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Femtosecond Differential Transmission Spectroscopy of α-Sexithienyl Single Crystals at Low Temperature

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Spectral relaxation of photogenerated excitations and stimulated emission is investigated in an α-sexithienyl single crystal. We have performed femtosecond differential transmission spectroscopy, probing the spectral region from 1.85 to 2.6 eV, and time-resolved photoluminescence measurements at low temperature. Stimulated emission with amplification of the probe light which results in a positive differential transmission signal is observed at two spectral positions for polarization parallel to the molecular *c*-axis. The observed stimulated emission decays with a time constant of 85 ps. Different kinetics of the rise of the stimulated emission and the superimposed excited-state absorption has been observed for excitation with 3.1 eV. This difference vanishes for excitation with 2.3 eV. Stimulated emission proceeds also via trap luminescence.

1. Introduction

Oligothiophenes attract large interest because of their role as a model compound for conjugated materials and their outstanding optical and electro-optical properties. They are promising candidates for device application such as light-emitting diodes or thin film field-effect transistors.[1−4] In comparison to conjugated polymers, oligothiophenes have a well-defined conjugation length. Furthermore, single crystals are available.[5]

Such single crystals of oligomer α-sexithienyl (T6) show a very low degree of structural and chemical disorder and have been investigated by a number of different experimental techniques.[6−14] Their electronic structure has been analyzed in detail.[7,15] The anisotropy of their optical properties according to the molecular ordering has been demonstrated in absorption[7] and in fluorescence.[8]

Stimulated emission (SE) has been observed in a single crystal of T6[10,12] and has been explained by a four-level model.[16] Time-resolved femtosecond differential transmission (DT) measurements up to now have been performed at room temperature,[9,14] and amplification of the probe light has been recently observed.[14] The excited-state decay following optical excitation has been proposed to be described by an exciton model.[9,14]

In this article we report on femtosecond DT measurements on a T6 single crystal at low temperature. The relaxation of photogenerated excitations and the resulting SE is investigated with respect to the anisotropy of a single crystal. Gain of the probe light at two spectral positions is observed in correspondence with the reported SE.[12,16] An influence of the excitation energy on the relaxation dynamics is found. The results are compared with time-resolved photoluminescence (PL) measurements.

2. Experimental Section

The T6 single-crystal platelet (thickness 15 μm) was grown by the sublimation technique described by Lipsett.[17] The *bc*-plane of the crystal is parallel to the plate surface.[5] The sample was mounted on a glass substrate and fixed on the tip of a coldfinger cryostat, which was cooled to 20 K.

