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Photoexcitations in *para*-hexaphenyl

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We investigate the absorption and emission of photoexcitations in polycrystalline hexaphenyl films. Transient and quasi-steady-state optical modulation spectroscopy is used to identify the photoexcited species and their time evolution. The observed photoinduced absorption spectrum can be assigned to at least three different species: (1) transitions between excited states ($S_1 \rightarrow S_n$) and (2) transitions between triplet states ($T_1 \rightarrow T_n$) which are formed by intersystem crossing from the singlet to the triplet regime in the 100 ps time domain. In addition we assign one peak to the (3) formation of aggregates in the oligomer films. The depopulation of the excited singlet states is responsible for both the dynamics of the initial photoinduced absorption and for stimulated emission. The stimulated emission found in the transient optical modulation spectroscopy shows a very limited spectral overlap with the photoinduced absorption. In contrast to doping experiments we find no evidence for long living polaronic states upon photoexcitation. [S0163-1829(97)09740-3]

I. INTRODUCTION

Due to its thermal stability *para*-hexaphenyl (PHP; see Fig. 1) can easily be evaporated to form layers on various substrates. The high photoluminescence quantum yield[1] of this oligomer makes it a promising candidate for active layers in light emitting diodes (LED's). These devices were built[2–4] and the inclusion of oligo phenylene vinylenes[5] or the use of color conversion layers[6] even allows to tune the color of the device emission.

Depending on the evaporation conditions different degrees of crystallinity[5,7] can be obtained for the oligomer layers. X-ray studies confirm that the growth of crystallites with arbitrary orientation and preferred orientation of the PHP chains at 0, 70, or 90° with respect to the substrate plane can be achieved.[8] Based on reliable band-structure calculations for poly(*para*-phenylene) (PPP),[9,10] the anisotropic dielectric function and consequently the absorption spectra of poly- and single crystalline PHP can be predicted and confirmed experimentally.[11] The absorption behavior of the polycrystalline films we used in our investigation is characterized by an integration over all orientations.

The intention of our study is to determine the photoexcited states governing the optical properties of PHP based on continuous wave (cw) and transient pump and probe spectroscopy. This approach does not require the observed species to be emissive. Light-induced time-resolved studies on *polymers* showed that the obtained transient spectra contained the superposed information of subsystems, i.e., a distribution of linear chain segments in heterogenic surroundings.[12–14] Therefore studies of oligomers provide an opportunity to eliminate the influence of chain length distribution.

II. EXPERIMENT

After purification the PHP was evaporated onto sapphire in high vacuum of pressure $<10^{-6}$ mbar. The substrate was at room temperature to obtain a ≈ 1 μm thick, homogeneous polycrystalline layer.

The transient pump and probe experiments were done at room temperature with the films in vacuum ($p < 10^{-2}$ mbar). Femtosecond pump and probe experiments were carried out in the usual interferometric geometry. We used a Ti:sapphire laser oscillator in Kerr lens modelocking with chirped pulse amplification which provides pulses of 150 fs duration at 780 nm and energies up to 750 μJ at 1 kHz repetition rate. The sample was excited by pulses at 390 nm of 120 fs duration obtained by frequency doubling a fraction of the fundamental beam by an LiB_3O_5 crystal. The pump-pulse energy used in the experiments was 10 nJ, and the beam diameter at the sample was about 250 μm. Probe tunability was obtained using a white light continuum generated by focusing the fundamental beam into a flowing water cell. Desired wavelengths are obtained using 10 nm bandwidth interference filters or a monochromator. The time dynamics of the excited states were monitored in a broad range of wavelengths from 460 to 810 nm using suitable detectors. Since the probe beam is unpolarized the measured decay curves show the time dynamics free from polarization memory artifact.

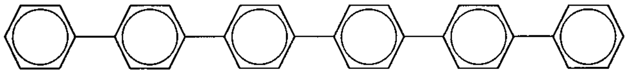

FIG. 1. *Para*-hexaphenyl (PHP) in its aromatic ground state.

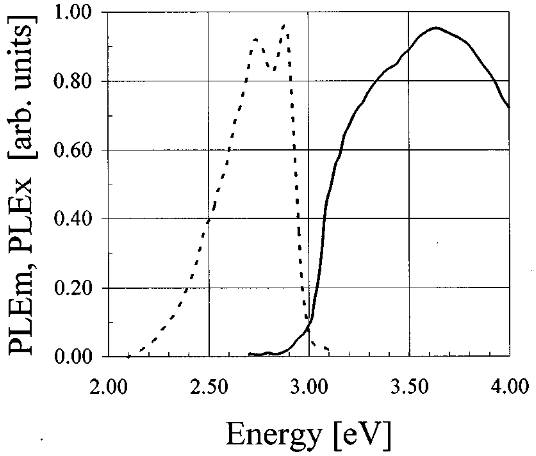

FIG. 2. Photoluminescence emission (PLEm, dashed line) and excitation (PLEx, solid line) spectra of polycrystalline PHP at room temperature.

