

Spontaneous and stimulated emission from a ladder-type conjugated polymer

B. Schweitzer

Institut für Physikalische Chemie and Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, D-35032 Marburg, Germany

G. Wegmann

Institut für Physikalische Chemie, Fachbereich Physik, and Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, D-35032 Marburg, Germany

D. Hertel, R. F. Mahrt, and H. Bässler

Institut für Physikalische Chemie and Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, D-35032 Marburg, Germany

F. Uckert, U. Scherf, and K. Müllen

Max-Planck-Institut für Polymerforschung Mainz, Ackermannweg 10, D-55128 Mainz, Germany

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Fluorescence from films as well as from a solid solution of a ladder-type poly(para-phenylene) has been studied as a function of pump energy upon excitation at variable spectral positions within the inhomogeneously broadened absorption band. Photoinduced transmission changes following excitation with 200 fs laser pulses at 25000 cm^{-1} have been recorded at variable delay time. The latter testify on the occurrence of optical gain in the spectral range of spontaneous emission and of absorption bleaching. The initial decay time of the gain is on the order of 1 ps. Above a certain pump power a 180 cm^{-1} broad emission feature emerges from the inhomogeneously broadened fluorescence spectrum of the film. Upon exciting within the low energy tail of the $S_1 \leftarrow S_0$ 0-0 absorption band sharp ($7\text{--}9\text{ cm}^{-1}$) emission features show up, off-set from the laser line by the energies of the dominant vibrational modes of the polymer. The phenomenon is identified as amplified spontaneous emission induced by spontaneous emission from polymer segments prior to the depopulation by energy transfer towards lower energy sites. [S0163-1829(99)12805-4]

I. INTRODUCTION

The conjecture that conjugated polymers differ from their low molecular weight analogs as far as the strength of electron-electron and electron-phonon interaction is concerned had a great impact on the research into their optoelectronic properties. Meanwhile there is abundant evidence that no such fundamental difference exists. Conjugated polymers can be considered as arrays of the respective oligomers, separated by topological faults of the polymer chain.¹ Their uniqueness as far as electro-optical properties are concerned relate to (i) the extended π -electron system, (ii) the possibility to tune absorption and fluorescence spectra across the entire visible spectral range by chemical modification, (iii) their high fluorescence quantum efficiencies, and, notably, (iv) their mechanical as well as film forming properties. After their successful use as active elements in light emitting diodes² it was straightforward to search for their potential application as substitutes for inorganic semiconductors in electrically pumped diode lasers or as optically pumped polymer lasers that would be easier to handle than conventional liquid dye lasers.

The statistical variation of the effective conjugation length of conjugated polymers as well as random chain packing gives rise to a distribution of optical transition energies, manifested in inhomogeneous band broadening both in absorption and emission. A specific feature of bulk systems is the occurrence of energy transfer among the chromophores, which leads to spectral relaxation. Site selective excitation

employing a spectrally narrow, tunable light source is a way to overcome inhomogeneous broadening in emission spectra provided that the chromophore density is low enough to avoid energy transfer. Since energy transfer can occur among different segments of both different chains and of the same chain this phenomenon erodes site selectivity in polymer spectra even in a matrix isolated system. Site selectivity is retained only if excitation occurs into the tail of the absorption band from where energy transfer towards sites of lower energy is negligible. It leads to spontaneous fluorescence features devoid of inhomogeneous broadening.

Yan *et al.*³ were the first to report on stimulated emission from the conjugated polymer polyphenylenevinylene. Occurrence of that effect has later been confirmed for a blend of a ladder-type poly(paraphenylene) with polycarbonate⁴ and for a soluble derivative of PPV.⁵ Subsequent work established gain at high irradiation dose. Its most obvious signature is the narrowing of the emission spectra of thin films of conjugated polymers. The importance of the enhancement of the optical path that spontaneously emitted fluorescence samples before leaving the film has been recognized. Ways to achieve this are by dispersing scattering TiO_2 particles inside the film^{6,7} and/or by making use of total internal reflection.⁸ Although superradiance has initially proposed as an explanation for spectral narrowing,⁹ there is growing consensus¹⁰ that this phenomenon, which has meanwhile been established to be a quite common one for conjugated polymers,¹¹⁻¹⁵ is related to stimulated emission. Major progress in this field has been the demonstration of laser

emission in a microcavity structure^{16,17} and upon placing the sample into an external resonator.^{18,19} Dilution of the active material turned out to be of advantage because of reduction of excited state quenching due to both energy migration towards inadvertent impurities and charge carrier formation.²⁰

In this work we report on site-selective fluorescence from a ladder-type poly(paraphenylene) as a function of the pump intensity combined with transient absorption. It will be shown that at high excitation dose resonant emission from site selectively excited chain segments can be used as a source of seeded, spectrally narrow, amplified stimulated emission from films of a ladder-type poly(paraphenylene).

