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Picosecond amplified spontaneous emission bursts from a molecularly doped organic semiconductor

C. Kallinger,^{a)} S. Riechel, O. Holderer, U. Lemmer,^{b)} and J. Feldmann

Lehrstuhl für Photonik und Optoelektronik, Sektion Physik und CeNS, Ludwig-Maximilians-Universität, Amalienstraße 54, D-80799 München, Germany

S. Berleb, A. G. Mückl, and W. Brütting

Lehrstuhl Experimentalphysik II, Universität Bayreuth, Universitätsstraße 30, D-95440 Bayreuth, Germany

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We report the dynamics of amplified spontaneous emission (ASE) in thin organic films of tris-(8-hydroxyquinoline)-aluminum (Alq_3) doped with small amounts of the laser dye 4-dicyanmethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM). The energy transfer from the initially photoexcited Alq_3 to the DCM molecules affects the high excitation density dynamics significantly. The time delay between pulsed photoexcitation and the ASE burst depends on the pumping level. For higher pumping levels the competition between depopulation by ASE and refilling of the DCM states via energy transfer leads to an oscillatory emission with a fundamental frequency of up to 0.2 THz. © 2002 American Institute of Physics. [DOI: 10.1063/1.1466879]

INTRODUCTION

Stimulated emission, amplified spontaneous emission (ASE) and lasing in luminescent organic semiconductors have recently attracted much interest.^{1–3} Thin films prepared by spin-coating conjugated polymers from liquid solution or by evaporating small organic molecules exhibit high optical gain and have been used as active materials in various resonator geometries. A particularly interesting system is tris-(8-hydroxyquinoline)-aluminum (Alq_3) molecularly doped with small amounts of the highly fluorescent dye 4-dicyanmethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM).⁴ This composite system Alq_3 :DCM is well suited for lasing purposes, as the red stimulated emission of DCM ($\lambda = 635$ nm) is shifted far away from the absorption of the Alq_3 host, whereas the absorption band of the DCM has good overlap with the emission of the Alq_3 (around 530 nm), thereby enabling an efficient Foerster-type energy transfer.^{5,6} The low percentage of doping (typically less than 3% by weight) also lowers the effects of concentration quenching and increases the luminescence and laser efficiencies.⁷ Since Alq_3 is widely used in organic electroluminescent devices,⁸ molecularly doped layers comprising Alq_3 are also promising candidates for future organic thin film injection lasers.

In this article we examine the effect of energy transfer on the dynamics of mirrorless lasing (ASE) in this guest host system using time resolved spectroscopy. The onset of ASE is time delayed due to the precursing energy transfer. For higher excitation densities the interplay of filling of the emitting states in the dye by energy transfer from Alq_3 and the depopulation by collective stimulated emission leads to ultrafast oscillations both in the transient population and the

emission. This behavior can be modeled if the energy transfer and the spatiotemporal evolution of the photon and population densities are accounted for. Our results are of relevance for the dynamic behavior of optically and electrically pumped organic solid state lasers.

EXPERIMENT

Samples were prepared by coevaporation of Alq_3 and DCM on glass substrates under high vacuum conditions. The concentration of the laser dye was adjusted to $\approx 2\%$ by weight corresponding to a density $N_{\text{DCM}} = 5 \times 10^{19} \text{ cm}^{-3}$ in the film. The sample consisting of the glass substrate with a refractive index of $n_{\text{Glass}} \approx 1.5$ and the organic semiconductor film with a thickness of approximately 200 nm and a refractive index of $n_{\text{Film}} \approx 1.75$ forms an asymmetric planar waveguide supporting only the TE_0 mode. Following a photoexcitation photons emitted from within the film can be coupled into the waveguide modes.

