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Picosecond Spectroscopy of Intermolecular Interactions in Dye Solutions

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Abstract. Some new experimental data on the time development of ultrashort superfluorescence (SF) in the dye solution are presented. The correlation between temporal behaviour change and the change of the spectral and spatial intensity distribution gives direct evidence of the important role of the selffocusing phenomenon in the formation of the ultrashort SF pulse synchronized with the pumping one. The oriental relaxation of solvent molecules in the dye solution not only influences the duration of the dye SF via the selffocusing mechanism but also causes a temporal change of spontaneous emission spectrum. At least two different relaxation times were found in the fluorescence spectrum of the dye in several polar solutions.

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The development of different picosecond spectroscopy techniques opened new interesting possibilities for the investigation of many ultrafast processes in dye solutions. In particular, the rotational movement of molecules in a solution may be directly measured by such technique. While a lot of attention was paid to the investigation of the rotational diffusion of dye molecules in a solution, the rotation of solvent molecules and its influence on the spectral and kinetic properties of the dissolved dye is still an opened problem in many respects.

Typically one of the two phenomena may cause the directed rotation of solvent molecules in a solution: 1) interaction of molecules with a strong optical field leading to the optical Kerr effect and/or 2) interaction of polar solvent molecules with the electric field of the dye molecules, which possess the permanent dipole moment. The first mechanism is the major one responsible for selffocusing of picosecond pulses in liquids while the other one plays an important role in the processes of formation of the solvate shell, surrounding the dye molecule.

There are almost no experimental data on the influence of these two types of the picosecond-scale rotations of the solvent molecules on the kinetic and spectral properties of emission of dissolved dyes. No comparison of the rotational relaxation processes in both cases was ever made.

This paper presents some new experimental results on picosecond spectroscopy of dye solutions, which demonstrate the important influence of the rotational motion of solvent molecules on the emission properties of dissolved dyes. At first, we shall discuss the specific features of the picosecond super-fluorescence (SF) formation in dye solution and then present the data showing the peculiar character of the orientational relaxation in alcohol solutions.

1. Experimental

The picosecond up-conversion method was employed for time resolved spectroscopy of dye SF [1]. The dye cell longitudinally pumped with the 2nd harmonic of the single amplified 5 ps pulse from a mode-locked Nd phosphate glass oscillator was tilted to avoid amplification of reflected fluorescence light. The sum frequency of the 1.054 μm pulse and SF was generated in the KDP crystal. Selected by a monochromator the sum frequency was registered with a photomultiplier as a function of the time delay between pumping the 0.527 μm and 1.054 μm pulses. The spectrum and far field distribution of SF were also detected at each shot.

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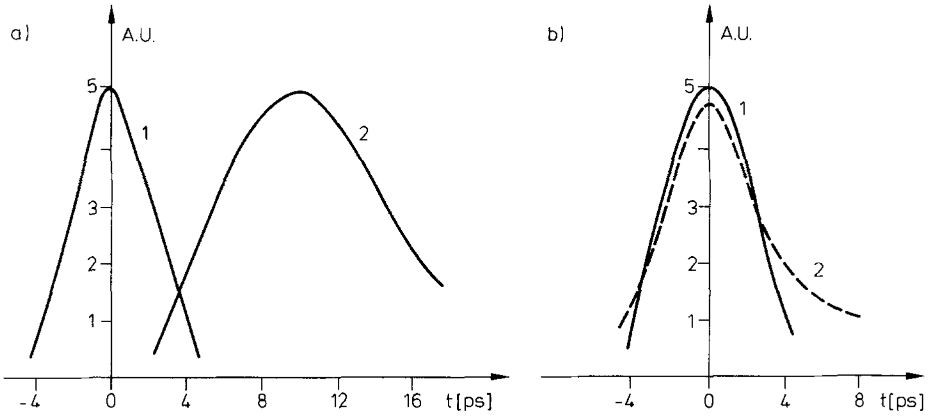

Fig. 1a and b. Kinetics of the superfluorescence maximum of Rhodamine 6G in ethanol at low (a) and high (b) level of pumping (*1* pumping pulse, *2* superfluorescence pulse)

