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ON THE EXCITONIC NATURE OF THE PHOTOLUMINESCENCE IN POLYTHIOPHENE REVEALED BY ODMR SPECTROSCOPY

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Abstract We used the photoluminescence (PL) and photoinduced absorption (PA) techniques, as well as their respective versions of optically detected magnetic resonance (ODMR), to elucidate the photoexcitation properties and the origin of the PL emission in films of poly(3 octhyl-thiophene). We identified the various PA bands in the PA spectrum as due to triplets, bipolarons and excitons, respectively. We show that the previous models used to explain the ODMR spectra in conjugated polymers are incompatible with our data. We offer a new model, in which the long-lived photoexcitations such as polarons, bipolarons, and triplets are non-radiative centers which compete with the excitonic PL emission.

INTRODUCTION

The properties and dynamics of optical excitations in conducting polymers are of fundamental interest since they play an important role in potential applications such as light emitting diodes (LED) and optical switches and modulators. However, in spite of intense studies of the linear and nonlinear optical properties, the basic model for the proper description of the electronic excitations in conjugated polymers is still unclear. One-dimensional semiconductor models[1], in which electron-electron (e-e) interaction has been ignored, have been successfully applied to interpret a variety of optical experiments in π-conjugated polymers[2]. In these models the strong electron-phonon (e-p) interaction leads to rapid self-localization of the charged excitations; the so called "polaronic effect". Then when electron-polaron (P^-) recombine with hole-polaron (P^+), emission from a "polaronic exciton" has been envisioned[4,5] in the form of relatively high efficiency photoluminescence (PL). The P^+ P^- recombination process is in principle spin dependent, resulting in relatively strong spin ½ optically

detected magnetic resonance (ODMR) signals[5-8].

In the pioneering work of ODMR spectroscopy in π-conjugated polymers[6], we only observed a spin ½ PL ODMR signal. Later Swanson et al.[7] observed both spin ½ and spin triplet PL enhancing signals in PL-ODMR (PDMR) of several polythiophene derivatives. The spin ½ PDMR signal was interpreted as due to intrachain "distant pair" (uncorrelated) polaron recombination[5,7], whereas the spin triplet signal was attributed to fusion of triplet polaronic excitons[8]. Following this work similar PDMR signals were measured in other π-conjugated polymers in the form of thin films and LEDs, and the same interpretation has been offered[5-8]. These measurements were then taken as evidence[5] that the "semiconductor picture" of π-conjugated polymers in which polaron recombination leads to PL emission[9], is applicable.

In this work we simultaneously apply two ODMR spectroscopies, PDMR for PL and ADMR[10] for photoinduced absorption (PA), to thin films of poly(3 octhyl-thiophene) (P3OT) to elucidate the recombination process which leads to PL emission. We found both spin ½ and spin triplet signals, as in previous works[5-8], and with the ADMR spectroscopic potential we identified the spin ½ and spin 1 PA bands in the PA spectrum. However, by comparing the ADMR and the PDMR magnetic field spectra, measured on the same sample and under the same resonant conditions, we demonstrate that the previous models used to interpret the PDMR data in π-conjugated polymers[5-8], cannot explain our new findings. Rather than distant polaron recombination[7,8], we show that the spin ½ PDMR is due to a parallel process in which polarons complete with exciton emission i.e. they are non-radiative centers. The same is true for the PDMR spin triplet signal.

EXPERIMENTAL

The ADMR experimental set-up is shown in Fig. 1[10]: A cw pump beam (from an Ar^+ laser) and a probe beam (from a tungsten lamp) constantly illuminate the sample, which is mounted in a high Q microwave cavity at (3GHz) equipped with optical windows and a superconducting magnet producing a field H. Microwave (μ-wave) resonant absorption, modulated at 500 Hz, leads to small changes δT in the probe

