

# Investigation of excited states in polymer/fullerene solar cells by means of photoinduced reflection-/absorption spectroscopy

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## Abstract

The discovery of a photoinduced charge transfer interaction between conjugated polymers and fullerenes has led to intensive spectroscopic investigations of solid state composites of these materials. Based on this charge transfer reaction, high efficient solar cell devices have been developed using the concept of bulk heterojunctions, i.e. blending of the conjugated polymer and fullerene. In this work, we present a spectroscopic study on such devices under working conditions. These devices were investigated by means of photoinduced absorption spectroscopy in reflection geometry at different temperatures and different applied external electric fields. Significant changes in the photoinduced signal were observed upon changing the applied voltage. These changes can be attributed to persistent charge carriers, charge carrier transport and charge carrier injection. From this the mean polaron lifetime, the built-in potential and the fraction of persistent charge carriers was estimated.

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**Keywords:** Photoinduced absorption; Conjugated polymers; Fullerenes; Organic solar cells; Photoinduced charge transfer

## 1. Introduction

The ultrafast photoinduced charge transfer between conjugated polymer and fullerene is the fundamental mechanism of charge separation in highly efficient bulk heterojunction solar cells [1]. Photoexcited electrons are transferred from the conjugated polymer to the fullerene molecules in a femtosecond timescale [2]. This leads to the formation of separated and mobile charge carriers, positive charges on the polymer backbone, so called polarons and negative charges on the fullerene molecule. These separated charge carriers are metastable because their recombination time is in the microsecond timescale at room temperature [3].

The positive polarons are related to two new energy levels in the bandgap, which are shown in Fig. 1 for a positively charged polaron. Two new optical allowed transitions can be observed by photoinduced absorption (PIA) measurements, indicated as low energy (LE) and high energy (HE) transition. Up to now, most spectro-

scopic investigations of this material composites have been reported on thin films [4–6], whereas little is known about their behaviour in photovoltaic devices under an external electrical field.

In this work PIA measurements in conjugated polymer/fullerene bulk heterojunction solar cells are presented. The influence of the temperature and the external electrical field on the HE transition is investigated. The temperature dependence of external electrical field effects on the photoinduced signal is discussed in comparison with the corresponding current–voltage curves of the device.

## 2. Experimental

The photovoltaic devices were prepared as reported by Shaheen et al. [7], yielding to 2.5% power conversion efficiency. The bulk heterojunction layer was spin cast from a chlorobenzene solution of poly[2-methoxy,5-(3,7-dimethyl-octyloxy)-*p*-phenylene-vinylene] (MDMO-PPV) and [6,6]-phenyl-C<sub>61</sub>-butyric acid-methylester (PCBM) blended 1:4 by weight. As the hole contact indium-tin-oxide (ITO) glass coated with

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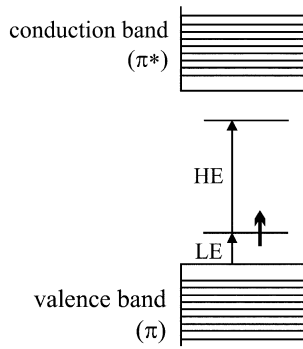


Fig. 1. Energy structure of a positive polaron on the conjugated polymer backbone. The characteristic HE and LE transitions are plotted.

poly(ethylene-dioxythiophene) doped with poly-(styrene-sulfonicacid) (PEDOT:PSS, Baytron P) spin cast from an aqueous solution was used. As top electrode, 0.6 nm of LiF followed by a 100 nm layer of Al or Au were evaporated. The active area of the device is approximately  $2 \times 4 \text{ mm}^2$ . An overview of the investigated samples are given in Table 1.

PIA spectra are usually measured in transmission geometry, i.e. the absorption of the transmitted probe beam is investigated. Since the top contacts of the investigated solar cells are not transparent, a modified set-up in reflection geometry is used in this work. The experimental set-up for this photoinduced reflection-/absorption (PIRA) spectroscopy is as follows. The 514 nm line of an  $\text{Ar}^+$  laser with a power between 50 and 100 mW was used as pump. This pump beam is mechanically chopped at 73 Hz and is focused on a spot diameter of approximately 2 mm onto the active area of the sample. The frequency of the chopper is adapted to measure close to steady state, i.e. with chopping cycles much longer than the inverse mean lifetime of the photoinduced species. A monochromatized radiation of a halogen lamp was used as the probe beam. The probe beam was detected with a  $\text{N}_2$  cooled Ge detector with an additional 1.8 eV cut-off filter in order to avoid any influence of the pump beam. The spectra were recorded with a lock-in amplifier and corrected for the photoluminescence. The sample was arranged in a cryostat in a helium atmosphere in order to investigate the signal at different temperatures between 5 and 150 K. The external voltage was applied between the ITO and the Al electrode.

