CH)_x$  optical gap is at  $\sim 1.5$  eV the sub-ps transient PM spectrum was measured in the mid-IR spectral range, where most of the action in this polymer takes place. We found that within 150 fs the transient PM spectrum is due to *excitons* and *polarons*, of which photogenerated quantum efficiency ratio depends on the excitation photon energy. This is in contrast to the cw PM spectrum which shows long-lived charge solitons that are formed at later times, as byproducts of the primary photoexcitations.

Semi-transparent trans-polyacetylene films were synthesized on IR substrates (sapphire, Caesium Iodide (CsI), and Barium Fluoride (BaF<sub>2</sub>)) by exposure of acetylene gas of six-nine grade to the Ziegler-Natta catalyst tetra-n-butoxytitanium (Ti(O-n-Bu)<sub>4</sub>) and triethylaluminum (AlEt<sub>3</sub>) [detailed sample preparation method is in Ref. [1] of supplemental materials]. The sample handling was done in a glovebox under N<sub>2</sub> atmosphere. All experiments were done with the sample at room temperature in a dynamic vacuum better than 0.1 Pa. Two femto-second laser systems based on Ti:Sapphire oscillator were applied for the optical measurements. A low power ( $\sim 0.1$  nJ of energy/pulse) high repetition rate ( $\sim 80$  MHz) laser for the mid-IR spectral range; and a high power (energy/pulse  $\sim 10$   $\mu$ J) low repetition rate ( $\sim 1$  kHz) laser for the near-IR/visible spectral range. The pump laser for both laser systems was set at  $\hbar\omega = 3.1$  eV, or at  $\hbar\omega = 1.55$  eV. For low power laser, we used an optical parametric oscillator (Opal, Spectral-Physics) and a difference frequency generation crystal that forms  $\hbar\omega$  (probe) ranging from 0.14 to 1.05 eV. Whereas for the high intensity measurements, white light super-continuum was generated for  $\hbar\omega$  (probe) ranging from 1.15 to 2.7 eV (Supp. Materials. [1]). The PM spectrum mainly contains photoinduced absorption (PA) bands with  $\Delta T < 0$  due to excited state absorption, where  $\Delta T$  is the change of the film transmission,  $T$ .

In Fig. 1(a) we show the absorption spectrum of  $t-(CH)_x$  thin film[16]. As seen, the absorption edge is at 1.55 eV; this calls to place the dominant allowed exciton transition, the  $1B_u$  at this energy. We also measured a weak polarized photoluminescence (PL) at 1.41 eV having a phonon side band at 1.37 eV. The  $t-(CH)_x$  film is not stretched-oriented, so that the polymer chains are not aligned. That the PL emission is polarized indicates that it occurs on the sub-ps time scale;

otherwise the PL polarization memory would be lost. The fast PL has been actually confirmed in the literature [17, 18]. We note that the PL emission is not predicted in the soliton SSH model, and this, by itself shows that SSH is not sufficient to describe the photophysics of  $t-(CH)_x$ . The PL polarization degree is defined as  $P_{PL} = (PL_{\parallel} - PL_{\perp}) / (PL_{\parallel} + PL_{\perp})$ , where  $PL_{\parallel}$  ( $PL_{\perp}$ ) is the PL component with polarization parallel (perpendicular) to that of the linearly polarized excitation laser beam. We measured  $P_{PL} \sim 0.25$  at the peak energy of 1.41 eV and remains approximately constant throughout the spectrum.

