# Mechanism of Carrier Photogeneration and Carrier Transport in Molecular Crystal Tetracene

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Models for the carrier photoexcitation mechanism in molecular crystals have been established initially on the bases of measurements on oligoacenes and later applied to conjugated polymers as well. These models emphasize the localized nature of photoexcitations and describe carrier generation as a secondary process involving exciton dissociation. The results of our photoconductivity studies of single crystal tetracene are at variance with these widely accepted models, and in fact indicate that the photocarrier quantum efficiency appears independent of temperature, photon energy, and light intensity, thus featuring the hallmarks of direct interband carrier photogeneration and coherent carrier transport at band states.

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Oligoacenes crystals have been studied extensively since the 1960s and are a model system for the class of molecular crystals [1,2]. In recent years, the recognition of their potential for device applications has created a renewed interest in their fundamental properties [3–5]. However, despite the extensive research, the nature of the charge transport and photoexcitations in organic molecular crystals as well as conjugated polymers remains controversial [6–10].

A particular research focus has been the mechanism of carrier photoexcitation, as it has been considered a sensitive gauge for the extent of the photocarrier delocalization [1,2]. The emerged picture has been of photoexcitations which are highly localized, forming tightly bound geminate electron-hole ($e$-$h$) pairs, and of mobile carrier photogeneration occurring via a secondary process of dissociation of these bound states due to phonon scattering, external electric field ($F$), and/or excess photon energy ($h\nu$). Indeed, the models developed initially for molecular crystals (e.g., the Onsager model) predicted carrier photoexcitation quantum efficiency ($\phi$) strongly dependent on temperature ($T$), $F$, and $h\nu$ [1,2].

This general picture has been applied later to conjugated polymers as well [6]. However, it has been found that the behavior of $\phi$ in conjugated polymers is at variance with the above predictions and, in particular, that $\phi$ is independent of $T$, [9,10] and the question of carrier generation in conjugated polymers is still debated [6]. In this Letter we present our studies of the carrier photoexcitation mechanism in crystalline tetracene. As will be demonstrated, our fast transient photoconductivity measurements are at variance with the ''exciton model'' of carrier photoexcitations and support carrier photoexcitation via interband excitation and transport at band states.

It is noteworthy that the initial scenario of carrier photoexcitation in oligoacenes was established mainly by the observation of thermally activated photocurrent, where the activation energy $\Delta E$ was found to be dependent on the excitation photon energy (i.e., $\Delta E$ decreasing with increasing $h\nu$). Based on this observation, it has been assumed that a greater thermalization radius (defined as the average distance between the geminate bound carriers) can be achieved when a larger excess energy is imparted to the carriers upon photoexcitation, leading to a lower binding potential between the carriers and thus higher carrier quantum efficiency [1,2].

In organic photoconductors, it is usual for more than a one transport mechanism to be operative, thus preventing a straightforward interpretation of the experimental data. The most important transport mechanisms include a short-lived one due to photocarriers occupying extended states, and long-lived carrier hopping (typically at $t >$ 100 ps after photoexcitation) that involves carrier trapping and detrapping from localized states [9–11]. Thus, in order to probe the carrier generation process before significant carrier recombination and carrier trapping occurs, the following experimental approaches can be used: (1) probing the transport in samples with low density of traps, so that the trap-limited transport is greatly minimized; (2) probing the transport promptly after pulsed photoexcitation. In the present studies, we have implemented both approaches by using single crystalline tetracene and probing the photoconductive response signal with $\sim$100 ps temporal resolution. In order to elucidate the distinct contribution of these carrier transport mechanisms at different time regimes, we also present the results of steady-state photoconductivity measurements obtained from the same sample used for the transient photoconductivity studies.

The tetracene crystals ($\sim 25$ $\mu$m thick) used were grown by the methods described elsewhere [12]. Two planar metallic electrodes consisting of a thin ''sticking'' Ti layer and a Au top layer were vacuum deposited onto the $ab$ crystalline plane of the crystals, leaving a gap of 30 mm long and 600 mm wide (which define the dimensions of the

 

tetracene photoconductor) [12]. The photoconductive Auston switch [13] used for the transient photoconductivity measurements was achieved by incorporating the sample onto the microstrip line electrodes that were predeposited on an alumina substrate. The optical excitation was generated by the second, third and fourth harmonic of a Ti:sapphire laser system (pulse duration of $\sim$100 fs) and the transient photocurrent was measured using a fast boxcar integrating system; the overall system temporal resolution ($\Delta t$) was about 100 ps. All measurements were performed while the sample was kept in vacuum (pressure of $<10^{-4}$ Torr). Low temperatures, down to 160 K, were obtained using a Helitran cryogenic system.

