Time-resolved studies of stimulated emission from colloidal dye solutions

Masood Siddique and R. R. Alfano

New York State Center for Advanced Technology for Ultrafast Photonic Materials and Applications, Institute for Ultrafast Spectroscopy and Lasers, Department of Physics and Department of Electrical Engineering, The City College of New York of the City University of New York, New York, New York 10031

G. A. Berger, M. Kempe, and A. Z. Genack

New York State Center for Advanced Technology for Ultrafast Photonic Materials and Applications, Department of Physics, Queens College of the City University of New York, Flushing, New York 11367

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The temporal profiles of the emission from titania particle suspensions in Rhodamine 640 perchlorate dye solutions excited by 10-ps pulses of 527-nm radiation were measured over a wide range of particle and dye concentrations and laser powers. The dynamics of stimulated emission from random media is modeled by a random walk of photons within the colloid and rate equations for molecular excitations. The pulse width and the dependence of the threshold for laser action on dye and scatter concentration are computed by a Monte Carlo simulation of the model and are found to be in qualitative agreement with experiment. © 1996 Optical Society of America

Lasing action in random amplifying media[1] has been observed in powdered phosphors[2] and in colloidal suspensions in dye solution.[3] The radiation following pulsed excitation is emitted in a short burst with a narrowed spectrum compared with those from spontaneously emitted radiation.[3,4] Because stimulated emission is induced at a pumping level below that required for the observation of significant amplified stimulated emission in a neat dye solution, such systems may find applications as novel displays, switches, and sensors.

In this Letter we explore the mechanism for lasing by comparing ultrafast emission measurements on a time scale comparable with the residence time of the pump photons in the medium and much shorter than the excited-state lifetime to a Monte Carlo simulation of photon migration and level occupation. The 10-ps excitation pulse used in these experiments was an order of magnitude shorter than in previous measurements. The temporal profile of emission was measured with a resolution of 10 ps in a series of samples of titania particles suspended in solutions of Rhodamine 640 perchlorate in which lasing was observed by Lawandy *et al.*[3] Suspensions are particularly useful because they allow one independently to change the transport mean free path l, in which the direction of propagation at the pump frequency is randomized, and the small-signal absorption length at the pump wavelength l_a, by varying the density of scatterers and the dye concentration, respectively.

We produced the colloid by mixing DuPont R960 powder of alumina-coated titania particles with an average diameter of 0.25 μm with Rhodamine perchlorate dye in methanol solution. The dye concentrations varied between 10^{-4} and 2.5×10^{-3} M, corresponding to absorption lengths l_a between 1400 and 50 μm. The density of scatterers was varied between 5×10^9 and 5×10^{11} cm^{-3}. The highest concentration studied had a volume fraction of 0.4%. The values of l that correspond to these concentrations were measured to be between 16 μm and 1.6 mm for the emitted light and 10 μm and 1 mm for the pump light.

A 10-ps pulse at 527 nm, obtained from a frequency-doubled single-shot Nd:glass laser, was focused onto the colloid contained within a 1 cm $\times$ 1 cm $\times$ 3 cm glass cuvette to a spot size of 0.5 mm. The incident beam made an angle of ~5 deg with the normal to the sample surface. We varied the pump pulse intensity from >400 to ~1 μJ by inserting neutral-density filters in the beam. A portion of the laser pulse was collected by an energy meter to monitor the incident pulse energy. The light that was backscattered from the front surface of the sample surface was collected and collimated by a lens. We removed light at the pump frequency by passing the collected light through three long-pass filters, which cut off wavelengths below 540 nm. This light was focused onto the slit of the streak camera along with a small portion of the incident pulse to provide a time reference. The Hamamatsu C979, with a silicon intensified target tube (C1000) and a temporal analyzer streak camera, had a temporal resolution of ~10 ps.

In the neat 10^{-4}-M dye solution a short pulse on the picosecond time scale was observed only for pump pulse energies above 25 μJ. The threshold for lasing action is defined as the pump energy for which the duration of the emitted pulse is 100 ps. As scatterers are added to the solution, laser action ceases up to the highest energies available with our laser for scatterer densities of 5×10^9 and 5×10^{10} cm^{-3}. As the density of the scatterers is further increased, laser action reappears at higher thresholds than in the neat dye solution. At higher dye concentrations lasing action requires a higher incident power in the neat solution, but the addition of scatterers lowers the threshold for lasing action significantly below the value in the neat solution, and pulses with widths comparable with that of the incident pulse are observed.

