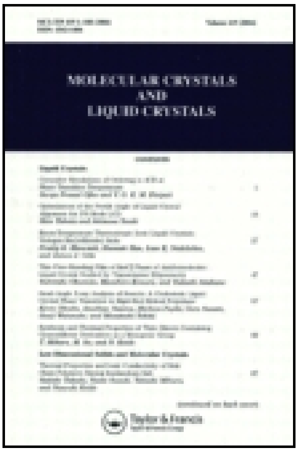

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Photoinduced Absorption Study of Sexithiophene; Evidence for Photogeneration of Polarons

J. Poplawski [a] , E. Ehrenfreund [a] , J. Cornil [b] , J. L. Brédas [b] , R. Pugh [c] [d] , M. Ibrahim [c] & A. J. Frank [c]

[a] Department of Physics and Solid State Institute, Technion-Israel Institute of Technology, Haifa, 32000, Israel

[b] Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut, B-7000, Mons, Belgium

[c] National Renewable Energy Laboratory (NREL), 1617 Cole Boulevard, Golden, CO, 80401, USA

[d] Tennessee Valley Authority, Muscle Shoals, AL, 35660, USA

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PHOTOINDUCED ABSORPTION STUDY OF SEXITHIOPHENE; EVIDENCE FOR PHOTOGENERATION OF POLARONS

J. POPLAWSKI[a], E. EHRENFREUND[a], J. CORNIL[b], J.L. BRÉDAS[b], R. PUGH[c,#], M. IBRAHIM[c] AND A.J. FRANK[c]

[a] Department of Physics and Solid State Institute, Technion–Israel Institute of Technology, Haifa 32000, Israel

[b] Service de Chimie des Matériaux Nouveaux, Université de Mons–Hainaut, B–7000 Mons, Belgium

[c] National Renewable Energy Laboratory (NREL), 1617 Cole Boulevard, Golden, CO 80401, USA

Abstract We have studied films of neutral $6T$ using photoinduced absorption spectroscopy. Two pairs of strong and weak narrow absorption lines are observed at 0.80 (strong), 0.96 (weak) and 1.54 (s), 1.68 (w) eV, respectively. They are very similar in energy, width and shape to those found in the radical cation $6T^{\bullet+}$. We therefore assign them to long lived photoinduced polarons (radical ions). The observed polaron spectrum is in very good agreement with energy level calculations of $6T$. In addition, there is a weak separate line at 1.1 eV that is close in energy to the position of the dication related band (1.2 eV).

INTRODUCTION

The model thiophene oligomer, sexithiophene, $6T$, and its alkyl substituted derivative didodecylsexithiophene, $D6T$, were shown to support polaron and bipolaron like defects when oxidized or reduced by various dopants.[1, 2] Fichou et al[1] have shown that the absorption spectrum of the radical cation $6T^{\bullet+}$ consists mainly of two strong bands (each with a pronounced shoulder on its high energy side) which collapse into a single band (again with a high energy pronounced shoulder) when the oligomer is further oxidized to its $6T^{++}$ spinless form. Recently, Bäuerle et al[2] observed similar behavior for the reduced forms of didodecylsexithiophene, $D6T^{\bullet-}$ and $D6T^{--}$. It therefore appears that for the six ring oligomer, the radical ions (positive and negative polarons) are characterized mainly by two electronic transitions, while the divalent ions (positive and negative bipolarons) show only a single absorption band. This observation is in apparent contrast with the generally assumed spectra of polarons[3] and bipolarons[4] in long polymers. Namely, that polarons are characterized by three optical transitions and the absorption spectrum of bipolarons is composed of two bands.[5]

In order to examine polaron/bipolaron defects without the presence of counter ions (as is the case in the doped oligomers, mentioned above), we have studied the absorption spectra of the photoexcited neutral oligomer. We have found that the photoinduced absorption (PA) spectrum is strikingly similar to that of $6T^{\bullet+}$, indicating the presence of photogenerated positive polaron. We have also found that the spectrum can be accounted for theoretically by calculating the energy levels and absorption spectrum of the singly oxidized sexithiophene oligomer.