II. EXPERIMENT

Most of the experiments were done on typically 300 nm thick spin-coated films of a methyl-substituted ladder-type poly(paraphenylene) MeLPPP.²¹ The advantage of this material as compared to unsubstituted LPPP is the reduced tendency to form aggregates that can act as traps for singlet excitations.²² The films were deposited onto quartz substrates and handled under air. The emission properties of isolated MeLPPP chains were studied on a vitrified 10⁻³% (by weight) solution of MeLPPP in MTHF. The samples were excited by a tunable dye laser pumped by an excimer laser delivering 20 ns pulses of spectral width [full width at half maximum (FWHM)] 0.5 cm⁻¹. The excitation dose within a circular spot of 0.15–0.5 mm diameter could be varied between 10⁻⁷ J and 10⁻⁴ J per pulse. Fluorescence was detected either by an optical multichannel analyzer (OMA) with 80 cm⁻¹ or 8 cm⁻¹ resolution or by a double monochromator-photomultiplier-boxcar system providing a spectral resolution of 0.2 cm⁻¹. All measurements were done in a cryostat at a pressure of 10⁻⁵ mbar and a temperature of either 6, 77, or 295 K. Pump and probe experiments were performed with a regenerative amplified Ti:sapphire laser system delivering 200 fs pulses of 1.55 eV (i.e., 12500 cm⁻¹) photons at a repetition rate of 1 kHz. The output beam was split into two parts. One of them passed a frequency doubler and was used for sample excitation while the second part was focused onto a sapphire crystal to generate a white light continuum for probing the transmission change of the sample as a function of the delay time. Differential transmission spectra were corrected for group velocity dispersion.

III. RESULTS

Figure 1 shows absorption and fluorescence spectra of a MeLPPP film at 295 K. Both reveal a vibronic progression built upon an inhomogeneously broadened origin feature with maximum at 22100 cm⁻¹ (absorption) and 21600 cm⁻¹ (emission). By extrapolating the $S_1 \leftarrow S_0$ 0–0 transition energies of LPPP oligomers^{23,24} plotted versus reciprocal chain length one arrives at 14.5 ± 1.5 phenylene units, equivalent to an effective conjugation length $L_{\text{eff}} = 6.5 \pm 0.6$ nm for the average absorbing chromophore.

The apparent energy of the vibrational feature, which is, in fact, the superposition of two strong and one weak vibrational bands, is 1400 cm⁻¹. Except for the tail region where scattering effects become important, the low energy wing of

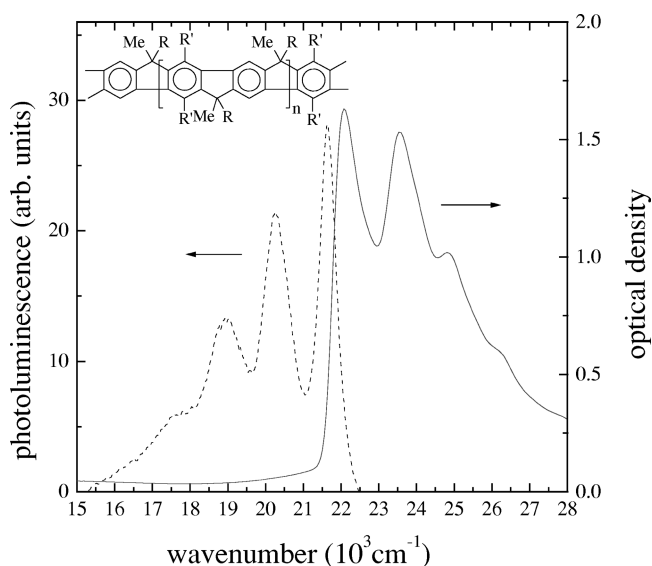


FIG. 1. Absorption and photoluminescence spectra of a MeLPPP film at 295 K. The chemical structure of MeLPPP is shown in the inset. (R : $-1.4\text{-C}_6\text{H}_4\text{-}n\text{-C}_{10}\text{H}_{21}$; R' : $-n\text{-C}_6\text{H}_{13}$.)

the $S_1 \leftarrow S_0$ 0–0 band can be fitted by a Gaussian envelope with (Gaussian) width $\sigma \approx 270$ cm⁻¹. This is about one-third of the inhomogeneous band width of PPV,²⁵ and testifies to the high degree of structural order of the film. The $S_1 \rightarrow S_0$ 0–0 emission feature is even narrower, the full width at half maximum (FWHM) being 560 cm⁻¹ at 295 K and 360 cm⁻¹ at 6 K. The latter value corresponds to a Gaussian width of 153 cm⁻¹.