We used a Ti:sapphire chirped pulse amplifier system with a 1 kHz repetition rate (Spectra Physics, Spitfire) as excitation source. Excitation pulses in the spectral range from 2.3 to 3.1 eV were generated by parametric frequency conversion. A white light continuum was used for the probe pulses, obtained by focusing a fraction of the fundamental output of the laser system into a sapphire plate. The white light continuum was detected after transmission through the sample with a diode array at the exit of a monochromator. The DT spectra were recorded in the range from 1.85 to 2.6 eV and are corrected for the chirp of the white light continuum afterward. The transmission of the sample for photon energies higher than 2.6 eV is too low to obtain reliable DT spectra due to the strong absorption of the T6 crystal. The noise of the measured DT spectra is mainly related to the intensity of the transmitted white light continuum, therefore, the DT spectra are much smoother in the transparent spectral region of the sample than for example in regions with strong absorption. Excitation power was on the order of 1.4 mJ/cm². The polarization of the pump and the probe pulses was adjusted with waveplates. It should be mentioned, that the birefringence of the T6 single crystal[18] may cause a spectrally dependent rotation of the polarization of the transmitted light. Therefore, we cannot exclude small deviations of the polarization direction of the spectrally broad white light continuum that may result from the uncertainty of adjusting the polarization with the waveplates. The probe beam is perpendicular to the plate surface. The spatial angle between the pump and the probe beam is 10°.
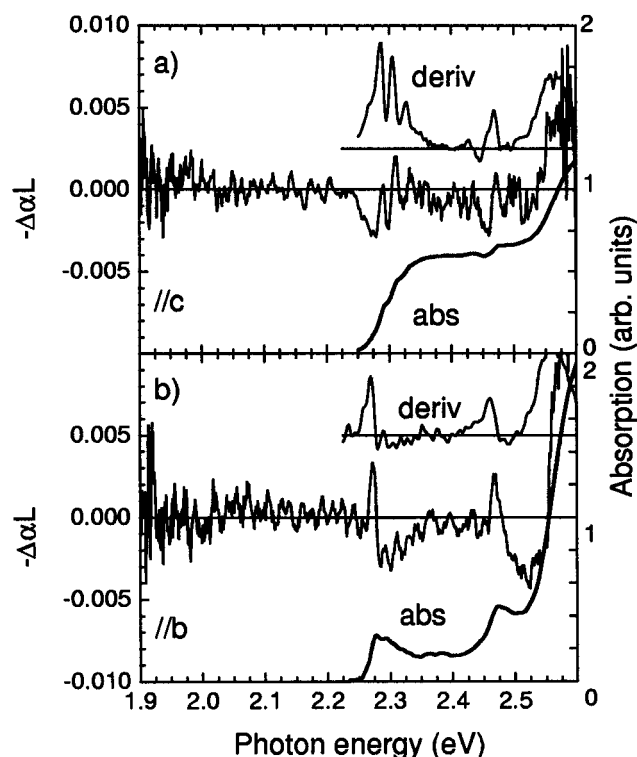
Linear absorption spectra were measured with the white light continuum.

Time-resolved PL spectra were measured with a streak-camera system with 10 ps time-resolution. The frequency-

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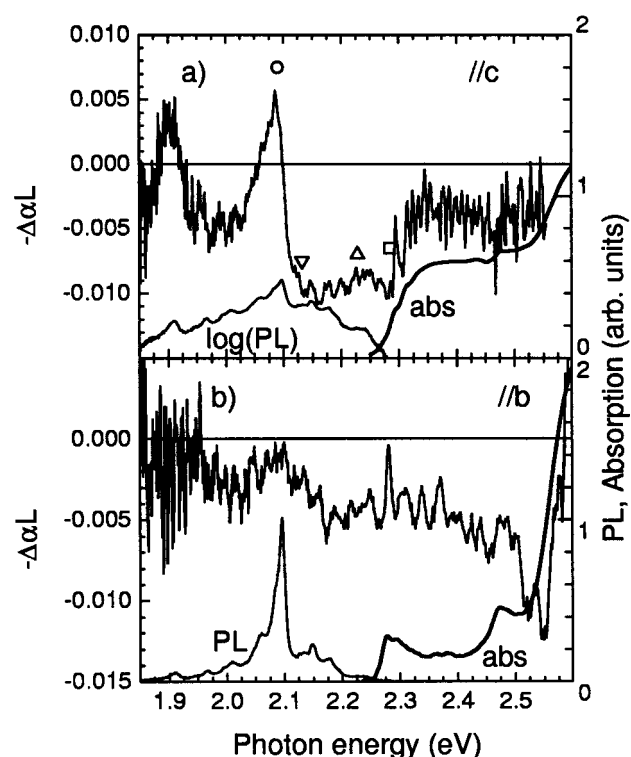‡ Max-Planck Institut für Polymerforschung.

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Figure 1. DT spectra of a T6 single crystal for a time delay of 1 ms and excitation at 3.1 eV. (a) Pump and probe polarization parallel to the *c*-axis. An absorption spectrum for polarization parallel to the *c*-axis (abs) and the first derivative of this spectrum (deriv) are also shown. (b) Pump and probe polarization parallel to the *b*-axis. An absorption spectrum for polarization parallel to the *b*-axis (abs) and the first derivative of this spectrum (deriv) are also shown.