Figure 1(b) presents the quasi steady state PM spectra of  $t-(CH)_x$  at 80 K and 200 K, respectively, which shows two dominant photoinduced absorption (PA) bands at 0.5 eV (low energy, LE) and at 1.4 eV (high energy, HE). Here the value of the PA signal ( $-\Delta T/T$ ) is of the order of  $10^{-3}$ , thus we have used  $10^3(-\Delta T/T)$  throughout the paper, which means  $10^3$  times ( $-\Delta T/T$ ), as the units in the y-axis. The LE and HE bands have been previously ascribed to the transitions of photogenerated charged soliton ( $S^{\pm}$ ) and neutral solitons ( $S^0\bar{S}^0$ ), respectively [13], the energy diagram of which is shown in Fig. 1(b) inset. The energy difference of 0.9 eV between LE and HE transitions, which has been ascribed as due to the effective electron correlation energy [19], is dramatically different from the zero energy predicted by the SSH model. Therefore, the e-e interaction cannot be ignored [13, 19]. The sharp feature around 0.17 eV is due to photoinduced absorption by infrared-active vibrational (IRAV) modes [20, 21], which result from Raman-active vibrational modes that become infrared-active by the presence of photogenerated charge carriers on the polymer chains. The excitation spectrum of the LE band ( $S^{\pm}$ ) is shown in Fig. 1(c), in which the PA value increases  $\sim$ two orders of magnitude for the excitation photon energy in the range of 1.5 eV to 3.5 eV. This result is consistent with the PM spectrum [22, 23] and photoconductivity action spectra measurements [24].

Figure 1(d) compares the steady state PM spectrum of the IRAV modes measured at 80 K, to the transient PM spectra at  $t=0$  pumped by 1.55 eV and 3.1 eV, respectively at room temperature. The two transient PM spectra are very different from one another. The PM spectrum excited at 3.1 eV shows strong PA at the same photon energy of the IRAV mode at 0.17 eV [20, 25]; whereas the PM spectrum excited at 1.55 eV does not show the increase at low energy. We conclude that the excitation dependence of the charged photoexcitations in the picosecond time

domain agrees with the steady state PM spectrum shown in Fig. 1(c). From this we conjecture that charge photoexcitations are photogenerated within the pulse duration when pumped at 3.1 eV. In contrast, when pumped at the band edge (1.55 eV), the primary photoexcitations are *neutral excitons*.

Figure 2(a) shows transient PM spectra of  $t\text{-(CH)}_x$  film pumped at 1.55 eV, at  $t = 0$  and  $t = 1$  ps, respectively. The PA spectrum is composed of two prominent PA bands in the mid infrared, namely PA<sub>1</sub> at 0.37 eV and PA<sub>2</sub> at 0.64 eV, as well as two PA features in the near infrared, PA<sub>3</sub> at 1.4 eV and two-photon absorption (TPA) with onset at  $\sim 0.9$  eV. Here the TPA is defined as a nonlinear optical process of one photon from the pump beam and one photon from the probe beam. The transient dynamics of the various PA features are shown in Fig. 2(c). The flat transient response at 0.17 eV indicates that charge photoexcitations are not generated when pumped at the band-edge (S.I., Fig. S3). We found that the dynamics of PA<sub>1</sub> and PA<sub>2</sub> are the same, both showing instantaneously photogeneration followed by a fast decay component of  $\sim 110$  fs (S.I., Fig. S4). However, the transient response of PA<sub>3</sub> consists of  $\sim 100$  fs *build-up*, followed by a much slower decay (S.I., Fig. S5). The similarity between the decay rate of PA<sub>1</sub> (or PA<sub>2</sub>) band and the build-up rate of PA<sub>3</sub> band suggests that the two features associated with these bands are connected via internal conversion. In contrast, the TPA feature shows an instantaneous response and fast decay dynamics which follows the cross-correlation trace of the pump and probe beams. This justifies the TPA feature to be ascribed to two photon absorption of pump and probe beams (S.I., Fig. S6 and discussion).

The main transient features shown in Fig. 2 can be fully explained by the exciton picture that has been used to describe the photophysics in most of homopolar  $\pi$ -conjugated polymers. In this picture, the exciton eigenstates are classified as even parity, A<sub>g</sub> and odd parity, B<sub>u</sub> states (Fig. 2(b)) [26-28]. We thus conclude that the 1B<sub>u</sub> exciton is instantaneously photogenerated in  $t\text{-(CH)}_x$  upon photon absorption with energy close to the optical gap ( $E_g$ ). Above the 1B<sub>u</sub> there are a number of B<sub>u</sub> and A<sub>g</sub> states; however the strongest coupling between the 1B<sub>u</sub> and these states is to an even state, so called mA<sub>g</sub>. Thus PA<sub>1</sub> band in Fig. 2(a) is the transition from 1B<sub>u</sub> to mA<sub>g</sub>. In this picture PA<sub>2</sub> band may be a transition from the 1B<sub>u</sub> to another, higher two-photon state, so called kA<sub>g</sub> [26-28]. Although the exciton in  $t\text{-(CH)}_x$  has characteristic PA bands similar to many other polymers in the  $\pi$ -conjugated polymer family, it is still unique because the photogenerated 1B<sub>u</sub> exciton decays within  $\sim 100$  fs to a “dark”, lower lying exciton (so called 2A<sub>g</sub> state) that is