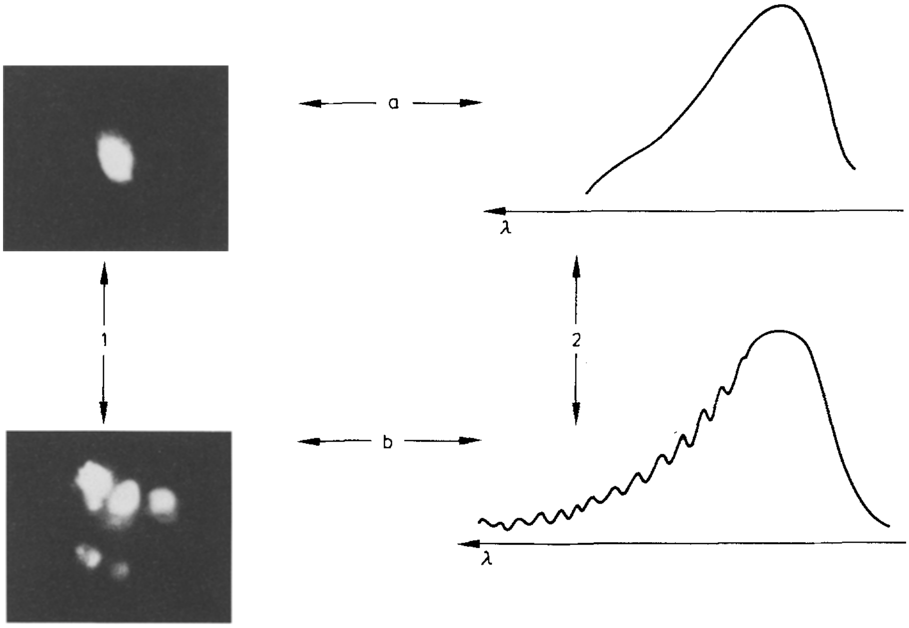

Fig. 2a and b. Far-field pattern *1* and spectra *2* of superfluorescence radiation at low (a) and high (b) level of pumping

2. Results and Discussion

As it was shown [2, 3] (including our own work [4]) two types of SF may develop under picosecond excitation. Sometimes the picosecond pulse develops synchronously with the pumping one while in other cases the maximum of SF is about 10 ps delayed with respect to the pumping one, the reason of this difference being not completely understood.

To explain the existence of the synchronized pulse the formation of a weak continuous background in the solution was assumed, the synchronous pulse being looked upon as an amplified part of this continuum in a spectral region of the gain maximum [5].

We have carried out accurate measurements of SF kinetics of Rhodamine 6G in ethanol under different levels of pumping and found that there are two types of SF really existing. Figure 1 shows the position and the shape of pumping 1) and SF 2) pulses in both cases. In the left part of Fig. 1 the SF behaviour at the pumping levels less than 10^9 W/cm^2 is demonstrated. In this case the SF pulse has typically a duration of 15 ps and is delayed for about 10 ps with respect to the pumping one. When the density of pump power exceeded the value of 10^9 W/cm^2 a drastic change of the SF parameters was observed. As it is seen from the right part of Fig. 1 in this case the SF pulse has practically the same duration as the pumping one and appears synchronously with it. The characteristic feature of the phenomenon is the threshold type of a transition from the first to the second type of lasing.

The change of the temporal behaviour of the SF pulse was followed by the drastic change of spatial and spectral characteristics of SF. Figure 2 shows the far-

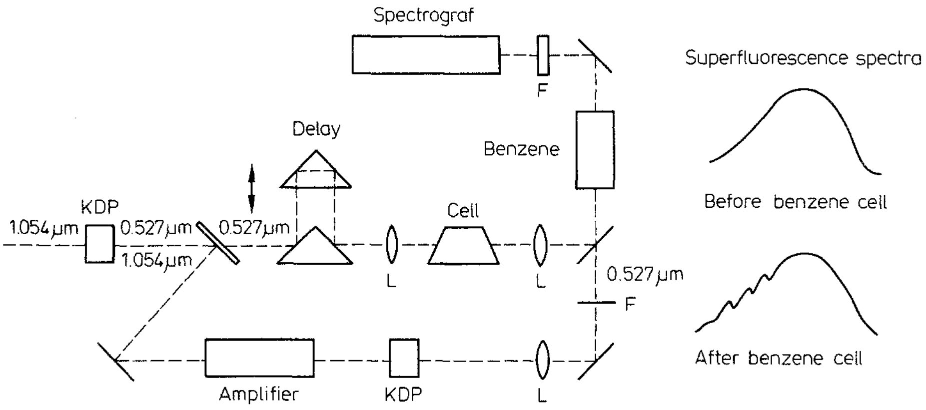

Fig. 3. Experimental set up (see text)

field pattern for both cases. It is seen that the smooth spatial distribution of SF which is typical for a delayed SF pulse changes to the "hot spots" type distribution in the case of the synchronous SF pulse. The characteristic pattern of Fig. 2b gives direct evidence of the waveguide filaments formation in a liquid due to the selffocusing phenomenon. The splitting of SF inside the solution into the number of separate filaments was also easily observed visually from the side of the cell.