The fluorescence of MeLPPP dispersed in MTHF glass recorded at 10 K are very similar to those of the film if excited above the $S_1 \leftarrow S_0$ 0–0 origin band (Fig. 2). There is an inhomogeneously broadened origin band centered at 21500 cm⁻¹ with a FWHM of ≈ 300 cm⁻¹ followed by the vibronic features. Except for weak vibronic satellites (see inset in Fig. 2) that appear at the high energy side of the main vibrational features and shift with ν_{ex} while growing in intensity as ν_{ex} decreases, the emission remains spectrally invariant upon excitation at $\nu \geq 21700$ cm⁻¹. For $\nu \leq 21700$ cm⁻¹ the dominant vibrational band splits into two features and shifts with ν_{ex} (Fig. 3). This is accompanied with some spectral narrowing. For $\nu = 21277$ cm⁻¹, which is the lowest energy chosen for reasons of an acceptable signal to noise ratio, the lower energy feature splits into a doublet (inset in the top spectrum of Fig. 2). The onset of the vibronic bands occurs at energies 1326, 1575, and 1607 cm⁻¹—identified as the dominant vibrational energies—below the laser line while emission band maxima are further displaced by about 30 cm⁻¹.

Site-selectively recorded fluorescence spectra of a MeLPPP film turn out to be dependent on the excitation intensity. Consider the case of excitation well above the localization energy ν_{loc} first. It is the energy that, on average, separates which chromophores participate in energy transfer and which do not. As the intensity increases from 1 to 10 μJ per a sample area of 2×10^{-4} cm² the width of the $S_1 \rightarrow S_0$ 0–1 transition decreases and saturates at 180 cm⁻¹ (i.e., 4.4 nm) (Fig. 4). Scanning ν_{ex} to the low energy tail of

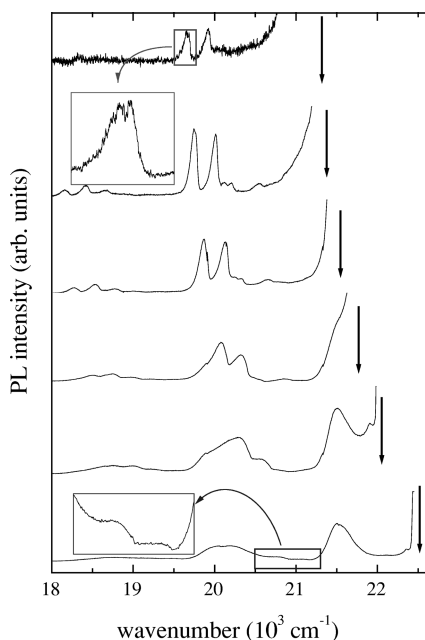


FIG. 2. Site-selective fluorescence spectra of MeLPPP embedded in a MTHF matrix at 10 K. The arrows indicate the excitation energy. The inset shows the weak quasiresonant features on an enlarged scale. The two narrow spectral features are identified as quasiresonant vibrational emissions.

the $S_1 \leftarrow S_0$ 0–0 band sharp features appear superimposed onto the nonresonant first (cumulative) vibronic band (Fig. 5). They are shifted from the laser line by 1326 and 1575 cm^{-1} , respectively. Their relative intensities change with ν_{exc} , obviously mapping their spectral overlap with the underlying nonresonant vibronic emission feature (Fig. 6).

