

Polaron photogeneration probed by picosecond infrared active vibrations in MEH-PPV

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Abstract

We report picosecond time resolved photoinduced absorption from infrared active vibrations in thin films ($\approx 0.1 \mu\text{m}$ thickness) of MEH-PPV. With an overall spectral resolution of 1 meV and temporal resolution of ≈ 4 psec both in the pump and probe channels, we followed the spectral evolution with time using 565 nm pulsed excitation applied at 80 MHz repetition rate with $\approx 2 \times 10^{13}$ photons/cm² per pulse. Under these experimental conditions, we found evidence for photogenerated polarons at times < 4 psec. The origin of these polarons is briefly discussed.

Key words: psec transient infrared spectroscopy, photoinduced infrared active vibrations, MEH-PPV

1. Introduction

In a previous work we reported the first picosecond time resolved photoinduced absorption (PIA) by infrared active vibrations (IRAV) in π -conjugated polymers [1]. In that preliminary study, we applied limited temporal resolution of ≈ 60 psec to poly[2-methoxy-5-(2-ethyl-hexyloxy)-p-phenylene-vinylene] (MEH-PPV) mixed with few percent of C₆₀, which did not fully quench the photoluminescence of these samples. We showed there that polarons are formed within our temporal resolution and decay on a sub-nsec time scale.

A subsequent study of spectrally and temporally resolved photoinduced IRAV absorption, similarly revealed charge separation within the system temporal resolution (≈ 200 psec) [2]. Another report on transient excited state absorption with temporal resolution of ≈ 0.1 psec, showed IR absorption at two discrete wavelengths in the spectral vicinity of the IRAV absorption peaks [3]. More recently, the same group reported [4] on time resolved measurements of limited spectral resolution (≈ 20 meV) IRAV spectra. From their results the authors

concluded that in photoexcited PPV-derivatives charges are separated on a time scale of 0.1 psec. Their conclusion contradicts the findings of a recent high sensitivity (relative transmission changes $\Delta T/T < 10^{-4}$) sub-psec photoinduced studies of DOO-PPV, in which no IRAV spectrum could be observed at room temperature [5].

In the present work we report on ≈ 4 psec time resolved high spectral resolution (≈ 1 meV [6]) PIA spectroscopy in pristine MEH-PPV at ≈ 10 K. We show that the IRAV spectrum is instantaneously (to within our temporal resolution) developed and it decays on a time scale of few hundred psec. We compare our psec IRAV results with recent studies of photoexcitations in the sub-psec time domain and conjecture that the photogeneration of polarons is a secondary process enhanced by the large pump photon density and/or by external defects.

2. Experimental

The time resolved PIA setup consists of three dye lasers which are synchronously pumped by the same frequency-doubled cw mode-locked Nd:YAG laser. The pulses from two dye-lasers are difference

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frequency mixed within a silver thiogallate crystal to produce ≈ 3 psec tunable mid-IR ($6 - 12 \mu\text{m}$) probe pulses, while the third laser is used to produce the pump pulses. The pump can be independently tuned from the UV through the visible and near IR by using various dyes and second harmonic generation. For the study reported here, a R6G dye at 565 nm was used for the pump. The system was operated at a repetition rate of 80 MHz and excitation fluence of $\approx 2 \times 10^{13}$ photons/cm² per pulse. An overall temporal resolution of ≈ 4 psec was achieved with this setup [7], which is shown in Fig. 1.

