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Femtosecond Time-Resolved Spectroscopic Studies on Thiophene Oligomers

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Thiophene oligomers (*n*T) with two to six units in solution are studied under pulse excitation (308 nm,350 fs) in the spectral range 430−830 nm. Transient absorption and induced fluorescence emerge within 1−2 ps. An “instant” absorption (A0), which shows a size dependent spectral structure superimposes the induced fluorescence during the first 500 fs. The fast kinetic processes of different *n*T are very similar during the first picosecond. They were interpreted as relaxation starting from the highest accessible electronic level down to the lowest excited-state S_1 of each oligomer.

Introduction

Oligothiophenes (*n*T, n = number of thiophene rings) are model compounds for polythiophene. They also show promising properties for device applications as field effect transistors,[1] luminescence diodes,[2] or fast optical switches.[3] The study of the ultrafast electronic relaxation channels is of great interest for the understanding of the electronic behavior, which is important to device properties.

Optical spectroscopic properties of oligothiophenes in solution were central to former investigations.[4−18] Picosecond time-resolved fluorescence measurements were presented in refs 4−7. It was found that fluorescence occurs from the lowest excited singlet state of 2T−6T and that the corresponding $S_1 \leftarrow S_0$ transitions are dipole allowed. No crossing of excited B and A energy level positions with oligomer size, as known for diphenylpolyenes,[32] was observed. The fluorescence lifetimes increase from about 50 ps in the case of 2T to about 1100 ps for 6T. The corresponding fluorescence quantum yields increase from 0.01 for 2T[12] to 0.35 ± 0.07 for 6T.[4] Several investigations showed that the intersystem crossing is very effective for oligothiophenes[9−12] and responsible for the high nonradiative decay rates. On the basis of the fluorescence kinetics[4−7] and using the reported triplet absorption spectra,[9−12] we were able to understand the transient spectral behavior of *n*T on a picosecond scale.[15] In picosecond pump−probe experiments we found two typical transient absorptions: A1, red-shifted to stationary absorption, and A2 located close to the respective fluorescence but of quite different time behavior. Additionally, there was the stimulated fluorescence F of each *n*T. The red band A1 decays monoexponentially and could be assigned to the transient absorption occurring from the S_1 state by comparing with the results of time-resolved fluorescence measurements of the corresponding *n*T.[4−7] The A2 bands appear in nearly the same spectral range of the fluorescence with considerable delay. The A2 bands show the same spectral band shape like that of the triplet−triplet absorption spectra of the respective *n*T.[9−12] By our picosecond time-resolved spectroscopic studies, we found the intersystem crossing process to proceed with the rate constants of S_1 depletion of the corresponding *n*T. The results of the picosecond spectroscopic studies of *n*T are summarized in Table 1. They demonstrate the size dependence of transient spectra and decay times. Both transient bands, A1 and A2, shift with increasing n to longer wavelengths. This behavior shows that even transitions between excited states follow the extended FEMO model.[19] The increase of the fluorescence lifetime with n is mainly caused by decreasing triplet formation.

Femtosecond experiments reported in this paper are expected to allow for the observation of relaxation processes between the state accessible by energy of excitation (4 eV) and the S_1 states known by their fluorescence and transient absorption bands (summarized in Table 1).

The first femtosecond pump−probe experiments were reported on 2T−4T and 6T1 in dioxane[20,21] and on 3T by Yamaguchi et al.[22] These studies showed that the transient absorption bands known from the picosecond studies emerge during the femtosecond excitation pulse. Spectral shifts during the first picosecond as reported in our previons work[20,21] were proved to be caused by delay time differences of the spectral parts of the white light femtosecond probe pulse.

The femtosecond time-resolved investigation has been performed to extend the knowledge of the transient optical behavior of the thiophenes to this ultrashort time region. Open questions, therefore, are how fast the occupation of the lowest excited singlet state takes place and whether there are processes to observe during this procedure. Furthermore, it is interesting to find out if higher electronic states predicted by semiempirical quantum chemical calculations of *n*T [23] influence the relaxation behavior.

