Picosecond Pulses and Applications

Experimental and Theoretical Study of the Mutual Interaction of Subpicosecond Pulses in Absorbing and Gain Media

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We use for this work a passively mode-locked dye laser providing an output composed of two interwoven pulse trains separated by 1/3 ns (the cavity round-trip time being 4 ns). The relevant parts of the autocorrelation of the laser output – the central part and one of two small sidebands – are shown in Fig. 1. The time delay associated with each sideband corresponds to an optical path length of 10 cm. The pulse train consists thus of a strong short pulse ($\simeq$0.2 ps duration) followed at 0.33 ns by a weak broad signal ($\simeq$0.8 ps duration). The second pulse being much longer than the first one, we have a unique possibility to determine accurately a subpicosecond pulse shape (by cross-correlating the first and second pulses) and to use it as a stringent test for theoretical models. Indeed, the two pulses being generated by mutual interaction in the same laser cavity, there is no possible source of jitter (in the time delay between the two pulses) as can occur in cross correlations between trains of synchronously mode-locked lasers [1] (when present, such a jitter can account for e.g. an asymmetrical cross-correlation, even if each pulse of the trains is perfectly symmetric).

The two pulse operation results from the coupling mechanism illustrated in Fig. 2. The main pulse traverses the dye jet (containing the gain medium together) first from right to left, is reflected by the end cavity mirror, and collides with the weaker pulse in the jet. Since the medium has been brought close to saturation already at the first passage, a population grating will be easily induced by the pulses meeting in the jet, resulting in one beam being diffracted into the other. A theoretical model of the cavity was made including saturable gain and absorption, mutual saturation, coupling between counterpropagating beams, linear cavity losses, jet thickness. Using the published values for the time constants of the absorbing and amplifying media, our theoretical steady-state pulse (Fig. 3) is seen to match accurately the experimental shape (Fig. 4). Other features that matched accurately the experiment are the ratio of amplitude (between 15 and 25 depending on the jet composition) and duration of the two pulses. The dissymmetry between the two pulses is due to the geometry of the cavity: with the sequence of passages shown in Fig. 2, the second pulse always experiences a more depleted gain medium.

We have studied the influence of the magnitude of mutual coupling (a parameter that is physically not adjustable) on the

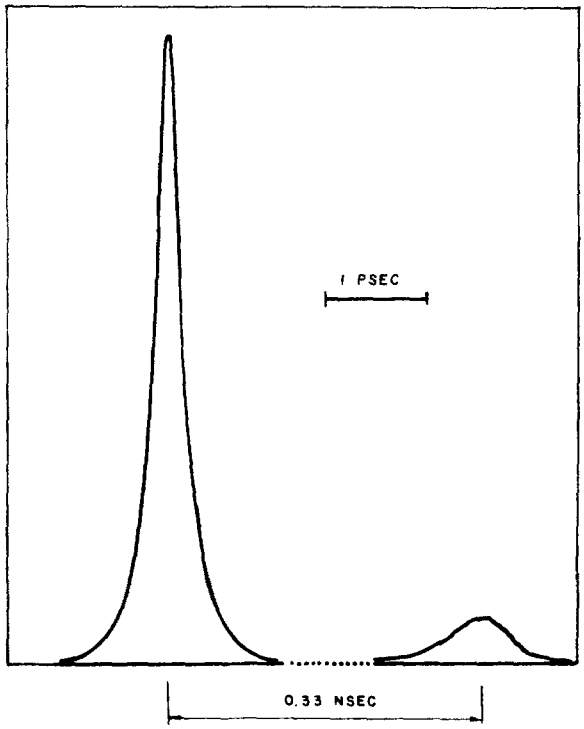

Fig. 1. Laser output (2 pulse trains)

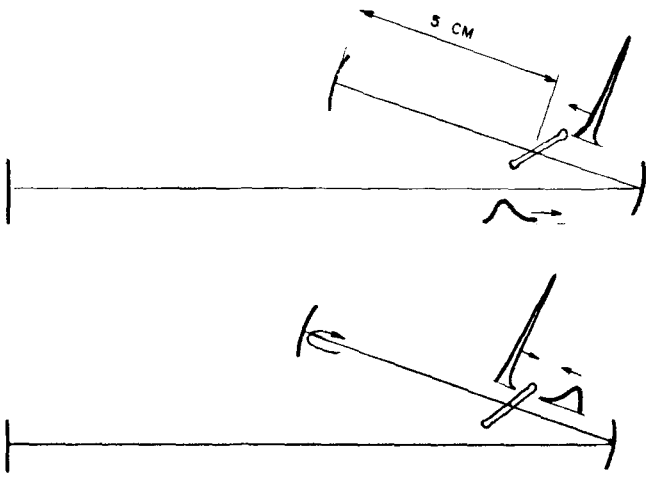

Fig. 2. Cavity configuration

pulse duration. The mutual coupling does not cause pulse shortening as is generally thought [2], but tends to make both pulses identical (the shorter one becoming longer, the longer shorter). Our theoretical study shows that, in the colliding pulse mode-locking [3], the requirement for an extremely thin jet is to prevent the attenuation in the region where the pulses do not overlap to bring the pulse intensity below (mutual) saturation in the region of collision.

