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Charge-induced dephasing in thin polythiophene films

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The third-order nonlinear susceptibility $\chi^{(3)}$ normalized to the absorption coefficient α displays a dramatic drop at 0.4 eV above the S_0-S_1 transition in polythiophene derivatives. Steady-state photoconductivity data show the intrinsic photocrent starting exactly where the decrease in $\chi^{(3)}/\alpha$ is seen. These results point to a change from bound excitons to free-electron hole pairs at 0.4 eV above the S_0-S_1 transition, and support the description of such disordered conjugated polymers using a molecular approach rather than as infinite one-dimensional semiconductors.

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I. INTRODUCTION

Organic materials are currently at the forefront of intense research in nonlinear optics because of their unique electronic and optical properties. Conjugated polymers comprise an important material system in this regard, combining the structural and mechanical properties of polymers with optoelectronic properties commonly associated with inorganic semiconductors.[1] The discovery of electroluminescence in conjugated polymers[2] has opened up a new field in which considerable attention has been given to the photophysical and electro-optical properties of these materials due to their potential application in light emitting devices.[3,4] An important recent development was the observation of stimulated emission from a variety of poly(p-phenylenevinylene) (PPV) and its derivatives.[5–7] Despite the amount of work in this area, there remain fundamental questions about the nature and the kinetics of the electronic excitations in these materials. In particular, an accurate description of the primary photoexcitations is critical to the application in light-emitting diodes (LED's) and lasers. Current debate centers on alternate descriptions of the conjugated chains as quasi-one-dimensional semiconductors, or using a molecular approach including the effects of random disorder.

The observed large energetic shift between absorption and emission spectra leads to the assumption that strong electron-phonon interaction is a characteristic feature of conjugated polymers and therefore, can be described in the traditional one-dimensional semiconductor model.[8] Here, the polymer is treated as a set of fully elongated infinite chains with negligible interchain interaction. The primary excitations are discussed as lattice stabilized quasiparticles, e.g., polarons and bipolarons. Photoluminescence is attributed to the decay of the so-called polaron exciton and the observed Stokes shift reflects the polaron binding energy.

An alternative model based upon results obtained by site-selective fluorescence (SSF) spectroscopy[9] focuses on a molecular approach. Within this model a conjugated polymer is treated as an array of localized subunits due to the inherently present disorder in noncrystalline polymers. The disorder leads to a localization of the electronic wave function and a broadening of the density of states (DOS). In this picture the elementary excitations are Coulombically bound electron-hole (*e-h*) pairs not different from the excited states of oligomeric model compounds.[10,11] Additionally, SSF spectra show a very small Stokes shift only, indicating that the electron-phonon interaction is weak and suggesting that the redshift between absorption and emission spectra observed in conventional photoluminescence spectroscopy reflects the loss of electronic energy in course of the spectral relaxation.[12] Within the context of this model charge generation is a secondary process as it is in molecular solids in general.[13]

II. EXPERIMENT

Polythiophene is an important member of the class of conjugated polymers. Although it generally shows weak luminescence, it has been extensively investigated for its good conductivity and relatively high optical nonlinearity.[14] Recently, polythiophene or its oligomers have been fabricated into thin-film organic transistors and smart pixels.[15] Here, we report a study undertaken to elucidate the photoexcitation and decay in a class of polythiophene derivatives. We use a combination of degenerate four wave mixing to determine $\chi^{(3)}$ and stationary photocurrent measurements in a sandwich configuration to measure the charge-carrier generation. We focus on trying to find a consistent description of the results of both experiments in terms of the photoexcited states, in particular using the molecular approach described above.