In this paper we report on the transient spectra and kinetics of the series of oligothiophenes that appear during and after excitation with 308 nm pulses of 350 fs duration. The transient absorption behavior of 2T could not be measured in our previous work by excitation with $\lambda = 349$ nm because of the small absorbance of 2T at this wavelength. Using the UV pulses of $\lambda = 308$ nm of the femtosecond spectrometer, we were able to include 2T in the investigation. For 2T we report the increase and decay behavior after excitation.

Additionally, the high excitation intensities of the amplified femtosecond light pulses allowed the investigation of the transient behavior after one- and two-photon excitation. The different excitation conditions may lead to the occupation of electronic states of different symmetry, which may affect the relaxation channels. Processes that proceed after one- and two-photon excitation were observed with 6T.

Experimental Section

Materials. The *n*T were produced by Naarmann et al. by Grignard coupling and were characterized by standard methods.[24] Instead of 6T, the β-substituted dodecylsexithiophene

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TABLE 1

oligomer	absorption E_{max}/eV (λ/nm)	fluorescence E_{max}/eV (λ/nm)	absorption A1 E_{max}/eV (λ/nm)	absorption A2 E_{max}/eV (λ/nm)	lifetime τ (ps)
2T	4.05 (306)		2.50 (495)		(51 ± 5)
3T	3.49 (355)	3.04 (408)	2.07 (600)	2.70 (460)	(135 ± 13)
4T	3.16 (392)	2.76 (450)	1.75 (710)	2.21 (560) 2.08 (595)	(531 ± 53)
5T	2.99 (414)	2.57 (483)	1.47 (845)	1.97 (630)	(880 ± 88)
6T	2.85 (435)	2.45 (507)	1.37 (905)		
6T1	2.91 (426)	2.44 (509)	1.38 (900)	1.82 (680)	(1018 ± 102)

(6T1) was used in the time-resolved experiments because of the better solubility of this material in organic solvents due to the side groups on the second and fifth thiophene ring. The *n*T were dissolved in dioxane (Aldrich, spectroscopic grade). The maximal concentration was 1 × 10^{-3} mol/L. Stationary absorption and fluorescence spectra in dioxane at room temperature are given in ref 15.

Experimental Equipment. The experiments were performed using a femtosecond laser spectrometer described elsewhere.[25] It is based on a CPM ring laser that generates red light pulses (wavelength $\lambda = 616$ nm, pulse duration $\tau = 80$ fs). Excimer laser pulses (Lambda Physics EMG 150, $E = 200$ mJ, $\tau = 20$ ns) were used for pumping a four-stage dye amplifier. After amplification the pulses were shortened in a recompression unit. The amplified pulses ($E = 50$ μJ, $\lambda = 616$ nm, $\tau = 80$ fs) were used for excitation in the two-photon experiments and a part of them for the generation of white light pulses (femtosecond continuum $\lambda = 400-800$ nm). UV pulses are necessary for one-photon excitation of thiophene oligomers. They were generated by frequency doubling in KDP and amplification of the UV pulses in a second excimer laser tube. In this way excitation pulses at $\lambda = 308$ nm with $E = 200$ μJ and $\tau = 350$ fs were available for pump−probe measurements. The transmitted white light pulses were registered as test I^{test} and reference I^{ref} intensities by an optical multichannel analyzer (OSMA Spectroscopic Instruments).

To improve the accuracy, about 40 test and reference spectra were accumulated and then used to determine the difference spectrum at each delay setting. From the transmission measurements with and without excitation the difference of the optical density $\Delta D(\lambda,t)$ averaged on *n* pulses was calculated by eq 1:

$$\Delta D(\lambda,t) = -\log \frac{\sum_{k=1}^{n} (I_k^{test,we}/I_k^{ref,we})}{\sum_{j=1}^{n} (I_j^{test,ne}/I_j^{ref,ne})} \qquad (1)$$

where the subscripts mean the following: we = with excitation, ne = no excitation, n = number of selected pulses, test = test beam, and ref = reference beam. The $\Delta D(\lambda,t)$ values were estimated with an accuracy of about 0.01. From the transient absorption spectra the kinetics at selected wavelengths were estimated and corrected for the dispersion of white light continuum (see below).