The steady-state photocurrent was measured using a conventional modulation technique, where an Argon laser beam (tuned at $h\nu = 2.71$ eV or 3.63 eV and chopped at 166 Hz) was used for photoexcitation in conjunction with a lock-in amplifier for measuring the photocurrent.

Figure 1 displays the transient photocurrent (PC) waveforms measured at various temperatures at an external field of $F = 83$ kV/cm, photon energy $h\nu = 3.10$ eV, and pulse excitation energy of $I = 53$ $\mu$J/cm$^2$. The data show an increasing prompt transient photoconductive signal at low temperatures where the peak PC (seen in the bottom of Fig. 2) could be fitted to a power law PC $\sim T^{-2.09}$. Considering that the measured mobility in tetracene follows a similar functional dependence on temperature, [4,5] i.e. $\mu \sim T^{-2}$ and that the PC signal is proportional to the product of $\mu\phi$, it follows that in tetracene $\phi$ is independent of $T$ in the temperature range studied, between 180–380 K. It is noteworthy that a weaker dependence than $\mu \sim T^{-2}$ (e.g., $\mu =$ const. or $\mu \alpha T$) was reported for relatively low quality samples [4]. We ruled out such a behavior in our samples since it would implied that $\phi$ increases sharply as $T$ is reduced, a behavior that to our knowledge has never been seen in any system (and would have been in even sharper disagreement with previous models for the carrier photoexcitation in molecular crystals). The dependence of $\mu \sim T^{-2}$ is expected theoretically when the acoustic phonon scattering dominates the carrier relaxation [14]. Increasing mobility at the low temperature regime has been found for other oligoacenes crystals as well [7,8,15–17]. Cooling below the structural phase transition at $T = 160$ K resulted in cracking the tetracene samples, which prevented measurements at lower temperatures. We note that a model based on an argument of local heating due to the excess photon energy has been suggested for the $T$-independent carrier quantum efficiency in conjugated polymers [18]. However, such a mechanism would predict a higher $\phi$ at higher

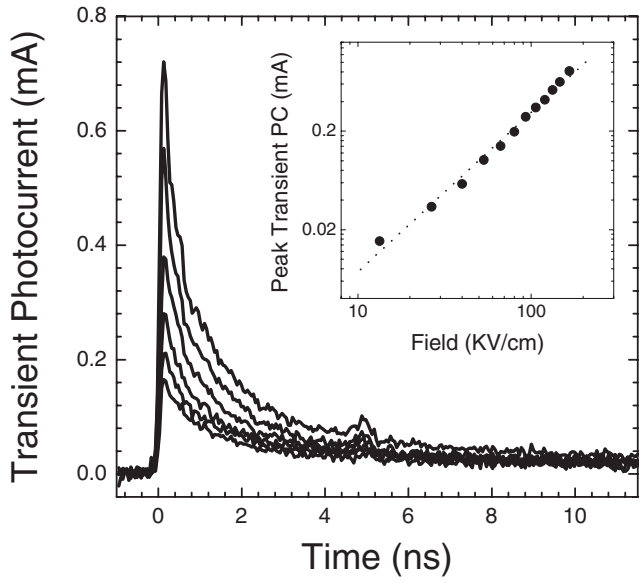


FIG. 1. Transient PC waveforms measured at various temperatures (listed from top to bottom): 181, 221, 262, 301, 341, and 378 K; $h\nu = 3.10$ eV, $I = 53$ $\mu$J/cm$^2$ per pulse and $F =$ 83 kV/cm; the inset depicts a logarithmic plot of the field dependence of the peak transient PC (dots) measured at room temperature with $I = 53$ $\mu$J/cm$^2$ per pulse as well as a fit to the data (dotted line) from which a power law dependence of PC $\sim F^{1.6}$ was deduced.