We look at a number of polythiophene derivatives in which the band gap, oscillator strength, and optical nonlinearity can be controlled to some degree.[16] These derivatives, prepared using the Stille coupling reaction, consist of randomly alternating units of unsubstituted thiophene or thieno[3,4-b]pyrazine rings. This method allows materials to be produced with minimum structural defects, doping, or overoxidation and a wide range of functional groups to be incorporated as side groups into the polymer. By adjusting the ratio between these units as well as the substituents on the pyrazine ring, the solubility and optical properties of the resulting polymer may be adjusted. Figure 1 shows the mo-

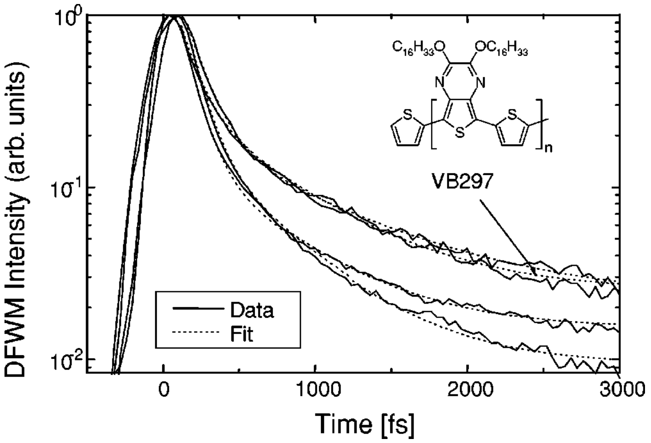

FIG. 1. Typical DFWM transients of some polythiophene derivatives with variable conjugation length. The transient observed for the VB 297 is marked by an arrow. The inset shows the chemical structure of the polythiophene derivative synthesized via the Stille coupling.

lecular structure of the polymer used in this investigation. Thin films were prepared by casting the solution in chloroform onto glass slides under controlled conditions and allowing a slow (several days) evaporation of the solvent. The resulting film had a thickness of 0.5 μm and an optical band gap of about 1.48 eV [see Fig. 2(a)].

Degenerate four wave mixing (DFWM) experiments were carried out in the folded box coherent anti-stokes Raman spectroscopy (CARS) geometry. More details of the experimental setup may be found in Ref. 16. Pulses with approximately 100 fs width were generated in the 720–900-nm wavelength region using a mode-locked Ti:sapphire (Mira 900F, Coherent Co.) followed by a pulse picker to reduce the repetition rate to 100 kHz. Pulses with similar widths were obtained in the 500–700-nm region with an optical parametric amplifier (OPA 9400, Coherent) pumped by a regenerative Ti:sapphire amplifier (RegA 9000, Coherent). The beam was split into three, which were focused onto the sample spot diameter of approximately 20 μm. Two of the beams "write" a grating through the third-order nonlinear optical susceptibility, $\chi^{(3)}$, with the third beam "reading" the grating. The deflected wave passed through a spatial filter and was detected by a silicon photodiode (Hamamatsu), the output of which was sent through a preamplifier followed by a lock-in amplifier (SR560, Stanford Research Systems) to improve signal-to-noise ratio.

For measuring the electronic response, the two write beams (irradiance I_1 and I_2) are polarized parallel to each other and are temporally and spatially overlapped on the sample. The read beam (I_3) can be delayed in time by a translation stage, allowing measurement of the temporal response of the nonlinearity. As a reference, we used $CS_2(\chi^{(3)} \approx 6 \times 10^{-13}$ esu), which is transparent in the wave-