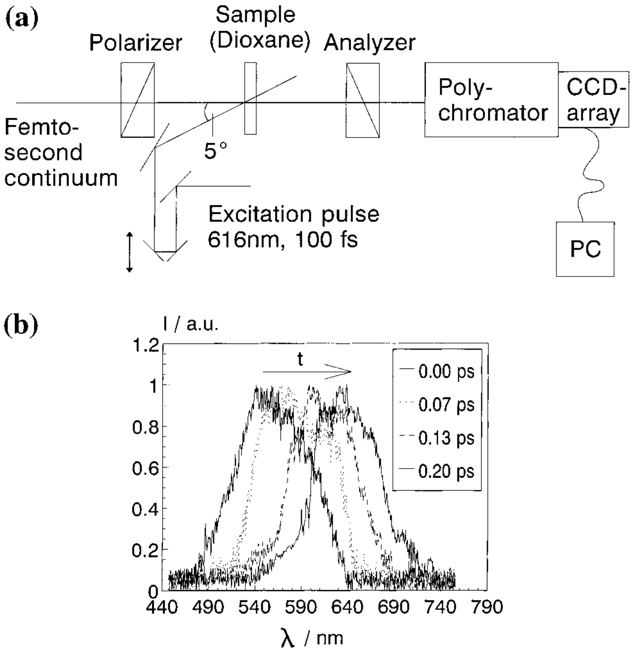

Figure 1. (a) Optical Kerr effect arrangement to correct for the dispersion of the femtosecond white light continuum. (b) Spectral parts of white light continuum measured by Kerr switch.

Experiments with UV excitation pulses of $E = 4.02$ eV ($\lambda = 308$ nm, $\tau = 350$ fs) were performed for 2T−6T1. Strong one-photon absorption at this wavelength takes place at all *n*T ($n = 2-6$), as expected from the stationary absorption spectra. Moreover, we tried to perform experiments using the red pulses of $E = 2 \times 2.01 = 4.02$ eV ($\lambda = 616$ nm, $\tau = 80$ fs). With two-photon excitation a measurable occupation of excited states was obtained only for 6T1. The two-photon absorption was less effective for the smaller molecules. Experiments with higher intensity could not be performed because of nonlinear interaction processes, e.g., induced Raman scattering, in the sample.

Kerr Effect Measurement of Dispersion of the White Light Pulse. The different wavelengths of a femtosecond white light pulse experience a temporal delay between each other when they cross optical elements with dispersion. We observed in our experiment a shift of the transient spectra during the first 2 ps. This shift was found to be caused by the dispersion of the femtosecond spectral continuum. In the experiments presented in this paper we diminished the shift by using Al mirrors instead of lenses. The remaining dispersion was measured by a Kerr gate experiment described below and was taken into account in the femtosecond kinetics and for the interpretation of femtosecond time- and spectral-resolved measurements. The polarizers (polarizer before and analyzer behind the sample) are crossed so that no signal of the white light pulse is registered by the CCD array. The polarization direction of the probe light spins in the Kerr cell during the propagation of the strong laser pulse. The spectral part of the white light probe pulse that cross the excitation pulse in the Kerr cell at the same time gives a signal. When the temporal position of the excitation pulse was changed to the position of the white light pulse, the different spectral parts of the continuum were registered (Figure 1b). A temporal shift of about 66 fs leads to a spectral shift of about 30 nm. This result was taken into consideration in the interpretation of the spectra and of the kinetic curves at selected wavelengths.

For the pump−probe measurements on the *n*T, we started with registration of the white light test pulse before the excitation

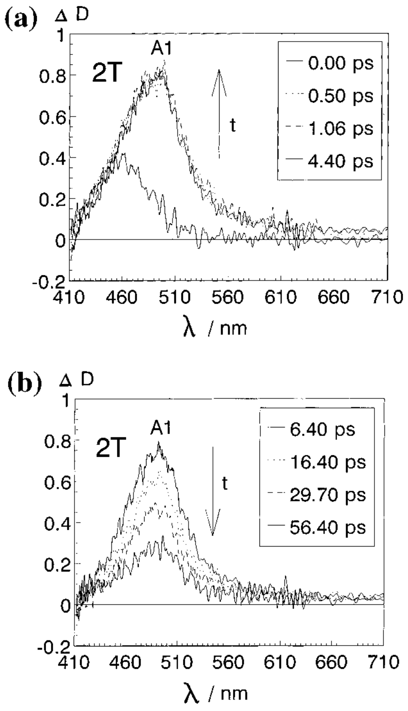

Figure 2. ΔD spectra of 2T (A1 band) at various delay times: (a) 0−4.4 ps; (b) 6.4−56.4 ps.

