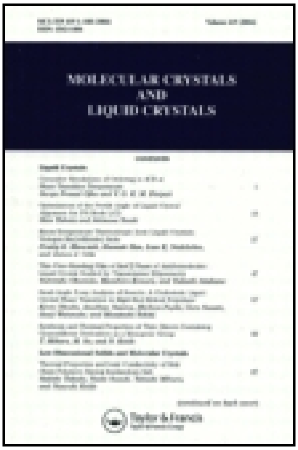

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Femtosecond Spectroscopy of Poly(3-Methylthiophene) Films

U. Stamm [a] [d] , M. Taiji [a] , M. Yoshizawa [a] , K. Yoshino [b] & T. Kobayashi [c]

[a] Department of Physics, Faculty of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113, Japan

[b] Department of Electrical Engineering, Osaka University, Yamada-Oka 2-1, Suita, Osaka, 565, Japan

[c] Department of Physics, Faculty of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113, Japan

[d] Sektion Physik, Friedrich-Schiller-Universitat Jena, Max-Wien-Platz 1, DDR-6900, Jena, German Democratic Republic

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Femtosecond Spectroscopy of Poly(3-Methylthiophene) Films

U. STAMM,† M. TAIJI, and M. YOSHIZAWA
Department of Physics, Faculty of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113 Japan

and

K. YOSHINO
Department of Electrical Engineering, Osaka University, Yamada-Oka 2-1, Suita, Osaka 565 Japan

and

T. KOBAYASHI‡
Department of Physics, Faculty of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113 Japan

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Femtosecond pump-probe experiments on poly(3-methylthiophene) films are reported. The effects of hole burning due to bleaching and gain due to stimulated Raman scattering on the transient absorption spectrum just after excitation in femtosecond pump-probe experiments on the conjugated polymers were observed. The decay time of the excited-state absorption is 800 ± 100 fs at 10 K and is temperature insensitive. It can be explained in terms of the nonradiative relaxation of a self-trapped exciton which has a formation time of 70 ± 50 fs at 10 K. The formation time is faster than that in polydiacetylene, poly-3BCMU reported as 150 ± 50 fs in a previous paper.

Keywords: Electron-phonon interaction, Self-trapped exciton, Femtosecond spectroscopy

I. INTRODUCTION

Recent progress in the field of high speed optoelectronics and information processing has encouraged the search for new materials with large nonresonant third-

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†Permanent address: Sektion Physik, Friedrich-Schiller-Universitat Jena, Max-Wien-Platz 1, DDR-6900 Jena, German Democratic Republic

‡To whom all correspondence should be addressed.

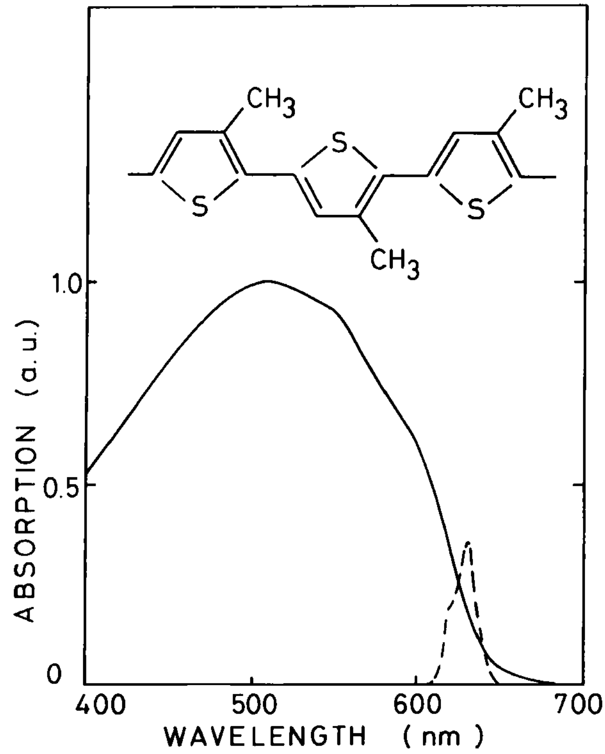

FIGURE 1 The structure and normalized steady-state absorption spectrum of P3MT. Additionally the spectrum of the excitation pulse is depicted as a dashed curve.