nonradiative [29-34]. The transient PM spectra and decay dynamics clearly show that the generation of  $2A_g$  exciton is at the expense of  $1B_u$  exciton. Importantly, the  $2A_g$ , which is the lowest two-photon state, occurs below the  $1B_u$  in most non-luminescent polymers [29-35]; whereas it lies above the  $1B_u$  in luminescent polymers [36, 37]. The relative ordering of the  $2A_g$  and  $1B_u$  states is a consequence of the relative strength of the e-e interactions [8, 31]. In this model the  $PA_3$  band is due to a transition from  $2A_g$  to higher  $B_u$  state, namely  $kB_u$ , with slower decay (S.I. Figs. S5(a) and Fig. S7); or, alternatively is due to a breather mode in the polymer chain [38].

We also measured the transient polarized PM with 1.55 eV pump excitation, as shown in Fig. 2(d). The Polarization memory degree,  $P$  is defined as  $P = [(\Delta T/T)_{||} - (\Delta T/T)_{\perp}] / [(\Delta T/T)_{||} + (\Delta T/T)_{\perp}]$ , where  $||$  and  $\perp$  denote the polarization of pump probe beams either parallel or perpendicular to each other. As seen in Fig. 2(d)  $P = 0.25$  during the  $PA_1$  lifetime ( $\sim 0.11$  ps). This supports the assignment of  $PA_1$  as due to excitons, since it agrees with the PL polarization degree of 0.25 shown in Fig. 1(a) inset.

Figure 3(a) presents the transient PM spectra of the same  $t-(CH)_x$  film at  $t = 0$  and  $t = 10$  ps, respectively, excited at 3.1 eV. The PM spectrum contains two PA bands, peaked at  $\sim 0.45$  eV ( $P_1$ ) and 0.9 eV ( $P_2$ ), which are different from the bands  $PA_1$  and  $PA_2$  as well as the LE PA band (0.5 eV) in the steady state PM shown in Fig. 1(b). Furthermore,  $P_1$ ,  $P_2$  and IRAV share the same dynamics (Fig. 3(c)), which suggests that they belong to the same photoexcitation species. Since the photoexcitations here are charged, but do not agree with charge solitons ( $S^{\pm}$ ), we identify the primary photoexcitations as polarons. The energy diagram model of charge polaron in the gap, and related optical transitions are well known in the literature as shown in Fig. 3(b) [8, 10, 13, 19, 29]. Following this model the energy difference between the polymer HOMO and LUMO may be estimated from the relation:  $E_g = 2P_1 + P_2$ . Consequently we get  $E_g = 1.81$  eV. This energy differs from the absorption edge  $\sim 1.55$  eV and the PL peak  $\sim 1.41$  eV. From these results it is possible to estimate the exciton binding energy,  $E_B$  in  $t-(CH)_x$  to be  $1.81 - (1.55 + 1.41)/2 = \sim 0.33 \pm 0.04$  eV (S.I., Fig.S8). The obtained  $E_B$  is smaller than that in other  $\pi$ -conjugated polymers [8], but is larger than  $k_B T$  at room temperature; therefore the excitons in  $t-(CH)_x$  are stable at ambient.