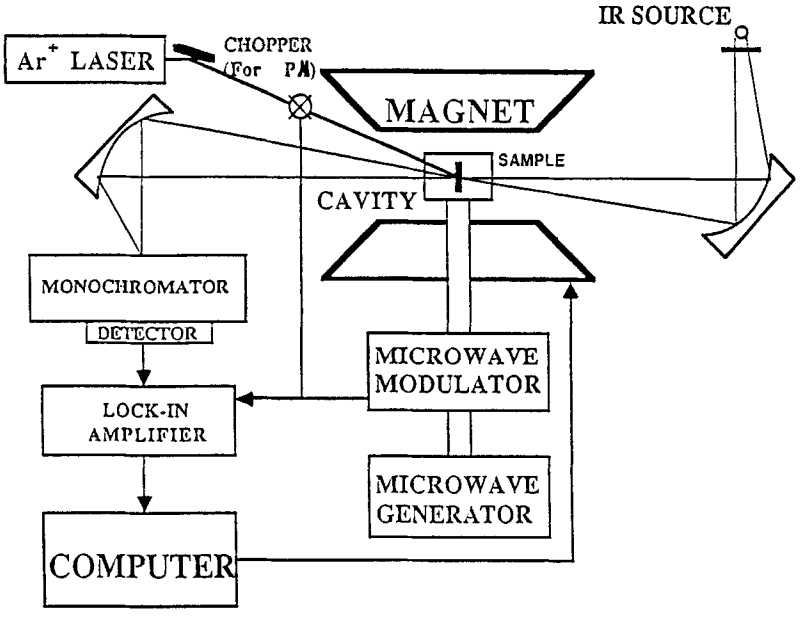

FIGURE 1 Schematic diagram of the ADMR experimental set-up[18].

transmission T proportional to δn, the change in the photoexcitation density n produced by the pump. δn is induced by transitions in the μ-wave range that change spin-dependent recombination rates. Two types of ADMR spectra are usually obtained: the H-ADMR spectrum in which δT is measured at a fixed probe wavelength λ while sweeping H, and the P-ADMR spectrum, in which δT is measured at a constant H, in resonance, while λ(probe) is changed. With suitable signal averaging, the system δT/T sensitivity was $3x10^{-8}$ in the visible to near ir range and $3x10^{-7}$ in the mid-ir spectral range. For the PDMR measurements the probe beam is blocked and PL is collected by the same set-up using a high efficiency collecting lens. Then the changes δPL in the PL emission are measured in the form of H-PDMR spectrum, where H is swept at a constant PL wavelength.

The polymer samples used in our ADMR studies were in the form of thin films (d≈1000 Å) polymerized (or spin casted) on sapphire substrates, which do not reduce the Q value of the μ-wave cavity. Several conducting polymers have been measured with similar results. These include oriented and unoriented poly(p-phenylene-vinylene) (PPV), poly(phenylene-acetylene) (PPA) and P3OT.

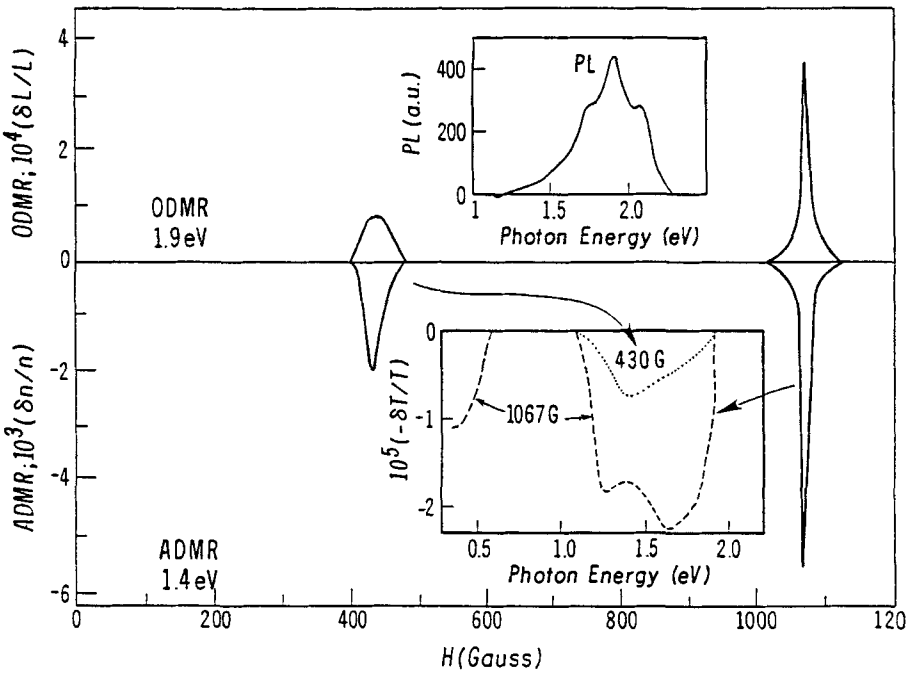

FIGURE 2 H-ADMR (at 1.4 eV) and H-PDMR (at 1.9 eV) of a P3OT film at 4K. The P-ADMR spectral of spin ½ at 1067G (broken line) and spin 1 at 430 G (dotted line) are given in the lower inset. The upper inset shows the PL emission spectrum of P3OT at 4K.