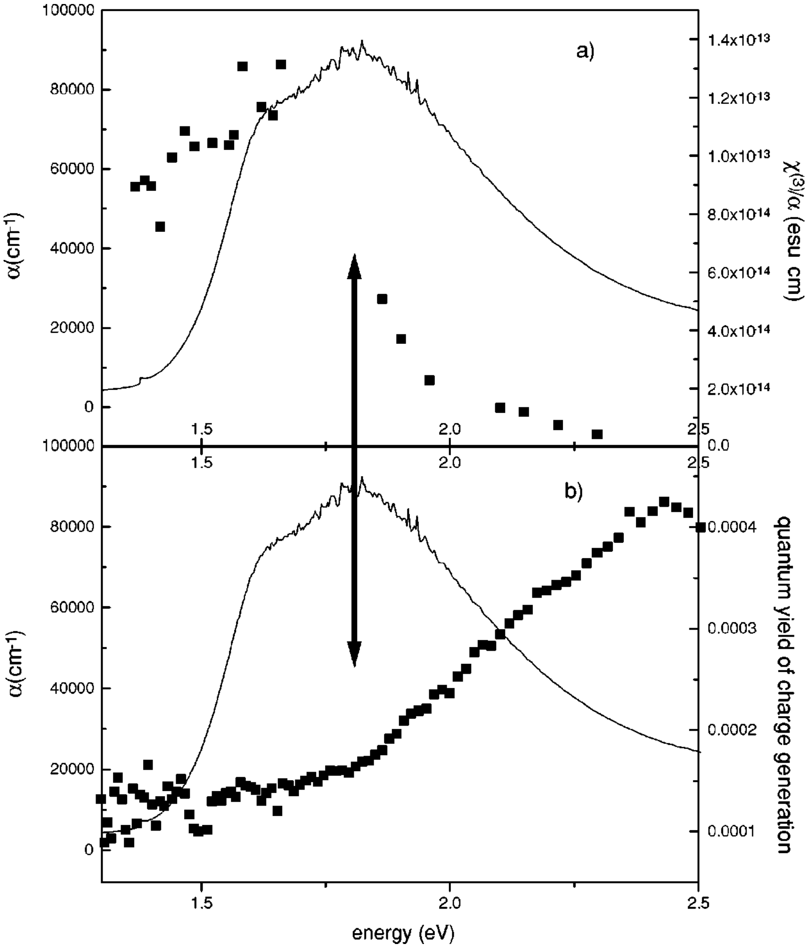

FIG. 2. (a) Energy dispersion of the $\chi^{(3)}/\alpha$ value of the VB 297. (b) Plot of the photocurrent action spectrum of the polythiophene film (VB 297) upon irradiating through the ITO/SiO anode. The absorption spectrum of the VB 297 is shown for comparison. The arrow is a guide to the eye and marks the onset of the photocurrent as well as the spectral position where the drop of the $\chi^{(3)}/\alpha$ value occurs.

length region of our experiments. The magnitude of the third-order susceptibility is determined using

$$|\chi_s^{(3)}| = |\chi_{\mathrm{ref}}^{(3)}| \left(\frac{n_s}{n_{\mathrm{ref}}}\right)^2 \sqrt{\frac{I_{4,s}}{I_{4,\mathrm{ref}}}} \sqrt{\frac{(I_1 I_2 I_3)_{\mathrm{ref}}}{(I_1 I_2 I_3)_s}} \times \alpha L_{\mathrm{ref}} \frac{\exp(\alpha L_s/2)}{1-\exp(-\alpha L_s)}, \tag{1}$$

where n_s and n_{ref} are the refractive indices of the sample and reference, respectively, α is the absorption coefficient, and L_s and L_{ref} are the thicknesses of the sample and reference, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the diffracted beam (I_4) for parallel-polarized writing beams as a function of the delay time τ of the reading beam with respect to the excitation pulses. The observed nonlinear response appears to be instantaneous (buildup) and is due to the generation of excitons. The decay of the nonlinear signal involves two time scales indicating that there is more than one relaxation channel involved in the decay process. The transient response (decay) can be well described in a first approximation by a biexponential decay with decay times of $\tau_1 \approx 100$ fs and $\tau_2 \approx 1$ ps, respectively. The ultrafast decay component may, in principle, be due to a coherent interaction (coherent artifact) between the three beams in the DFWM experiment. By changing the polarization of I_3 with respect to I_1 and I_2 the coherent artifact should be eliminated. However, no change in the dynamics of the ultrafast component has been found in our measurements. Therefore we attribute this ultrafast component to a genuine intrinsic process. Theoretical considerations show that, by contrast with linear optics, nonlinear optics may in principle exhibit critical behavior related to localization, a phenomenon which is strongly connected to disorder.[17] The material under investigation is strongly inhomogeneously broadened as can be seen from the absorption spectrum in Fig. 2(a). Therefore we have to take into account the inherently present disorder in the interpretation of the irreversible decay of the nonlinear signal in this class of materials.

