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Picosecond Dye Laser Emission in the Infrared between 1.4 and 1.8 μm

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Abstract. The stimulated emission of new infrared dyes was investigated. The dyes have short S_1-lifetimes between 5 and 12 ps with corresponding low fluorescence quantum efficiencies of 10^{-3} to 10^{-4}. In spite of this, 2% of the pumping energy were converted to an intense infrared pulse with frequencies between 5550 cm^{-1} (1.8 μm) and 7150 cm^{-1} (1.4 μm). The dye solutions were excited by single picosecond pulses of a Nd:glass laser in a travelling wave system consisting of a diffraction grating and a transversely pumped dye cell. The pulse duration at 6250 cm^{-1} was measured to be 6 ps.

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In numerous experiments with picosecond light pulses a tunability in frequencies is of major importance. For the infrared part of the spectrum several tuning schemes have been investigated: Parametric amplification [1], stimulated Raman scattering [2], and color-center lasers [3]. Tunable dye lasers [4] have encountered difficulties in the infrared because of the small fluorescence lifetime (small quantum efficiency) and the poor photochemical stability of infrared dyes.

Recently, substantial progress has been made in synthesizing new infrared dyes with superior photochemical stability. With one of these dyes it was possible to operate a cw dye-laser system tunable around 1.3 μm [5]. Continuing the systematic synthesis of infrared dyes we found new compounds [6] with an electronic absorption band as far as 1.5 μm suggesting infrared emission at even longer wavelengths. Data on absorption and fluorescence properties and photochemical stability will be published in detail elsewhere [7]. In this paper we discuss stimulated emission of three new laser dyes. Using a travelling-wave system pumped by a single picosecond laser pulse, amplified spontaneous emission was found between 1.4 and 1.8 μm. Approximately 2% of the pumping energy were converted to an intense ultrashort infrared pulse. The duration of the Gaussian shaped pulse was 6 ps at 1.6 μm.

Experimental

The experimental set-up for the study of amplified spontaneous emission is depicted schematically in the upper part of Fig. 1. Single picosecond light pulses generated by a mode-locked Nd:glass laser system ($\tilde{\nu}_L = 9485\,\mathrm{cm}^{-1}$) are used for excitation of our infrared dyes. The duration of the pump pulse is 4 ps, the pulse energy was varied between 30 and 500 μJ. The energy of these laser pulses is controlled by the photodetector PD1.

The pump beam passes a beam expander (L_1, L_2) and the diffraction grating GR and is subsequently focussed into the dye cell S by a cylindrical lens L_3 (excited volume $1.5 \times 0.01 \times 0.01\,\mathrm{cm}^3$). Spontaneous emission of excited dye molecules is amplified along the length of the cell. The high amplification leads to an intense, highly collimated infrared emission.

The grating GR introduces a continuous differential time delay across the horizontal diameter of the laser beam. This delay is caused by the difference in optical

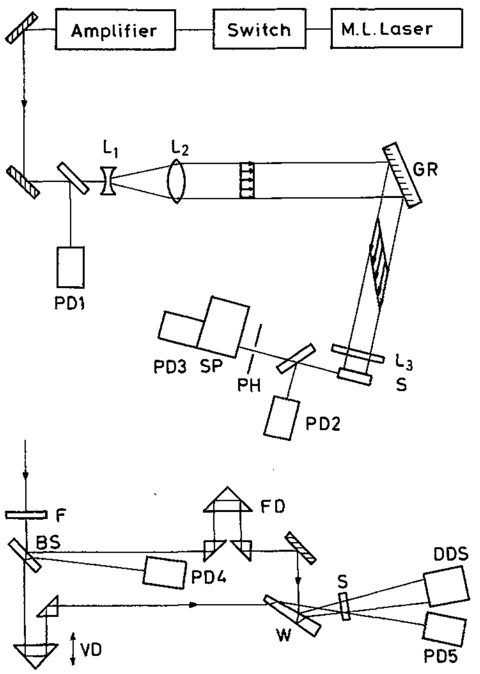

Fig. 1a and b. Schematic of the experimental set-up. (a) System for generation of dye laser pulses: Nd : glass laser system, beam expander L_1, L_2, travelling-wave system consisting of the grating GR, cylindrical lens L_3 and dye cell S. The stimulated emission is analyzed by the monochromator SP, pinhole PH and photodetectors PD2, PD3. (b) System for measuring the absorption recovery time: Filter F, beamsplitter BS, delay lines VD and FD, wedge W, sample S, and differential detector system DDS

path length of different parts of the pumping wave front [8]. By proper adjustment of the grating in relation to the dye cell a well-defined temporal relation between pump light and stimulated emission in the dye cell may be achieved. For instance, it is possible that the delay across the pumping wave front is equal to the travelling time of the fluorescence emission along the dye cell. The exact temporal overlap between pump pulse and the infrared pulse in the medium leads to an effective use of the pump energy, even for S_1 lifetimes of only a few picoseconds. Further, the short S_1 lifetimes and the exact temporal adjustment reduce the jitter between pump pulse and stimulated emission. We expect values of less than 1 ps.