RESULTS

Photoinduced absorption

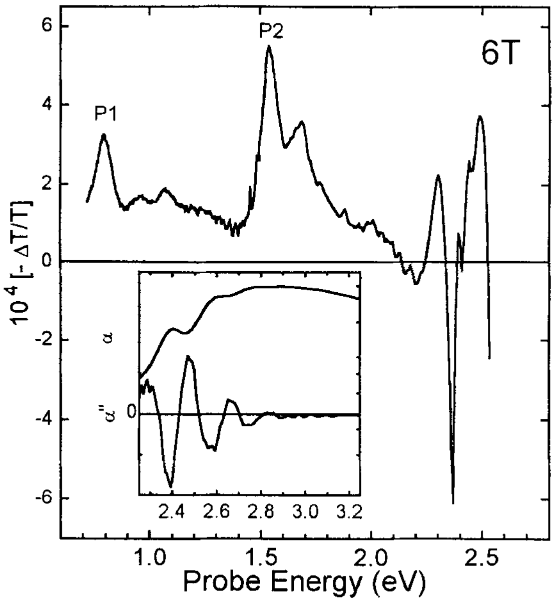

Fig. 1 The photoinduced absorption spectrum, $-\Delta T/T$, of $6T$ film taken at ≃85 K, excited at 2.708 eV @$0.2 W/cm^2$. The inset shows the film linear absorbance (upper trace) and its second derivative with respect to energy (lower trace).

The $6T$ was prepared by a literature method[6] and was purified by sublimation. Thin films were vapor deposited onto glass slides at reduced pressure (10^{-6} Torr). The photoinduced changes in the transmission were measured using a phase sensitive detection technique recording both the in-phase and out of phase components. The exciting pump beam (4579 Å of the ion argon laser) was modulated by an acousto optic modulator in the frequency range 10 Hz–120 kHz.

In Fig. 1 we display the photoinduced absorption spectrum of $6T$ at ≃85 K, in the energy range 0.7–2.6 eV. The spectrum consists of two strong bands, marked P1 (at 0.80 eV) and P2 (at 1.54 eV), and additional smaller absorption bands at 0.96, 1.08 and 1.68 eV. In addition, there is a derivative-like strong feature in the vicinity of ≃2.4 eV. This last feature appears to be related to the second derivative of the film absorption spectrum, shown in the inset of Fig. 1. The upper part of the inset shows the linear absorption spectrum of the film in the vicinity of the HOMO–LUMO transition. The spectrum shows typical vibronic structure, and we identify the 0-0 transition at 2.40 eV, with the 0-1 transition at 2.58 eV and the 0-2 at $\simeq$2.75–2.80 eV. The lower inset shows the second derivative of this spectrum. As can be seen, it is similar to the derivative-like feature of the PA. We therefore associate the derivative like feature with electro-absorption arising from photoexcited charge species. Further evidence for the photogeneration of charged defects, is obtained from the photoinduced infrared active vibration absorption spectrum observed in films with KBr substrates (not shown here). We note that Lanzani et al[8] have observed a similar PA spectrum for 6*T* (in the overlapping range of measurements, 0.6–1.6 eV), while Janssen et al[9] have observed totally different PA spectrum in alkyl-substituted sexithiophene, which was attributed to triplet excitons.