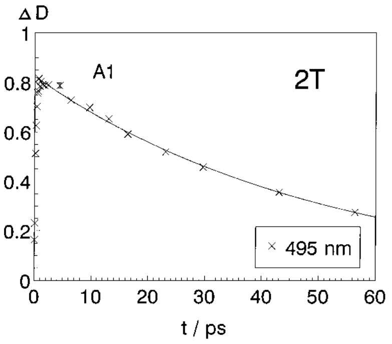

Figure 3. Time dependence of transient absorption A1 that gives the S1 decay time of 50 ps.

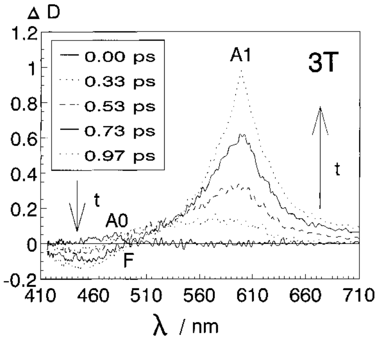

Figure 4. ΔD spectra of 3T at various delay times showing wide absorption A0, absorption A1 at 600 nm, and induced fluorescence (negative values) F below 500 nm.

pulses have arrived at the sample. By changing the delay, we registered the first effect on the blue side of the continuum because the temporal end of the pulse (blue part of the pulse) at first crosses the excited sample.

Results

We measured the optical density difference $\Delta D(\lambda,t)$ during and after excitation with 350 fs pulses at 308 nm with subpicosecond delay steps. The measurements were performed on *n*T in solution. The photon energy of 4.02 eV of the 350 fs pulses was remarkably larger than the energy of the S_1 states of the *n*T ($n = 3-6$) (see Table 1). The photon energy in the experiment described here is much higher than in preliminary experiments where 3.5 eV (347 nm) in ref 15 and 3.2 eV (388 nm) in ref 22 were used. From our picosecond spectroscopy studies the spectral positions of the stimulated fluorescence F and the excited state absorption A1 are known. Therefore, the femtosecond experiments enable us to study processes that may proceed in the time interval between the population of the initially excited state at 4 eV and the population of the lowest excited state due to relaxation processes.

The transient spectra of 2T−6T observed by femtosecond spectroscopy are now described in detail.

For 2T the emergence of the transient absorption A1 of 2T is shown in Figure 2. Stimulated fluorescence and triplet absorptions of 2T are located at shorter wavelengths[10] and were not observed here. Owing to the dispersion of the white light probe pulse, a spectral shift was observed during the first 500 fs after excitation. The maximum of A1 is located at $\lambda = 495$ nm. The decay of A1 was found to be single exponential with a decay time of 51 ps (Figure 3). A similar decay time was found for the fluorescence of 2T.[6] Therefore, A1 was assigned to an absorption from the relaxed S_1 state to a higher electronic state.

For 3T the formation of the excited-state absorption A1 and of the stimulated fluorescence F are shown in Figure 4. We observed a broad A1 band that becomes spectrally narrower within the first picosecond. A spectral narrowing of 3T excited-state absorption was also found by Yamaguchi et al.[22] and explained by vibrational relaxation of higher vibrational levels of the S1 state. The maximum of A1 lies at $\lambda = 600$ nm as observed on the picosecond time scale. The ΔD spectrum F appears delayed from that of A1 under consideration of the white light pulse dispersion. We found additionally small positive values of ΔD at very small delay times, indicating a further transient absorption A0.

The transient behavior of 4T is shown between 440 and 830 nm in Figure 5. Here, the spectral width of A1 is very broad as already observed on the picosecond time scale. The maximum of A1 was found at about $\lambda = 770$ nm, which is larger than observed by picosecond spectroscopy ($\lambda = 700$ nm). To take into account the white light continuum dispersion, all parts of the excited-state absorption A1 of the whole band arise at the same time. By picosecond spectroscopy, it was found that the whole absorption band A1 decays simultaneously and single exponentially with $\tau = 530$ ps.[15] Both observations show that the broad excited-state absorption A1 stems from the same state. Positive ΔD values due to an absorption A0 seem to appear weak at zero decay, but as in the case of 3T the induced fluorescence is delayed relative to the transient absorption.