We argue that the fast initial process is related to disorder present in our samples. The influence of disorder on the dynamics of optical excitation on an ultrafast time scale has been studied theoretically in the context of four wave mixing in the spontaneous photonecho configuration and for noninteracting particles.[17] In this case the dephasing of the optical polarization is of primary interest, while in our present configuration the dynamics of the optically excited density is monitored. Nevertheless, the fundamental principles also apply here.

The electronic eigenstates in a disordered environment can be localized and are then characterized by a localization length that depends on disorder. We assume that the wavelength of the population grating is comparable to the localization length of the relevant optical excitations being determined by the conjugation length of the underlying polymer segments. The population grating responsible for the diffracted signal is then composed of an ensemble of eigenstates with energies in the spectrum of the laser pulse and phases such that the sinusoidal grating is produced during the duration of the optical pulse. The grating can then be viewed as a wave packet given by a suitable light-induced superposition of the excited eigenstates. After the pulse the individual eigenstates develop in time according to their eigenenergies, i.e., the phase factors in the linear superposition change in time and the wave packet tends to be smeared out, thus decreasing the diffraction efficiency of the grating which leads to a decay of the signal. The time scale of this decay is given by the bandwidth of energies of the eigenstates building up the grating, which in turn are determined by the laser spectrum. Since this is given by the duration of the laser pulse the decay takes place on a time scale comparable with the duration of the pulse. The decay is the more pronounced, the larger the localization length is. For strongly localized excitations with localization length much smaller than the wavelength of the grating no effect of this ultrafast decay is expected, since an effective smearing out of the packet is not possible. For large localization length exceeding the wavelength of the grating there can be a total decay of the signal on the ultrashort time scale of the pulse. For intermediate cases the decay is still fast, however, not complete, such that a finite diffraction efficiency remains in the long-time limit. This finite value is the smaller the more extended the eigenstates are. In Fig. 1 this behavior can be clearly seen in polythiophene derivatives with varying degrees of disorder. For the upper two traces the crossover from the short-time to the long-time regime appears at a larger DFWM intensity, while for the lower two traces, which correspond to more delocalized states this cross over happens at a lower intensity.

In the long-time regime the phonon assisted hopping processes become important leading to a decay with a time scale given by the hopping rates, which is, depending on spatial arrangement of the optical excitations, their density of states (DOS) and on temperature, usually much longer. From Fig. 1 one obtains decay rates in the long-time regime that are on the order of about 1 ps. This compares favorably with the rates deduced from PL upconversion measurements.[12]

Taking into account that the large resonant nonlinearities in these conjugated materials are usually attributed to saturation of the absorption as can be inferred from *Z*-scan measurements,[18] the scenario described above can be summarized as follows: localized excitonic states will give a larger nonlinear polarization than extended excitonic states. In ordered semiconductors, similar effects are due to excitonic enhancement,[19] however, the inherent disorder present in polymers such as these makes the discussion of the dropoff in terms of dephasing described by Lonsky *et al.*[17] more appropriate.

Wavelength-dependent DFWM experiments show that the main contribution to the nonlinear response comes from the low-energy side of the absorption spectrum. Normalizing the measured $\chi^{(3)}$ value with the absorption coefficient at a certain wavelength leads to a constant $\chi^{(3)}/\alpha$ value [see Fig. 2(a)] well known from the literature.[20] By scanning the wavelength of the DFWM experiment further across the absorption profile a dramatic decrease of the $\chi^{(3)}/\alpha$ value appears around 0.4 eV above the $S_1 \leftarrow S_0$ 0-0 absorption edge. Taking into account that the exciton binding energy in this class of materials is of the order of about 0.3–0.5 eV as has been revealed by time-resolved luminescence spectroscopy,[21,22] it is likely that intrinsic charge generation leads to the decay of the coherence in the nonlinear response. Support for this assumption comes from the decay time $\tau_2 \approx 1$ ps which concurs well with the hopping time (dwell time) of an excitation residing on a site having lower energy neighbors, as can be inferred from luminescence upconversion spectroscopy.