order nonlinear optical susceptibilities.[1] Among several classes of materials, conjugated polymers seem to be very promising candidates for future practical applications in nonlinear optical devices. Because of their often large nonlinear optical susceptibilities and their role as model compounds for quasi-one-dimensional semiconductors, considerable interest has been directed to their electrical and optical properties in order to clarify the relevant energy level/band structure and the mechanisms of the optical nonlinearity.[2]

Polythiophene (PT) and poly(3-methylthiophene) (P3MT) belong to the class of rather well studied conjugated polymers. They possess a simple backbone geometry resembling that of cis-polyacetylene (Figure 1). The *cis*-like structure is stabilized by the sulfur which is known to interact only weakly with the π-electron system of the backbone[3] so that polythiophenes can be considered as a type of pseudo-polyenes.[4]

Most knowledge of elementary excitations in PT and P3MT has been gained from steady-state photoluminescence and photoinduced absorption spectroscopies and from light-induced electron-spin resonance experiments.[4–13] It is well established that polarons and bipolarons are formed in PT and P3MT after photoexcitation or electrochemical doping.[4–9,11,12] The appearance of bipolarons is directly caused by the nondegenerate ground state of PT and P3MT which leads to a confinement of soliton-antisoliton pairs. Bipolaron formation is known to give rise to localized vibrational modes connected with local structural distortions[7,12,13] and to the appearance of symmetric gap states[4,5,13]. There is evidence that bipolarons rather than polarons are the dominant charge storage configurations in PT and P3MT after steady-state photoexcitation or electrochemical doping[4-6,8,11] and thus the energy of the bipolaron state is lower than the energy of two polarons.[13]

The results of photoluminescence measurements on PT and P3MT have been reported recently[5,10] indicating that the fluorescence is due to either free charge carriers or excitons. It has been suggested that the generation of photoluminescent excitons may be independent of the formation of polarons or bipolarons.[10] In order to obtain more insight into the elementary processes involved after photoexcitation, it is important to investigate the excited-state dynamics by time-resolved methods. From time-resolved fluorescence experiments it is known that PT shows a fast fluorescence decay which has been estimated to possess a decay time shorter than 9 ps[14].

In this paper, the first direct measurement of the excited-state dynamics of poly(3-methylthiophene) thin films after excitation by a high intensity femtosecond pulse is reported.

II. EXPERIMENTAL

Sample films of P3MT of thickness about 1 μm were prepared by electrochemical polymerization[15] on glass substrates. Whether the polymer chains are randomly distributed over the whole sample volume or whether there are some microcrystalline regions of the sample is unknown.

The laser system consists of a colliding pulse mode-locked (CPM) ring laser (pulse width 50 fs). The output pulses of the CPM laser are amplified in a four-stage dye amplifier pumped by a Q-switched Nd:YAG-laser at 10 Hz. The duration of the amplified pulses is 70–100 fs and the energy per pulse amounts to about 200 μJ[16,17]. The center wavelength (628 nm) of the laser pulse lies very close above the band edge of P3MT (see Figure 1). Even though a pronounced exciton peak is not clear in the absorption spectrum of P3MT, the major excitations generated via light absorption near the band edge are considered to be excitons[10] which have a zero-phonon line and one- and two-phonon line at approximately 595, 550, and 510 nm respectively in the spectrum. The exciton peak may have been broadened in the steady-state absorption spectrum by inhomogeneous distribution of the transition energy. It may also be due to intrachain interaction by which P3MT cannot be considered as an ideal one-dimensional system. The photoinduced change in the absorption spectrum $\Delta A = A - A_0$ was measured by probing the absorption with a weak white light continuum pulse generated by focusing a fractionally split amplified pulse into a 1 mm-cell containing carbon tetrachloride. The transmitted signal was detected with a poly chromator/multichannel detection system in the photon energy range 1.3–2.1 eV. Temporal overlap of the pump and probe pulse as well as the pulse duration have been adjusted by using a potassium dihydrogenphosphate (KH_2PO_3, KDP) crystal at the sample position for the determination of the cross-correlation function between the pump and probe pulses. All the following spectra obtained using the white light continuum pulse are corrected for the group delay which results from the group velocity dispersion in the probe-beam path. Measurements have been carried out at 295 K or 10 K. The laser spot diameter on the sample was roughly 300 μm. In order to avoid damage or irreversible change of the films during the experiments, the excitation pulses were attenuated by appropriate neutral density filters down to a pulse energy of about 2 μJ.