Another interesting information from our theory is the shape of the shorter intense pulse. In agreement with previous bandwidth-

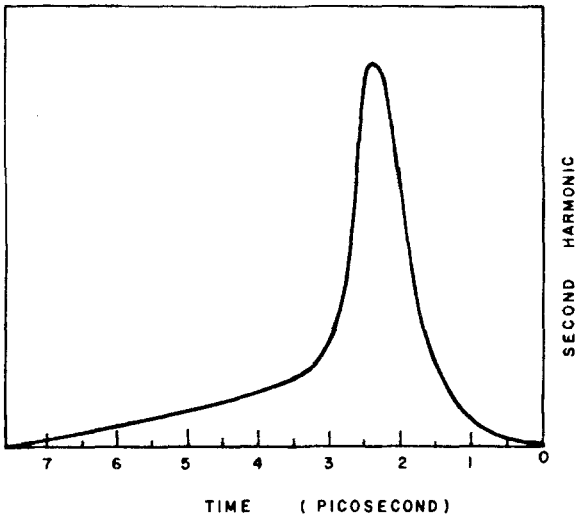

Fig. 3. Cross-correlation: Shape of the weak pulse. Theory

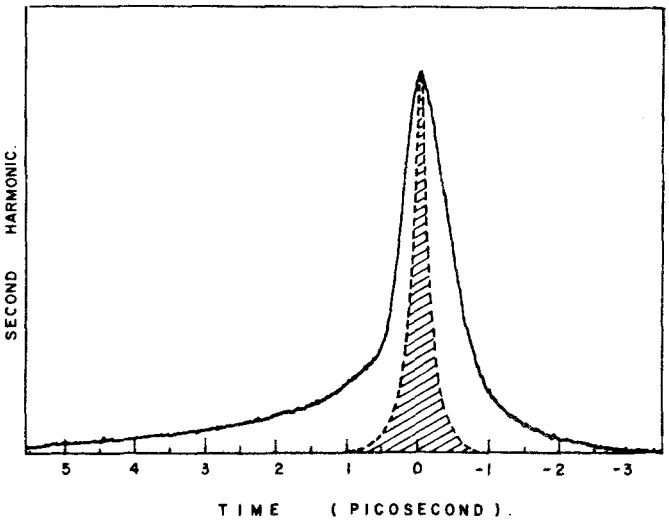

Fig. 4. Cross correlation: Shape of the weak pulse. Experiment

autocorrelation measurements [4], the shorter pulse appears to be essentially symmetric.

In conclusion, we have measured the shape of a subpicosecond pulse by a cross-correlation technique, and we have constructed a theoretical model for the passively mode-locked dye laser, including mutual coupling of counterpropagating pulses, that accurately matches the measured pulse shape. Our model does not apply to our particular laser, but can also be used to describe the operation of other passively mode-locked dye lasers (for instance the colliding pulse mode locked dyes laser of [3]).

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High Resolution Single-Photon Measurements of Fluorescent Decays with Solid-State Detectors and Sinchronously Pumped Mode-Locked Lasers

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Single-photon timing has been applied to measurements of fluorescent lifetimes since many years [1, 2]. A major advantage of this technique is a higher time resolution, in comparison to other methods employing photodetectors. After the development of laser systems for the generation of picosecond light pulses, the resolution is limited mainly by the photodetector. The limit for presently available photo-multiplier tubes (PMTs) is somewhat more than 200 ps, due to the transit time jitter [3, 4].

Higher resolution can be expected by using some types of avalanche photodiodes to detect single-photons. These devices have uniform breakdown over the junction area (diameters from 40 to 80 μm) and the transit time in the junction can be as low as a few 10 ps [5]. By using the active-quenching method, these single-photon avalanche diodes (SPADs) can be operated with short deadtimes (<20 ns) and well-defined parameters [6, 7]; preliminary tests have confirmed the possibility of obtaining high resolution.

In this paper experimental results are reported, which demonstrate a time resolution of ~90 ps and the suitability of SPADs to measure subnanosecond fluorescence decays. A synchronously pumped mode-locked Rhodamine 6G dye laser has been used both for testing the time resolution and to excite the fluorescences. The time duration of the dye laser pulse was measured by SHG autocorrelation function and resulted to be less than 5 ps FWHM, assuming a gaussian shape. Conventional electronics (time-to-amplitude converter and multichannel analyzer) was used to measure the delay distribution of the single photons. The start pulses were obtained by using a beam splitter and an ordinary photodiode, associated to electronic circuitry that provided synchronisation to the optical pulses at suitable reduced repetition rate (about 10 kHz). The synchronism jitter was checked by using an identical system in the stop channel: FWHM between 35 and 70 ps were observed, depending on various side effects.