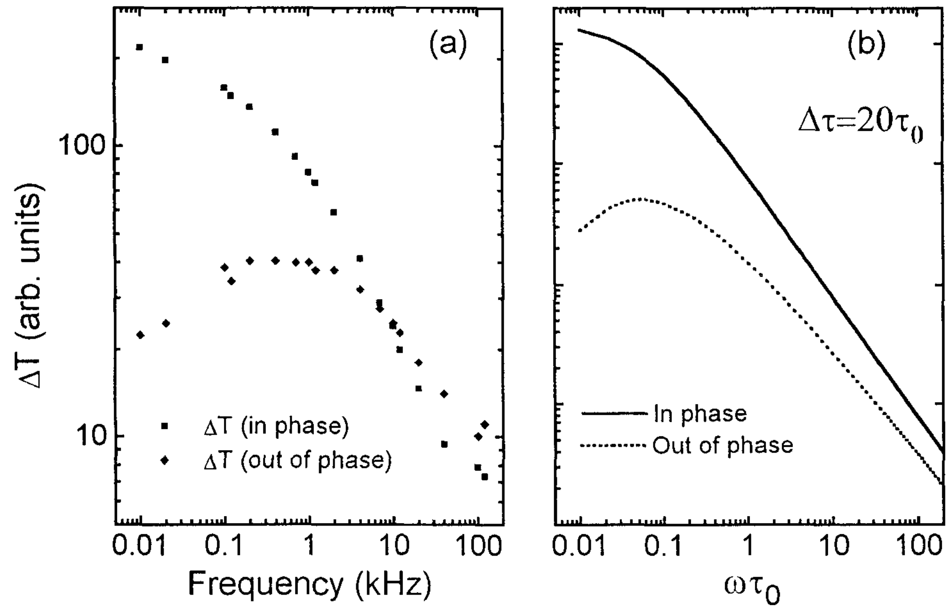

Fig. 2 (a) The modulation frequency, ν, dependence of the PA of the lower energy band, P1 (Fig. 1). Both the in-phase and out of phase signals (with respect to the pump beam) are shown. Note the log–log scale.

(b) Model prediction for the in-phase and out of phase signals, assuming a Lorentzian distribution of lifetimes, as a function of $\omega\tau_0$ ($\omega = 2\pi\nu$ and τ_0 is the distribution center). The distribution width is $\Delta\tau = 20\tau_0$. Note the log–log scale.

The two bands P1 and P2 are correlated via their pump intensity and modulation frequency dependencies. They both show similar sublinear dependence on the laser intensity, with a tendency towards saturation at high photon flux. Their dependence on the pump modulation frequency is also similar and in Fig. 2a we show that of P1. The out of phase signal has a maximum at $\nu_{max} \simeq 0.8$ kHz, indicating an effective lifetime of $\simeq (2\pi\nu_{max})^{-1} = 0.2$ msec. Yet, the in-phase signal increases with decreasing frequency even for the slowest modulation used (10 Hz). At very high frequencies ($\nu > 10$ kHz) the in-phase signal decreases as $\nu^{-0.6}$. We note here that for a simple mono-molecular recombination process, the in-phase signal should approach a constant value for $\nu << \nu_{max}$ and should behave as ν^{-2} for $\nu >> \nu_{max}$. Thus the modulation frequency dependence of both the in-phase and out of phase PA, strongly suggests that there is a distribution of characteristic life times for the charged photoinduced defects. We shall discuss this point in more detail below.