Table 1  
Sample parameters

Sample	1	2	3
Top electrode material	Al	Al	Au
Active layer thickness (nm)	140	70	70

PIRA measurements provide information about the number of polarons in the device. The polarons are created by the pump beam and afterwards they are excited by the probe beam. The absorption of the probe beam by excitation of the created polarons is proportional to the number of polarons.

### 3. Results and discussion

PIRA spectra from MDMO-PPV:PCBM solar cells, recorded at 5 K in the spectral range 1–1.75 eV of the probe beam for two different applied external voltages are shown in Fig. 2. The signal  $\Delta R$  is normalised to the mean reflected intensity of the probe beam  $R$ . The absorption of the polaronic transition HE shown in Fig. 1 leads to a peak in the measured signal  $-\Delta R/R$  at approximately 1.35 eV as shown in Fig. 2. The LE transition at approximately 0.3–0.4 eV is not observable due to the spectral limits of the experimental set-up. An increase of the photoinduced signal occurs upon applying an external voltage. For example, the PIRA spectra at short circuit conditions (solid line) and at an applied external voltage of  $-6 \text{ V}$  (dashed line) are shown. The corresponding internal electric field strength is  $0.7 \times 10^5 \text{ V cm}^{-1}$  at short circuit conditions and  $5 \times 10^5 \text{ V cm}^{-1}$  at a voltage of  $-6 \text{ V}$  (dashed line). A constant field over the active layer is assumed.

In order to do a closer investigation of this voltage dependence the PIRA spectrum at a fixed spectral position was recorded as a function of the applied external voltage in the range of  $-10$  to  $+10 \text{ V}$ . The spectral position was close to the HE peak at 1.3 eV because of the highest sensitivity on  $\Delta R$  of the set-up at this energy. These spectra are similar for all samples. For example the spectrum of sample 2 for different temperatures between 5 and 150 K is shown on Fig. 3.

The symmetry of the photoinduced signal  $-\Delta R$  in respect of applied external voltage is shifted to positive

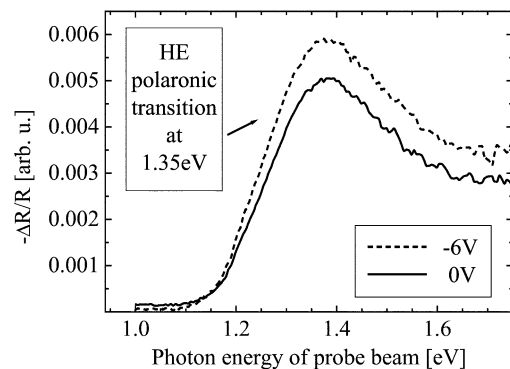


Fig. 2. PIRA spectra of a MDMO-PPV:PCBM bulk heterojunction solar cell with gold top contact (sample 3) at 5 K under short circuit conditions (solid line) and under applied external voltage  $V_{\text{ext}} = -6 \text{ V}$  (dashed line).

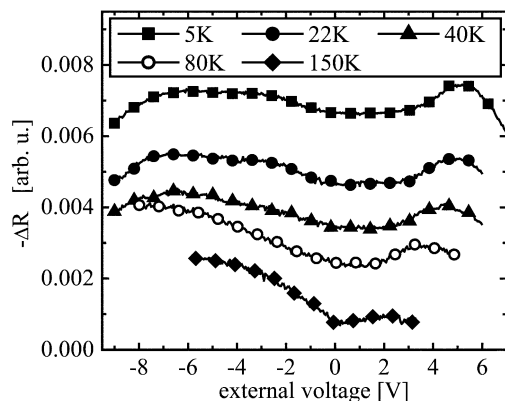


Fig. 3. PIRA measurement at a probe photon energy of 1.3 eV in dependence on applied external voltage. The additional parameter is the temperature in the range of 5–150 K.

voltages. This shift is caused by the built-in potential, the flat band potential is therefore approximately 1 V bias. The symmetry is not perfect between positive and negative external voltage. This is assigned to the rectifying behaviour of the device.