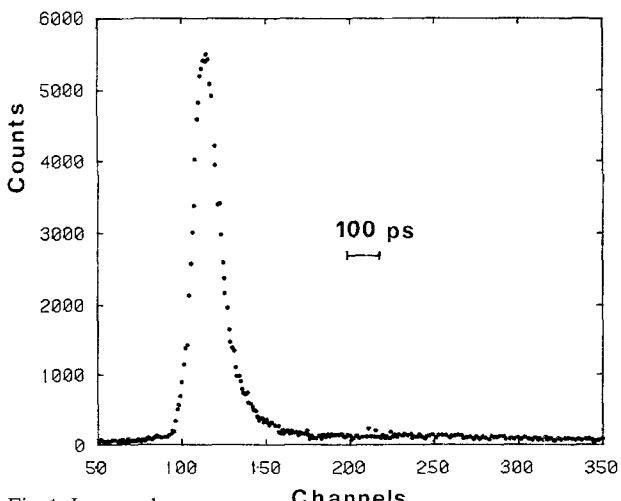

Fig. 1. Laser pulse

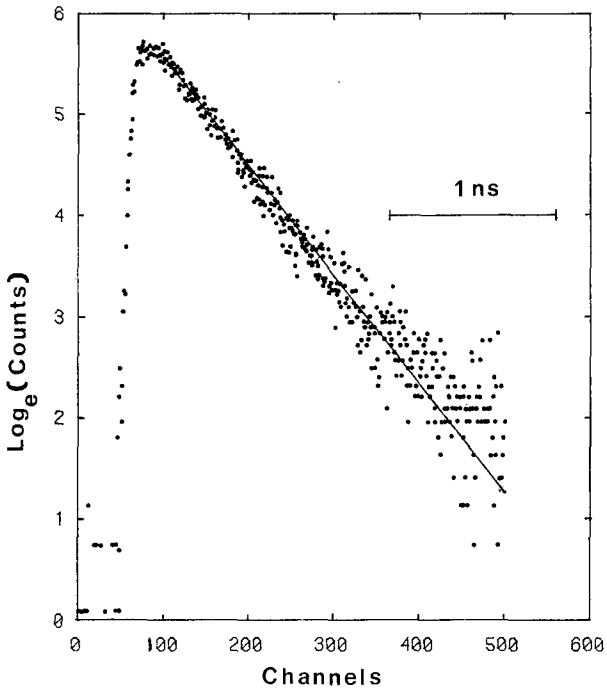

Fig. 2. Fluorescence decay of Erythrosin B

Such a synchronism was sufficient at this stage, though susceptible of further improvement. During the measurements, the stop pulses were provided by the SPAD. Figure 1 shows a representative result obtained by measuring the laser pulse. The curve has ~90 ps FWHM and exhibits some "tailing", due to carrier diffusion effects [7]. Fluorescent decays excited by the laser have then been measured. Figure 2 depicts the measurement on Erythrosin B (10^{-3} M solution in Ethanol), performed with 5.165 ps/channel; the lifetime is 0.96 ns. Measurements on DODCI showed a lifetime of 1.58 ns. The lifetime values are in agreement with data reported in the literature.

The results obtained demonstrate that SPHADs can be used for measurements of fast decays and provide considerably higher resolution than PMTs. Further improvements (larger area, lower tailing, etc.) may be expected from developments in the device technology.

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Applications of the Jitter-Free Signal Averaging Streak Camera in Solid State Physics, Biophysics, and Chemistry

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In the case of single-shot streak cameras, the application of signal averaging techniques is in general complicated and limited in accuracy by shot-to-shot jitter, or errors in synchronization of the camera to the picosecond transient being recorded (typically ±100 ps). We have developed a single-shot streak camera with 2 ps jitter [1] and complete absence of short or long term drift using picosecond high power switching in semi-insulating GaAs [2].

We have studied luminescence from solids in three classes: color centers in alkali halides, amorphous materials, and semiconductors. In color center luminescence, we have used the absolute timing capability of the streak camera to compare the luminescence rise of M centers in NaF to the excitation pulse, and find a time delay of less than 1 ps, indicating rapid vibrational relaxation. In amorphous As_2S_3, we have made the first luminescence measurement of recombination kinetics on the picosecond time scale, and find again less than 1 ps delay and a strongly temperature dependent decay time. In this experiment, the single-shot signal to noise ratio was considerably less than 1, and it was necessary to average 300 shots to obtain an acceptable signal. In $CdS_{0.5}Se_{0.5}$ it has been possible to accumulate the time-resolved