We found that the polaron transient PA(t) decays as a power law  $(t/t_0)^{-\alpha}$ , with  $\alpha \sim 0.5$  for  $t < 10$  ps, followed by  $\alpha \sim 0.13$  for  $t > 10$  ps (see Fig. 3(c) and Fig. S9). In general, a power law decay of the form  $(t/t_0)^{-\alpha}$  may originate from a distribution of lifetime,  $g(\tau)$  with the form of  $\tau^{-(1+\alpha)}$  [39], or dispersive diffusion towards recombination centers [40]. We adopt the former explanation since the polymer film is disordered. In addition we found that the transient response of the photogenerated polarons also has polarization memory (Fig. S10), where  $\Delta T_{\parallel} > \Delta T_{\perp}$ . Since the photoinduced anisotropy decays relatively slow we therefore believe that the photogenerated polarons are still subjected to quasi-one-dimensional environment even at 3.1 eV pump excitation. The polarons may be photogenerated directly by the high energy photons because the 3.1 eV is much larger than the continuum band in  $t-(CH)_x$  [41, 42]. Alternatively, the photogenerated polarons may be a byproduct of hot exciton dissociation since the exciton binding energy is  $\sim 0.33$  eV, whereas the photon energy is 1.5 eV higher than the optical gap [43]. It is worth noting that no PA related to charge soliton pairs (characterized schematically in Fig. S1(d)) has been observed in the transient PM spectra, irrespective of the pump photon energy [44]. We thus conclude that the SSH model is *unable* to describe the intrinsic photophysics of  $t-(CH)_x$ .

In conclusion; depending on the excitation photon energy, both singlet excitons (binding energy of about  $\sim 0.33$  eV) and polarons are instantaneously photogenerated in  $t-(CH)_x$ . Importantly, no soliton-antisoliton pairs are photogenerated directly upon photon absorption. With these findings the saga of photoexcitations in  $t-(CH)_x$  has been solved. The photophysics of  $t-(CH)_x$  in the ps time domain is governed by a dark exciton that lie below the allowed exciton state, but otherwise is in agreement with other homopolar  $\pi$ -conjugated polymers.

### Acknowledgements:

This work was supported by the National Science Foundation grant (DMR-1701427). C.X.S. thanks the support of National Natural Science Foundation of China (Nos. 61874056, 61574078, 61627802). Y.M.P. thanks the support of the Korean-Swedish Basic Research Cooperative Program of the NRF (No. NRF-2017R1A2A1A18070721), Korea. K.H.K thanks the support of the Swedish Foundation for Strategic Research (SSF) (No. IS14-0053, RMA15-0024).