For excitation we use the frequency doubled output of a regeneratively amplified Ti:sapphire laser producing laser pulses with a duration of 150 fs at a wavelength of 400 nm and a repetition rate of 1 kHz. Time integrated emission spectra are recorded in a direction perpendicular to the substrate with a spectrometer and a subsequent charge-coupled device detector. Thus the spectra consist of a superposition of light which is directly emitted into the direction of the detector and light that is first waveguided and subsequently scattered out of the waveguide by imperfections into the direction of the detector. We employ two complementary time-resolved techniques to monitor the dynamics of excited state population and emission: Pump-probe experiments monitoring the excited state population of the DCM molecules are performed using a small spectral fraction of a whitelight continuum generated by focusing a small portion of the fundamental femtosecond laser pulse onto a sapphire crystal. Time resolved emission transients are measured with a temporal

^{a)}Present address: Deutsches Patent-und Markenamt, 80297 München, Germany.

^{b)}Electronic mail: uli.lemmer@physik.uni-muenchen.de

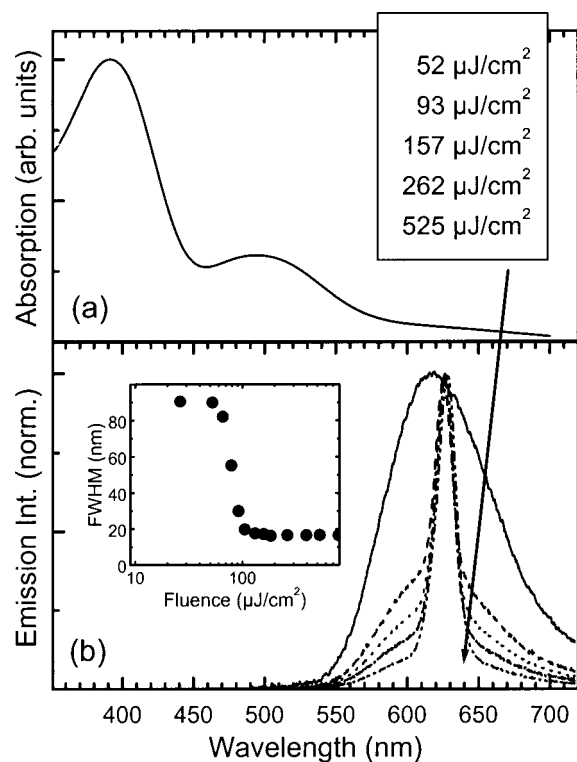


FIG. 1. (a) Normalized absorption spectrum of Alq_3 :DCM. (b) Emission spectra of Alq_3 :DCM for various excitation fluences. Femtosecond laser pulses at 400 nm are used for excitation. The inset shows the linewidth for the various pumping conditions. Gain narrowing is observed for higher excitation levels. The inset shows the linewidth as a function of excitation fluence.

resolution of ≈ 2 ps using an optical Kerr gate setup containing a CS_2 cell.⁹ In both experiments time delay zero is defined by analyzing the curve measured for the highest pump intensity. Since a small portion of the DCM molecules is directly excited an almost instantaneous signal arises. The very first occurrence of a signal above the noise level was set to $\Delta t = -400$ fs. We estimate the error in this procedure to ± 300 fs. All experiments are performed at room temperature and the samples are kept under dynamic vacuum at a pressure below 10^{-4} mbar.

RESULTS AND DISCUSSION

Figure 1(a) shows the absorption spectrum of the sample. Two broadened bands due to the lowest lying optical transitions in Alq_3 (around 390 nm) and DCM (around 500 nm) can be distinguished. Excitation pulses with a wavelength of 400 nm are thus mainly absorbed by Alq_3 molecules.