The line shape of the sharp features can best be described by a Gaussian profile (Fig. 7). The linewidth is almost temperature independent, FWHM values being 7.1 cm^{-1} (6 K),

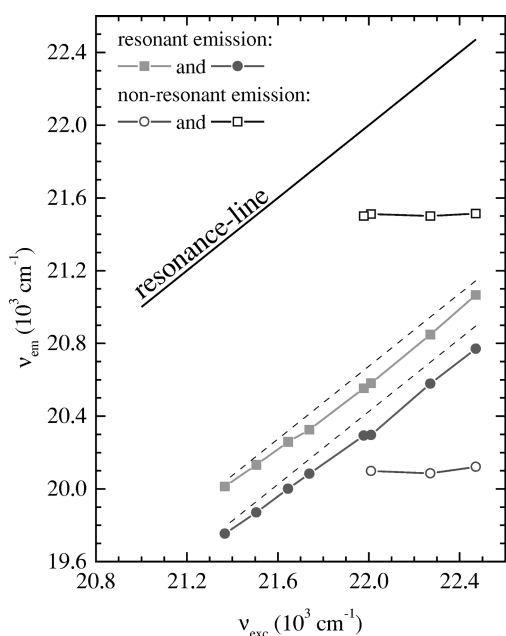


FIG. 3. A plot of the energy of the dominant vibrational features in the fluorescence spectra of MeLPPP in MTHF as a function of the excitation energy.

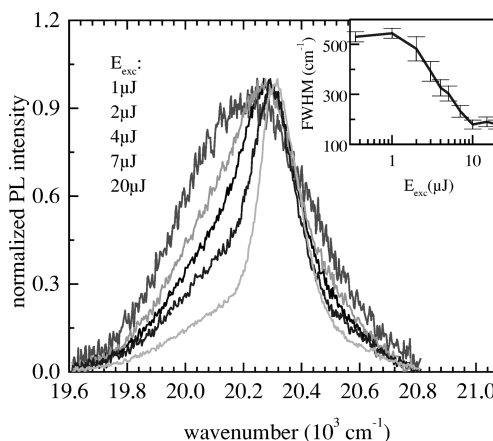


FIG. 4. Evolution of the $S_1 \rightarrow S_0$ 0–1 emission band in a MeLPPP film as a function on the energy of the pump pulse ($T = 77$ K). The sample was excited at $\nu_{\text{exc}} = 22222$ cm^{-1} . The inset shows the linewidth as a function of pump-pulse energy.

8.8 cm^{-1} (77 K), and 9.0 cm^{-1} (295 K). Figure 8 illustrates how the $S_1 \rightarrow S_0$ 0–1 emission feature evolves as function of the pump intensity on a semilogarithmic scale. The above experiments were all done under front detection. Side face detection demonstrates, however, that waveguiding effects are important.

Basically, the same phenomena are observed with 2,7-poly-(trans-4,9-dioctyl-4,5,9,10-tetrahydropyrene) (trans-PTHP). Due to steric repulsion between adjacent biphenyl-units the polymer is not planar. Quantitatively, disorder broadening overrides the vibronic splitting and the entire spectrum is blue-shifted as compared to MeLPPP (Fig. 9).

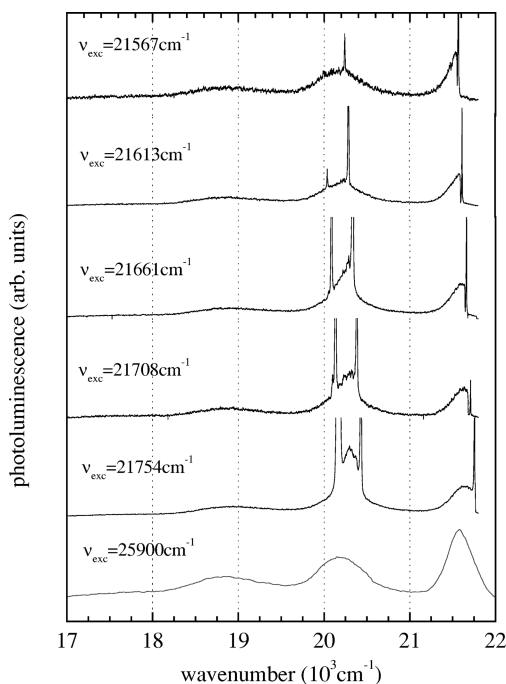


FIG. 5. Photoluminescence spectra of a MeLPPP film at $T = 6$ K for various excitation energies. For lower excitation energies sharp features appear superimposed onto the broad $S_1 \rightarrow S_0$ 0–0 emission band. Because of the big differences in signal ratio the maxima of the sharp features are cut off.