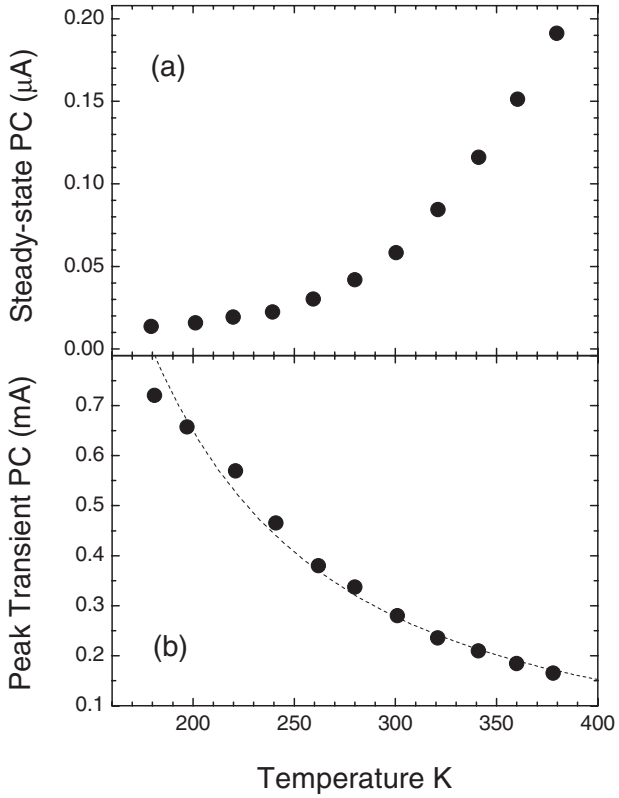


FIG. 2. Temperature dependence of the steady-state PC measured at $h\nu = 2.71$ eV using $F = 10$ kV/cm, $I =$ 2.7 mW/cm$^2$, and modulation frequency of 166 Hz (a) and of the peak transient PC measured using $h\nu = 3.10$ eV, $I =$ 53 $\mu$J/cm$^2$ per pulse, and $F = 83$ kV/cm (b); the dashed line represents the best power law fit to the data from which a $T^{-2.09}$ dependence was deduced.

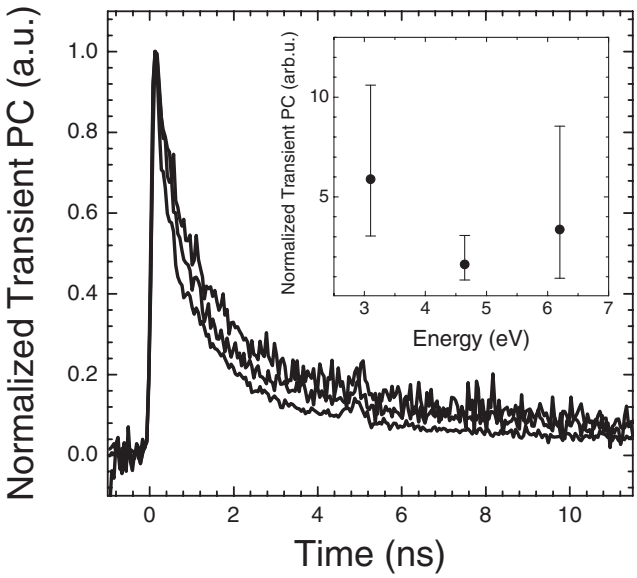


FIG. 3. The transient PC waveforms displayed in Fig. 1 (181, 301, and 378 K) normalized at the peak PC; the inset shows the excitation spectrum of the peak transient PC at few excitation photon energies measured, normalized to the number of incident photons per unit area.

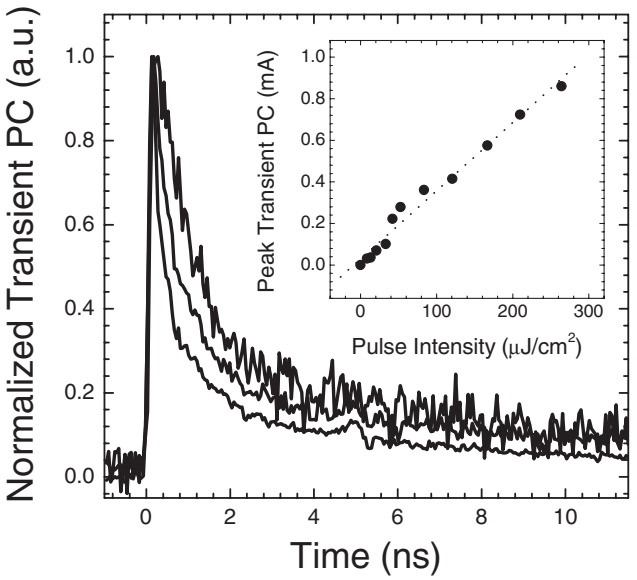


FIG. 4. Normalized transient PC waveforms obtained at various excitation intensities ($h\nu = 3.10$ eV, $T = 330$ K, $F = 83$ kV/cm); the pulse intensities used from top to bottom were: 33 $\mu$J/cm$^2$, 83 $\mu$J/cm$^2$, and 264 $\mu$J/cm$^2$; the inset shows the dependence of the peak transient PC on excitation intensity (dots) and a linear fit to the data (dotted line).

photon energies, contrary to the observations described in the following.

The PC waveforms shown in Fig. 1, normalized to a constant PC peak value, are shown in Fig. 3; the data indicate a second longer-lived transport mechanism characterized by an opposite $T$ dependence than that of the peak PC, as evidenced by the reduction of the PC "tail" at the low temperature regime. The above data thus identify two transport mechanisms corresponding to an initial short-lived one due to carriers occupying extended states and a longer-lived one due to hopping among localized states as well as between localized states and extended states. The carrier "freeze out" at trap sites at low temperatures is manifested by the decrease of the photocurrent "tail" [9–11].