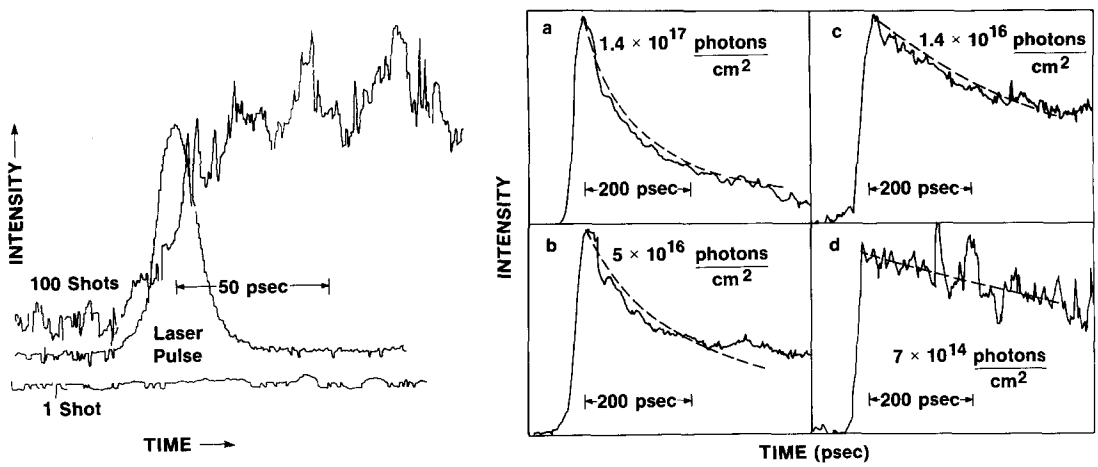

Fig. 1a and b. Signal averaging: Light harvesting chlorophyll aggregates. (a) one and 100 shots of fluorescence and 10 shots of attenuated laser pulse, (b) intensity dependence of fluorescence signal indicating exciton annihilation. Dashed curves are fits to $N(t)=[(1/n(0)+\gamma/2k)\exp(Kt)-\gamma/2k]^{-1}$ with $K=8\times10^8\,s^{-1}$ and $\gamma=3\times10^{-9}\,cm^3\,s^{-1}$ (from [3])

luminescence spectrum in a simple way using a set of interference filters by taking advantage of the absolute timing capability of the streak camera.

In biophysics, we have studied exciton annihilation in light-harvesting chlorophyll *a/b* proteins [3] (Fig. 1), the temperature dependence of purple membrane fluorescence, and the detailed kinetics of energy transfer on the picosecond time scale in spinach chloroplasts. Acquisition of high signal-to-noise ratio data allows for a detailed comparison of the signals with kinetic theory with a greater accuracy than has been possible.

In low quantum yield systems ($\phi \lesssim 10^{-4}$) such as phthalazine, we have measured fluorescence kinetics using a 3ω excitation. Fluorescence depolarization can be measured to a high degree of accuracy with the jitter-free streak camera. We performed a study of Rhodamine-B fluorescence depolarization in solutions of varying ionic concentration.

The jitter-free streak camera enables detailed studies in previously inaccessable areas, offering the versatility of a high-power system with the sensitivity of a signal-averaging system. We have recently acquired data over a dynamic range of $>10^4$ using the averaging technique.

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The Self-Injected Laser for High Power Short Pulse Generation

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Adiabatic pulse compression by a large factor (~ 10) has been achieved in a simple and reliable way in conventional lasers by a suitable driving of the cavity Q-factor with a Pockels cell. This is the effect of the unconventional technique of "self injection" (or "cavity flipping") [1, 2]. In the cavity configuration we used a single polarizing Pockels cell (PC) inserted in the cavity and driven by an appropriate HV circuit provided at successive times the actions of Q-switching, cavity flipping and cavity dumping of the selected short pulse generated in the cavity. The cavity configuration of the self-injected Nd:YAG laser is presented in Fig. 1. At first a convenient voltage V applied to PC triggers the Q-switch action. Then, after an appropriate delay, a square pulse is applied to PC. The frustrated Q-switch action results in the generation and in the regernative amplification of a "seed" optical pulse of duration 2 Lc. A train of pulses with envelope reproducing the shape of the corresponding normal Q-switched pulse then develops in the cavity. Extracting of one (or more) of such pulses is provided by cavity dumping due to PC. With Nd:YAG ($6.3 \times 60\,\mathrm{mm}^2$ rod) as active medium it was possible to reach 85 MW, 1 ns pulses, in the same operating conditions that would have allowed, in normal Q-switching operation, the generation of 8.5 MW peak power, 10 ns pulses. The same method has been applied to a 2-frequencies flash pumped dye laser [2] (Fig. 2). With this type of active medium we obtained 200 kW, 1 ns pulses with a loss of energy of $\sim 20\%$. The same technique has been applied successfully also to the unstable cavity laser. A further pulse-compression due to the action of an intracavity saturable absorption cell resulted in the generation of 15 ps bandwidth limited pulses with a 4 GW peak power using Nd:YAG as active medium [1].