ADMR and PDMR Spectra in P3OT

The H-ADMR and H-PDMR spectra of a P3OT film at 4K are shown in Fig. 2 as $\delta n/n$ and $\delta L/L$, respectively. Two prominent resonance bands were observed, one at 1067 Gauss which is associated with spin ½ at g=2.0023, and the other at 430 Gauss which is the "half-field" powder pattern resonance signal associated with photo-excited spin triplets; its related full-field powder pattern was also measured[11], but is too small to show in Fig. 2. We note that the H-ADMR and H-PDMR spectra are the same[11] except for the sign and relative magnitude: $\delta n<0$, whereas $\delta PL>0$. Also $|\delta n/n|$ is larger than $|\delta PL/PL|$.

In Fig. 2 (insets) we show the P-ADMR spectra at 1067 (spin ½) and 430 Gauss (spin 1), respectively; the PL emission band is also shown for comparison.

The spin 1 P-ADMR spectrum shows a band at 1.4 eV and we thus identified it as a transition in the triplet manifold, associated with photogenerated triplet excitons in P3OT. The spin ½ ADMR spectrum, on the contrary, consists of three bands. We identify the PA bands at 0.4 and 1.2 eV, respectively, as two correlated transitions known to exist for bipolarons (BP)[12]. The band at 1.6 eV is either due to photogenerated polarons[13] or to long-lived excitons.

DISCUSSION

The main question that we would like to address here is the underlying mechanism for the similarity that we have found in the H-ADMR and H-PDMR spectra (Fig. 2). The magnitude of the resonances leave little doubt that they originate from unthermalized (non Boltzmann) spins[14]. We note that ODMR is an excited state dynamical technique, which is not based on photoexcitations in thermal equilibrium. In this respect it is not similar to ESR, of which signal follows the Boltzmann statistics. In ODMR we must actively provide spin polarization, or different population of spin sublevels of the photoexcitations[15]. This can be achieved either during the generation process, or the recombination, or both. We will discuss spin ½ and spin 1 cases separately, under the assumption that the spin-lattice relaxation time is much longer than the photoexcitation lifetime.

(i) Spin ½

Two spin ½ particles produce pairs with spins either parallel (P) or anti-parallel (AP) to each other. In the case of "geminate" pair, the photoexcited electron-hole are correlated after photon absorption, hence their spins are in an AP configuration. The reason for that is that the ground state (GS) is spin singlet and the photon absorption process conserves spin. Spin polarization is achieved, therefore, by generation[14]: μ-wave absorption flips the spin of one carrier, thus reducing the recombination rate of the pair to the GS. Consequently $\delta n > 0$; but this is not applicable for our data. In the cases of uncorrelated carriers[14], usually with bimolecular recombination kinetics, there are pairs with P or AP spin configuration, initially generated with equal probability. With time, the pairs with P configuration prevail, since their recombination rate to the GS is smaller. Spin polarization is therefore achieved by

recombination, and any μ-wave induced spin-flip increases recombination and consequently $\delta n < 0$ as in our case. Then, assuming that only AP pairs radiatively recombine and we have saturation conditions at resonance, we can calculate $\delta n/n$ and $\delta PL/PL$ at resonance. We found[11]

$$\delta n/n = -(\Delta R/R)^2 \quad (1)$$

$$\delta PL/PL = \Delta R/R \quad (2)$$

Here $\Delta R = R_{AP} - R_P$ and $R = R_{AP} + R_P$, where R_{AP} and R_P are the recombination rates for a spin ½ pair with AP and P spins, respectively. From Eqs. (1) and (2) we get $|\delta n/n| = |\delta PL/PL|^2$. But since $\delta PL/PL << 1$ (Fig. 1) this relation leads to $\delta n/n << \delta PL/PL$, in disagreement with our findings for spin ½ (Fig. 2). We emphasize that the ADMR signal can be readily explained by the "distant-pair" model with $\delta n < 0$ (Eq. 1)[10-13], the PDMR signal, however, cannot. We conclude that the PL emission in P3OT is not due to direct polaron recombination[7,8].