The selffocusing of the filaments in the liquid was also followed by a change of the spectral structure of SF. Figure 2 shows the SF spectra of Rhodamine 6G for both cases. The upper spectrum corresponds to the delayed SF pulse while the lower to the synchronous one. One can see that the periodic structure in the spectrum is observed in the case of synchronous SF lasing. The appearance of a periodic structure indicates that SF is developed in a waveguide structure which is induced in the liquid by the intense pumping beam [6]. To prove that the observed periodic structure of SF corresponds to the modes of the selffocusing waveguide we have carried out an additional experiment, shown in Fig. 3.

The SF pulse generated in a regime of the smooth spectrum, passed through the benzene cell to which an additional 0.527 μm pulse was directed by a side optical arm. While the power of the SF pulse was much lower than the value of selffocusing threshold, the power of the 0.527 μm pulse essentially exceeded this value. If SF and 0.527 μm pulses overlapped in space and time inside the benzene cell the initially smooth spectrum of SF acquired the characteristic structure at the exit of the cell. The SF spectra before and after the benzene cell are shown for this case in Fig. 3. The result is expected because at the selffocusing conditions the maximum transition of the cell appears to be only for the own waveguide modes while the rest of the incident light experiences essential losses caused by the scattering in the optically perturbed media.

Thus it follows from the presented data that the selffocusing phenomenon is the mechanism responsible for the time compression of the SF pulse and its synchronization with the pumping one under high enough levels of pumping.

Now, the question arises whether the duration of the SF pulse is directly connected with a lifetime of selffocusing filaments.

As the optical Kerr effect is a main mechanism for selffocusing of picosecond pulses in liquids one can expect that the upper limit for duration of the SF pulse will correspond to the Kerr relaxation time. As the observed SF pulse of dye in ethanol almost coincides with the pumping one in time, it indicates that the rotational relaxation time for ethanol molecules is very small (of the order of 1–2 ps). To observe the influence of the orientational relaxation time of solvent molecules on the duration of the SF pulse we repeated the experiment with Rhodamine 6G, but substituted the ethanol with nitrobenzene as a solvent. The Kerr relaxation time of nitrobenzene is known to be of 35–40 ps [7] so one may expect the substantial increase of the SF pulse duration of the dye in this solvent in comparison with the ethanol solution. The dye concentration was kept the same in ethanol and nitrobenzene solutions, and the pumping level was adjusted to produce similar output in both cases. By this the equality of the gain factors for both solutions was ensured. On the other hand, the level of pumping well exceeded the selffocusing threshold for nitrobenzene. The dye SF pulse shape at the selffocusing conditions is shown in Fig. 4. We see that the duration of the SF pulse in this case is much longer than in an ethanol solution and the time of the pulse decay appears to be close to the orientational relaxation time of the solvent. On the basis of these data one may draw the conclusion that the development of the SF pulse closely follows the dynamics of the build up and the decay of the selffocusing filaments in the liquid.

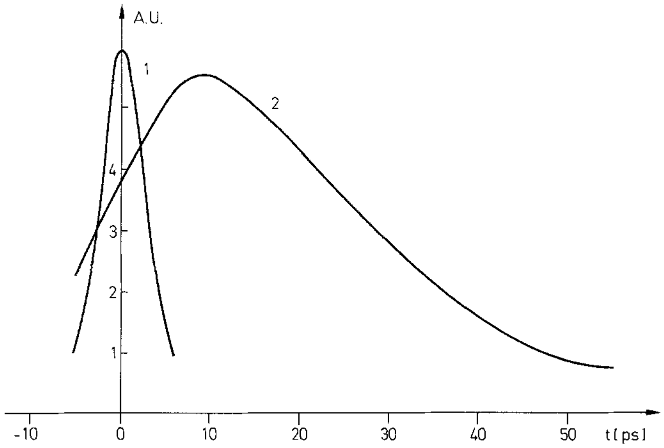

Fig. 4. Kinetics of superfluorescence of Rhodamine 6G in nitrobenzene *2* at high level of pumping (*1* pumping pulse)