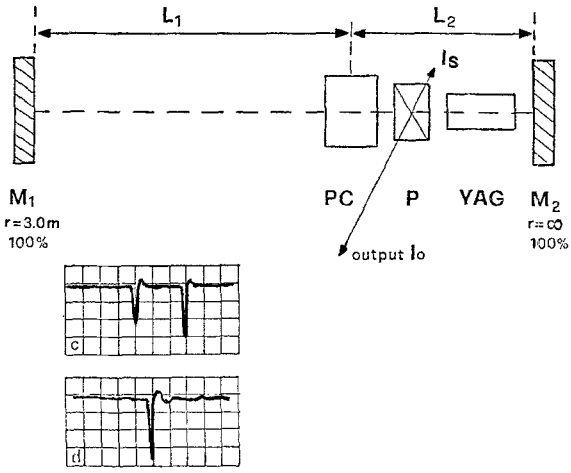

Fig. 1

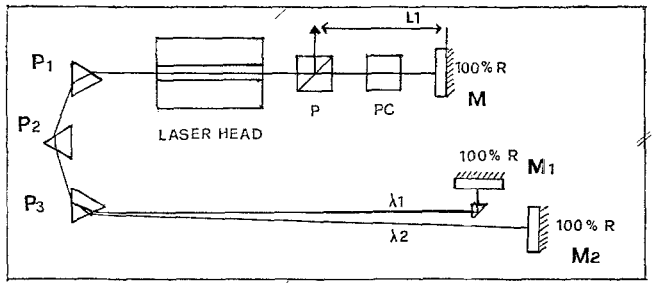

Fig. 2

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A New Approach to the Theory of Mode-Locking by Synchronous Pumping

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We have developed a new theoretical technique for the case of mode-locking by synchronous pumping that allows complete pulse profiles to be computed simply and essentially without approximation. The results cast serious doubt on the validity of previous theoretical work on this problem and have wide implications within the whole field of mode-locking.

The theory of mode-locking by synchronous pumping (MLSP) has been studied by various authors [1–5], with particular reference to the effect of mismatch in the lengths of the pumping and slave laser cavities defined here as $t_m = T_{\text{slave}} - T_{\text{pump}}$. The self-consistency requirement determining the pulse profile $V(t)$ under steady-state conditions is

$$V(t+t_m) = F \exp((A(t)-\Gamma)/2) V(t), \quad (1)$$

where F represents the action of a bandwidth-limiting filter and the amplification coefficient $A(t)$ is controlled by a standard rate equation containing pumping and saturation terms. We represent the pulse by a mesh of values V_i separated in local time by t_m, and we model the filter by an ideal Fabry-Perot device whose storage time is t_f, and whose transit time is chosen as t_m without significant loss of generality. It is now simple to show from (1) that the profile is determined (for the case where $t_m > 0$) by the difference equation

$$V_{i+1} = (R + g_i(1-R)) V_i, \quad (2)$$

where $R = \exp(-|t_m|/t_f)$. Equation (2) is approximately equivalent to the differential equation

$$dV/dt = V(A(t)-\Gamma)/2t_c, \quad (3)$$

where $t_c = t_m/(1-R)$. The pulse dynamics are now seen to be controlled by the familiar Wagner-Lengyel equations [6] and it therefore emerges that the pulses in the case of MLSP are "mini-" giant pulses in which the cavity transit time in standard Q-switching theory is replaced by the time t_c. An equation similar to (4) applies in the case where (t_m/t_f) is small and negative.

Curves a and b in Fig. 1 show profiles generated from (3) for different initial values of $V(t_1)$, where t_1 is the time relative to the pumping pulse at which net gain is first achieved. This boundary value is determined by the level of spontaneous emission far out on the leading edge of the pulse. Curve c is the (Gaussian) profile produced by a refined version of the MLSP analysis of Kim et al. [4]. Plotting the profiles on a logarithmic scale highlights the major differences between Curves a and b, and Curve c. The two theoretical approaches lead to different functional dependences of the pulse widths on key parameters.

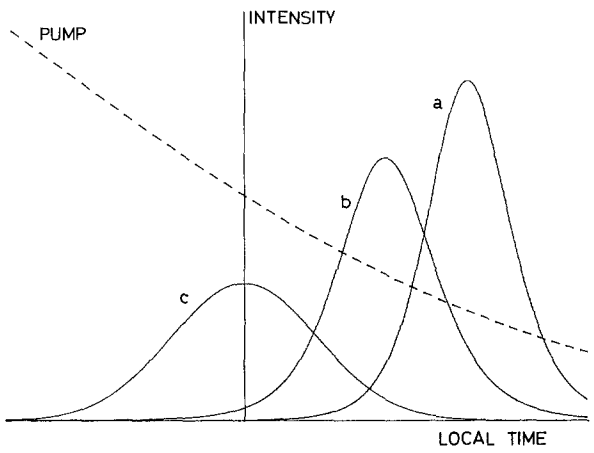

Fig. 1. Curves a and b: Pulse profiles generated by (2). Curve c: Gaussian pulse predicted by the method of [4]

Like other authors [3, 5], Kim et al. [4] used a technique that has been applied widely and with apparent success elsewhere in the theory of mode-locking. A particular (symmetrical) functional form for the pulse is defined at the outset, and the filter and shift operations are represented by truncated differential operators. We show how the exclusion of asymmetry causes the standard approach to fail, in the case of MLSP at least. The implications of this conclusion in other areas of mode-locking theory will be discussed.