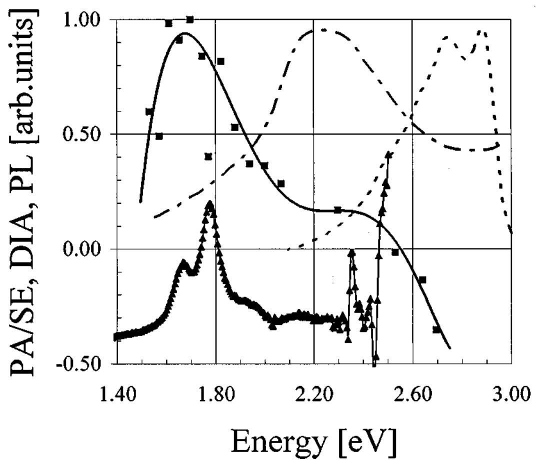

FIG. 3. cw-PA spectrum (triangles, displaced vertically for clarity) of a polycrystalline PHP film at 90 K, doping induced absorption (DIA) of PHP (dash-dotted line) in solution as obtained by Khanna *et al.* (Ref. 19), PL emission spectrum (broken line) from Fig. 2; points (■) denote the results of transient spectroscopy with zero delay between pump and probe pulse on a polycrystalline (PHP) film (solid line guides the eye; see Sec. III B).

The steady-state fluorescence spectra were measured in conventional source–monochromator–sample–monochromator–detector geometry, correcting for the spectral throughput/response of the components. For the cw-pump and probe experiments the ultraviolet lines (351.1 and 363.8 nm) of a Spectra Physics argon ion laser were utilized as pump source. The probe beam from a tungsten source was guided through the sample at 90 K and in vacuum ($p < 10^{-5}$ mbar) and after being dispersed by a grating monochromator picked up by a silicon photodiode. The pump beam was chopped mechanically at a frequency of 93 Hz, using the chopper frequency as the reference for an EG&G Princeton Applied Research lock-in amplifier 5210 which measures the pump beam induced modulation of the probe beam. To extend the spectral range of the probe beam to the infrared we also conducted cw-pump and probe experiments using a Fourier transform infrared (FTIR) spectrometer, covering the region of 200–5000 cm^{-1} (25–620 meV) as described in Ref. 15.

III. RESULTS

A. Steady-state photoexcitations

In Fig. 2 the photoluminescence (PL) emission and excitation spectra of PHP at room temperature are shown. Efficient excitation of photoluminescence is observed for quantum energies above 3 eV. The excitation spectrum does not show any vibrational replica which can be explained by the torsional degree of freedom of neighboring phenyl rings in the ground state.[16] This torsion is hindered by the more quinoidal structure of the excited, emitting state[17,18] which leads to a deviation from the mirror image rule.[19] In addition there is substantial migration of excitation energy to the PHP sites, lowest in energy, prior to emission.[20] Therefore the PL emission shows vibrational structure, mainly determined by the C=C stretching of the backbone. The peak position of the PL excitation spectrum is determined by a superposition of absorption parallel and perpendicular to the backbone as expected for a polycrystalline film [the absorption perpendicular to the backbone peaks at about 4.4 eV (Ref. 11)].

In order to probe the nonemissive photoexcited states in PHP we performed cw-PA experiments. In Fig. 3 we show a cw-PA spectrum of a polycrystalline PHP film at 90 K. The signal at room temperature was also recorded but is below the noise level. The low-temperature spectrum can be described by two Gaussian peaks centered at 1.78 and 1.67 eV with full widths at half maximum (FWHM) of 69 and 98 meV, respectively. There is an additional weak shoulder at about 1.95 eV but no further features are found in the spectral range of 1.1 to 2.5 eV. The strong photoluminescence, excited by the pump beam, has to be subtracted from the photoinduced absorption spectrum. This causes the noise seen above 2.3 eV. In order to illustrate where polaronic states are to be expected we show the doping induced spectra of hexaphenyl radical anions in solution as obtained by Khanna *et al.*,[19] which are in accordance with the electron energy loss spectra for Rb^+-doped PHP.[21] A comparison of the recorded PA spectrum, peaking at 1.67 and 1.78 eV, with the doping induced spectrum in solution shows that the doping induced absorbance occurs at higher energy by about 0.4 eV and with much broader linewidth. Although doping is known to introduce disorder, which influences the shape of the observed optical absorption spectra, we conclude that the large deviation between photoinduced and doping induced spectra rules out singly charged states as possible candidates for the observed PA. This conclusion is backed by the absence of any photoinduced infrared active vibrational modes in the range of 200–5000 cm^{-1} under the same measurement conditions as for the experiments in the visible range (sample at 90 K, same excitation conditions).