The photoinduced signal under steady state condition can be described by Eq. (1).

$$-\Delta R \sim g\tau\sigma \quad (1)$$

The signal  $-\Delta R$  is proportional to the number of polarons in the device. It is described by the product of the number of generated polarons per second  $g$  and the mean polaron lifetime  $\tau$ . And it is proportional to the absorption cross section for the HE transition of a polaron  $\sigma$ . The probability of ultrafast electron transfer and therefore of polaron generation is almost unity. For this reason no significant change in  $g$  in dependence on temperature and external voltage is expected. For  $\sigma$ , there is also no change expected due to the action of the electric field or due to the change in temperature [9]. From this follows that the increase of the photoinduced signal for decreasing temperature is caused by an increase of the mean polaron lifetime.

The decay of the signal at high external voltage is due to charge carrier injection. The injected charge carriers recombine with polarons, the mean polaron lifetime is decreasing and the signal drops off. This is shown by the correlation between the drop off of the signal and the rise of current in current–voltage characteristics for different temperatures (Fig. 4).

The mean polaron lifetime can be estimated from the signal dependence on chopper frequency [10] and was measured for a MDMO-PPV:PCBM solar cell at 80 K in dependence on external voltage. The mean polaron lifetime at open circuit conditions corresponding to the flat band condition, where no internal field exists, is 3.3 ms and decreases with increasing internal field [8].

Charge transport to the electrodes followed by discharge of these charge carriers is the reason for the observed decrease of mean polaron lifetime when the absolute value of external voltage increases. The discharge of charge carriers at the electrodes is an additional relaxation path for polarons, which reduces the mean polaron lifetime and therefore the photoinduced signal.

In contrast to this, the photoinduced signal in the PIRA spectra does not decrease when the external voltage increases. This is due to persistent charge carriers with a lifetime in the range of seconds and longer for low temperatures. These persistent charge carriers were identified by light induced electron spin resonance measurements as polarons, captured in deep trap states with a low probability of thermally activated recombination [11]. Trapped polarons contribute to the absorption of probe beam but do not contribute to the difference signal  $\Delta R$ , because their lifetime is much larger than the inverse chopper frequency. Under the influence of the electric field, these persistent charge carriers are liberated due to a lowering of the trap energy by the high internal electric field. These detrapped polarons recombine with a lifetime less than the inverse chopper frequency of 7 ms and become therefore detectable by the photomodulation experiment. This leads to an additional contribution to the signal  $\Delta R$  and thus to the maximum in  $\Delta R$ , when an electrical field is applied. This additional contribution to  $\Delta R$  gives an estimation of the fraction of persistent charge carriers. From the relative difference of the maximum and the minimum in the photoinduced signal for the investigated samples the fraction of persistent charge carriers of 15% at low temperatures is estimated (it is taken, that all polarons with a lifetime larger than the inverse chopper frequency are persistent charge carriers).

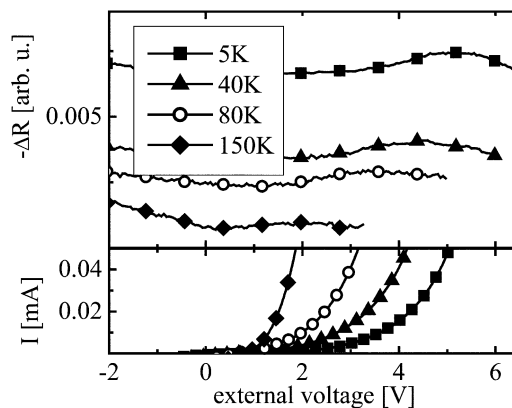


Fig. 4. PIRA measurement in dependence on applied external voltage (above). Current–voltage characteristic of the corresponding photovoltaic device (below). Correlation between the drop off of the photoinduced signal at high applied external voltages and the onset for current injection into the device for different temperatures.

#### 4. Conclusion

The effect of an external voltage on the recombination of the photoinduced charge carriers in MDMO-PPV:PCBM solar cells was investigated by means of PIRA spectroscopy. Charge carrier transport and discharge at the contacts at applied external field lead to a decrease of mean polaron lifetime from 3.3 ms at flat band condition to 1.8 ms at internal electric fields of the order of  $10^5 \text{ V cm}^{-1}$  (at 80 K). An expected decrease of the photoinduced signal could not be observed due to detrapping of persistent charge carriers. From the relative difference of maximum and minimum of photoinduced signal the fraction of persistent charge carriers was estimated. The photoinduced signal decreases again for higher voltages due to charge carrier injection at the contacts. This was proven by the correlation between the drop off of the photoinduced signal and the onset of the current in current–voltage characteristics at different temperatures.

#### Acknowledgments

The authors thank the BMBF under grant ZE98 and the Christian Doppler Society for their financial support.

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