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Tunable Picosecond Pulse Generation by Distributed Feedback Dye Lasers

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Recently it has been shown that N_2-laser pumped distributed feedback dye laser (DFL) are capable of producing transform-limited laser pulses having a duration of the order of ten picoseconds [1, 2]. In this paper we wish to report a detailed experimental and theoretical study of the DFDL [4, 5].

The experimental arrangement (Fig. 1) which uses a holographic grating as a beam splitter ensures that the visibility of the pumping interference fringes produced on the dye cell approaches unity even with N_2 or XeCl-excimer lasers as pump sources. Other pump configurations are also presented. Tuning of the DFDL can be accomplished by rotating the mirrors or by changing the

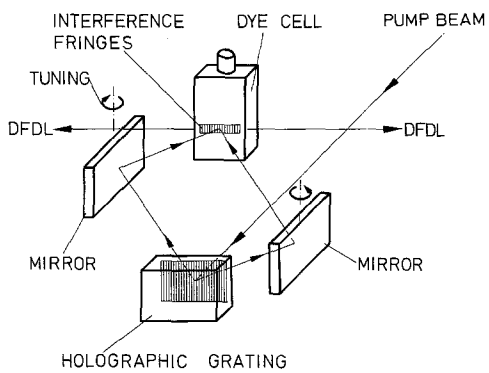

Fig. 1. Experimental arrangement of the DFDL

refractive index of the dye solution. The pressure dependence of the refractive index of solvents was also used for fine tuning. In the DFDL no longitudinal modes are built up and therefore tuning without mode-hopping over a spectral range of several nanometers is very straightforward.

In the DFDL feedback is provided by the spatially periodic gain modulation produced by the pumping interference fringes. It was shown [1] that $\tau_c \sim \alpha^2$, where τ_c is the equivalent cavity lifetime of the DFDL and α is the gain coefficient. Both τ and α are time dependent quantities. This specific feature of the DFDL results in the production of stable ultrashort pulses instead of relaxation oscillation spikes. The formation of ultrashort pulses was described by a rate equation model. The calculated and measured effects of various parameters (pump power, pump pulse duration, dye concentration, fluorescence lifetime and geometry dimensions of the laser) on the temporal and energy characteristics of the DFDL were found to be in good agreement [3, 4].

Calculated and measured DFDL pulse shapes [Ref. 3, Fig. 2] show that the number of DFDL pulses increases with increasing pump power. Single pulses are produced if the pump power does not exceed threshold by more than 20%. The shot-to-shot energy stability of single pulses was found to be $\pm 7\%$.

The duration of single pulses was measured to be 78 ps, 42 ps, and 28 ps when 3.5 ns, 1.8 ns, and 1.2 ns long pump pulses were used, respectively. We obtained pulses considerably shorter than the resolution of our streak camera when the DFDL was pumped with the 0.7 ns long pulses from a TEA–N_2 laser. Preliminary experimental results indicate that the DFDL pumped with single pulses from a mode-locked Nd:YAG laser is capable to produce subpicosecond pulses.

The operation of synchronously pumped mode-locked dye lasers in the blue and near uv part of the spectrum is strongly impeded by the absence of suitable pump sources and mode-locking absorbers. DFDLs are capable to operate at any wavelength where laser dyes exist. Single picosecond pulses were obtained not only in the visible but also in the 360–420 nm spectral range.

The threshold pump energy of the DFDL is about 0.2 mJ. The rest of the N_2 laser pulse energy was used to pump a two stage amplifier. The single DFDL pulses were amplified up to 0.5 MW peak power at 200 pps repetition rate. Special care was taken to suppress amplified spontaneous emission and to avoid pulse broadening in the amplifier. Since the DFDL and the amplifier was pumped with the same N_2 laser synchronization problems did not arise. The construction of a XeCl-excimer laser pumped regenerative ring amplifier is nearly completed. Amplification up to 1 mJ pulse energy is feasible.

The DFDL emits a train of closely spaced pulses when threshold is exceeded considerably [1]. A comparative study of N_2-laser pumped grating-tuned dye lasers and DFDLs showed that the DFDL has a much lower amplified spontaneous emission background level and about twice the efficiency and tuning range of grating tuned dye lasers.

Distributed feedback laser action has been also demonstrated in a passive optical fiber surrounded by a gain modulated dye solution of lower refractive index [5]. Both the mechanisms of feedback and gain are accomplished by evanescent wave interaction. Such a device can be useful for measurement of dispersion of ultrashort pulses in optical fibers.

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Coherence Peak and Excited State Absorption of Dye Molecules

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The transient propagation of picosecond probe pulses in dye solutions after weak excitation by a pump pulse is studied theoretically and experimentally. Two kinds of experiments are reported.