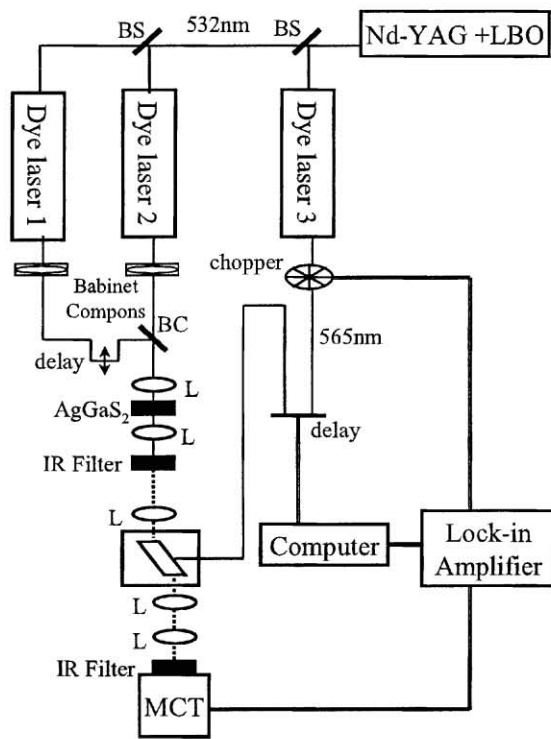


Fig. 1. The picosecond visible-pump/mid-IR-probe experimental setup. The pulse repetition rate is 80 MHz, and the pulse duration, both visible and mid-IR, is 3–5 psec. The probe energy resolution is better than 1 meV in the 6–12 μm wavelength range.

Polymer films were obtained by dissolving MEH-PPV in chloroform solution and subsequently drop casting onto a specially prepared reference semiconducting superlattice (SL) grown on ≈ 0.5 mm thick *InP* substrate. The polarized photoinduced intersubband absorption of the SL served as a reference signal for calibration and for optimization of the pump-probe overlap [1]. The negative rela-

tive differential transmission through the polymer-substrate assembly, $-\Delta T/T$, was used to obtain the PIA of the sample, which was held in a cold-finger cryostat at ambient temperature of ≈ 10 K.

3. Experimental results

Fig. 2 shows the PIA of pristine MEH-PPV as a function of probe energy and probe delay time. The values of $-\Delta T/T$ are given by the gray color scale bar. Three spectral lines, marked as SL, A and B are clearly observed. The reference SL line at ≈ 150 meV is identified from our previous measurements [8]. The other two PIA bands are due to the photoinduced IRAV in the polymer. The higher energy line (A), at ≈ 185 meV, is relatively narrow and appears at the same energy as in steady state PIA measurements [1,9]. The lower energy line (B), however, is much broader and peaks at ≈ 120 meV, some 10 meV lower than its steady state PIA analog [1]. All the PIA features are instantaneous to within our temporal resolution.

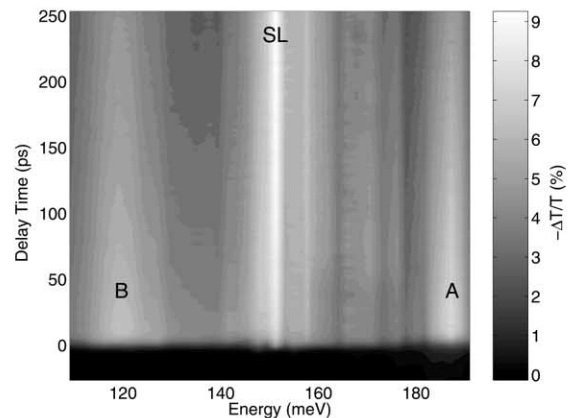


Fig. 2. Picosecond PIA as a function of probe photon energy and delay time for MEH-PPV film at 10 K. The PIA magnitude is given by the gray color scale bar on the right. SL marks the photoinduced superlattice intersubband absorption, A and B mark the polymer photoinduced IRAV lines.

Fig. 3 shows several PIA spectra at selected delay times as marked in the figure. Again, the spectra show the photoinduced SL, A and B spectral lines. It is readily seen, that already at probe delay time of 3 psec all three lines are resolved. All the lines decay with characteristic lifetimes which are shorter than the time interval between two consecutive pulses (≈ 12 nsec), as can be seen from their absence in the negative delay time spectrum (the

–17 psec curve).

Fig. 4 shows the temporal evolution of the PIA bands. As expected, the SL reference line shows a relatively long decay time [7]. The IRAV lines, on the contrary, decay on a much shorter time scale. We note that the IRAV line A appears to decay somewhat faster than line B.