B. Transient PA

To gain insight into the temporal evolution of the photoexcited states we have also performed transient pump and probe experiments. In Fig. 3 we show the change of the probe beam transmission upon photoexcitation by the 120 fs pulses for a zero delay (i.e., maximum temporal overlap) of pump and probe beam. When we compare these data points

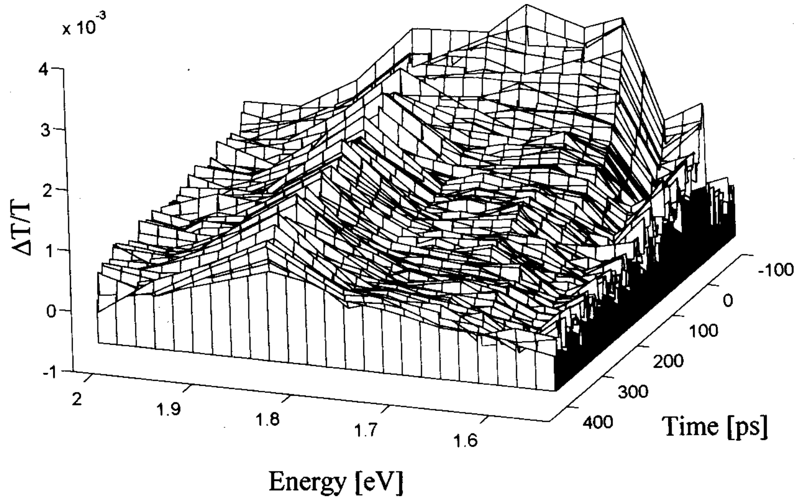

FIG. 4. Time resolved photoinduced absorption in a PHP film at room temperature excited at 390 nm.

to the obtained cw-PA spectrum we see that the peaks match quite well in both measurements although the transient experiments were conducted at room temperature.

The development in time for this PA band is shown in a three-dimensional (3D) plot in Fig. 4. Please note that the double peak structure seen in the cw-PA is also clearly present in the transient spectra. But whereas the peak at 1.67 eV dominates the transient PA spectrum at zero delay, it is found to be very small in the cw-PA, i.e., it decays much faster than the 1.78 eV peak, which is the pronounced one in the cw-PA. Therefore we will examine the $\Delta T/T(t)$ traces near these probe wavelengths (680 and 750 nm).

Figure 5 shows the time evolution of PA at 680 and 750 nm. Assuming a biexponential decay, the trace at 750 nm can be described very well by 24 and 279 ps while the curve at 680 nm yields time constants of 29 and 895 ps (smooth curves in Fig. 5).

IV. DISCUSSION

The PL quantum yield in PHP films is 30%.[1] A slightly higher value of 37% is found for solutions of hexathiophene.[12] For the oligothiophenes it is well established that the intersystem crossing (ISC) to the triplet manifold is the main nonradiative decay process of the excited singlet state S_1.[12,22] In this case PA bands due to $T_1 \rightarrow T_n$ transitions are expected in the near infrared. Due to the forbidden character of the spin flip, population of the lower lying triplet state usually occurs on a hundred ps time scale. The faster decay of the singlet state prevents a sizable triplet state population. Alternatively in the condensed phase other excitations like charged states or intermolecular species (photoinduced dimers or charge transfer excitons) may quench the PI.

For photoexcited long living charged states, which show lifetimes of the order of 1 μs and above, we expect a cw-PA spectrum with electronic transitions and infrared active vibrational modes, very similar to the doping induced effects. From Fig. 3 we see that there is no cw-PA peak, similar to the doping induced transitions in PHP. We also could not detect any IR activity of the photoexcited species with a relative transmission change greater than 2×10^{-5}.