Figure 2. DT spectra of a T6 single crystal for a delay time of 1 ps and excitation at 3.1 eV. (a) Pump and probe polarization parallel to the *c*-axis. An absorption spectrum for polarization parallel to the *c*-axis (abs) and a time-resolved PL spectrum taken at $t = 0$ ps in a logarithmic scale (log(PL)) are shown also. The symbols mark the energetic positions of the transients shown in Figure 4. (b) Pump and probe polarization parallel to the *b*-axis. An absorption spectrum for polarization parallel to the *b*-axis (abs) and a time-resolved PL spectrum taken at $t = 0$ ps (PL) are also shown.

doubled output of a Ti:sapphire oscillator with 2 ps pulse duration was used for excitation.

3. Results and Discussion

Single crystals of T6 show anisotropic absorption.[7] We have measured absorption spectra with the white light continuum and varied its polarization with a waveplate to identify the *b*- and *c*-axis of the crystal. We could reproduce the well-known absorption spectra for polarization parallel to the molecular *c*- and *b*-axis[7,15] for two polarization directions, which are perpendicular to each other (Figure 1, parts a and b).

Figure 1 shows DT spectra for a negative time delay between pump and probe pulse for excitation at 3.1 eV. Here the pump and the probe pulse were in fact delayed by 1 ms, which is the inverse of the repetition rate of our laser system. Despite this very long time delay these DT spectra consist of reproducible features that show no dynamics on a time scale of several tens of picoseconds. The sample does not recover completely after excitation by the pump pulse. For DT measurements of T6 evaporated thin films heating within a few hundred picoseconds after excitation is observed due to thermalization of photoexcitations.[19−21] After each excitation pulse the temperature rises due to the thermalization and then after passing a maximum in temperature the sample cools until the next excitation pulse because of heat flow. Heating induces shifts as well as broadening of the absorption peaks.[21] The changes in absorption due to the temperature difference result in spectral features in the DT spectra that match approximately the first derivative of the absorption spectrum.[19,21] The spectral features of the measured DT spectra for a time delay of 1 ms and the calculated first derivative of the absorption spectrum (Figure 1, parts a

and b) are coincident for both polarizations investigated. Therefore, we conclude that heating is observed for the T6 single crystal, too. Here, the DT signal for negative time delays results because during the DT measurement the intensity of several hundred probe pulses is integrated in the detector. The sample is at a different average temperature when the pump pulses excite the sample if compared with the temperature when the pump pulses are blocked. The spectral features for negative time delays show no dynamics on a time scale of several tens of picoseconds because their dynamics governed by heat flow is very slow.

Therefore, the temperature of the coldfinger of the cryostat is not the actual temperature of the sample during the DT measurement. Although the probe pulses are much weaker than the pump pulses they may also prevent the sample from reaching the temperature of the coldfinger. This might explain the different resolution of our measured absorption spectra (Figure 1) if compared with the spectra measured by Muccini et al.[7] Another reason might be a different quality of the sample.

The following DT spectra are always subtracted by a DT spectrum for a negative time delay to investigate the fast dynamical changes following the pump pulse.