In our experiment we used a reflection grating with 600 grooves/mm in first order. This grating generates a total delay of 72 ps over the beam cross-section. In order to adjust the travelling time of the fluorescence to that of the pump pulse to an accuracy better than ±1 ps, the angle between the pump beam and the axis of the dye cell has to have an accuracy of ±1/200 radian.

The frequency and spectral bandwidth of the amplified emission was analyzed by an IR monochromator SP ($f = 25$ cm, Fig. 1) and a PbS photodetector PC 3. The detector PD2 monitors the energy of the spectrally integrated emission.

Measurements of the pulse duration were performed by the background-free autocorrelation technique using a $LiIO_3$ crystal. In an independent experiment the absorption recovery time of the new dyes was measured directly by an improved two-pulse, excite and probe technique [9]. A first intense pulse partially populates the S_1 level of the dye molecules. A second probe pulse, which is weaker in intensity (1/500) and delayed with respect to the first pulse, interrogates the instantaneous transmission of the medium. Measuring the transmission of the probe pulse as a function of the delay time one deduces the absorption recovery time of the dye.

The experimental system is shown schematically in the lower part of Fig. 1. The laser pulse is divided in an excitation and a probing pulse by the beamsplitter BS. The delay lines VD and FD introduce a variable time delay between these two pulses. The probe pulse is divided once more by the wedge W; the first pulse probes the excited volume of the dye solution, whereas the second one passes an unexcited part of the sample. The two probing beams are registered by a differential detector system DDS, which measures the energy difference between the two pulses with high accuracy. The signal of the differential detector is independent of changes in probing intensity. With this system we are able to measure relative transmission changes of less than 3×10^{-4}. In this way measurements may be performed on a very low level of excitation.

Results and Discussion

While a series of new infrared dyes was investigated, we present data on three typical compounds, the dyes S 301, S 401, and S 501. In Fig. 2 the structures of these molecules are depicted. The chromophores contain symmetrical π-electron systems of the cyanine type. ClO_4^- is used throughout as counterion for the cationic chromophore. Long conjugated chains of double bonds tend to be rather unstable; for this reason we incorporated part of the chain in 5- and 6-membered rings. Although our new dyes have absorption maxima up to 1.5 µm, they are surprisingly stable. It is interesting from a theoretical point of view that the absorption of these dyes can be fully understood on the basis of the simple electron-gas model. Dissolved in suitable solvents the oscillator strength is as high as predicted by the theory. Table 1 summarizes the photophysical properties of the three dyes investigated here. They show high extinction coefficients of nearly 5×10^4 $cm^{-1} M^{-1}$ at the pump wavelength, which is important for efficient laser action.

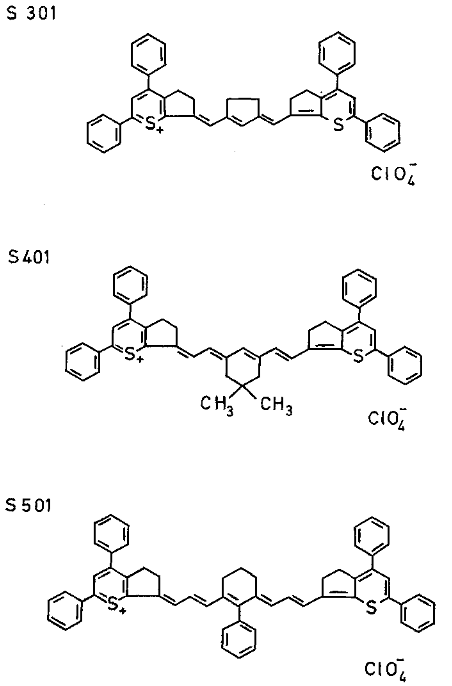

Fig. 2. Structure of the investigated infrared dyes

In Fig. 3 we present measurements of the absorption recovery time. The change of transmission of the dye solutions is plotted as a function of delay time between excitation and probe pulse. The two molecules S301 and S501 show an exponential relaxation with time constants of 5.4 and 12.5 ps, respectively (Table 1). It should be emphasized that the dye solutions were bleached by ≈4% only (from 50% initial transmission to 52% maximum transmission). We recall from previous investigations of IR dyes [10] that the absorption recovery time was equal to the lifetime of S_1, the first excited electronic state of the molecule. From the very short S_1 lifetimes we estimate very small fluorescence quantum yields of approximately 10^{-4}.