For 5T the emergence of the transient absorptions A0 and A1 is clearly seen in Figure 6. A0 decays within about 500 fs, whereas A1 increases to a terminal value within about 2 ps. The induced fluorescence appears delayed because of the superposition by A0. The spectral maximum of the excited-state absorption A1 was not measured in this experiment. It was found by picosecond spectroscopy to be located at about 850 nm. The whole absorption A1 was found to decay single exponentialy with a decay time of about $\tau = 900$ ps.[15]

In the case of 6T1 one- and two-photon excitation experiments were performed.[21] The results for 6T1 after one-photon excitation (Figure 7) are very similar to that of 5T. At first, the transient absorption A0 was observed. The maximum of the excited-state absorption A1 was found by picosecond

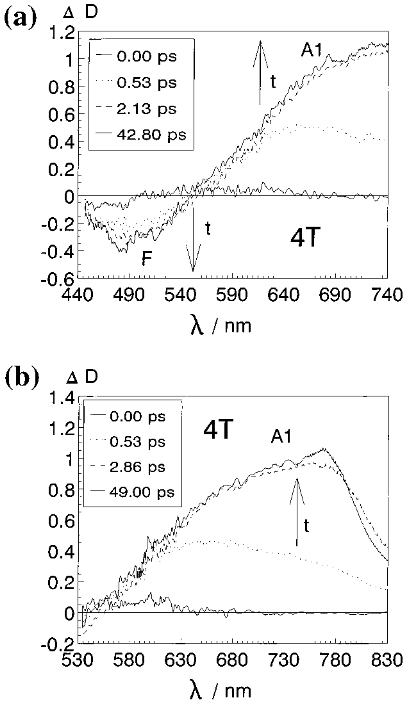

Figure 5. (a) ΔD spectra of 4T at various delay times with fluorescence F (negative values) and absorption A1 and (b) transient absorption at longer wavelengths (530−830 nm).

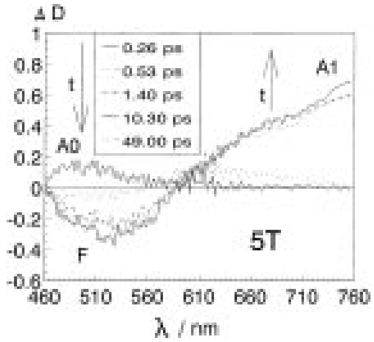

Figure 6. ΔD spectra of 5T at various delay times with absorptions A0 and A1 and fluorescence F.

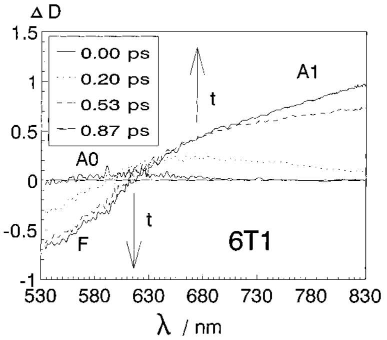

Figure 7. ΔD spectra of 6T at various delay times with absorptions A0 and A1 and fluorescence F.

spectroscopy at 900 nm with a decay time $\tau = 1100$ ps.[15] The stimulated fluorescence F forms with delay owing to the existence of A0.

With excitation by two photons ($\lambda_{ex} = 616$ nm, 80 fs) a broad A0 band appears first[21] followed by the A1 and fluorescence bands. The time behavior at a selected wavelength shows the strong increase of A0 and A1 (Figure 8). A0 is seen for about 500 fs; later, the fluorescence predominates. Though in this experiment the laser pulse amounts to only 80 fs (compared to 350 fs at one-photon excitation), the existence of A0 is observable as long as it is the case of one-photon excitation, i.e., the A0 band exists longer than the excitation pulse.