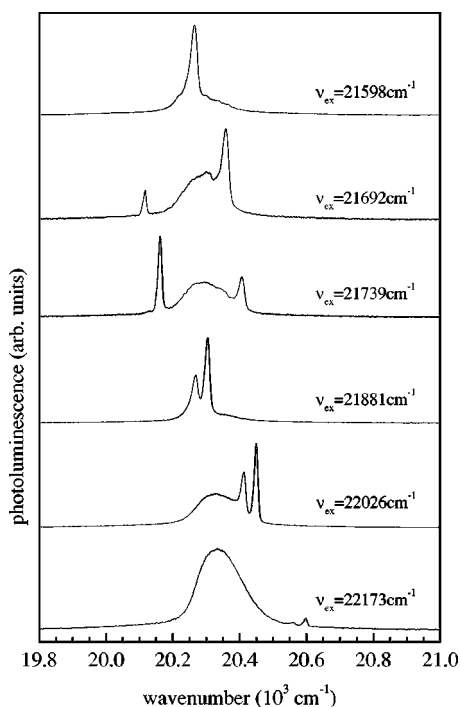


FIG. 6. A series of fluorescence spectra of a MeLPPP film restricted to the spectral region of the $S_1 \rightarrow S_0$ 0-1 band for high excitation intensities ($T=295$ K).

This translates into a smaller effective conjugation length. Fluorescence is emitted from the higher ordered segments as evidenced by the appearance of vibronic structure. With increasing pump energy per pulse spectral narrowing is observed irrespective of ν_{ex} . If excitation occurs at a spectral position such as to guarantee that the accompanying resonant vibronic line overlap with the inhomogeneously broadened $S_1 \rightarrow S_0$ 0-0 band sharp features evolve.

Finally the transient differential absorption (DA) spectra recorded on MeLPPP films employing the pump and probe technique shall be reported. The DA spectrum shown in Fig. 10 bears out a positive change of the sample transmission for

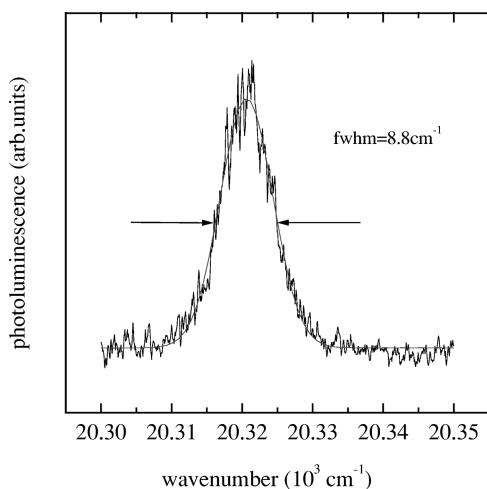


FIG. 7. Line shape of the sharp emission feature of a MeLPPP film related to the 1575 cm^{-1} vibrational mode. The spectrum was recorded at $T=77$ K upon exciting at $\nu_{\text{ex}}=21895$ cm^{-1} with high intensity.

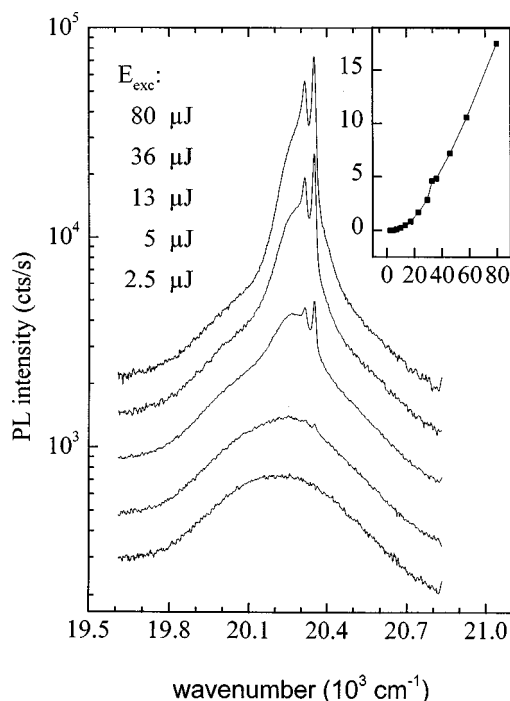


FIG. 8. The $S_1 \rightarrow S_0$ 0-1-band of a MeLPPP film for various energies of the pump pulse ($\nu_{\text{ex}}=21928$ cm^{-1} , $T=77$ K). Note the logarithmic ordinate scale. The inset shows the dependence of the intensity of the superimposed sharp emission feature recorded at 23350 cm^{-1} on the energy of the pump pulse. (The ordinate scale is in a.u., the abscissa scale is in μJ units.)