Figure 1(b) shows emission spectra for various excitation intensities with the pump beam focussed to a circular spot of ≈ 160 μm diameter. For low excitation conditions (pump fluence $F_{\text{pump}} \leq 52$ $\mu\text{J}/\text{cm}^2$) a broad emission spectrum is observed spanning from 530 nm to over 700 nm. This emission band is attributed to the radiative deactivation of excited DCM molecules. The emission band of Alq_3 exhibits significant spectral weight at wavelengths below 525 nm and is not observed here. This indicates that all neutral excita-

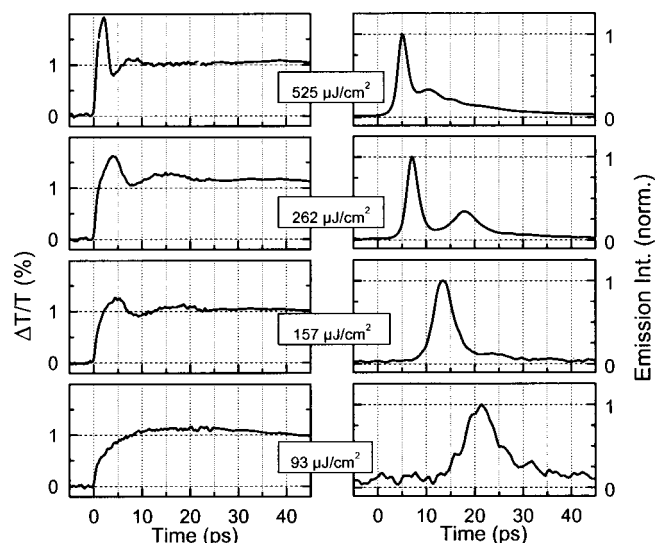


FIG. 2. Left: Pump-probe transients of Alq_3 :DCM for various excitation levels. The pump pulse has a wavelength of 400 nm while the probe pulse is spectrally located at 635 nm. At this wavelength optical amplification due to stimulated emission by DCM molecules is observed. Right: Emission transients at 630 nm after photoexcitation at 400 nm. The transients are measured with the technique of optical Kerr gating.

tions are funneled from Alq_3 to DCM by diffusion within the Alq_3 manifold and subsequent Foerster-type energy transfer. The high efficiency of this process indicates that the energy transfer occurs on a time scale considerably shorter than the radiative lifetime of excited states in Alq_3 .¹⁰

Increasing the pump level to higher values ($E_{\text{pump}} > 52$ $\mu\text{J}/\text{cm}^2$) results in a gradual spectral narrowing of the emission band from 90 nm full width at half maximum (FWHM) to a rather narrow band with a FWHM of 16.5 nm centered at 628 nm. The dependence of the spectral width on the excitation energy is shown in the inset of Fig. 1(b). This emission line narrowing is attributed to ASE: spontaneously emitted photons propagate through the optically excited region and stimulate the collective radiative decay of further excitations. Spectral gain narrowing can be observed if ASE becomes the dominant deactivation pathway.¹¹

Further insight into the process of ASE in Alq_3 :DCM is gained by time resolved measurements. A comparison of the pump-probe transients measured at the spectral position of stimulated emission in DCM ($\lambda_{\text{probe}} = 635$ nm)¹² and a direct time resolved measurement of the DCM emission detected at 630 nm for the same excitation conditions are shown in Fig. 2. The pump-probe data are shown on the left-hand side while the transient emission measured with the Kerr-gate technique is depicted on the right-hand side.

Just above the threshold for ASE, at an excitation fluence of 93 $\mu\text{J}/\text{cm}^2$, the population of the DCM molecules rises slowly and reaches a maximum after approximately 20 ps. While the (nonamplified) spontaneous emission of DCM is below the detection limit in our time-resolved emission measurements an emission-burst due to ASE is observed in the temporal window between 15 and 35 ps after the initial excitation.

At higher pumping levels the threshold for the emission of an ASE burst is reached at earlier times. This is clearly

seen in the emission transients on the right-hand side of Fig. 2. The time delay between the pump pulse and the onset for the (first) burst of ASE decreases with increasing pump pulse energy. For higher excitation densities ASE leads to a significant ultrafast depopulation of the DCM molecules. This can be seen directly in the pump-probe transients on the left-hand side. For increasing excitation densities a maximum is reached more and more rapidly followed by a picosecond depopulation due to ASE.