Subsequently, we focus on the scenario described above. Therefore steady-state photoconduction measurements have been performed on an 80-nm-thick VB 297 film spin coated from a hot chloroform solution (1% weight/weight). The film was deposited on top of an indium tin oxide (ITO) coated glass slide. On the ITO a 6–8-nm-thick layer of silicon monoxide (SiO) was evaporated, to block charge injection.[23] At the same time SiO affects discharge of carriers only marginally, due to its lower band gap and its higher dark conductivity as compared to that of polymeric materials $[10^{-13}$ vs $10^{-15}(\Omega\ \mathrm{cm}^{-1})]$. Before completing the sandwich configuration by evaporating aluminum (Al) top electrodes of 0.07 cm^2 the device was kept in a vacuum chamber at a pressure of about 10^{-6} mbar at 295 K for 12 h to remove residual solvent.

The stationary photocurrent measurements were carried out in a temperature-controlled cryostat using a calibrated xenon lamp as a light source and quartz optics. Lock-in techniques were employed for signal detection and the photocurrent action spectrum was recorded in a pointwise manner from low to high photon energies. In order to minimize space charge effects the device was shorted after each measurement and kept in the dark for 5 min before the next data point was taken immediately after turning on the light. Dark currents were of the order of 10^{-10} A/cm^2 typically two orders of magnitude lower than the lowest photocurrent considered for data evaluation. This rather low value of the dark current demonstrates the purity of our device.

Figure 2(b) shows the photocurrent action spectrum of a 80-nm-thick VB 297 film recorded upon irradiating through the ITO/SiO anode ($j_{+,\mathrm{SiO}}$) at $E = 2.5 \times 10^5$ V/cm together with the absorption spectrum. The photocurrent is normalized to the number of photons absorbed in the bulk. The yield spectrum displays some fluctuations in the range of the $S_1 \leftarrow S_0$ 0-0 absorption edge followed by a plateau up to $E_{\mathrm{exc}} \cong 1.68$ eV and an additional monotonous increase at $E_{\mathrm{exc}} > 1.68$ eV. The photocurrent fluctuations in the range of the absorption edge may result both from the low signal-to-noise ratio in this spectral range and from residual extrinsic contributions to the photocurrent. From previous work[23] it is known that $j_{+,\mathrm{SiO}}$ can be attribute to volume photoionization. In VB 297 the intrinsic photogeneration starts 0.35–0.40 eV above the $S_1 \leftarrow S_0$ 0-0 absorption threshold. This is in accord with the photoionization in polydiacetylenes[24] where the intrinsic charge carrier generation starts ≈0.5 eV above the absorption edge and confirms that an energy $\gg kT$ is necessary for generating a free *e-h* pair from an excitonic precursor state. Comparable results recently obtained on PPV derivatives corroborate this.[23,25]

A comparison between DFWM and photocurrent measurements clearly shows the coincidence of the severe decrease in the $\chi^{(3)}/\alpha$ values and the onset of the intrinsic photogeneration. We have directly observed this drop when the exciting beams in the DFWM experiment are about 0.4 eV above the $S_1 \leftarrow S_0$ 0-0 absorption edge of the polythiophene derivative. The roughly constant $\chi^{(3)}/\alpha$ value below the band edge and the dramatic decrease above suggest a change in the nature of the photoexcited state at this point. This behavior can be consistently explained using a molecular approach as due to the onset of intrinsic photogeneration of free *e-h* pairs leading to the decay of the coherent nonlinear response. Our data indicate that the exciton binding energy in this class of materials is on the order of 0.4 eV.

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