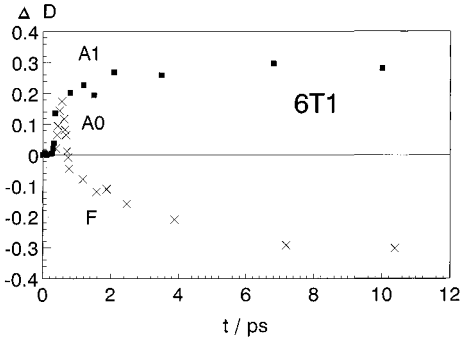

Figure 8. Time dependence of transient bands of 6T1 after excitation with 80 fs pulses (616 nm) by two-photon absorption at 550 (×) and 720 nm (■).

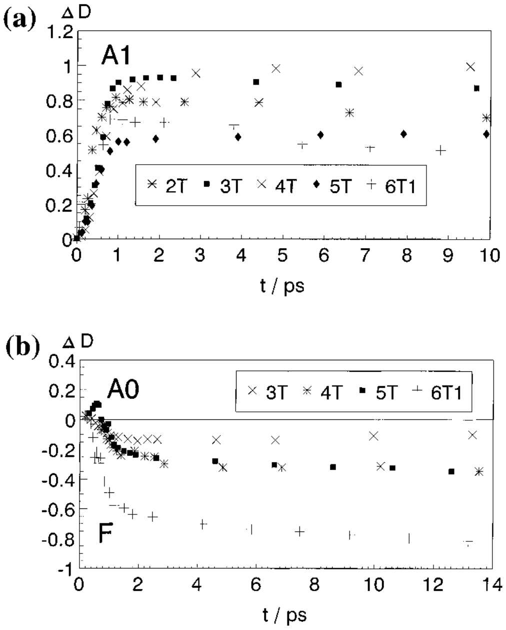

Figure 9. (a) Time course of A1 bands of thiophene oligomers *n*T ($n = 2$−6). (b) Time course in the spectral regions of induced fluorescence F of *n*T ($n = 3$−6). The early absorption is largest at 5T.

To compare the kinetic behavior of the *n*T, the time dependent ΔD values were taken out at selected wavelengths of the corresponding A1 bands and fluorescence bands. In Figure 9a the kinetics of the excited-state absorptions of 2T−6T after one-photon excitation is shown. For all *n*T A1 increases immediately after excitation and the formation of A1 is finished after a little more than 1 ps. The decay of these bands A1, which stems from the lowest excited singlet state, demands several hundred picoseconds and is dependent on size of the oligomer.[15]

The appearance of the stimulated fluorescence was found to be late in comparison to A1 for 3T−6T (Figure 9b). The positive ΔD values at the beginning of the spectral range of the stimulated fluorescence were registered clearly for 3T, 5T, and 6T1 after one-photon absorption.

Discussion

The transient absorption bands ($S_n \leftarrow S_1$) as well as the stimulated fluorescence of the thiophene oligomers *n*T known from picosecond experiments were observed after excitation by femtosecond pulses (380nm, 350 fs) during their emergence.