III. RESULTS AND DISCUSSION

Figure 2 displays a series of absorption difference spectra at 10 K measured at various delay times between the excitation and probe pulses. When the probe pulse arrives at the sample before the peak of the excitation pulse, clear oscillations in the differential absorption spectra are observed around the photon energy of the

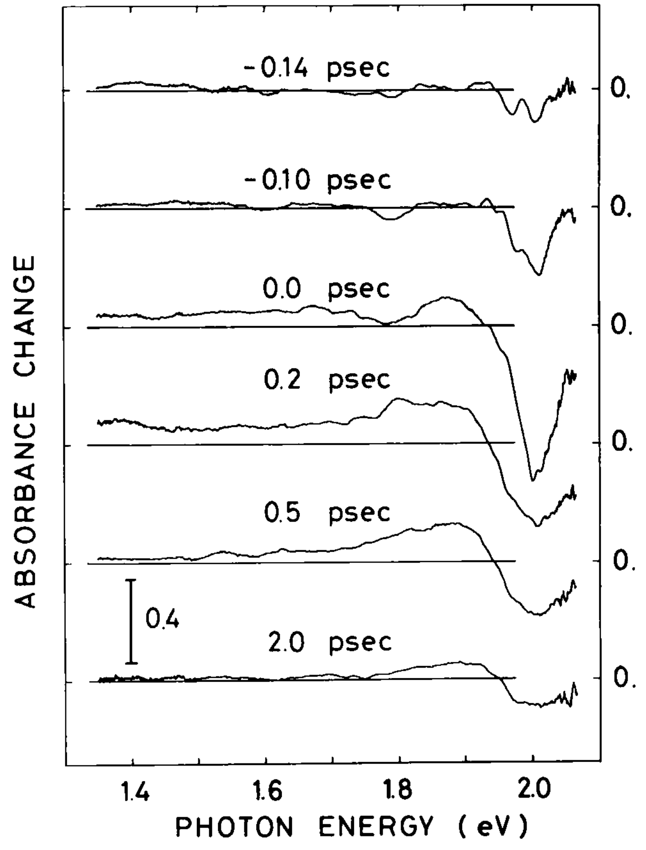

FIGURE 2 The differential absorption spectrum of P3MT at various delay times at 10 K. The photon energy of the excitation pulse was 1.98 eV.

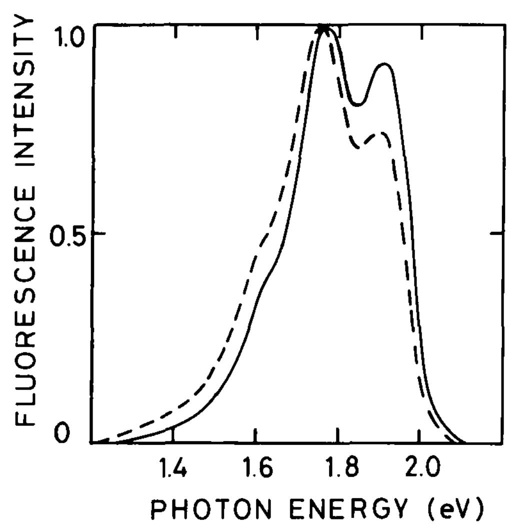

FIGURE 3 The normalized steady-state spontaneous fluorescence spectrum (solid line) and the calculated spectrum of the stimulated emission (dashed line) of P3MT.

excitation pulse. These oscillations turn out to be very similar to those observed in femtosecond pump-probe experiments on semiconductors near the band edge.[18-21] They result from the coherent interaction of the weak probe pulse with the polarization induced by the intense pump pulse in the P3MT film. As is expected from theory[21,22] the coherent oscillation vanishes when the maximum of the probe pulse arrives at the sample later than the pump pulse.