When comparing the doping induced electronic transition in PHP with the transient spectrum at zero delay of pump and probe beam (Fig. 3) one can see that the transient spectrum shows a shoulder at 2.3 eV in the region where the polaronic transition is expected. Therefore in accordance with photoconductivity data on PHP,[23] which show that *mobile charged states* decay within 110 ps this may be the absorption signature of the photocreated polarons. The fact that this signal is not observed in cw-PA can be attributed to the absence of significant trapping of these polarons, which would enable to see them in a cw-pump/probe experiment. This phenomenon is common for conjugated materials of a very low defect content.[24,15] Furthermore we can conclude for the transient spectra that only the short components (up to 110 ps) can be attributed to mobile charges while the long living component (e.g., 895 ps at 680 nm) can only be due to trapped charges or neutral states.

Another point indicating that the observed peaks in the cw-pump/probe spectrum at 1.78 and 1.67 are not due to charged transitions is their energy spacing of 0.11 eV. For doped *quaterphenyl* the two absorption bands with a spacing

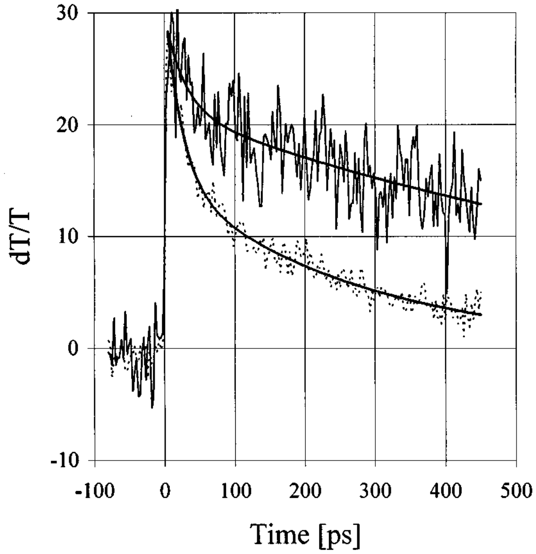

FIG. 5. $\Delta T/T(t)$ traces at probe wavelengths 680 (solid line) and 750 nm (dashed line) corresponding to the time behavior of the two peaks of the cw-PA. The spectra are normalized for equal intensity at zero delay; smooth solid lines are biexponential fits (see text).

of about 0.2 eV (Ref. 19) are attributed to vibrational splitting of the C—C stretching mode of planar-quinoid radical ions which is strongly coupled to the electronic structure.[25] In accordance with that we find a vibrational spacing of 0.18 eV for planar *polyphenyls* for the polaronic transitions,[26] while a considerably lower spacing of 0.08 eV is found for the triplet-triplet transitions in these planar polyphenyls.

An additional indication against the assignment of the 1.78 eV peak as due to polarons is the *mere existence of a well resolved apparent vibrational splitting*, because the vibrational replica, seen in the absorption spectrum of charged states in conjugated oligomers becomes less prominent upon increasing the size of the molecule. In quaterphenyl it is seen but it is completely lost for hexaphenyl (see Fig. 3). This behavior is also seen in oligothiophenes.[27]

Therefore, (1) the missing IR activity, (2) the apparent vibrational splitting, (3) the magnitude of the splitting, and finally (4) the energetic position of both the peaks at 1.67 and 1.78 eV lead us to rule out *singly charged states* to be responsible for the cw-PA spectra. *Doubly charged* dications of PHP are found to absorb at 1.54 eV (Ref. 19) and show a FWHM of 160 meV. Again this does not correspond to what we find in cw-PA. Here, however, we have to mention that studies on hexathiophene[28] have revealed that by either cooling the sample to 10 K or by using a highly ordered film a bipolaronic absorption can be seen. In the case of the highly ordered film bipolarons seem to be the only detectable species in the cw-PA. Therefore we cannot exclude that one of the peaks at 1.67 or 1.78 eV might be due to a bipolaronic transition. This assignment is however problematic since in this case photoinduced infrared modes should also be detectable. Finally we want to mention that the absence of photoinduced infrared modes is in agreement with the absence of any pronounced peaks in the subgap region of the electromodulation spectra obtained on PHP. Although performed at room temperature these experiments show a clear polaron signal for planar polyphenyls, but no charge induced states for PHP.[29,30]

Based on the previous reasoning and since interpolating the energetic positions of the triplet-triplet transition of terphenyl, quaterphenyl, and the planar polyphenyls plotted versus conjugation length,[31] leads to an expected value of around 1.8 eV in good agreement with the 1.78 eV, we conclude that the 1.78 eV peak in the cw-PA is due to a triplet triplet transition. Also for α-sexithiophene a narrow PA peak of 0.1 eV FWHM was reported[32] and in agreement with the interpretation by other groups[12,33,34] this peak was attributed to absorption by the T_1 triplet state after a relaxation of the lowest singlet excited state S_1 via intersystem crossing. The sharp absorption band is the consequence of the strong localization of the triplet wave function, which has an extension of 3.6 Å for sexithiophene.