energies ≥ 18300 cm^{-1} and a negative signal for lower energies. The high energy feature with maximum near 22000 cm^{-1} correlates with the $S_1 \leftarrow S_0$ 0-0 absorption feature (Fig. 1) and is obviously related to bleaching of that transition at high pump intensities. The lower energy features with maxima near 20400 and 19000 cm^{-1} overlap with the

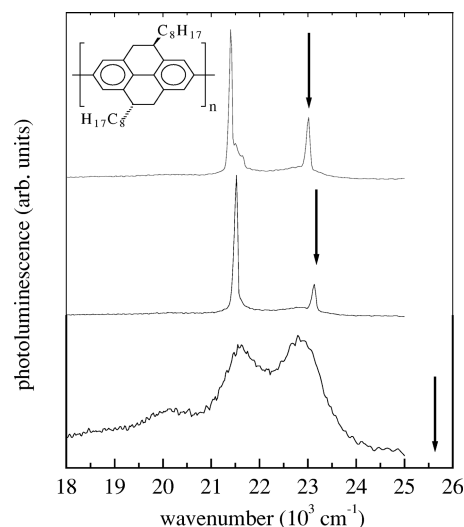


FIG. 9. Photoluminescence spectra of a trans-PTHP film at $T=295$ K. Bottom: Recorded upon nonresonant excitation at $\nu_{\text{ex}}=25640$ cm^{-1} . Middle and top: Excitation at the low energy tail of absorption with high intensity. The dominant sharp feature shifts with excitation energy and is shifted from the laser line by ≈ 1600 cm^{-1} . Inset: chemical structure of trans-PTHP.

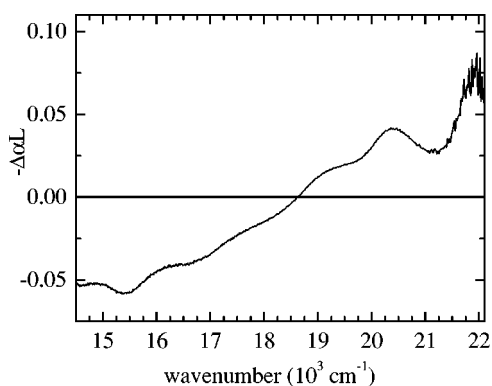


FIG. 10. Differential transmission spectrum of MeLPPP at 5 ps after the excitation recorded at 295 K. Optical gain occurs within the spectral region between 18600 and 21200 cm^{-1} . The pump intensity was 100 μW at a repetition rate of 1 kHz.

(cumulative) $S_1 \rightarrow S_0$ 0–1 and 0–2 emission bands. In this spectral region the temporal decay of the positive transmission change is nonexponential, the initial decay to one-half of the peak value occurring within 0.5–1 ps (bottom spectrum in Fig. 11). The negative transmission change for $\nu < 18500 \text{ cm}^{-1}$ has to be attributed to photoinduced absorption.

IV. DISCUSSION

The series of site-selectively recorded fluorescence spectra of MeLPPP dispersed in a MTHF glass concurs with previous results on conjugated polymers.²³ As the excitation energy ν_{ex} is scanned across the $S_1 \leftarrow S_0$ absorption band, known from film absorption spectra, towards lower energies an inhomogeneously broadened fluorescence spectrum with 0-0 maximum at 21500 cm^{-1} followed by a poorly resolved vibronic doublet is observed. No dependence on ν_{ex} is noted except for the two weak vibronic features, off-set from the laser line by about 1300 and 1600 cm^{-1} that appear superimposed onto the dominant emission (inset in bottom spectrum in Fig. 2). They grow in intensity as ν_{ex} gets lower and shifts with ν_{ex} . They are assigned to the emission from those chromophores from which energy transfer is unfavorable

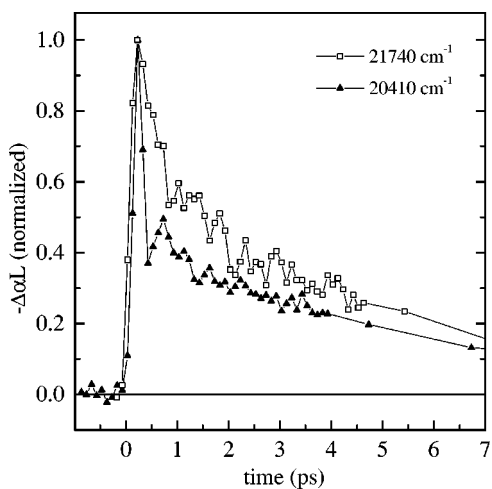


FIG. 11. Decay of the transient differential transmission (DT) signal for different probe energies.