A striking feature of the photoinduced absorption spectra at early delay times (very pronounced at -0.1 and 0 ps) is the appearance of a strong minimum at 1.8 eV and a weaker one at 1.62 eV. The minimum at 1.8 eV reaches negative absorbance values while there is no absorption of the ground state at 1.8 eV. Therefore this minimum is due to a gain mechanism that will be discussed later. The gain was observed only when the excitation and the probe pulses overlapped. The disappearance of the gain at zero delay is a result of the superposition of the gain and the consequent excited state absorption. It has been reported[14] that the fluorescence quantum yield of P3MT is small, about 10^{-5}, due to efficient nonradiative relaxation channels. In Figure 3 the normalized steady-state fluorescence spectrum of P3MT is shown. The fluorescence spectrum is rather broad in width with half maxima at 1.61 and 1.98 eV. The spectrum has peaks at 1.91, 1.77, and 1.63 eV, due to the strong electron-phonon coupling.[5] The stimulated emission spectrum ($B(E)$) can be calculated from the spontaneous fluorescence spectrum ($A(E)$) using equation (1)

$$B(E) = A(E) \cdot E^{-3}\, \pi^2 \hbar^3 c^3 \tag{1}$$

where E is photon energy and π and the universal constants $\hbar$ and c have ordinary meanings. The calculated result is shown in Figure 3. Thus, if there is amplification

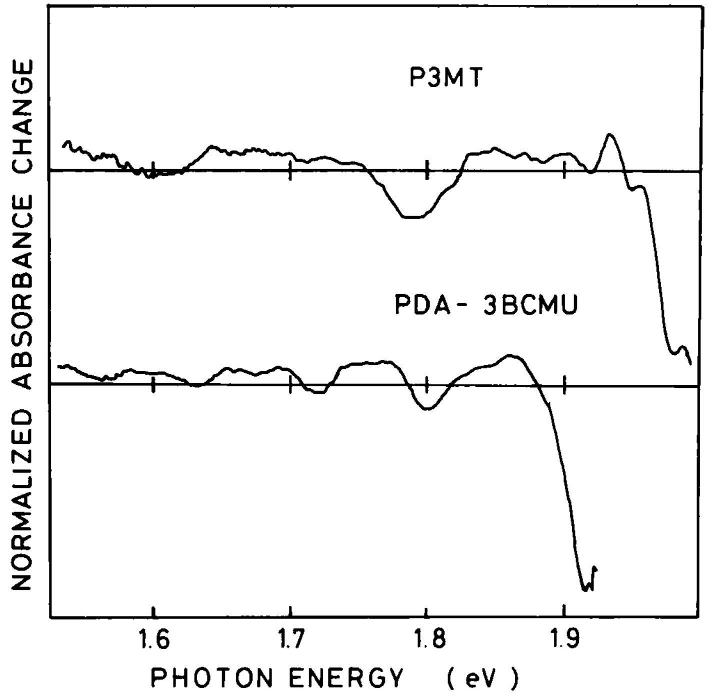

FIGURE 4 Normalized photoinduced absorption change of P3MT and PDA-3BCMU at −0.1 ps delay time.

of the probe pulse due to stimulated emission, it should give rise to a broad band feature of about 0.33 eV FWHM with a peak around 1.75 eV. Therefore, it is concluded that stimulated emission plays only a minor role in the displayed spectra.

The situation becomes clearer if the differential absorption spectra of various polymers are compared. In Figure 4 the transient absorption spectrum at −0.1 ps delay of P3MT together with that obtained in experiments on a polydiacetylene with the side group 3-butoxycarbonylmethylurethane (PDA-3BCMU)[16,17] under the same conditions are shown. It is obvious in both spectra that there is a coincidence of the minima at 1.8 eV. The PDA-3BCMU spectrum in addition has several minima but none is located at 1.62 eV. However, the equidistance of the minima suggests the cause to be Raman gain, which has been discussed previously for a polydiacetylene, PDA-3BCMU[16,17]. This assignment is also supported by the resonance Raman scattering spectrum of P3MT measured by Steigmeier *et al.*[23] Their result shows that the phonon energy of the C═C stretching mode which has the strongest coupling with an exciton is 0.18 eV, the same photon energy shift which we observed. The one dominant mode in the Raman gain spectra suggests that only one phonon mode with an energy of about 0.18 eV is much more strongly associated with the excitation of P3MT than any other modes as was observed in the resonance Raman spectrum by Steigmeier *et al.*[23]

Recent experiments in which polydiacetylene toluene sulfonate (PTS) was excited at photon energies below the excitonic resonance have in addition proved the importance of the inverse Raman effect, called phonon-mediated optical nonlinearities.[24] The results offered here can be explained by a similar mechanism. In the present case, two pump photons with higher energy and one probe photon with lower energy lead to the amplification of the probe light, while in their experiment two pump photons with lower energy and one probe photon with higher energy result in the loss of the probe light.

