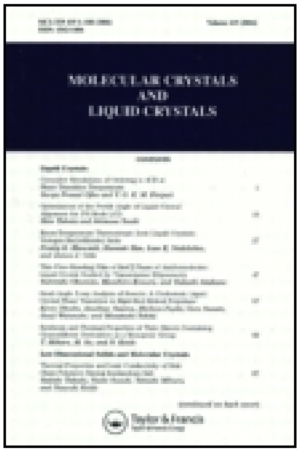

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Polaron Pairs as Intermediate States in the Process of Photogeneration of Free Charge Carriers in Semiconducting Polymers

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Polaron Pairs as Intermediate States in the Process of Photogeneration of Free Charge Carriers in Semiconducting Polymers

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Properties of polaron pairs (PP) are considered. PP are intermediate states between electron excited state of molecules and free charge carriers in conducting polymers of the PPV type. PP are shown to be important for generation of the free charge carriers at photoexcitation of polymers; recombination of free charge carriers; intra-chain triplet exciton generation; delayed luminescence of mono- and bimolecular nature; displacement current in the transient photoconductivity experiments; spin-dependent reactions.

Keywords charge carriers, polaron pairs, excitons, photoconductivity, electroluminescence, spin-dependent reactions

INTRODUCTION

Photoexcitation of conducting polymers with nondegenerated ground state of the chain results in generation of intra-chain singlet excitons localized on the conjugated part of the polymer chain. Because of a small overlapping of electron clouds an electron transfer to the next neighbor conjugated part of the same or adjacent molecule is possible. The latter process leads to formation of inter-chain charge-transfer excitons or polaron pairs. Polarons have a chance to jump to neighbor chains, still retaining a high probability of geminate recombination, or by other words, belonging to the polaron pair. Rates of the geminate recombination and dissociation of the pair define the lifetime of the pair. Figure 1 shows the scheme of energy levels of a polaron pair formed by electron transfer from an excited singlet precursor.

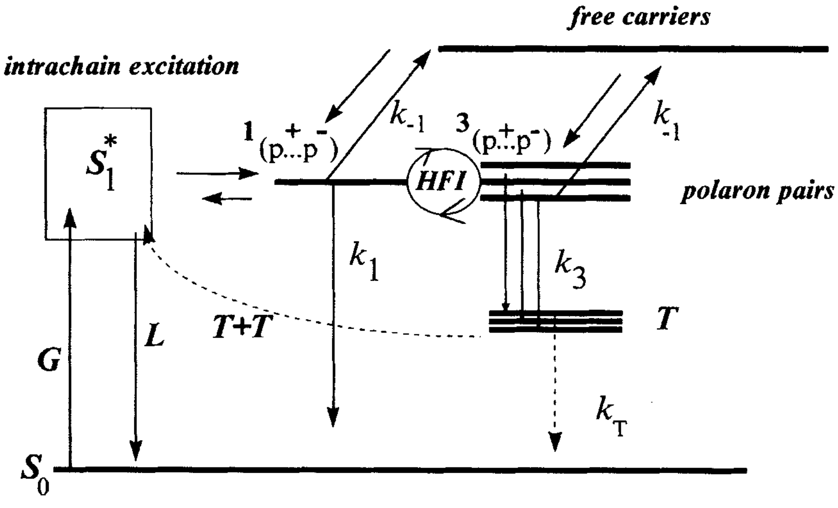

FIGURE 1. Spin substates of polaron pairs ($p^+...p^-$) are shown, which are mixed by hyperfine interaction (HFI); k_1 and k_3 are rate constants of geminate recombination of singlet and triplet polaron pairs; k_{-1} is dissociation rate constant. S and T are intrachain excited states.

Hypothesis on the polaron pairs in conjugated polymers was suggested firstly on the basis of the magnetic field spin effect on the photoconductivity of polyacetylene[1] and polyarylenevinylenes[2]. A role played by polaron pairs in the photoconductivity was analyzed also in[3]. Papers[4,5] report on photoinduced absorption caused by polaron pairs. Results obtained by the technique of magnetic resonance detected by fluorescence[6] have shown that polaron pairs are formed under photoexcitation of polyphenylenevinylene (PPV) even at liquid helium temperature.

PHOTOGENERATION OF FREE CHARGE CARRIERS

Polaron pairs are precursors of free charge carriers. The probability of dissociation of a pair is usually small, that results in a low yield of free charge carriers. The yield can be significantly improved by applying of an electric field. High increase of the yield of free carriers can be achieved by doping of the polymer by electron acceptor molecules. Addition of C_{60} molecules to PPV leads to quenching of the fluorescence of the polymer and to appearance of high photoconductivity[7, 8]. Even higher increase of the photoconductivity can be achieved by adding molecular oxygen to the polymer[9], though photochemical reactions with O_2 destroy the material soon. These facts may be described as superfast formation of pairs of the (D^+...A^-)-type, which have a high rate of dissociation and slow rate of recombination. Formation of (polaron$^+$...C_{60}^-) pairs was evidenced by the observation of magnetic resonant transitions in the pairs detected by photoinduced absorption of light in[10]. Such sensitivity can be expected only due to existence of dynamically polarised polaron pairs.