The peak PC (observed at $t \sim 100$ ps following a pulsed excitation) is linearly dependent on excitation intensity (as seen from the inset of Fig. 4), consistent with a direct interband carrier photogeneration process. However, the PC rate of decay increases at higher intensities as is evidenced from the normalized PC data shown in Fig. 4, a behavior that indicates a bimolecular carrier recombination process operating at relatively high intensities.

So far we have described the data generated using the second harmonic of the Ti-sapphire laser fundamental, at $h\nu = 3.10$ eV. We have measured also the room temperature photoconductive response at the third and the fourth harmonics, at 4.64 and 6.20 eV, respectively, while keeping identical external field of $F = 83$ kV/cm. At high photon energies the probability of electron photoemission and the acceleration of the emitted electrons by the fringe external field above the sample increases. Such an extrinsic photoeffect can contribute positively to the overall measured photocurrent, [19] and to mitigate this effect for the purpose of determining bulk photoconductivity, we conducted the measurements while the sample chamber was filled with the electron quenching gas mixture of $CO_2 + SF_6$ (90%:10%). The results for the peak transient PC (normalized for a constant number of incident photons per unit area) measured at the above photon energies are depicted in the inset of Fig. 3. The data indicate that within experimental error (originating mostly from the variation in the laser beam profile at the different photon energies), the peak PC was found insensitive to excitation energy.

In contrast to the linear dependence of the photoconductivity in conjugated polymer poly(phenylene vinylene) (PPV), we find the PC in tetracene to be moderately dependent on applied field $F$, following PC $\sim F^{1.6}$ (as depicted in the inset of Fig. 1). The origin of this behavior is not clear. It is noteworthy that if exciton dissociation due to the external field is the reason for this behavior, the field regime in which this functional dependence is observed would imply an exceedingly small exciton binding energy, [20] much smaller than the one expected from systems supporting localize excitations but akin systems described by a band model.

In the following we present the results of steady-state PC measurements. The dependence of the steady-state PC on $T$ obtained from measurements where the laser was tuned at $h\nu = 2.71$ eV is shown in the top panel of Fig. 2(a); similar $T$ dependence was observed when the Argon laser

beam was tuned at its UV output range (comprising mostly $h\nu = 3.63$ eV). The results indicate a decreasing steady-state photocurrent as the temperature is reduced (an opposite behavior to that displayed by the peak transient PC) that eventually starts to level off at the lowest temperatures. This behavior can be understood considering that the steady-state PC consists of two transport mechanisms due the short- and long-lived carriers, characterized by an opposite $T$ dependence. At room temperature, the steady-state PC is dominated by the thermally activated long-lived transport. However, as $T$ is reduced, the contribution of the long-lived transport decreases, while that due to the short-lived one (arising from carriers occupying extended states) increases, resulting in a modified PC dependence on $T$.

Assuming the sum of the electron and hole mobility at room temperature is $\mu \sim 0.7$ cm$^2$/V s, [4,5] and considering that the peak transient photocurrent density is given by $J^{\text{peak}} = e\phi N\mu F$, where $e$ is the electron charge and $N$ is the absorbed photon density, we estimate a lower bound value for the carrier quantum efficiency in tetracene as measured at 100 ps after excitation to be $\phi > 5 \times 10^{-2}$; this is a lower bound value as it was derived assuming complete optical absorption of the excitation light in the sample (i.e., zero optical reflection and transmission from the sample) and zero carrier recombination and trapping promptly after photoexcitation, during a time span comparable to the measuring system temporal resolution ($\Delta t =$ 100 ps).

The observations of photocarrier quantum efficiency independent of temperature, photon energy, and light intensity suggest a direct interband carrier photoexcitation mechanism operating in tetracene. The $T$ dependence of the mobility at short times following pulsed excitation and its relatively large magnitude indicate the existence of a coherent transport operating in crystalline tetracene. No indication of a transition from hopping to a band transport is indicated by the experimental data, [14,21] as the photocurrent was found to increase monotonically as $T$ was reduced, in the studied temperature range of 180–380 K. The behavior of the transport suggests a greater spatial extent of the carrier delocalization in crystalline tetracene as compared to the one tacitly assumed before, and carrier photoexcitation via interband transition, in agreement with previous studies of anthracene [7], pentacene [8], as well as conjugated polymers [9,10,19,22,23]. Finally, our studies elucidate the role of the two transport mechanisms operating in molecular crystals and the way they are manifested in transient and steady-state photoconductivity measurements.

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