Calculated structure and absorption of $6T^{\bullet+}$

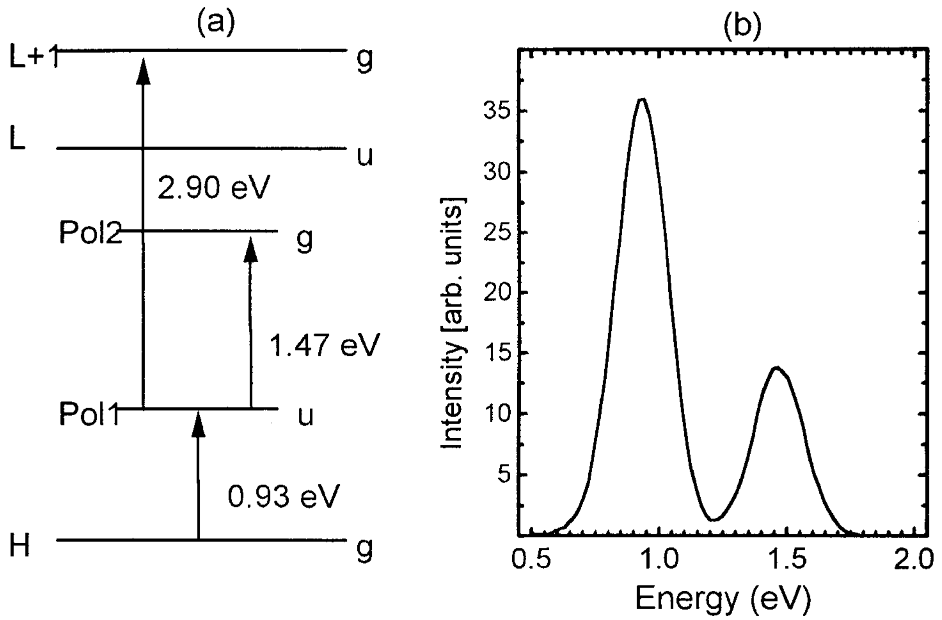

Fig. 3 (a) Energy level diagram and transition energies calculated by the VEH method for the sexithiophene radical cation. The parity of the molecular levels are also indicated.

(b) Optical absorption calculated at the INDO/SCI level for $6T^{\bullet+}$.

We have carried out geometry optimization of the oligothiophene radical cation by means of the semiempirical Hartree-Fock Austin Model 1 (AM1) method, parametrized to reproduce the correct geometries at the ground state. The detailed calculations will be presented elsewhere. [7] On the basis of this geometry, the transition energies are calculated by means of the nonempirical valence effective Hamiltonian (VEH) technique. The AM1 optimized geometry of the radical cation reveals the appearance of a semiquinoidic character for the C-C bonds while the C-S bonds are only slightly affected. The geometry relaxation induced by the polaron progressively softens away from the center of the oligomer. Owing to the C_{2h} symmetry of the system, the molecular levels alternately present a different parity (g or u) versus the inversion center, as shown schematically in Fig. 3a. Consequently, the spectrum shows only the transitions between the HOMO level (H) and the lower polaronic level (Pol1) and the transition between the two polaronic levels (Pol1 → Pol2). The transition H→ Pol2 is totally forbidden (Fig. 3a). A third transition between Pol1 and the LUMO+1 (L+1) level is also allowed, however, its transition energy is above the neutral oligomer HOMO–LUMO energy difference. The absorption spectrum is obtained following correlated calculations performed at the INDO/SCI level on the basis of the VEH energies and is displayed in Fig. 3b. The spectrum shown is simulated by means of a convolution with a Gaussian whose full width at half maximum is 0.1 eV. The two transitions H→ Pol1 and Pol1 → Pol2 are clearly observed.

DISCUSSION

The observed PA spectrum of our films is very similar to that observed for the singly oxidized forms of sexithiophene and didodecylthiophene. All of these spectra show the lower energy band (P1) and the higher energy band (P2), each with shoulders at higher energies. Fichou et al[1] have shown that the singly oxidized sexithiophene is a spin bearing species with S=1/2, and thus it represents almost entirely the radical cation $6T^{\bullet +}$. The peak values of all the bands observed in the absorption spectra are very similar (those of the radical cations are ≃50 meV lower in energy than those observed in PA). The full width at half maximum of the two main bands P1 and P2 are of the order of 7 meV, in all the experiments. Moreover, the calculations presented above show that the singly oxidized oligomer should be characterized by only two absorption bands within the HOMO-LUMO gap (Fig. 3b), while the doubly oxidized oligomer should have only a single absorption band. [7] We therefore conclude that the features associated with the two bands P1 and P2 (Fig. 1) are due to photogenerated polarons. Since the absorption spectrum of the didodecylsexithiophene radical cation is not identical to that of the radical anion (P1 appears at 0.87 eV for the cation and 0.72 eV for the anion),[2] we conclude that there is probably no charge conjugation symmetry. Based on this observation, we assign the P1 and P2 bands to positive polarons. We conjecture that the negative charge, created by photoexcitation, is probably trapped by impurities (e.g. oxygen) outside the oligomer molecule and does not contribute to the PA. The trapped electrons cannot then recombine with the positive charge situated on the oligomer, giving rise to the very long lifetimes observed in the PA experiment (Fig. 2a).