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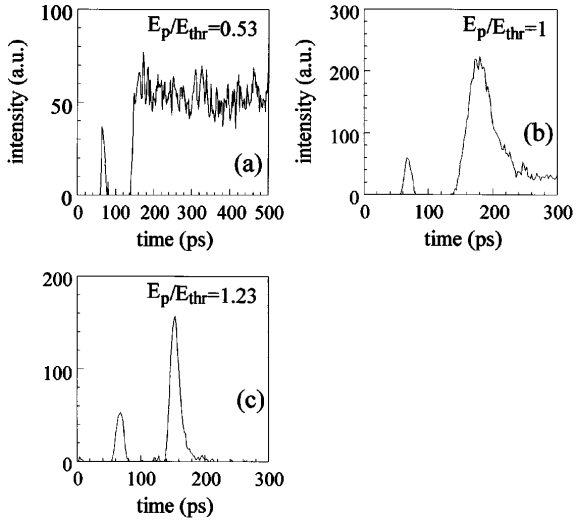

Fig. 1. Time-resolved emission from Rhodamine 640 dye in methanol (10^{-3} M, $l_a = 140$ μm) with titania particles (5×10^{11} cm^{-3}, $l = 16$ μm). (a) Spontaneous emission after excitation with 7 μJ of pump light. (b) Emission at threshold of ~13-μJ pump energy. (c) Short pulse at a pump energy above threshold (16 μJ). The reference pulse shown in each figure indicates the input pulse duration and the time resolution of the detection system. Its timing with respect to the onset of the emission varies from (a) to (c). E_p/E_{thr} is the ratio of pump to threshold energies.

Examples of the change in the emission profile as the pump energy increases are shown in Fig. 1. Table 1 gives the pulse width, uncorrected for the temporal resolution of the streak camera, as well as the threshold energy for lasing for a wide range of values of l and l_a.

In the weak-scattering regime in which the transport mean free path is much larger than the wavelength, one can therefore ignore wave interference in computing average transport within the medium. The energy flow of pump and emitted photons can then be modeled by a random walk of photons.[1,5] The neglect of wave coherence is in accord with the observation that local intensity fluctuations in reflection from powdered samples are small.[2]

The random walk of photons is computed with a temporal step size equal to the mean free time $\tau = l/v$, where v is the phase velocity in the solution. The values of l at the incident and the emitted frequencies are taken to be the same. The incident beam is assumed to be random after penetrating a distance l into the sample. We further assume that the incident beam is a plane wave with incident intensity equal to the fluence of the incident pulse divided by the equivalent area of the beam at the laser surface, which is taken to be πw_0^2, where w_0 is the beam waist. Thus this model focuses exclusively on the evolution of the sample along the longitudinal direction normal to the surface. The average magnitude of the projection of the displacement of diffusing photons along the longitudinal dimension during one mean free time is $l/2$. After each mean free time, photons that are not absorbed and that do not pass through the sample surface have moved either to the right or to the left by $l/2$ with equal probability. The internal reflectivity of the sample boundaries is 0.15. The sample thickness is taken to be 1 mm, which is much larger than the intensity attenuation length $L_a = (\frac{1}{3} l l_a)^{1/2}$ for the range of parameters considered.

The dye molecule is modeled as a four-level system. Because the relaxation times from the terminal levels of the pumped and emitting transitions, levels 4 and 2, respectively, are generally on a subpicosecond time scale, we assume that only ground state, level 1, and the emitting state, level 3, have significant population, $n_1 + n_3 = n$, where n is the density of dye molecules and n_i is the density of molecules in the ith level. The level populations and the emission and absorption of photons are governed by rate equations that involve the cross sections for absorption of the pump radiation and for emission as well as the level populations and the densities of pump and emitted photons.

In the Monte Carlo computation we keep track of the density of incident and emitted photons and of the population density n_3 at points with depths in the medium that are multiples of $l/2$ at time intervals that are multiples of τ. The emission spectrum of Rhodamine 640 (Ref. 4) is divided into 20 segments of equal area. The spatial and temporal evolution of the photon density of each of these segments of the spectrum is followed separately. We take the threshold to be the pump energy at which the ratio of the total number of stimulated and spontaneously emitted photons is unity. At this point we find that the emission spectrum has narrowed to a few nanometers and the emission has a width of less than

Table 1. Threshold Pump Energies and Measured FWHM of the Emission for Various Particle Densities and Dye Concentrations[a]

Particle density (cm^{-3})/1 (μm)	Dye Concentrations (mol/L)/la (μm) at the Following Threshold Energies (μJ)/Emission FWHM (ps)[b]		
	10^{-4}/1400	10^{-3}/140	2.5×10^{-3}/50
0	25/56	45/30	50/30
5×10^{9}/1600	NL	35/16	15/18
10^{18}/800	NL	25/16	10/18
5×10^{10}/160	90/80	17/26	8/18
10^{11}/80	50/50	15/22	12/18
5×10^{11}/16	50/24	13/20	6/20

[a]The transport mean free path given is for the emitted light. The duration of the emitted pulse was the shortest obtained at pump energies up to 400 μJ. In most cases the shortest pulse width was reached well below this pump energy.

[b]NL, Lasing was not observed for pump energies as high as 400 μJ.