while the dominant emission comes from chromophores that were populated via energy transfer. The center of the inhomogeneously broadened $S_1 \rightarrow S_0$ 0–0 emission marks the threshold energy ν_{loc} below which, on average, energy transfer is no longer competitive with spontaneous emission. For $\nu_{\text{ex}} < \nu_{\text{loc}}$ the emission spectrum becomes narrower and shifts linearly with ν_{ex} . However, in no case were zero phonon features observed as they were with matrix-isolated oligomers of LPPP.²³ Their high energy tail is off-set from the laser line by the vibrational frequencies 1326 and 1575 cm^{-1} , known from the stimulated emission feature discussed below as well as from Raman spectra.²⁶ Absence of zero phonon features might be an indication of sufficiently strong coupling to lattice phonons. We consider this possibility unlikely, since zero phonon lines do show up in the site-selective fluorescence spectrum of LPPP oligomers. This suggests that residual line broadening is a polymer related phenomenon. A segment of a polymer chain that acts as a chromophore is unlikely to be a perfect ordered entity of exactly the length indicated by effective conjugation length. It is more realistic to envisage it as a group of monomers separated from the neighboring segment by topological faults but being elastically deformed due to packing constraints. Upon optical excitation further planarization may occur, equivalent to a lowering of the transition energy. Support for this notion comes from the observation that in polyphenylenevinylene related systems the residual Stokes shift of site selectively recorded fluorescence spectra increases with the overall inhomogeneous band broadening.²⁵

The emission spectra of a MeLPPP film differ from those of matrix-isolated chains in several important aspects. Upon exciting well above the anticipated localization energy ν_{loc} the first vibronic feature of the inhomogeneously broadened emission narrows and becomes an $\approx 180 \text{ cm}^{-1}$ (i.e., 4.4 nm) broad feature that grows superlinearly with pump power. It is identified as amplified spontaneous emission (ASE). This assignment derives from the similarity of the positive DT spectrum and the inhomogeneously broadened fluorescence spectrum as well as the nonlinear intensity dependence of the signal. The gain mechanism is the same as the one involved in a conventional dye laser.²⁷ The primary pump pulse populates a vibrationally hot S_1' state that relaxes rapidly to an S_1 state of a chromophore absorbing near ν_{loc} . Since the vibrational energy quanta are $\gg kT$ inversion exists relative to any vibrational level that couples to the electronic ground state. Stimulated emission is triggered by the spontaneous inhomogeneously broadened first vibronic fluorescence band involving waveguiding. The bandwidth of the stimulated emission band is determined by the quality of the internal resonator.

As ν_{ex} approaches ν_{loc} a sharp doublet appears superimposed onto the ASE mode and becomes the dominant feature at high pump energy per pulse. Comparing the energy offsets of both lines from the laser line with the energies of the dominant skeleton vibrations of LPPP oligomers known from site-selective spectroscopy (Table I) confirms that these vibronic satellites are associated with an emission that is resonant with excitation. The minor decrease of the vibrational energies with increasing chain length is an effect well known for conjugated polymers, and is related to excited state delocalization.^{28,29} Recall that we attribute this phenomenon to ASE induced, i.e., seeded by resonant emission of

TABLE I. Comparison of the energies (in cm^{-1}) of the dominant vibrational modes coupling to the ground state of matrix-isolated LPPP oligomers (from Ref. 23) and to the S_0 state of MeLPPP (present work).

Monomer	LPPP Dimer	Trimer	MeLPPP Polymer
175	145	120	
260			
710			
780			
1370	1350	1320	1326
1483	1490		
1640	1620	1600	1575 1607

MeLPPP chromophores before energy transfer occurs. The threshold character testifies on the involvement of stimulated emission. Upon scanning the excitation energy ν_{ex} across the $S_1 \leftarrow S_0$ 0-0 absorption band the seed effect maps the intensity distribution of the ASE mode. This is obvious from Fig. 6. Upon shifting ν_{ex} from the absorption maximum towards ν_{loc} the 1575 cm^{-1} vibronic line appears first and is dominant as long as it overlaps with the ASE mode. Subsequently, the 1326 cm^{-1} line takes over. The effect vanishes upon scanning ν_{ex} significantly below ν_{loc} . In that case there is neither a sufficiently large population of spectrally relaxed S_1 excitations available for stimulated emission nor is the total density of excitations sufficient to establish gain.