In Figure 2, DT spectra for a time delay of 1 ps are shown. The anisotropy observed in absorption can be found in the DT spectra, too. For both investigated polarizations, the spectra consist of three superimposed components.[9,14] A dominant excited-state absorption is observable in the whole spectral region, resulting in a nearly overall negative spectrum. Bleaching of the absorption is found energetically above 2.27 eV. The bleaching is only faintly observed for polarization parallel to
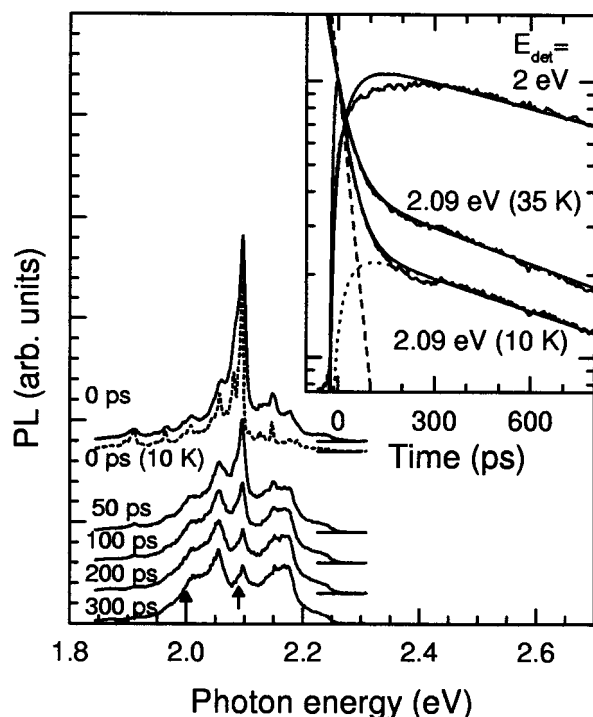
Figure 3. Time-resolved photoluminescence spectra at 35 K (except for the dashed spectrum) for a series of times after excitation at 3.1 eV. The times are given in the figure. The spectra are shifted vertically for clarity. The inset shows the decay of the luminescence detected at 2 eV at a temperature of 35 K and at 2.09 eV at 10 and 35 K, respectively. The smooth lines are exponential fits (see text).
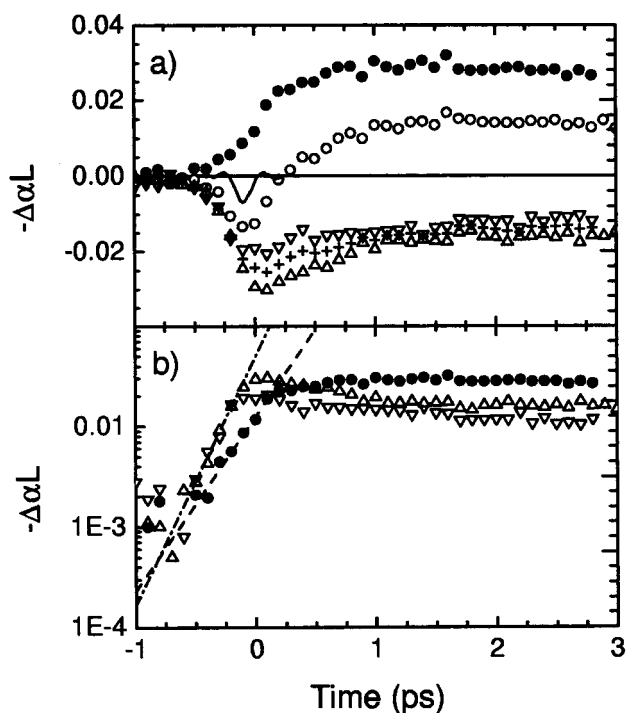

Figure 4. Measured DT decay curves at 2.090 eV (○), 2.132 eV (▽), 2.228 eV (△), and 2.284 eV (□) for excitation at 3.1 eV. Also shown are calculated decay DT curves of the difference between 2.228 and 2.284 eV (+) and the difference between 2.090 and 2.284 eV (●). Pump and probe polarization was parallel to the *c*-axis. The lines are explained in the text.

the *b*-axis due to the low absorption. The most pronounced spectral features for polarization parallel to the *c*-axis are the positive peaks at 2.09 and 1.9 eV. These peaks (although much weaker and therefore below zero) are observed for polarization parallel to the *b*-axis, too. They are located at the same spectral positions where in time-resolved PL spectra strong and sharp emission bands are observed instantaneously after excitation (Figure 3). Therefore, we attribute these DT peaks to SE.