The origin of the additional weak lines observed in our PA spectrum is not entirely clear. The two "shoulders" at 0.96 eV and 1.68 eV may originate from vibronic overtones of the two polaron bands P1 and P2, respectively. The corresponding excited state vibration energy of ≃0.15 eV is slightly smaller than that observed for the linear absorption (0.18 eV, Fig. 1). The line at 1.1 eV is close to the dication related line (at 1.2 eV)[1] and may thus signify a photogenerated bipolaron; this assignment is also supported by by VEH calculations, indicating a transition at 1.08

eV in the doubly charged oligomer.[7]

We turn now to the modulation frequency behavior of the P1 and P2 bands. In a simple monomolecular recombination process, the polaron density, p, is governed by the following rate equation,

$$\frac{dp}{dt} = G(t) - \frac{p}{\tau} , \tag{1}$$

where τ is the recombination time and $G(t)$ is the time dependent generation rate of the polarons. In our photomodulation experiment we approximate $G(t)$ by $G(t) = g(1 + cos\omega t)/2$, where $\nu = \omega/2\pi$ is the pump modulation frequency. In this case, the resulting in-phase and out of phase polaron population are given by,

$$p_{in} = \frac{g\tau}{1 + \omega^2\tau^2} , \quad p_{out} = \frac{g\omega\tau^2}{1 + \omega^2\tau^2} . \tag{2}$$

The PA signal, which is proportional to the polaron density, should then behave according to eq. 2. Specifically, ΔT(in-phase) should reach a constant value for $\omega << \omega_{max} = \tau^{-1}$, and decrease as ω^{-2} for $\omega >> \omega_{max}$. We note here that for other recombination mechanisms (such as bimolecular or multiple trapping[10]) we also expect a constant value of the in-phase PA at low frequencies and $\omega^{-\beta}$ (with β close to 2) behavior at high frequencies. Since our measured in-phase PA increases with decreasing frequency even for $\omega << \omega_{max}$ and behave as $\omega^{-0.6}$ at high frequencies, we believe that there is a wide distribution of recombination lifetimes that controls the dynamics of the long lived polaron population.

In order to account for the frequency behavior of the PA, we have assumed a Lorentzian distribution of recombination times τ. Performing the convolution we obtained the results shown in Fig. 2b for $\Delta\tau = 20\tau_0$, where τ_0 and $\Delta\tau$ are the mean and half width of the distribution, respectively. We see that with such a distribution of lifetimes, the in-phase signal does not reach a constant value even at frequencies as low as $\omega < 0.1\omega_{max}$, where ω_{max} is the frequency at which the out of phase PA reaches its maximum. Also, at high frequencies the decrease of the in-phase signal is approximately $\omega^{-0.8}$, i.e. close to the experimental value and far below the exponent of -2 expected when no distribution is taken into account. These results thus demonstrate that by measuring the PA modulation frequency dependence one can study the recombination processes that govern the photogenerated species at relatively long times. These results do not prove, of course, that the lifetime distribution is Lorentzian, nor do they uncover the main recombination mechanism. More work, including the laser intensity dependence, is now under way in order to study the recombination processes.

SUMMARY

We have shown that polarons are the main species photogenerated in sexithiophene. Based on comparison with absorption spectra of both the radical cation and anion forms of 6T, we have concluded that the observed photoinduced absorption spectrum is due to positive polaron (radical cations). We suggest that the photogenerated negative charge is trapped outside the oligomer molecule and does not contribute to the PA spectrum. The theoretical energy level and absorption spectrum calculations presented here are in very good agreement with the observed polaron spectrum and confirm that the polaron spectrum in 6*T* should consist of two electronic transitions. In this context, it is worthwhile mentioning that upon oxidation of β-carotene, which may be looked upon as a finite degenerate ground state polyene, a single midgap absorption band was observed.[11] It corresponds to the absorption spectrum of the doubly oxidized state, i.e. a bipolaron (or a pair of like-charge solitons).

We have also shown by studying the modulation frequency dependence of the PA that there is a wide distribution of characteristic lifetimes for photogenerated polarons.

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[#] Present address: Tennessee Valley Authority, Muscle Shoals, AL 35660, USA.

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