There is no clear understanding of the mechanism of molecule rotation in liquid. The picosecond measurements of light induced dichroism in different solvents showed the single exponential relaxation in all cases. On the other hand, for all molecules of nonspherical shape one can expect the existence at least of two different relaxation times for rotational movement. The question was discussed, for example, in a review by Lessing and von Jena [8] and is easily understood. For all shapes of molecule except the spherical one the resistance of media to the rotational movement of molecule depends on the molecular plane of rotation. In other words, a rotational anisotropy must exist for such molecules. Figure 5 shows schematically the way the molecule is expected to rotate in this case. Let us assume that the molecule has a permanent dipole moment and interacts with the external electric field directed along the axis x. The force of electrical interaction rotates the molecule until it will be aligned along x-axis. The quickest way for the molecule to get aligned along this direction is to rotate by a certain angle α first in the plane of the fastest rotation, and then to finish the alignment by the rotation by an angle β in a perpendicular plane. This two step rotational movement of a molecule corresponds to two different rotational relaxation times of the liquid.

In the case of short (picosecond) pulses the molecular rotation induced in liquid by the optical Kerr effect is most probably developed only in its first, fastest stage. It means that in this case the optical Kerr effect may lead only to a partial alignment of molecules, corresponding to the rotation of all of them in the "fastest" molecular plane (of course, in the isotropic liquid there is a random distribution of molecules by the orientations of this plane in space).

To investigate the molecular rotation in a liquid on a full time scale another phenomenon may be used instead of the Kerr effect, namely the orientational relaxation of solvent molecules in a solvate shell surrounding a dye molecule in the solution. It is known [9], that in polar dye solutions the solvate shell of specific structure is formed of solvent molecules around the dye molecule. After excitation the dye molecule changes its dipole moment either by value or by direction or both. This leads to the reorientation of solvent molecules of the shell immediately after the excitation. The process of reorientation may be detected by the temporal shift of fluorescence or the gain spectrum of the dye.

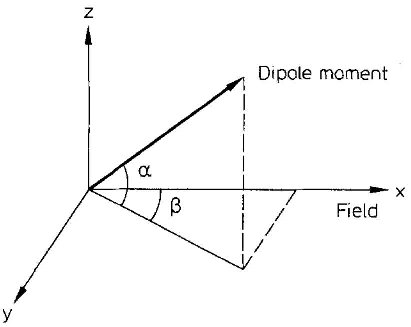

Fig. 5. Diagram of molecule rotation in space

In most cases the temporal shift of the fluorescence (or gain) spectrum to the red occurs though the blue shift also may happen if the dye is excited in the anti-Stokes spectral region [10].

It may be shown that the shift of instantaneous gain (fluoresence) spectrum about its stationary position follows the same law of relaxation as the electric field inside the solvate shell. So the spectral kinetics of dye molecules in a solution gives direct information about the orientational relaxation of solvent molecules in the shell. On the basis of these considerations we have measured the spectral kinetics of the dye nileblue oxazon A in different solvents.

Nileblue oxazone A was chosen for the experiment as it may be conveniently excited with the 2^{nd} harmonic of the Nd laser and has extremely high sensitivity of the fluorescnece spectrum to the local electric field of the shell due to the large difference between dipole moments of the molecule in the ground and excited states.

The conventional method for exciting and probing, using a picosecond probing pulse, was employed for measurements.

Figure 6 shows the temporal change of the gain spectral maximum of the nileblue oxazone A in four different alcohols: ethanole (a), isoamil alcohol (b), propanol (c), and butanol (d). The logarithmic plot of λ^{max} on time demonstrates the existence of a two-exponential decay for three solutions with a shorter