The stronger SE component for polarization parallel to the molecular *c*-axis compared to polarization parallel to the molecular *b*-axis is in accordance to measured PL ratios.[7,9] We find a positive DT signal $-\Delta\alpha L$ for polarization parallel to the *c*-axis for both of the SE peaks at 2.09 and 1.9 eV, demonstrating amplification of the probe light at these energetic positions. This agrees well with the reported SE spectra of a T6 single crystal,[12,16] although we cannot measure the absorption in this spectral region precisely enough to decide whether the absorption is smaller than the induced change in absorption $-\Delta\alpha L$.[22]

From the time-resolved PL spectrum plotted on a logarithmic scale in Figure 2, it follows that SE may contribute in the whole spectral region below 2.3 eV to the observed DT spectrum as stressed by Klein et al.[9] Furthermore, measured DT decay curves for probe energies of 2.132 and 2.228 eV show a different recovery if compared with the decay curve for 2.284 eV (Figure 4). We have measured time-resolved PL to investigate this in more detail.

Figure 3 shows time-resolved PL spectra of a T6 single crystal at low temperature. These measurements were not performed in a polarization-dependent way. The spectra reveal that luminescence consists of emission from different species. Energetically sharp PL bands result from molecular transitions, whereas broad luminescence bands result from traps.[6,23] At a temperature of 10 K the PL bands of the molecular transitions
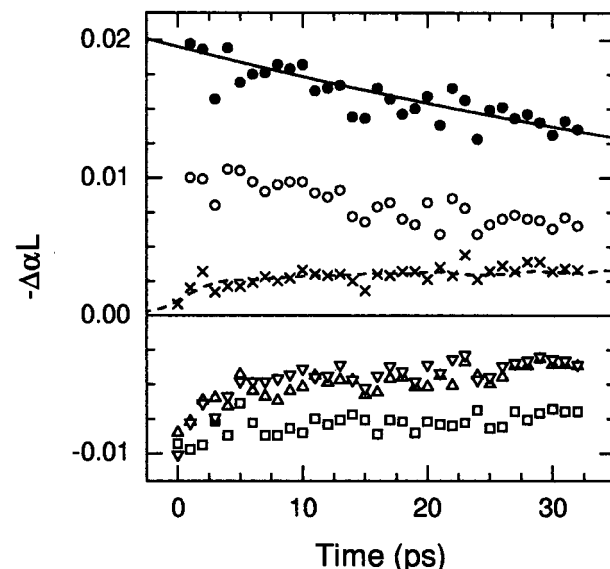
are as sharp as the peaks of the linear absorption spectrum,[7] The sharp luminescence bands are only observed during a short time interval after excitation. They show up instantaneously while the broad bands appear after a finite rise and evolve in time.

Similar time-resolved PL spectra of a T6 film have been explained by a transfer of excitations into traps.[23] With rising temperature a thermally activated detrapping of the excitations is possible. This detrapping results in a slower decay of the molecular emission (see for example the inset of Figure 3). Fitting the decay curves in Figure 3 according to a rate equation model reveals that a single time constant of 45 ps for a temperature of 35 K (40 ps for 10 K) describes the decay of the sharp PL bands at 2.09 eV (dashed line in inset of Figure 3) and the rise of the PL at energetic positions of the broad bands at 2 eV (solid line). Furthermore, the PL intensity at the energetic position of the sharp PL band at 2.09 eV can be very well described in the whole time interval (solid line in inset of Figure 3), assuming a superimposed PL component related to trap luminescence at this energetic position (dotted line). The time constant describing the decay of the trap luminescence is on the order of a nanosecond.