A different model that can successfully explain our ODMR data is based on excitonic PL emission[16]. In this model[11] P, PB and triplets with respective densities n_i (i=1, 2 or 3) are efficient non-radiative centers for the excitons and therefore compete with the PL. Then changes in their steady state population δn_i caused by μ-wave resonance, in turn induce changes δPL in the PL efficiency. In this model[11] it is easy to understand why $\delta PL > 0$ when $\delta n_i < 0$; the reason is the reduced density of non-radiative centers. Assuming a simple model, where the PL is proportional to the exciton density, which in turn is determined by the radiative and non-radiative recombination rates, respectively, we found[11] $|\delta PL/PL| < |\delta n_i/n_i|$, in agreement with the experimental results (Fig. 2).

(ii) Spin 1 (triplets)

The spin Hamiltonian for spin 1 (triplet) states is more complex than that of doublets, due to spin dipole interaction[17]:

$$\mathcal{H} = \mathcal{H}_0 + g\beta\, \bar{H}\cdot\bar{S} + D\,(S_z^2 - \tfrac{1}{3}S^2) + E\,(S_x^2 - S_y^2) \quad (3)$$

where $\mathcal{H}_0$ denotes the atomic Hamiltonian, $g\beta\, \bar{H}\cdot\bar{S}$ is the magnetic Zeeman splitting term, and D and E are the zero field splitting (ZFS) parameters. The spin states are

hence split into three sublevels (denoted x,y and z) even in the absence of $\vec{H}$.

Spin triplet excitons cannot be generated directly from the singlet GS by photoabsorption. They are produced, therefore, by intersystem crossing from the singlet manifold due to the spin-orbit (LS) coupling. LS coupling is usually different for each of the triplet sublevel states x,y,z, causing spin polarization by generation. Then μ-wave absorption among the triplet sublevels causes ADMR signals with either $\delta n_T > 0$ or $\delta n_T < 0$ (or $\delta n_T = 0$) depending whether the recombination rate R decreases, or increases (or stays put), respectively. Even if the generation of the triplet sublevels is homogeneous, spin-polarization can be still achieved by recombination [17], since the sublevel recombination rates to the GS are different ($R_x \neq R_y \neq R_z$). In this case, only ADMR signal with $\delta n_T < 0$ is observed, similar to the case discussed above for spin ½ distant pair recombination.

From Fig. 2 $\delta n_T < 0$ and $\delta(PL)_T > 0$ for the triplet resonance at "half field" (H≈430 Gauss), which is due to a powder pattern average of μ-wave transitions between the extreme Zeeman-split triplet sublevels (T_1 and T_3)[7]. We can again apply a similar model as for spin ½ above where the levels T_1 and T_3 replace the P and AP spin ½ pairs, respectively. Then Eq. (1) is valid resulting in $\delta n_T < 0$. The model used previously[5] to explain the triplet PDMR resonance assumed singlet exciton formation from triplets fusion. In this model $PL = PL_0 + \Delta PL$ where PL_0 is related to direct singlet exciton generation and ΔPL results from triplets fusion. In the steady state ΔPL is proportional to $(n_t)^2$, where n_t is the steady state triplet density. Then in resonance, $\delta(PL)_T = 2\Delta PL\ \delta n_t$, with the same sign as δn_t. This cannot explain our data with $\delta n_T < 0$ and $\delta(PL)_T > 0$ (Fig. 2). On the other hand if we apply again the above model used for spin ½ where the triplet are the non-radiative recombination centers, which compete with exciton PL, we find $\delta(PL) > 0$ when $\delta n_T < 0$, with $|\delta PL/PL| < |\delta n_T/n_T|$, in agreement with our data in Fig. 2.

CONCLUSIONS

In conclusion, simultaneously applying the PDMR and ADMR spectroscopies to thin films of P3OT, we elucidated the properties of long-lived photoexcitations, as well as the recombination process leading to PL emission. We identified the various PA

bands in the PA spectrum as follows: triplets at 1.4 eV, BP (or polarons) at 0.4 and 1.2 eV, respectively, and excitons (or polarons) at 1.6 eV. We showed that the model of distant-polaron recombination for the PDMR cannot explain the similarity between the PDMR and ADMR spectra. In contrast, a model where P, BP and triplets are non-radiative centers, which compete with the excitonic PL emission, is in perfect agreement with all our ODMR results.

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