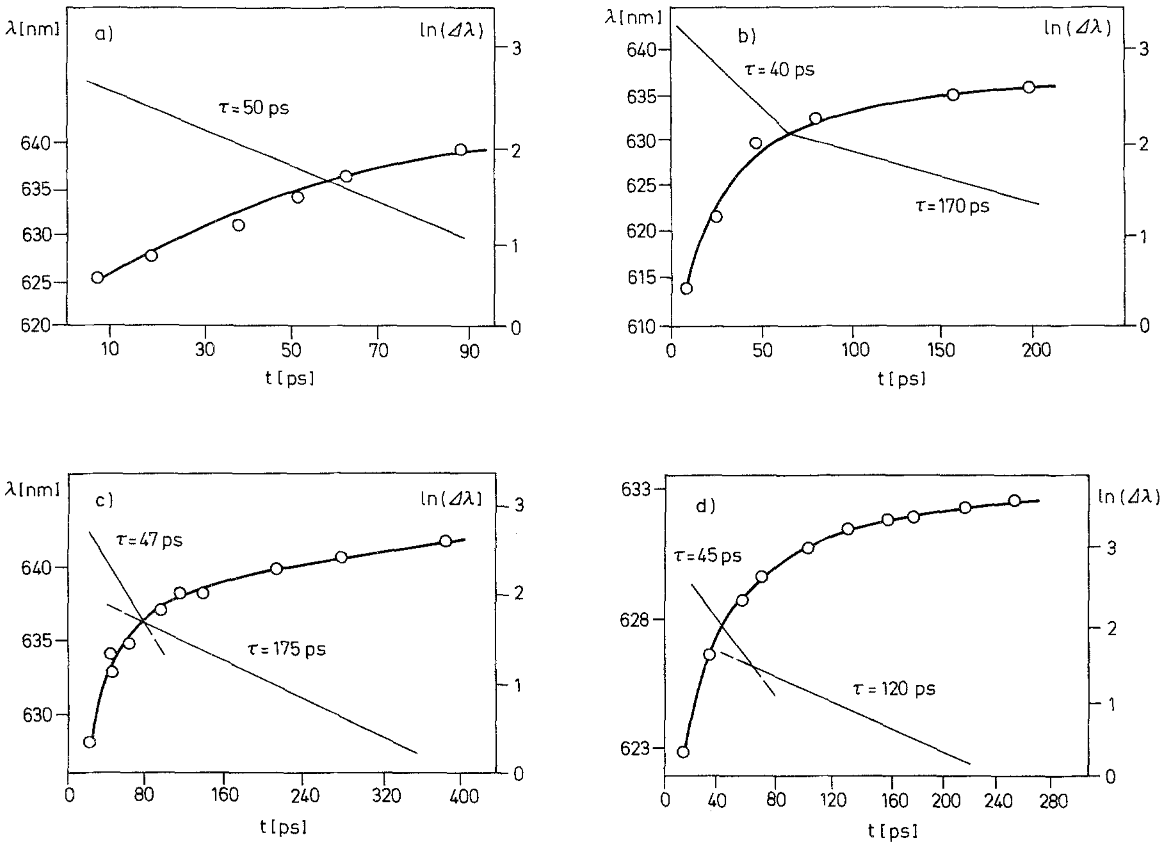

Fig. 6a–d. Kinetics of gain band maximum of nileblue oxazone A in ethanole (a), isoanil alcohol (b), propanol (c), and butanol (d)

relaxation time of 40–47 ps and a longer one of 120–175 ps.

In contrast to that single-exponential decay with a relaxation time of 50 ps was observed for ethanol.

The obtained data are in a qualitative agreement with the considerations discussed above. The two-stage orientational relaxation is clearly seen for the heavy alcohols, which corresponds to the expected sequence of molecule rotations: at first in the "fastest" plane and then the conclusive rotation in the perpendicular plane. The characteristic time of the fastest rotation appears to be close to the expected Kerr relaxation time for such large alcohol molecules and so one may consider that both processes are going on due to the same type of molecular rotation. One may also expect that the selffocusing of picosecond pulses in heavy alcohols is be characterized by a time of about 40 – 45 ps, i.e. by the shortest of two relaxation times. But, of course, for longer light pulses both types of rotation should make a contribution to the selffocusing phenomenon.

Most probably, ethanol has also two different relaxation times but the shorter one is too short to be observed in our experiment. This hypothesis agrees with our earlier conclusion about the fast relaxation of the selffocusing filaments, based on the observation of the synchronous SF pulse.

Conclusions

In conclusion, we have demonstrated the two-exponential relaxation of rotations of heavy alcohol molecules caused by the rotational anisotropy of the molecules. As it was shown, the faster rotational component is responsible for the selffocusing of picosecond pulses in a liquid; if this component is fast enough the latter process may lead to the compression of the dye superfluorescent pulse and its synchronization with pumping one.

Of course, the problem discussed here needs further thorough experimental investigation so that the exact relationship between the process of the Kerr effect relaxation and the orientational relaxation of solvent molecules in a solvate shell could be established. These investigations should lead to the further development of the hydrodynamic model of the molecule rotation in liquid.

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Erratum

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The title of the contribution by
J. D. Spalink, M. L. Applebury, W. Sperling, A. H. Reynolds, and P. M. Rentzepis should read
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