The other features of the spectra displayed in Figure 2 are now discussed. The strong bleaching around the excitation energy results from the generation of excitations near the band edge as well as from the ground-state depopulation. The sharp line bleached at zero delay time is due to unthermalized free excitons. The bleached spectral region at later times after thermalization becomes much broader. On the low energy side a broad absorption band arises during excitation caused by the onset of a strong excited-state absorption.

The absorbance change spectrum has been measured with parallel and perpendicular polarizations of the pump and probe pulse. There is no clear difference in the spectral shapes and the dynamics between these two polarizations. Thus further discussion is restricted to data obtained for parallel polarization directions.

The transient behavior of the photoinduced absorbance change is discussed in more detail using Figure 5, which shows the absorbance changes at five different photon energies. It was found that the rise of the bleaching following the excitation pulse may already be influenced by a rapid relaxation process and that the finite rise time of the induced absorption. The time constant of this process is estimated at 70 ± 50 fs. The variance is large because the lifetime is close to the resolution of the experimental system.

Because in such a one-dimensional system the lattice is "limp", the self-trapping process can have no barrier and is expected to be very fast.[25] Therefore, the experimentally observed fast relaxation can be considered to correspond to the exciton self-trapping process, of which the time constant has been determined to be 150 ± 50 fs in PDA-3BCMU.[16,17] Just after excitation (0 ps), broad featureless absorption spectra were observed in the photon energy region of 1.35–1.9 eV in both P3MT and PDA. The common feature indicates that the absorption is due to the same transition, i.e. the free exciton to higher excite states. At a delay time of 0.2–0.5 ps, the spectrum of the self-trapped exciton can be seen with a peak in the spectral region 1.8–1.95 eV. This absorption is due to the transition from the self-trapped exciton to the excitons of higher energies or to the conduction band.

A second fast component is clearly apparent in the relaxation of the recovery of the bleached absorbance with a time constant of 800 ± 100 fs. The component of the same decay time was found in the broad band excited-state absorption. Thus this decay indicates the relaxation of self-trapped excitons to the ground state or to other long lived species.

The time-resolved fluorescence measurement of PT has been reported by Wong *et al.*[14] They estimated the fluorescence lifetime only to be shorter than 9 ps, which is the temporal resolution of their system. Since the excited-state absorption has

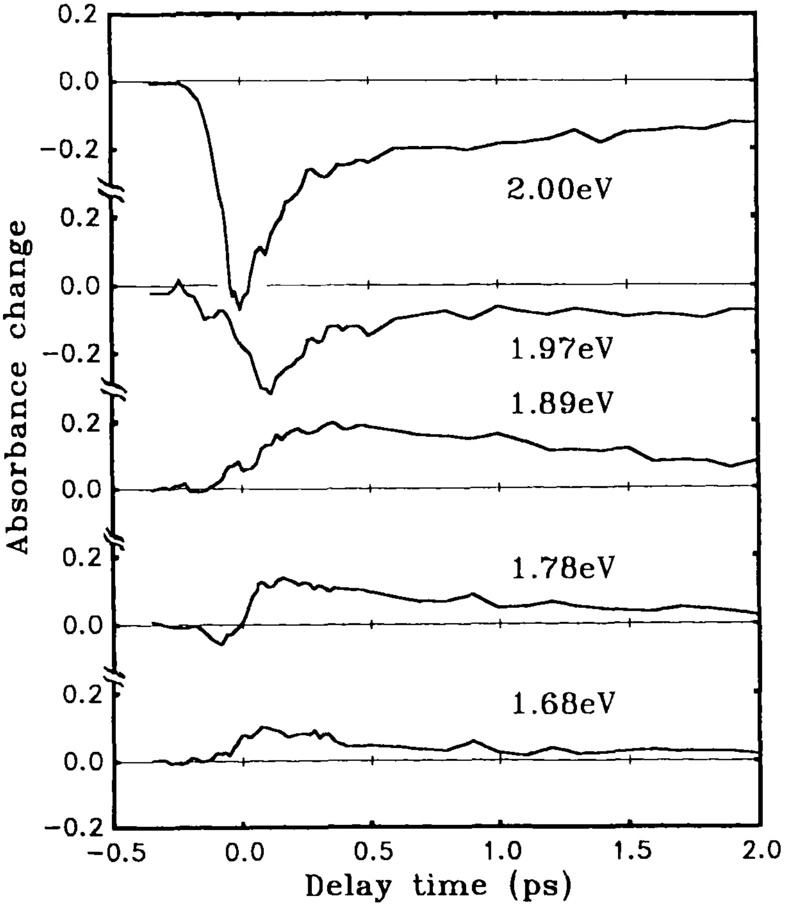

FIGURE 5 The time dependence of the photoinduced absorption of P3MT at 10 K for various photon energies of the probe pulse.