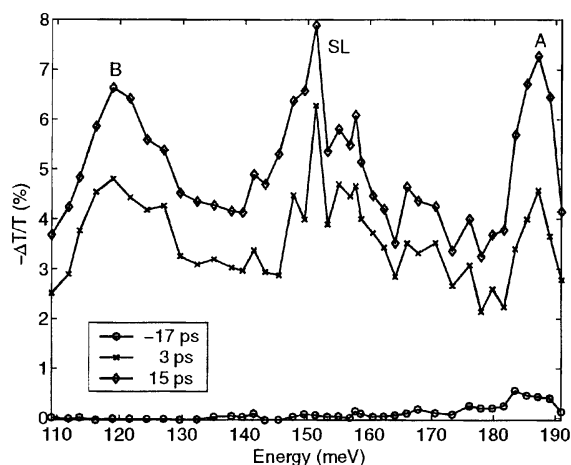


Fig. 3. Picosecond PIA spectra at selected probe delay times for MEH-PPV films at 10 K.

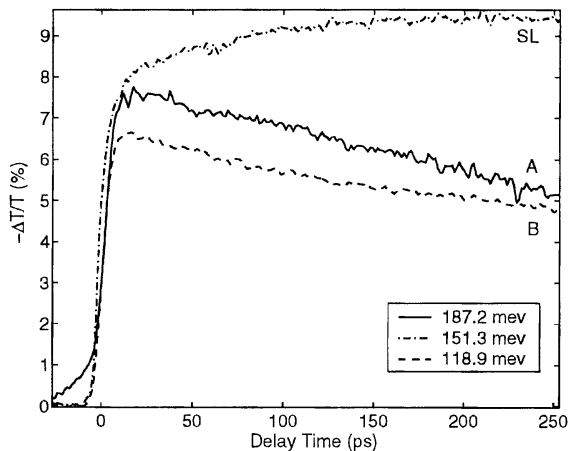


Fig. 4. Picosecond transient PIA probed at the peaks of the A, B and SL bands, shown in Fig. 2.

4. Discussion

In π -conjugated polymers, charged excitations, such as polarons, locally convert the symmetrical Raman active modes into IR active vibrations [10,11]. On the other hand, neutral excitations, such as a pair of positively and negatively charged solitons [12] or an exciton [13], do not lead to such

a conversion and consequently do not show IRAV. IR absorption is possible once the pair becomes “incoherent” and the charges can be considered as separated. Photoinduced or doping induced IRAV absorption serves, therefore, as a unique evidence for the existence of charged excitations.

In this respect, the data presented here give an unambiguous evidence for the presence of polarons in MEH-PPV on a time scale of less than 4 psec following a pulsed excitation. The data, however, do not give any clue as to the sequence of events prior to that time scale.

The efficiency at which polarons are produced following pulsed photoexcitation may depend on various factors, such as the excitation photon fluence, the presence of charge traps and ambient temperature. At high photon fluences, the initially photogenerated excitons interact with each other possibly forming biexcitons which then quickly break into pair of separate charges. Also, at high photon fluence, a second photon may excite an already photogenerated exciton, thus bringing it to a very high excited state, which then quickly disintegrates into a pair of polarons. Recent studies at the sub-psec time domain [14] indicated that such effects are already operative at exciton densities of as low as 10^{18} cm^{-3} . In addition, in the presence of impurities and at low temperatures, very high density of long lived photogenerated trapped polarons and triplet excitons may be created by the intense excitation. These long lived species may serve as exciton quenchers and thereby give rise to fast polaron formation.

The time resolved PIA measurement presented here for MEH-PPV were performed at 10 K with intense pulses at a repetition rate of 80 MHz. Using the SL absorption as a calibration for the photon fluence through the polymer and the magnitude of the measured $\Delta T/T$, we estimate the polaron density to be $\simeq 10^{18} \text{ cm}^{-3}$ per pulse. Under these conditions, it is plausible that the observed IRAV absorption is due to secondary polarons which are the result of the high fluence induced exciton disintegration. The reported IRAV signal within 0.1 psec [3,4] may imply that such disintegration possibly occurs within the first 0.1 psec after the pulsed excitation. Also, the absence of IRAV in the low fluence experiments [5] is yet another indication that polaron formation after photoexcitation is a secondary process.

5. Summary

We used picosecond time resolved photoinduced absorption spectroscopy to measure the infrared active vibrations in pristine films of MEH-PPV. We found an evidence for the existence of polarons immediately (<4 psec) after the excitation pulse. These charge carrying polarons are possibly formed by a fast disintegration of the initially photoexcited excitons.

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