I. The signal enhancement observed in measurements of induced dichroism [1, 2] for short time delay t_D between excitation and probe pulse ("coherence peak") is investigated. Model calculations are presented considering moecular transitions from the ground state to a distribution of vibronic levels in the first excited electronic state S_1 with subsequent vibrational relaxation. Excited state absorption (ESA) to higher lying levels is included in our treatment, taking into account the large density of states of dye molecules via generalized (complex) absorption cross sections.

Our results are summarized as follows:

(i) The signal enhancement around $t_D = 0$ occurs for equal frequencies of probe and pump; it is strongly effected by the transient population of vibrationally excited levels in the S_1 state and by excited state absorption. The decisive parameters are the vibronic relaxation time and the difference between ground state and excited state absorption cross sections. A certain contribution to the signal maximum results from a population grating produced by the superposition of pump and probe field [2, 3]. For large beam diameter where scattering off the induced grating is fully effective and in the absence of vibrational relaxation, a small signal enhancement of ~ 1.4 is expected for Gaussian pulses.

(ii) In our measurements we use single pulses of 5 ps duration at 18,990 cm^{-1} generated by a mode-locked Nd:glass system with subsequent frequency doubling. The E-vector of the linearly polarized probe beam is oriented at 45° with respect to the excitation field and the transmitted probe pulse is measured behind an analyzing polarizer. Enhancement factors of 1.8 to 4 are reported for the laser dyes rhodamine 6G and phenoxazone 9 in various solvents. Comparison with our calculations using excited state absorption data (see below) yields values of the vibrational relaxation time in the S_1 state [4].

In part of the investigation, the frequency of the probe pulse was shifted to 17,645 cm^{-1} using stimulated Raman scattering in nitrobenzene. For this situation no signal enhancement is observed at the low intensity level ($\sim 10^7$ W/cm^2) considered here. It is concluded that additional nonlinear effects of the solvent and solute molecules are negligible.

II. We have investigated the generalized excited state absorption cross sections of dye molecules studying the nonlinear transmission of the probe pulse. A double beam set-up has been devised so that small changes of probe transmission are readily detected in single pulse measurements where only a small fraction of the molecules (a few 10^{-2}) is promoted to the S_1 level. For this situation a linear dependence of the probe transmission on the

excitation intensity is expected, allowing the determination of the conventional ESA cross section (real part of the generalized cross section). Experimental data on the ESA of rhodamine 6G and phenoxazone 9 in various solvents are reported. We emphasize the low excitation level of several 10^7 W/cm^2 in our measurements so that competing nonlinear effects may be neglected.

The imaginary part of the generalized ESA cross section is of particular interest. Information on this quantity is supplied by the first time studying the ellipticity of the transmitted probe pulse in the induced dichroism experiment. The results demonstrate the validity of our theoretical approach which takes into account the high density of states of dye molecules.

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Orientational Dynamics in Microemulsion Droplets with Picosecond Time Resolution

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In despite of their fundamental interest as well as their many possible applications, predictive understanding of the microemulsion structure is only emerging. Those media, basically constituted of a mixture on an oil, water, and a surfactant, are characterized by a thermodynamically stable, optically transparent, phase. It is generally admitted that, in the case of low water concentration, the water is concentrated inside nearly spherical droplets isolated from the oil phase by a shell of surfactant molecules. The droplet sizes (few tens of Å) suggest that the structure of the water in the droplet core should be different than for a pure liquid phase. This fundamental problem has already been investigated by several techniques, and particulary by the fluorescence polarization analysis of probe dye molecules preferently soluble in water [1]. These experiments, presenting a low time resolution, cannot be interpreted with a simple model. Moreover, the results are strongly depending on the location of the dye molecule which cannot be precisely determined.

We report on what we believe to be the first analysis of the water structure in a microemulsion, using a time resolved spectroscopy method [2] with a resolution in the picosecond range. Similarly to the polarization fluorescence experiment, we use dye marker molecules to probe the properties of the intramicellar medium. The characteristic reorientational time of the probe molecules is investigated by monitoring, versus the delay time, the absorption of a picosecond pulse through the medium, following an excitation by a first saturing pulse. The reorientation time is very sensitive to the surrounding of the probe molecule, in such a way that informations can be obtained on their environmental situation. In particular, the effects of various parameters, like the nature of the dye, the droplet size and the surfactant polarity on the probe molecules location in the droplet core can be investigated to give a correct interpretation of the water structure in the core.

In the actual experiment, the linearly polarized probe and saturating pulses are counterpropagating through the sample cell. The dichroism induced by the saturating pulse is directly obtained by periodically switching the respective polarization of the two pulses from parallel to perpendicular, and by detecting, with a phase detection device, the modulated part of the probe absorption. The absorption recovery is obtained by imposing the 54.7° magic angle between the polarization of the two counter propagating beams [3].