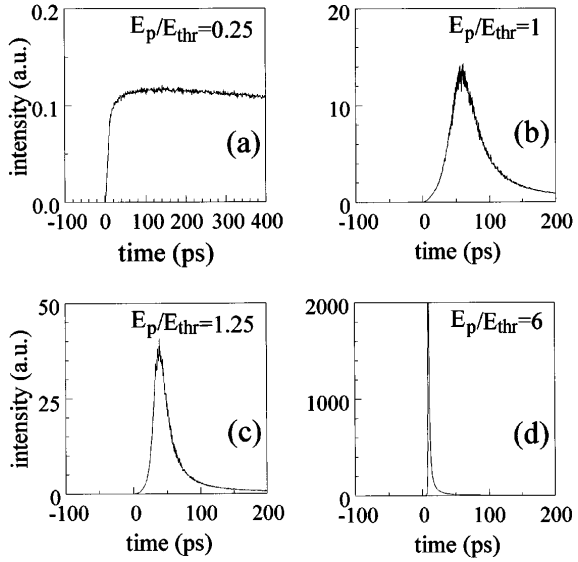

Fig. 2. Emission profiles from the Monte Carlo simulations for $l = 18\ \mu$m and $l_a = 140\ \mu$m. Emission for a pump energy (a) below threshold (0.12 μJ), (b) at threshold (0.47 μJ), (c) slightly above threshold (0.59 μJ), and (d) far above threshold (2.8 μJ).

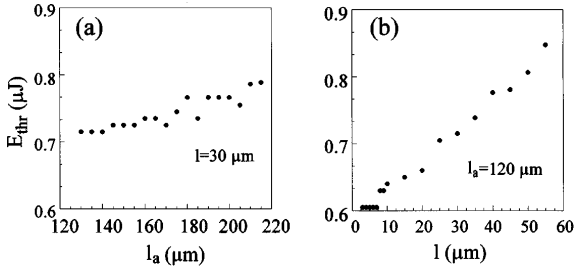

Fig. 3. Calculated threshold pump energy versus (a) l_a for fixed $l = 30\ \mu$m and (b) l for fixed $l_a = 120\ \mu$m.

100 ps. Thus the transition in temporal and spectral features of emission appears to occur at the same pump energies, and our criterion for the threshold in consistent with that used in this and previous experiments.[3,4]

The Monte Carlo simulation allows use to study the dynamics of molecular excitation and deactivation and wave transport in the medium on the same footing and is equivalent to solving the coupled nonlinear photon diffusion and molecular rate equations when diffusion theory is applicable.

The temporal profile of the total number of emitted photons at all frequencies is shown in Fig. 2 for a 10-ps incident pulse for incident power levels that correspond to excitation below, at, and above threshold in a sample with values of l and l_a similar to those in Fig. 1. At low pump energy the emerging photons are produced predominantly by spontaneous emission with the molecular lifetime of 4 ns (Ref. 4) [Fig. 2(a)]. At the threshold for laser action we find an emission pulse of width 40 ps, which reaches its peak 60 ps after the arrival of the leading edge of the pump pulse [Fig. 2(b)]. Above threshold the emission shortens dramatically and reaches its peak value at earlier times. At pump energies six times above threshold the peak of the pulse is delayed by 10 ps and its width narrows to 3 ps, which is shorter than the incident pulse [Fig. 2(d)]. The emission spectrum narrows from the width of 40 nm associated with spontaneous emission below threshold to 7 nm above threshold. The temporal profiles in the experiment and in the simulations are similar. The principal difference is that the lasing thresholds found in the simulations are an order of magnitude lower than observed experimentally. This difference cannot be explained by absorption of the emitted light in the medium, which was omitted in the above calculations. We find that including the absorption typically raises the threshold by only 40%. However, the difference in the thresholds between experiment and our model may be due to the neglect of the transverse excitation profile. Because this omission results in a flat transverse gain profile, the emitted photons cannot escape the gain region by transverse diffusion. The difference between the experiments and the simulations should diminish when l and l_a become significantly smaller than the beam diameter.

In Fig. 3 the results of the computation of the threshold energy as a functions of l with l_a held constant at 120 μm and as a function of l_a with l held constant at 30 μm are shown. In these calculations the actual spectral distribution of the spontaneous emission was represented by an effective cross section of $\sigma_e = 4.2 \times 10^{-16}$ cm^2. The threshold depends only weakly on l and l_a. This can be anticipated by considering the limit in which bleaching of the pump transition is negligible.[4] In the absence of gain or loss for the emitted photons the average path length of photons that are spontaneously emitted in the excited region of depth L_a is $\langle s \rangle \sim {L_a}^2/l \propto l_a$. The small-signal gain in the medium is inversely proportional to l_a. Thus the pump energy threshold, which depends on the gain–path length product, would be independent of l and l_a.

In the present measurements, as well as in previous reports of lasing in random media, the lasing threshold is reached at the point at which the pump transition is bleached. Such bleaching increases the penetration of the pump and consequently leads to longer path lengths for emitted photons within the gain region, which results in a reduced threshold in these systems. This effect is taken into account in the present Monte Carlo simulation, which we find is in qualitative agreement with measurements of pulsed emission.

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