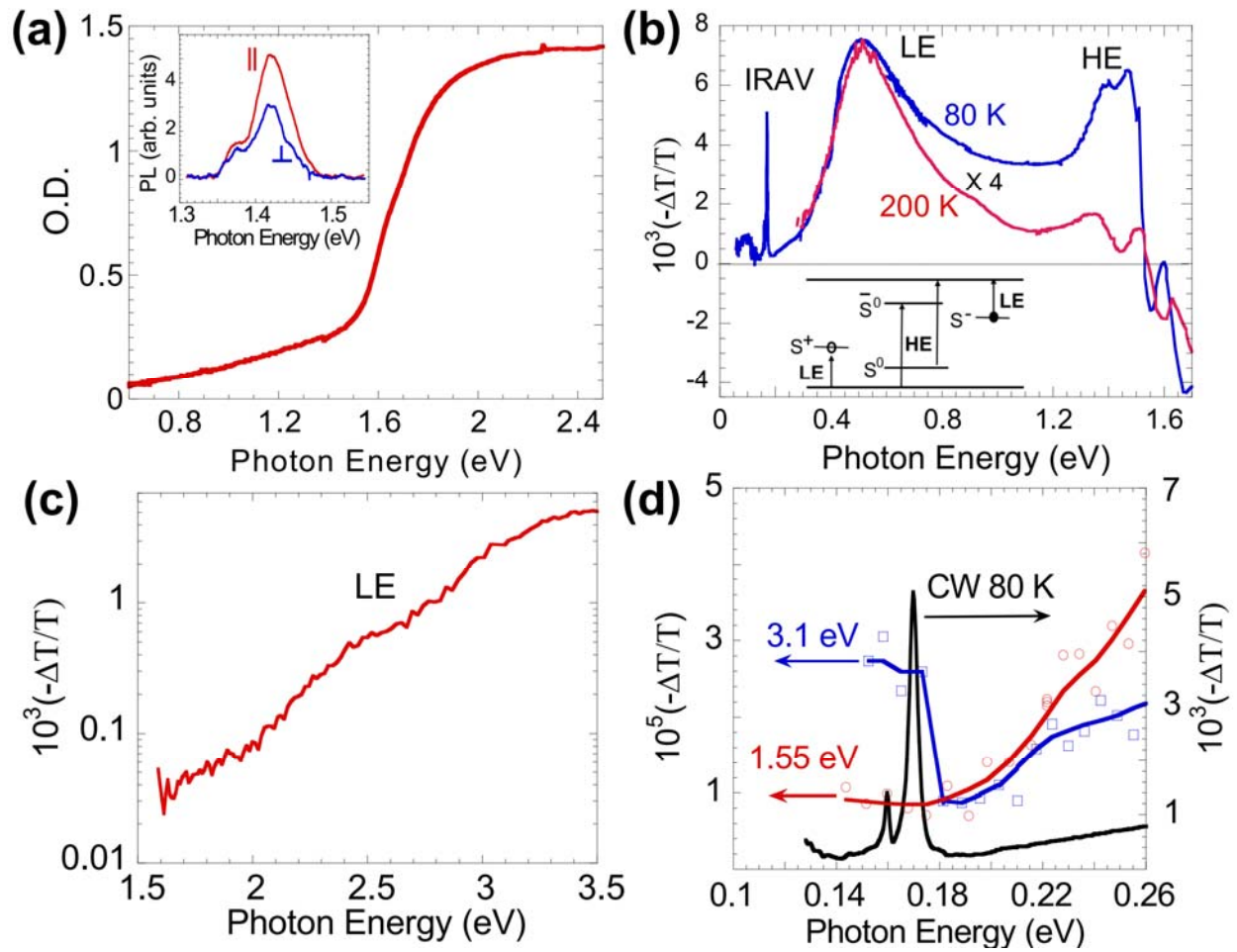


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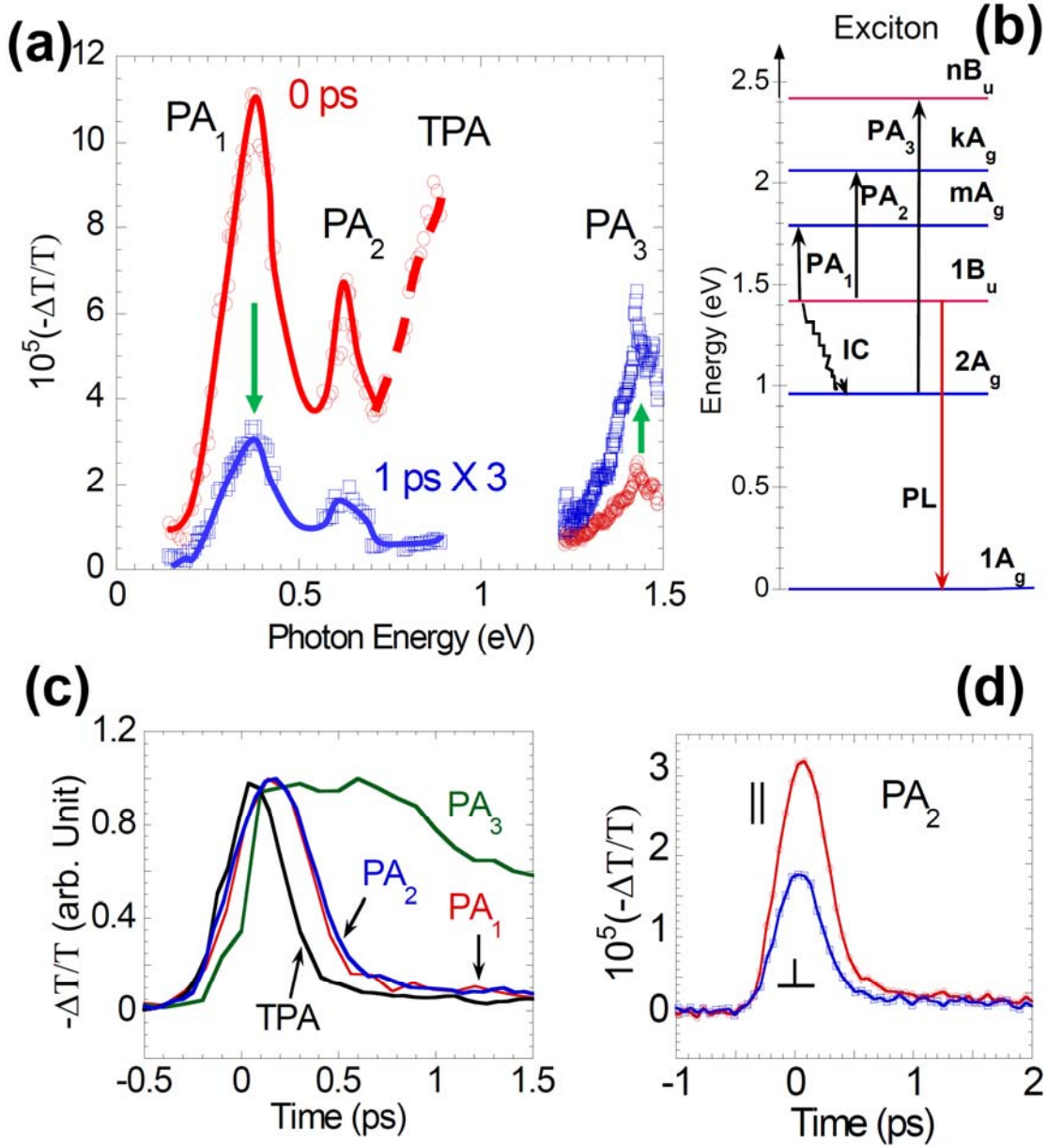
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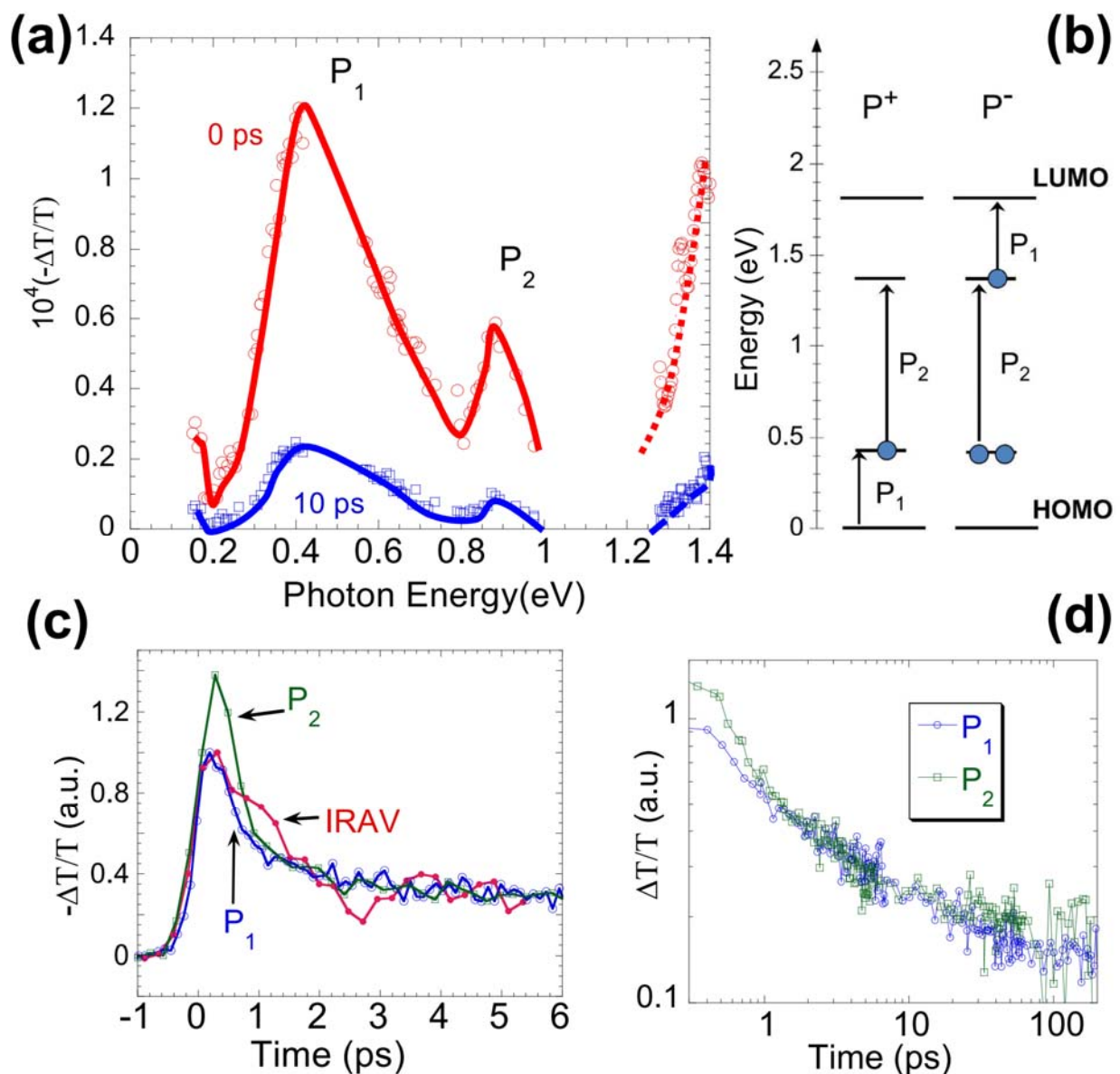
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**Figure 1** (a) The absorption spectrum of  $t-(CH)_x$  thin film. The inset is the parallel (||) and perpendicular (⊥) components of the polarized PL emission spectrum respect to the polarization of the pump excitation. (b) CW photomodulation spectra of  $t-(CH)_x$  at 80K and 200K, respectively. The LE PA band was identified as due to  $S^\pm$  [13, 19], whereas the HE PA band was ascribed to  $S^0$  [13]. (c) Action spectrum of the LE PA band in the steady state PM spectrum. (d) Transient PM spectra of  $t-(CH)_x$  film pumped at 3.1 eV (blue squares and line) and 1.55 eV (red circles and line) compared with the steady state PM spectrum (black line) measured at 80 K. The lines through the data points are to ‘guide the eye’.