At a pump fluence of $262 \mu\text{J}/\text{cm}^2$ the first burst of ASE is terminated after less than 10 ps, i.e., well before all excitations are transferred from Alq₃ to DCM. After depopulation of the DCM states by the first ASE burst the DCM manifold can be populated a second time to a value above the threshold for ASE. A second weaker ASE burst can evolve and is observed with a time delay of ≈ 10 ps after the first burst. With increasing excitation intensity the time delay between the bursts decreases; the oscillation frequency rises to approximately 0.2 THz.

The pump pulse energy dependent delay of the emission burst and the oscillatory transient is a gain switching behavior similar to the relaxation oscillations which are observed during the switch-on processes in a variety of lasers.¹¹ In a typical laser relaxation oscillation, population of the active medium by continuous pumping and depopulation due to stimulated emission compete with each other leading to an oscillatory behavior of both the inversion and the density of emitted photons. In our case the situation is related, but qualitatively different since neither a resonator is present nor do we have a continuous pumping scheme. The series of emission bursts is mainly determined by the temporal evolution of the gain in the material given by the density of excited DCM molecules. This density is determined by the competition between “pumping” by energy transfer from excited Alq₃ molecules and depopulation by ASE. Additionally, the geometry of the photoexcited area affects the dynamics.

For a quantitative understanding of the experimental results, we have performed numerical simulations of ASE in this composite system using a model that accounts for the dynamics of the spatially dependent densities of excited states in the two molecular species and the photon density. For any given position (x,y) in the excited area a spatiotemporal system of coupled rate equations has to be solved. We adapt a system of rate equations that has been previously used for describing ASE in conjugated polymer films.¹³

First the evolution of the density of excited states $N_{\text{Alq}}(x,y)$ in Alq₃ is considered. Following an instantaneous excitation, the density of excited states in Alq₃ decays due to intrinsic deactivation processes or via energy transfer to DCM. The corresponding equation reads

$$\frac{\partial N_{\text{Alq}}}{\partial t} = - \left[\tau_{\text{Alq}}^{-1} + \frac{(N_{\text{DCM}}^{\text{max}} - N_{\text{DCM}})}{N_{\text{DCM}}^{\text{max}}} \tau_{\text{transfer}}^{-1} \right] N_{\text{Alq}}, \quad (1)$$

where τ_{Alq} denotes the excited state lifetime in Alq₃ and τ_{transfer} is the excitation transfer time from Alq₃ to DCM. Here, we have chosen a constant transfer time in order to account for excitation diffusion within the Alq₃ manifold prior to the Förster-type energy transfer.^{4,14} At low excitation conditions the density of excited DCM molecules N_{DCM} is

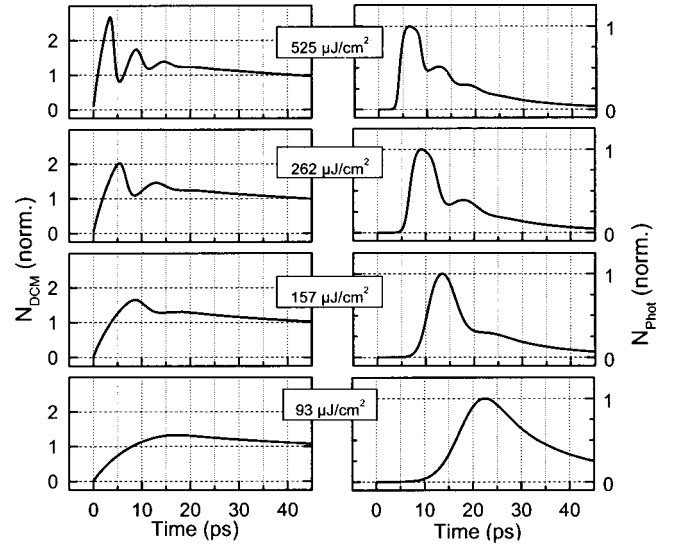


FIG. 3. Left: Calculated transient population of the DCM molecules. Right: Calculated total transient number of emitted photons. A system of rate equations is used to model the excitation and emission dynamics in Alq₃:DCM.