Using a synchronous pumped, cavity dumped, R6G mode locked dye laser providing pulses of few picosecond duration, two ternary microemulsions have been investigated [4]. The first one consisted of a mixture of water, heptane and A.O.T. (sodium 1,4 bis-2 ethyl hexylsulfoccinate), and anionic surfactant. The markers were the cations of the DODCI or thionine dye molecule. The opposite polarity between dye and surfactant makes more probable the location of the dye molecule close to the surfactant shell than inside the water core. This behavior is confirmed by the experiments where the reorientation relaxation time in the micellar medium (1,1 ns) is found to be much larger than in pure water (200 ps), and nearly independant of the hydrodynamic radius of the droplets determined by photon correlation light scattering experiments [5]. The second microemulsion consisted of a mixture of benzene, water and BHDC [6] (benzyl hexadecyl dimethyl amonium chloride) as surfactant. The cationic nature of the surfactant, repulsing the cation of the dye molecule used as a marker, should lead to a real probing of the water structure in the droplet core. It is found that the relaxation time of the dye marker, larger than in the pure liquid case (60 ps), is now strongly depending on the hydrodynamical radius r_H of the droplets and not on the droplet concentration, within the range of the volumic fractions investigated. The experimental results are well fitted with a single exponential lying on a constant background, suggesting that, in the case of even polarities, part of the dye marker molecules are still located close to the surfactant interface. The results have been interpreted in terms of the change in the water structuration with the droplet size.

From the above experiments, a certain number of informations concerning the photochemistry of the dyes employed have been obtained. For example, the measurements of the absorption recovery time of DODCI in the first microemulsion shows that, because of internal conversion quenching, the relaxation towards the ground state – which is well fitted with a single exponential and a constant background – is twice larger than in pure water. A quantitative measurement of the rate of formation of the photoisomer specie is directly given by the amplitude of the background. This rate has been found close to the value of the pure water case.

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Measurement of Level Kinetics and Reorientation Processes with High Time Resolution

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Fluorescence spectroscopy is advantageously applied in order to measure excited state lifetime and reorientation of the transition moment after excitation (see, e.g., [1, 2]). Applying ultrashort light pulses the time resolution is limited in most cases by the signal detection system. Mahr et al. [3] proposed a method in which an excite-and-probe scheme is combined with fluorescence observation. The dependence of the integrated fluorescence signal between two successive exciting light pulses is measured. That dependence arises under the condition that the second pulse views a ground state population depleted by the first pulse. The time resolution is only limited by the pulse duration and hence values in the sub-ps-range can be achieved.

In [3] a special modulation of the high repetition rate pulse trains has been applied using a third reference pulse train with a fixed delay being large in comparison with the signal relaxation time. A very precise adjustment of the pulse intensities in the different channels is needed. To avoid this requirement we modified the method by modulating two exciting beams with frequencies ω_1 and ω_2, respectively, and measuring the fluorescence signal at one of the frequencies $\omega_1 \pm \omega_2$.

Both methods have been investigated by us with respect to the measurement of level kinetics and reorientation of the transition moment after excitation. The reorientation influences the absorption of the second pulse and emission of light due to the first and second pulses. The time-integrated signal depends on the polarization direction of the second pulse with respect to the first one and on the polarization chosen in the detection channel. Assuming isotropic rotational diffusion (coefficient D) in both the ground and excited states, single exponential decay of the excited level

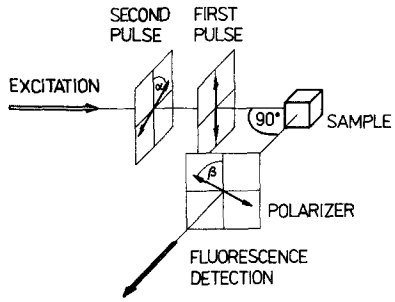

Fig. 1. Geometrical configuration (polarization directions are indicated by ↔)

(lifetime τ) and weak δ-pulse excitation the following delay time dependence of the signal under the polarization geometry specified in Fig. 1 results:

$$S(t) \sim e^{-t/\tau}\Big(1+\tfrac{2}{5}e^{-6D\tau}(3\cos^2\alpha-1)+\tfrac{2}{5}\frac{1}{1+6D\tau} \cdot\{\tfrac{3}{2}\sin^2\alpha\sin^2\beta+\tfrac{1}{2}(3\cos^2\alpha-1)(3\cos^2\beta-1) +e^{-6D\tau}[-\tfrac{6}{7}\sin^2\alpha\sin^2\beta+\tfrac{1}{7}(6\cos^2\alpha+5)(3\cos^2\beta-1)]\}\Big).$$

For $\alpha_0 = 54.7°$ and $\beta_0 = 65.2°$ the signal decay depends only on the level kinetics. (Measurements at other angles provide a mixture of level and orientation kinetics and hence might be misinterpreted. Concerning cresyl violet, disagreement between our measurements and data given in [3] might be explained in this way.) Then, using the level kinetics determined the reorientation time can be extracted by forming certain linear combinations of signals with different polarization directions.

Measurements on several dyes in solution will be discussed.

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