This concept is supported by the band shape of the sharp emission features. The band profile is a Gaussian whose width is almost temperature independent, its 6 K value translating into a dephasing time of 750 fs, and is virtually independent on the spectral position. Not only does this time correlate with the initial decay time of the optical gain, it also agrees within a factor of 2 with the hopping time of singlet excitation inferred from spectral relaxation studies on a film of LPPP.²² For $\nu_{\text{ex}} \geq \nu_{\text{loc}}$ the fastest energy transfer events occur among nearest neighbors, this being an exothermic process irrespective of temperature. Temperature should therefore hardly affect the transfer rate as should variation of ν_{ex} since upon downward scanning of ν_{ex} only the number of chromophores that are able to transfer their energy to an adjacent chromophore changes rather than the rate of the transfer event itself.

The observed phenomenon is reminiscent of resonant Raman scattering. In fact, on the time scale of the dephasing time of an excited state fluorescence and resonant Raman scattering are indistinguishable. It is obvious, though, that the sharp vibronic features cannot be assigned to conventional Raman scattering because the intensity ratio of those lines varies within the broad ASE feature while the intensity pattern of a Raman spectrum would be independent of spectral position. This proves that the sharp vibronic doublet must gain intensity via stimulation due to nonresonant ASE.

The threshold pump power for seeded ASE ($10 \mu\text{J}$ within a spot size of $\approx 7 \times 10^{-4} \text{ cm}^2$) corresponds to 3×10^{16} quanta per cm^2 delivered during 20 ns. Taking 2 ps as a crude estimate of the decay time of the optical gain a stationary density of active S_1 states during the excitation

pulse on the order of $N_{\text{exc}} = 2 \times 10^{17}$ is obtained for excitation at 21770 cm^{-1} , where the absorption coefficient is $7 \times 10^4 \text{ cm}^{-1}$. Assuming $\sigma = 10^{-16} \text{ cm}^2$ as an estimate of the cross section for stimulated emission³⁰ one ends up with a gain coefficient $g = \sigma N_{\text{exc}} \approx 20 \text{ cm}^{-1}$. Being much smaller than the reciprocal film thickness this implies stimulation involving waveguiding, consistent with the observation that most of the emission leaves the film from the side faces.

Finally, the transient differential transmission (DT) change should be addressed. There is (i) a high energy bleaching feature at 22000 cm^{-1} , followed by (ii) two broader positive $-\Delta\alpha L$ features near 20200 cm^{-1} and 18800 cm^{-1} and (iii) a photoinduced absorption signal below 18400 cm^{-1} . Coincidence of the former with the $S_1 \leftarrow S_0$ 0-0 band in absorption testifies on bleaching due to S_1 excitations prior to spectral relaxation towards the tail states of the distribution. In fact, time resolved fluorescence spectroscopy has been known to occur nonexponentially featuring a $1/e$ -decay time of the order of 1 ps.²² The positive DT signal between 21000 cm^{-1} and 18400 cm^{-1} , i.e., below the absorption edge, decays faster than the bleaching signal (i) (Fig. 11) and, thus, can neither be due to depletion of tail states of the manifold of S_1 states nor to spontaneous fluorescence from relaxed S_1 excitons. Consistent with the dependence of the ASE signal it has been assigned to optical gain associated with vibronic bands of the fluorescence spectrum. At lower energies the gain spectrum merges into photoinduced absorption.³¹

V. CONCLUDING REMARKS

The present work substantiates the conclusion that stimulated emission is a common phenomenon for conjugated polymers as it is with conventional organic dyes. The novel effect reported herein relates to the disorder that exists in a solid film of a particular conjugated polymer and which implies branching between resonant emission and energy transfer from a chromophore that absorbs at the low energy side of the inhomogeneously broadened $S_1 \leftarrow S_0$ 0-0 transition. At sufficiently high excitation density those excitations that relaxed within the relevant distribution of states via energy transfer act as a reservoir that can be forced to emit by stimulation via either nonresonant or resonant spontaneous emission. The latter effect results in spectrally narrow stimulated emission that is amplified via waveguiding effects inside the film. Observing the same phenomenon also with trans-PTHPP indicates that it is not bound to a special type of conjugated polymer but, rather, to the mode of excitation and to sample geometry as far as waveguiding effects are concerned.

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