Stimulated emission was investigated in dye solutions of high concentration of approximately 10^{-3} M; this concentration gives a transmission at 1.054 μm of 10^{-4} for a cell thickness of 0.1 cm. In the solvents 1,2-dichloroethane and orthodichlorobenzene no significant aggregation of dye molecules occured. The dye concentration is a critical parameter; dilution to half the concentration reduces the amplification drastically [11].

In Fig. 4 the normalized absorption spectrum (l.h.s.) and the stimulated emission (r.h.s.) of the dye S301 are depicted. The normalized emission spectrum with maximum at 1.6 μm was measured with a pump energy of 200 μJ. The frequency profile is symmetric with a spectral bandwidth of 190 cm^{-1}.

Table 1. Photophysical properties of new infrared dyes. Absorption maximum λ_{max}, corresponding extinction coefficient $\varepsilon(\lambda_{max})$, extinction coefficient $\varepsilon(\lambda_p)$ at the pumping wavelength $\lambda_p = 1.054$ μm, and absorption recovery time

Molecule	S 301	S 401	S 501
Solvent	1,2-dichloro-ethane	1,2-dichloro-ethane	*o*-dichloro-benzene
λ_{max} [nm]	1,270	1,250	1,420
$\varepsilon(\lambda_{max})$ [$cm^{-1} M^{-1}$]	109,000	107,000	71,000
$\varepsilon(\lambda_p)/\varepsilon(\lambda_{max})$	0.43	0.62	0.35
τ [ps]	5.4±0.5	5.2±0.5	12.5±1.5

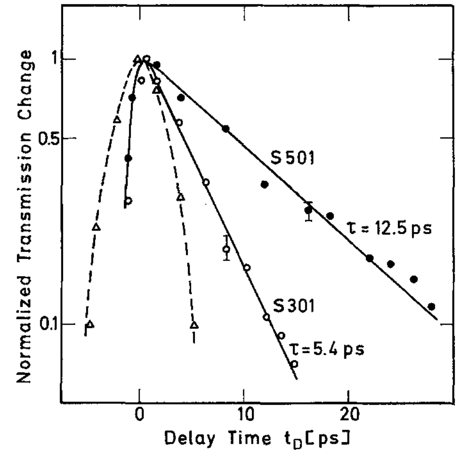

Fig. 3. Normalized change in transmission of the dyes S301 and S501 (solvents given in Table 1). The transmission change is plotted as a function of the delay time between excitation and probe pulse. The dashed curve represents the autocorrelation function of the laser pulses

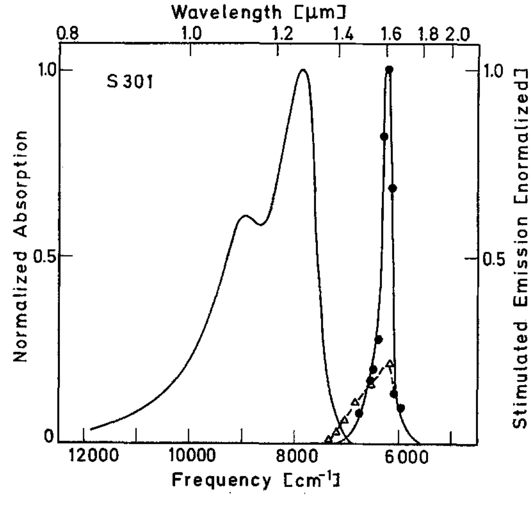

Fig. 4. Normalized absorption (l.h.s.) and stimulated emission (r.h.s.) of dye S301. Profiles of stimulated emission are given for two dye cells of different length *l*. Solid line: $l = 1.5 cm^{-1}$; broken line: $l = 0.5$ cm

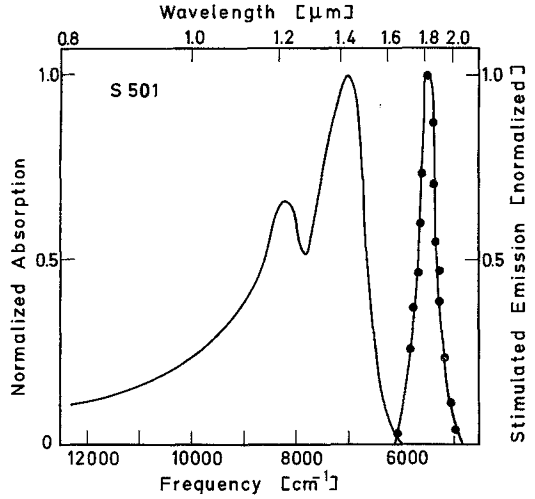

Fig. 5. Normalized absorption and stimulated emission spectrum of the dye S501. The stimulated emission peaks at 1.8 µm

Table 2. Parameters of stimulated emission. Typical pump energy E_p, maximum of stimulated emission λ_E, spectral bandwidth FWHM, energy conversion efficiency η, pump energy threshold E_{thr}, beam divergence angle α_D