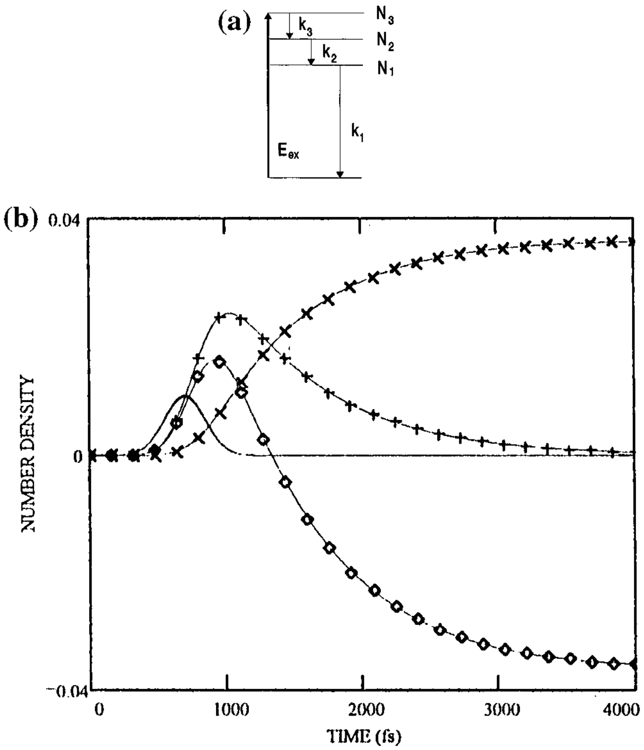

Figure 10. Simulation of decay processes between higher electronic levels: (a) scheme for occupation and decay of levels 3, 2, and 1 with number densities N_3, N_2, and N_1 and rate constants k_3, k_2, and k_1; (b) number densities of N_1 (×) with $k_1 = (100\ \text{ps})^{-1}$, N_2 (+) with $k_2 = (750\ \text{fs})^{-1}$, and the difference $(N_2 - N_1)$ (◇) for an excitation pulse of 350 fs. $(N_2 - N_1)$ simulates the superposition of absorption A0 and fluorescence F.

We found that the bands of the different nT increase within 1−2 ps, which is longer than the doubled half widths of the pulse.

The stimulated fluorescence appears with a delay of about 500 fs relative to the A1 absorption, although both absorption and fluorescence stem from the same state, proved by decay measurements with picosecond time-resolved spectroscopy.[15] This delayed appearance of stimulated fluorescence is caused by a quickly increasing and short-lived absorption A0 located in nearly the same spectral range as the fluorescence.

We do not think that A0 is an artifact because it appears at different nT at different wavelengths and with different quantity of ΔD.

We try to explain the experimental findings with a relaxation cascade between the levels 3, 2, and 1 (Figure 10a) described by rate equations for the occupation densities N_i: $dN_3/dt = G(t) - k_3N_3$; $dN_2/dt = k_3N_3 - k_2N_2$; $dN_1/dt = k_2N_2 - k_1N$. We assume that the “instant” absorption A0 is caused by a state located slightly below that level reached by excitation with 4 eV. This state 2, occupied by relaxation of the excited state 3, decays down to the known electronic state 1 from which the fluorescence and the $(S_n \leftarrow S_1)$ − absorption start.

A simulation of this situation by the rate equations demonstrates the experimentally observed time dependence of ΔD by means of the occupation numbers of the initially excited-state N_3, the absorbing state N_2 from which A0 starts, and the fluorescence state N_1.

The exciting Gaussian pulse $G(t)$ (350 and 80 fs), the known decay rate k_1 of S_1, and the estimated time constants for $k_3 \approx (100\ \text{fs})^{-1}$ and $k_2 \approx (750\ \text{fs})^{-1}$ were included in the rate equations.

The experimental observed time function of the $(S_n \leftarrow S_1)$ − absorption corresponds to the time function of $N_1(t)$, whereas the superimposed A0 and F bands are demonstrated by the difference $N_2(t) - N_1(t)$ in Figure 10.

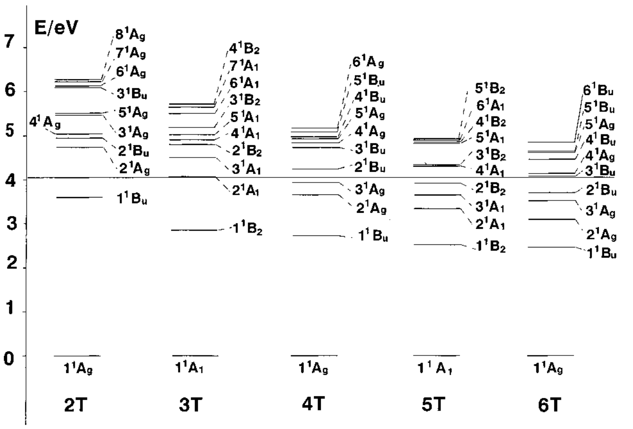

Figure 11. Scheme of energy levels calculated (by CNDO/S) for nT ($n = 2-6$).[23] The line at 4.02 eV marks the energy of the excitation photon.

For comparison the Gaussian excitation pulse is also shown. Without use of any quantitative values of the absorption or emission cross section it can be seen already that the rise of N_1 exceeds the pulse duration and the fluorescence appears delayed. The situation in Figure 10b resembles the $\Delta D(t)$ curves obtained for 5T in Figure 9.