In frozen solutions of oligothiophenes a PA band is found below the energy of the triplet-triplet absorption.[33] Its intensity depends on the oligomer concentration and it completely dominates the cw-PA of the pure films. Therefore Janssen *et al.*[33] conclude that upon aggregation of the oligothiophenes, small clusters or microcrystallites are formed, which give rise to a PA band below the triplet absorption. Based on the previous arguments we assign the 1.78 eV band to triplet absorption in accordance with the expected position and FWHM, and the 1.67 eV band to aggregate states formed in the PHP films.

While both cw and transient photoinduced absorption data probe the population of absorbing species additional insight can be obtained by looking at the $S_1 \rightarrow S_0$ transition (i.e., emission). We find a positive $\Delta T/T$ above 2.5 eV. As can be seen in Fig. 3, we find cw-PL in this region. However, there is no significant absorption of PHP in this region (Fig. 2). Therefore we exclude photobleaching of absorptive transitions as a possible reason for the positive $\Delta T/T$ and we attribute the latter to stimulated emission (SE). Spontaneous emission is excluded since the positive signal disappears when the probe beam is blocked and spontaneous emission shows no dependence on the temporal pump-probe delay. In contrast to the PA signal, which probes the induced *population of an absorbing species* (n_a), the SE signal yields the population of an *emitting species* (n_e). This population is described by a nonexponential decay with a initial time constant of 29 ps, which is similar to lifetimes reported for hexathiophene films [40 ps (Ref. 32)]. We expect PA which is exclusively due to excited states to show the same decay time, and in fact the PA curves shown in Fig. 5 show initial decay times of 24 and 29 ps, respectively. Therefore the initial PA is partly due to excited states absorption $(S_1 \rightarrow S_n)$ as well as to triplet absorption. The observed dynamics reflect two different processes: at 680 nm the ISC to the triplet, with the triplet absorption fully superimposed on the broader singlet absorption. At 750 nm the decay of the singlet towards a plateau which is due to trapped excitons within the aggregates.

Nonexponential behavior in general is typical of disordered organic solids and can be related to a distribution of lifetimes. The slower dynamics observed at 680 nm is determined by the buildup of the triplet population which is expected to be nonexponential as well. In fact the distribution of recombination times for the singlet excitons implies a distribution of ISC times to the triplet. As a consequence we cannot extrapolate a single time constant for the triplet population buildup, which describes the process, but determine the time scale: it is approximately a few hundred ps.

Concerning the SE we want to add that competition between SE and PA is intensely debated for conjugated polymer films where—depending on the synthesis and purification—in some cases the broad distribution of conjugation lengths influences the observed photophysics.[14] For poly(*para*-phenylene vinylene) (PPV) homopolymers PA is observed to overwhelm SE,[35] for dilute PPV/polystyrene *blends*[36] and PPP-type *blends*[37] this competition is not observed. We have also demonstrated recently that for a pure homopolymer with high intrachain order in the solid state, a ladder-type methyl substituted PPP, no such competition is observed.[38] In the transient pump and probe experiments on PHP we do also only observe competition between PA and SE in the very limited energy range of 2.2–2.5 eV, where the cw PI intensity is down to about one-fifth of its maximum and the transient pump and probe spectrum shows PA, probably due to polarons. Therefore we observe a nearly complete spectral separation of PA and SE.

V. CONCLUSIONS

We have presented and discussed photoinduced transmission difference spectra of PHP which shows PA and SE on the ps scale, while only PA is seen on a ms scale. From the identical decay behavior of SE and PA during the first 100 ps we conclude that the initial PA is due to $S_1 \rightarrow S_n$ optical transitions. The main deactivation path is proposed to be ISC to the triplet manifold. Due to the sample inhomogeneity the dynamics is nonexponential, preventing the determination of simple time constants. Our transient results show that in about 400 ps the initial PA becomes equal to the ms PA, providing an estimation for the ISC time scale. Differences in the peak shape are mainly attributable to the difference in sample temperature. A residual fraction of singlet excitons is long lived, appearing in the ms PA and it is assigned to trapped species within aggregates of PHP molecules.

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