**Figure 2** Transient PM spectra and decay dynamics of  $t-(CH)_x$  film in the mid-IR spectral range excited at 1.55 eV. (a) The transient PM spectra at  $t=0$  (red circles) and  $t=1$  ps (blue squares); the lines through the data points are to guide the eye. Various bands are assigned (defined in the text) TPA is pump-probe two photon absorption (b) Schematic of the energy levels and optical transitions of singlet excitons.  $1B_u$ ,  $nB_u$ ,  $1A_g$ ,  $2A_g$ ,  $mA_g$  and  $kA_g$  are odd and even parity exciton states in the neutral manifold. IC is the Internal Conversion from  $1B_u$  state to  $2A_g$  state. (c) The transient rise and decay dynamics of the main PA bands assigned in (a). (d) Transient polarized response of  $PA_2$ ; both  $\Delta T_{\parallel}$  and  $\Delta T_{\perp}$  components are shown.



**Figure 3** Transient PM spectra and decay dynamics of  $t-(CH)_x$  film in the mid-IR spectral range excited at 3.1 eV. (a) The transient PM spectra at  $t=0$  (red circles) and  $t=10$  ps (blue squares); the lines through the data points are to guide the eye. Various PA bands are assigned. (b) Schematic of the energy levels and optical transitions of charge polaron excitation. HOMO (LUMO) is the highest (lowest) occupied (unoccupied) molecular orbital in the charge manifold. (c) The transient decay dynamics of the main PA bands assigned in (a). (d) Transient decay dynamics of the  $P_1$  and  $P_2$  bands plotted in log-log scale.