POLARON PAIRS AS A SOURCE OF DELAYED FLUORESCENCE

Recombination of polarons inside a polaron pair can result in formation of intra-chain electronically excited states. The requirements are a suitable energy position and conservation of the spin. A delayed fluorescence of PPV in the time domain of 50 ns has been observed in[11], accounted for as due to electron back transfer in polaron pairs. If the electron in the pair is localised on acceptor molecule, the energy level of the pair is lower than that of intra-chain singlet exciton and only non-radiative decay of singlet state of the pair is possible. Magnetic field spin effect on the photoluminescence was observed in[12] and explained as originated from spin-dependent recombination in polaron pairs. Energy level of a polaron pair lies in most cases higher than that of triplet intra-chain exciton, and formation of the latter is allowed and observed in[6]. Delayed fluorescence connected with recombination of triplet polaron pairs, formation of intra-chain triplet excitons and their annihilation have been observed in PPV[13].

INFLUENCE OF POLARON PAIRS ON THE QUANTUM YIELD OF ELECTROLUMINESCENCE

According to a simplified point of view that neglects the very existence of polaron pairs one quarter of the recombination collision rate $k_{rec}p^+p^-$ of free charge carriers leads to the formation of singlet, excited states. It is not so if formation of intermediate polaron pairs at combination of free polarons of opposite sign is taken into account. Then the rate of recombination into the singlet channel is $R_S = \frac{1}{2}k_{rec}p^+p^-\frac{k_1}{k_1+k_3+2k_{-1}} = \Phi k_{rec}p^+p^-$. It is desirable to have $k_1 \gg k_3$, k_{-1} in order to make the highest possible value of electroluminescence quantum yield $\Phi = 0.5$.

POLARISATION OF POLARON PAIRS IN AN EXTERNAL ELECTRIC FIELD

In experiments on excitation of transient photoconductivity by pico-to-nanosecond light pulses, polaron pairs are expected to show themselves by the electric current due to polarisation of the pairs by the electric field in the sample (displacement current). Though the polarisation of polaron pairs formed in electric field proceeds extremely fast ($\tau_{pol} \approx 10^{-14}$ s), electric response will be delayed by RC-time of the electric circuit. The response is expected to look very similar to that induced by a drift of the free charge carrier with the lifetime $\tau \approx RC$. Values of the total charge Q transferred into the external circuit due to appearance of these two kinds of species can be comparable: $Q_{pair} = \frac{\alpha V}{d^2} N_{pair}$ for N_{pair} pairs with the polarisability α, and $Q_{free} = \frac{e\mu\tau V}{d^2} N_{free}$ for N_{free} free carriers with the mobility μ and the life time before trapping τ; V is the voltage applied, and d is the gap between electrodes of the sample. Polarisability α of polaron pairs in conjugated polymers is expected to be as high as up to 10^{-19} cm^3.due to the possibility to shift the electron density along the conjugated part of the polymer chain. The process of decay of polaron pairs having the lifetime τ_{exc} starts right at the moment of their formation. The decay is accompanied by the distraction of the polarization produced, which looks like the displacement current but has opposite direction.

Kinetics of the displacement current looks like the next formula

$$i_p = N_{pol}\alpha \frac{V}{l^2 \tau_{pol}} \left(e^{-\frac{t}{\tau_{pol}}} - \frac{\tau_{pol}}{\tau_{exc}} e^{-\frac{t}{\tau_{exc}}}\right)$$

Here N_{pol} is an amount of polarizable species formed in the sample, l is the distance between electrodes.

One can expect that the signal caused by the polarisation will not depend on the temperature and will depend on the light intensity and the electric field strength linearly. Photocurrent signals with such properties were observed in works[14,15], though described as originated from free charge carriers produced by inter-band light absorption. Further studies are necessary in order to find out their nature unambiguously.

MAGNETIC FIELD SPIN EFFECT AND MAGNETIC RESONANCE ON POLARON PAIRS

The effect takes place when the lifetime of the pairs is shorter than spin-lattice relaxation time T_1 (T_1 is about 10^{-7} s for molecular solids). Pairs are produced from their precursors in the pure singlet state as it is shown in Figure 1. But during their lifetime spins evolute, and all four spin states of the pair (one singlet and three triplets) become populated in zero external magnetic field. Spin evolution takes place due to hyperfine interaction (HFI) of a polaron spin with magnetic nuclei (protons), and it causes mixing or periodical transitions, between singlet and triplet states of the pair. An external magnetic field lifts the degeneracy of the triplet state, and thus prevents mixing of the singlet and T_{+1} , T_{-1} substates. Only singlet and T_0-substate remain mixed. Singlet and triplet pairs have different rates of geminate recombination, k_1 and k_3. Thus, an external magnetic field can affect the relative amount of triplet and singlet pairs. Rates of kinetically connected processes, such as dissociation of pairs into free charge carriers, geminate recombination into singlet and triplet channels, and delayed fluorescence are changed as well. Spin state of the pair can be altered also by microwave induced resonant transitions between magnetic sublevels of the triplet polaron pair [6]. No absorption of microwave energy is possible by singlet polaron pairs. Resonant transitions act in the opposite direction to that of the action of permanent magnetic field. At saturating microwave power, all spin substates become mixed again, as they were before switching-on the magnetic field. Magnetic resonance spectra of polaron pairs detected by photoluminescence, photoinduced absorption, or by photoconductivity were obtained [6, 10, 16] and served as the main source of information on properties of the pairs.

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