We discuss now fast intramolecular processes that may be responsible for A0 and the observed fast kinetics. In large molecules the density of vibronic states is high and increases with energy. Therefore, vibrational relaxation of excited electronic states is known to be very fast, a few 100 fs. The observed “instant” absorption A0 exists longer than a typical vibrational relaxation time. It demands an electronic state of a finite lifetime.

We assume higher electronic levels with a lifetime slightly shorter than 1 ps. The assumption is supported by the semiempirical CNDO/S calculation. In Figure 11 the electronic level system of the nT calculated in ref 23 is shown. The calculation gives the electronic levels without consideration of the vibrational parts. No alteration of nuclear coordinates after excitation was considered. Therefore, it must be assumed that the real electronic levels lie somewhat lower. The level scheme shows that the high excitation energy of 4.02 eV allows the occupation of higher electronic energy levels at all nT. The levels nearest the excitation energy are of A symmetry for 3T and 4T but of B symmetry for 5T and 6T.

In the case of 5T and 6T the excited states with B symmetry near 4 eV can be occupied by allowed a one-photon excitation from the A ground state. For 3T and 4T, states of A symmetry lie next to the excited state. They need vibromic coupling to be excited. The initially occurring absorption A0 is assumed to start from one of the higher electronic states near 4 eV. Relaxation processes from these states may be responsible for the decay of A0 during the first picosecond and for the delayed increase of stimulated fluorescence of 3T−6T. The two-photon experiments at 6T support this assumption.[21] We were able to observe the absorption A0 in the case of 6T1 after two-photon excitation with a time resolution of about 80 fs. At 6T the density of electronic states is higher than at smaller nT. At 4 eV above the ground state the A and B states of 6T are very close. Therefore, one- and two-photon processes may proceed as well. A direct excitation of A states by allowed two-photon absorption seems to result in an effective population of an A_g state of 6T accompanied by a strong A0 absorption band.

The depletion of the absorbing electronic state proceeds by vibronic coupling to the vibrational manifold of S_1. Fast intramolecular vibrational relaxation leads to a high effective "vibrational" temperature. In their femtosecond time-resolved investigations of 3T Yamaguchi et al. found a broad transient absorption band at 600 nm that becames smaller in the first 5 ps owing to intermolecular vibrational relaxation processes.[22] In ref 22 a delay of the induced fluorescence is observable too, though the early absorption A0 was not seen. We think that the population of the "fast absorbing" state was probably lower than in our experiment because of lower excitation energy of the photons (3.2 eV).

The existence of electronic levels close above the first excited B levels is reported from quantum chemical calculation on oligothiophenes. From two-photon absorption measurements on polythiophene in solution, the existence of an A level close above the first excited B level was observed.[8] It seems understandable that these electronic levels have finite lifetimes somewhat longer than those of the vibrational levels, and therefore, they are observable by their own absorption.

Summary

Thiophene oligomers with $n = 2-6$ monomer units were excited with femtosecond pulses (350 fs,308 nm) with photon energy (4.02 eV) higher than the S_1 state of these compounds ($\Delta E \approx 3-2.5$ eV) except for 2T. The population of the S_1 state was detected by kinetics of the ($S_n \leftarrow S_1$) $-$ absorption A1 and stimulated fluorescence F. The increase of the A1 bands proceeds in 1−2 ps, i.e., somewhat longer than the doubled half widths of the pulse. The stimulated fluorescence, which stems from the same S_1 state as A1, is superposed by an instant absorption A0.

The kinetics of that spectral region shows the superposition of absorption A0 and fluorescence in different quantities for the different *n*T. We think that we have observed not only a simple vibrational relaxation process but a fast relaxation from a higher electronic state of a finite short lifetime to the S_1 state.

The absorption A0 is more pronounced with the larger thiophene oligomers ($n = 5$, 6). The oligomer 6T1 showed a strong A0 absorption even at two-photon excitation with shorter excitation pulses (80 fs) at 616 nm but with an observable A0 band of about 500 fs. These experimental findings were compared with calculated level schemes of the *n*T. Thereby, we found indeed suitable energy levels below the excitation energy (4 eV) that could be responsible for the absorption A0 and their fast decay.

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