always distinctly lower than the total density $N_{\text{DCM}}^{\text{max}}$ of DCM molecules in the film. At high pumping levels, however, a considerable part of the DCM molecules is excited leading to a saturation of the transfer rate. This is accounted for by a correction factor.

The corresponding rate equation for the density N_{DCM} of excited DCM molecules reads

$$\begin{aligned} \frac{\partial N_{\text{DCM}}}{\partial t} = & \frac{(N_{\text{DCM}}^{\text{max}} - N_{\text{DCM}})}{N_{\text{DCM}}^{\text{max}}} \tau_{\text{transfer}}^{-1} N_{\text{Alq}} - \tau_{\text{DCM}}^{-1} N_{\text{DCM}} \\ & - c \int \sigma_{\text{SE}} N_{\text{DCM}} M d\lambda d\varphi. \end{aligned} \quad (2)$$

Here the last term on the right-hand side couples the excitation density N_{DCM} with $M(x,y,\varphi,\lambda,t)$ being the number of photons per volume, per propagation angle in direction $\mathbf{u}(\varphi)$, and per wavelength λ . σ_{SE} is the (wavelength dependent) cross section for stimulated emission in DCM and c is the velocity of light in the waveguide. The rate equation for the photon density is then given by

$$\begin{aligned} \frac{\partial M}{\partial t} = & -c \mathbf{u}(\varphi) \cdot \nabla_{x,y} M + f \tau_{\text{spont}}^{-1} \frac{1}{2\pi} g N_{\text{DCM}} \\ & + c \sigma_{\text{SE}} N_{\text{DCM}} M, \end{aligned} \quad (3)$$

where the first term on the right side describes the photon propagation in $\mathbf{u}(\varphi)$, the second term considers the spontaneous emission and the last term describes stimulated emission. f is the probability that a spontaneously emitted photon is coupled into the waveguide, $g(\lambda)$ is the normalized lineshape function and $\sigma_{\text{SE}} \propto g(\lambda)$ is the cross section for stimulated emission.

In the calculation the lifetime τ_{DCM} of DCM has been set to 4 ns¹⁵ while the nonradiative lifetime was assumed to be 1 ns in order to match a lifetime of 800 ps as measured in time resolved emission measurements at low excitation levels. The transfer time was adjusted to $\tau_{\text{transfer}} = 9.5$ ps such that

pump probe transients below the ASE threshold could be fitted. Using these parameters and taking into account the excitation conditions both the transient population as well as the total number of emitted photons can be calculated. The numerical data are shown in Fig. 3. All main experimental observations (cf. Fig. 2) are reproduced by the calculated curves. When the pumping level is exceeding a threshold value, ASE sets in and leads to an emission burst and a rapid depopulation of the excited states. For the lowest pump level ($93 \mu\text{J}/\text{cm}^2$) ASE only depopulates a small part of the excited states while the emission transient is already dominated by the ASE burst. The calculated curves also exhibit the increasing relevance of ASE for higher intensities and the oscillatory behavior is also well reproduced. We conclude that our model considering ASE in a highly excited organic guest host semiconductor gives a complete picture of the underlying processes.

In conclusion we have shown that the organic composite semiconductor $\text{Alq}_3\text{:DCM}$ shows an unusual collective emission behavior under high excitation conditions. The energy transfer from photoexcited Alq_3 to DCM leads to a pumping level dependent delay between a femtosecond pump pulse and the amplified spontaneous emission. A series of picosecond ASE bursts similar to relaxation oscillations observed in conventional lasers has been observed.

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