The difference in the recovery of measured DT decay curves at 2.132 and 2.228 eV compared to the decay curve at 2.284 eV (Figure 4) can be explained by the onset of a SE component at probe energies of 2.132 and 2.228 eV and by absence of SE at 2.284 eV. The dashed line in Figure 4 shows the temporal evolution of the PL emission at 2.228 eV from Figure 3 which has been normalized to the signal amplitude of the calculated difference between the DT decay curves at 2.284 eV and at 2.228 eV. The dynamics of the time-resolved PL match those of the difference of the DT transients. The rise of the signals on a time scale of a few tens of picoseconds indicates that at this spectral position the SE proceeds via trap luminescence, too.
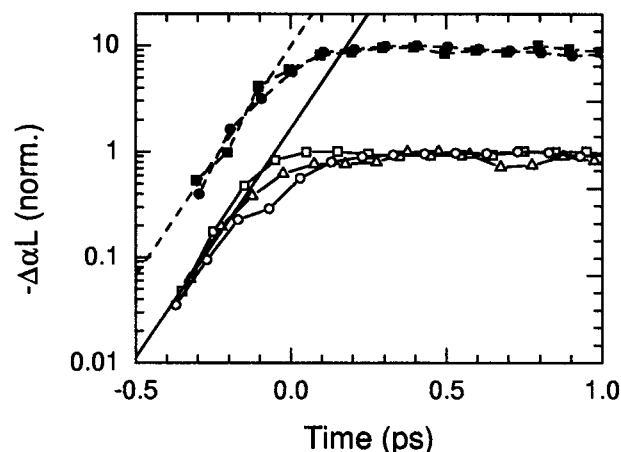
The SE component at 2.09 eV is instantaneously detected (Figure 4), similar to the instantaneously detected emission in the time-resolved PL at this energetic position. The SE component is superimposed onto a component of excited-state
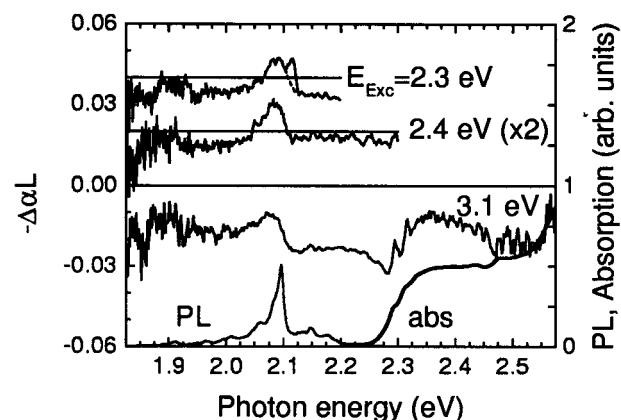
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Figure 5. (a) Measured DT decay curves at 2.093 eV (○), 1.986 eV (△), and 2.125 eV (▽) for excitation at 3.1 eV. Also shown are calculated DT decay curves of the average of 1.986 and 2.125 eV (+) and the difference between 2.093 eV and average of 1.986 and 2.125 eV (●). Pump and probe polarization was parallel to the c-axis. The solid line is explained in the text. (b) Three of the transients from (a) in a logarithmic scale. The transients at 1.986 and 2.125 eV have been inverted. The lines are explained in the text.

Figure 6. Normalized inverted DT transients of the rise of the excited-state absorption at 2.171 eV for excitation with 2.3 eV (■) and with 3.1 eV (●) and normalized DT transients of the rise of the SE component for excitation with 2.3 eV (□), 2.4 eV (△) and 3.1 eV (○). The transients of the SE component are calculated as the difference of the measured transient at 2.087 and 2.147 eV. Pump and probe polarization was parallel to the c-axis.

Figure 7. DT spectra of a T6 single crystal for a delay time of 0 ps. The spectra are shifted vertically for clarity. The excitation energy is given in the figure. Pump and probe polarization was parallel to the c-axis. An absorption spectrum for polarization parallel to the c-axis (abs) and a time-resolved PL spectrum taken at $t = 0$ ps (PL) are also shown.