only one fast decay component shorter than 9 ps this fast relaxation process is identical to that reported by Wong *et al.* for PT.[14] The Stokes shift of the transient fluorescence from PT is similar to that of the steady-state fluorescence from P3MT. Therefore both fluorescence spectra are considered to be due to the self-trapped excitons. The steady-state fluorescence of P3MT has a peak around 1.9 eV (Figure 3). Assuming that the curvature of the self-trapped exciton is the same as that of the ground-state and that the free exciton energy is 2.1 eV, the deactivation energy due to the self-trapping is estimated to be 0.1 eV.

After the 800 fs relaxation, a long-persisting absorbance change was observed. Its time constant is longer than a few tens picoseconds, but it may obey nonexponential decay kinetics. The induced absorption is considered to be due to triplet excitons, polarons, and/or bipolarons.[17] In the case of higher excitation pulse energy, the electron-hole pair is generated by two-photon absorption. Therefore the induced absorption in the region 1.35–1.8 eV has some contribution from the triplet excitons in such a case.[17] However, a similar absorbance change can still be observed in the case of weak excitation; thus it seems that other species also exist. It should have some contributions from polarons or bipolarons since the small absorbance change observed with a high pulse energy nanosecond laser indicates a small number of polarons or bipolarons.[26] The injection of a single charge always occurs via the formation of polarons which can build up charged bipolarons. However, the time for the formation of bipolarons should strongly depend on the density of excitations generated in the material. As known from steady-state photoinduced absorption spectra measured during electrochemical doping, the formation of bipolarons in P3MT gives rise to the appearance of an absorption band around 1.6 eV and a stronger one with a peak around 0.65 eV.[6,9] If polarons remain, an additional peak at about 1.2 eV should be observed. The spectrum observed by the present femtosecond spectroscopy is so featureless that it is difficult to determine which is the major long-lived species, triplet-exciton, bipolaron, or polaron.

Since the fast decay results in a rather long-lived excitation, the time dependence of the photoinduced absorbance on a femtosecond time scale is rather complicated and more detailed measurements are necessary to fit the experimental data to theoretical calculations.

Finally it is noted that neither the decay kinetics nor the spectrum measured at 295 K show significant differences from that at low temperature. At room temperature, again the 800 fs decay component followed by a long persisting absorption and bleaching around the band-edge energy is found. This leads to the conclusion that the involved relaxation channel is temperature independent. The fact that there is no clear temperature dependence in the formation of the self-trapped exciton is consistent with a barrierless potential of the self-trapped exciton in one-dimensional chain due to strong electron-phonon coupling. The temperature insensitive ultrafast decay of the self-trapped exciton of the order of one picosecond may be explained by assuming that the position of the crossing point of two potential surfaces between the ground state and the self-trapped exciton is located below or only slightly higher than the bottom of the free exciton.

IV. CONCLUSION

The first results of femtosecond pump-probe experiments on P3MT have been reported. The stimulated Raman scattering processes on the measured differential absorption spectra at early delay times were found.

The data discussed here indicate the dynamics after pumping with an intense femtosecond pulse near the absorption edge. The self-trapping of free excitons takes place with a time constant of 70 ± 50 fs. The relaxation time constant of the self-trapped exciton is 800 ± 100 fs. The self-trapped exciton relaxes mainly into the ground state nonradiatively. The remaining long-lived absorbance change may be due to triplet excitons, polarons, and/or bipolarons. From the given data, triplet exciton, polaron, and charged bipolaron formation cannot be distinguished. More detailed measurements of the functional shape of the transient absorbance change and its dependence on the delay time and excitation energy and measurements of the temporal development of the absorbance around 0.65 eV should allow polaron and bipolaron formation to be distinguished.

Experiments to separate these processes are in progress.

Acknowledgments

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