Molecule	S 301	S 401	S 501
E_p [µJ]	200	200	100
λ_E [nm]	1600	1550	1800
FWHM [cm^{-1}]	190	400	320
η	2%	4%	1%
E_{thr} [µJ]	15	$\simeq$ 20	$\simeq$ 20
α_D [mrad]	20	20	20

To demonstrate the influence of the interaction length on the properties of the stimulated emission, dye cells of various lengths between 0.5 and 1.5 cm were investigated. We observed a strong reduction of stimulated emission and a spectral broadening for the shorter dye cells. The broken line in Fig. 4 shows the broadened, asymmetric emission profile (FWHM $= 800\,\text{cm}^{-1}$) of a dye cell of 0.5 cm length. The short-wavelength wing of this spectrum is determined by reabsorption of the dye, whereas the long-wavelength side falls off with the fluorescence band.

Table 2 summarizes important emission parameters. We obtained energy conversion efficiencies of pump light to the infrared of 2% corresponding to 10^{14} infrared photons for a pump energy of 1 mJ. The three dyes show similar conversion efficiencies. We note that the conversion efficiency appears to be independent of the absorption recovery times. This fact is due to the short pumping pulses of 4 ps and the accurate temporal adjustment of our travelling wave pumping system.

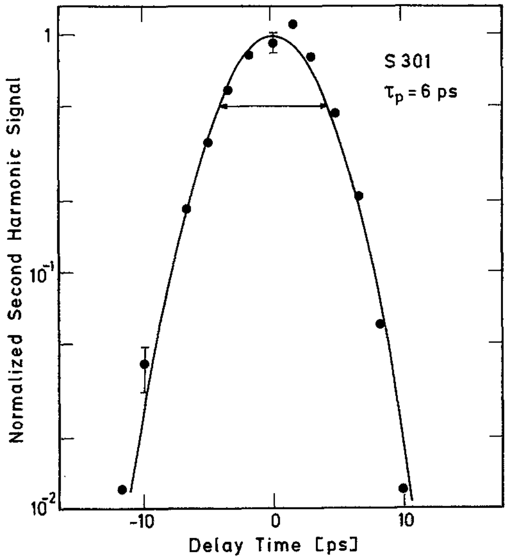

Fig. 6. Autocorrelation trace of the stimulated emission of dye S301. The experimental points are well accounted for by a Gaussian autocorrelation function. A pulse duration of 6 ps is derived

Of special interest are the optical properties of dye S501. Due to its longer π-electron system (Fig. 2) the absorption is shifted to 1.42 µm. Absorption spectrum and stimulated emission are depicted in Fig. 5. The stimulated emission is centered around 1.8 µm with a bandwidth of $320\,\text{cm}^{-1}$ (FWHM). Stimulated emission of a dye molecule at this long wavelength has never been observed (and anticipated) previously.

The chemical structure and photophysical properties of dye number S401 are similar to that of S301. The stimulated emission was found at a somewhat shorter wavelength at 1.55 µm. Picosecond pulses at this wavelength are of interest for applications in fiber optics.

It is interesting to estimate the gain factor of amplified spontaneous emission from the energy conversion efficiency, the spectra of spontaneous and stimulated emission, and the fluorescence quantum yield. For a quantum yield of 10^{-4} we estimate a gain factor of 10^7 to 10^8. At the pump energy of 100 µJ saturation of the amplification process is observed. A variation of the pump energy by a factor of two leads to small changes in the energy conversion efficiency. The threshold of laser action is determined by strongly reducing the intensity of the pump beam. We find a low threshold energy of 15–20 µJ.

The beam divergence of the stimulated emission is determined by the dimensions of the pumped volume, i.e., by the penetration depth and the interaction length. In our experiment a full divergence angle of 20 mrad was measured. It could be compensated to a residual value of 1–2 mrad by an external lens of $f = 10\,\text{cm}$.

An autocorrelation trace of the emission of the dye molecule S301 is given in Fig. 6. The experimental points agree with the Gaussian autocorrelation function over a signal range of two orders of magnitude. We deduce a pulse duration of 6 ± 0.5 ps and a Gaussian temporal shape of the generated infrared pulses. The pulse duration is close to the lifetime of the S_1 level of the dye molecule.

The application of dye molecules in laser systems requires high photochemical stability. During our experiment we worked many hours with the same dye solution without decrease of emission efficiency. Detailed data on the photochemical stability will be published at a later date [7].

Summary

The travelling wave geometry for pumping a dye laser proves to be an efficient method to generate picosecond pulses in the infrared. In spite of the very short S_1 lifetimes of these dyes the threshold of 10–20 μJ for stimulated emission is very low. The new dye molecules extend the available spectral range to 1.85 μm.

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