absorption. To evaluate the decay time constant of the pure SE component at 2.09 eV, the knowledge of the temporal evolution of the exited-state absorption is necessary. We assume the temporal evolution of the excited-state absorption at 2.09 eV to be similar to the temporal evolution at 2.284 eV. Therefore, we calculated the difference of the measured decay curves at 2.09 and 2.284 eV in order to correct the measured decay curve at 2.09 eV for the superimposed component of the excited-state absorption. The resulting decay curve for the pure SE component can be described by a time constant on the order of 85 ps (solid line in Figure 4). The observed decay of the SE is slower than the initial decay of the sharp PL structures observed in time-resolved PL measurements (Figure 3). This contradiction may be explained by the temperature of the sample that might be higher than 35 K. The decay of the emission at 2.09 eV becomes slower for higher temperatures because of the more efficient detrapping (Figure 3). Furthermore, traps might be filled because of the higher excitation density in the DT measurements if compared with the PL measurements.

Figure 5a shows the evolution of the DT signal during the first few picoseconds in detail. At energies of 1.986 and 2.125 eV, the rise time of the DT transient to its negative maximum is comparable to the time-resolution of our set-up. The time-resolution can be directly inferred from the solid line in Figure 5a which shows a DT transient determined by the temporal overlap of pump and probe pulse[24] and measured with the same set-up. In contrast, the transient at 2.093 eV falls during the first few hundred femtoseconds below zero and then starts to rise up to positive values. We explain this behavior by different rise times of the excited-state absorption with its negative sign and the SE with positive sign. In Figures 5a and 5b we calculated the difference of the measured transient at 2.093 eV and the

average of the measured transients at 1.986 and 2.125 eV to describe the pure SE component which is superimposed onto the excited-state absorption. The dashed line in Figure 5b shows that the rise time of the SE component is 250 fs and therefore longer than the time-resolution of our set-up, resulting in a different influence of the internal conversion and the relaxation dynamics for the SE and the excited-state absorption.[9]

Figure 6 shows DT transients from measurements with different excitation energies. The observed rise time of the transient at 2.171 eV is the same for excitation with 3.1 and 2.3 eV. The signal of the excited-state absorption, which is the dominant component at 2.171 eV, rises with the time-resolution of the set-up independently of the excitation energy. We then calculated the difference of the measured transients at 2.087 and 2.147 eV to investigate the rise of the pure SE component as a function of excitation energy. These calculated transients in Figure 6 show that the difference between the rise time of the SE and the excited-state absorption observed for an excitation energy of 3.1 eV vanishes for excitation at 2.3 eV.

The vanishing difference between the rise time of SE and the excited-state absorption for excitation around 2.3 eV is also

observable by comparing DT spectra during the temporal overlap of pump and probe pulse for different excitation energies (Figure 7). For an excitation energy of 3.1 eV the excited-state absorption grows faster than the SE as shown in Figure 5. This results in a SE peak below zero for early delay times (Figure 7). In contrast, for excitation energies of 2.3 and 2.4 eV the SE peak at 2.09 eV is positive already *during* temporal overlap of the pump and the probe pulse (Figure 5).

The temporal overlap of the pump and the probe pulse for the spectrum with excitation energy of 2.3 eV can be inferred directly from the spectrum. A peak observed as a shoulder next to the SE peak 180 meV below the pump energy (Figure 7, see dashed line) is due to Raman gain which is a coherent, phonon-mediated process.[25] This signal is present only during temporal overlap of pump and probe pulse.[24] The energy separation of 180 meV below the excitation energy is given by the C=C breathing mode, which is the strongest vibron in T6.[7]

4. Conclusions

The spectral relaxation of photogenerated excitations and the stimulated emission is investigated in an α-sexithienyl single crystal using femtosecond differential transmission spectroscopy and time-resolved spectroscopy at low temperature. Stimulated emission with amplification of the probe light is observed at two spectral positions only for polarization parallel to the molecular *c*-axis. The stimulated emission and a superimposed excited-state absorption are governed by different kinetics for excitation with 3.1 eV. This difference vanishes for excitation at 2.3 eV. The stimulated emission decays with a time constant of 85 ps. Stimulated emission proceeds also via trap luminescence.

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