TIME EVOLUTION OF TRANSPARENCY OF DYE LASER SOLUTIONS AFTER INTENSE NITROGEN LASER IRRADIATION

By

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The time behaviour of transparency of dye laser solutions irradiated by intense nitrogen laser pulses shows a complicated complex character in the nanosecond and millisecond time range. This time evolution is in all likelihood the result of several intra- and intermolecular processes. Thermal process is considered as the main contribution to these processes, in which a transfer of excess excitation energy from an excited molecule to solvent molecules takes place.

Introduction

The characteristics of the output beam of lasers depend on several factors, some of which refer to the active medium and other to the cavity and pumping source. Flash-lamp is often used in dye laser systems as an intense light source that excites the dye solution. Such broad-band, intense exciting sources, although provide population inversion, produce many undesirable, time-dependent changes, too, *e.g.* irregular change of the refractive index of the active medium (due to shoch-wave [1] and thermal effects [2]), photobleaching of the solution [3, 4], and triplet population [5, 6]. These effects lead to a decrease of laser pulse duration, an increase of divergence of the beam, a lowering of laser efficiency, *etc.* Investigations of the time dependence of transparency of dye solution after an intense excitation can give many useful information (especially for practical purposes) about the processes that take place in the solution.

In this paper the time behaviour of the transparency of dye solutions after intense excitation by nitrogen laser pulses is reported. In such investigations the nitrogen laser is preferred to flash-lamp of its shorter pulse duration and well defined wavelength (337.1 nm). (There is no considerable absorption by solvent).

Using short probing pulses after the primary exciting pulse enables one to investigate the time behaviour of transparency in small time intervals close to the excitation (50—500 ns), while using a continuous laser makes possible the investigaions over longer time intervals (10—100 ms).

Experimental arrangements and materials

Two experimental set-ups are shown in Fig. 1. In both cases the investigated solutions in the cuvette (C) and the nitrogen laser (NL_1) were the same (600 kW peak-power, 10 ns time duration). The power flux of the exciting beam was about 10 MW/cm².

One of the probing light sources was a tuned dye laser (DL) pumped by a nitrogen laser (NL_2) (Fig. 1a). The dye laser pulses passed through a pinhole and then the excited volume of the investigated solution. In this arrangement the intensity of the probing pulses was measured by a photcdiode (PD) and oscilloscope (OS). The two nitrogen lasers were switched with the same pulse generator (G). The delay time between the timing of the exciting and probing pulses was varied with an electrical delay line (EDL). The delay time was adjustable from -2 µs to 15 µs. For measuring the time dependence of transparency the intensity of the probing pulses was followed as a function of delay time. As additional control of the delay time, fluorescence pulses from dye solution placed in cuvette C' (excited by NL_1) were used.
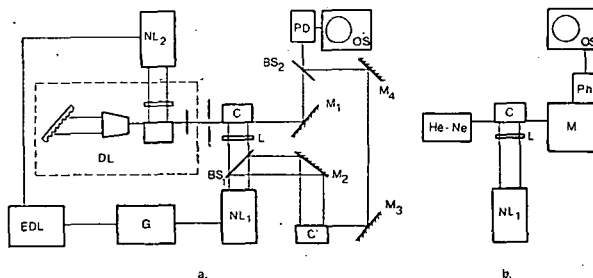

Fig. 1. Experimental set-ups. NL_1, NL_2 — nitrogen lasers, DL — dye laser, Ne-Ne — He-He laser, G — double-pulse generator, C, C' — dye cells, BS_1, BS_2 — beam splitters, M_1, M_2, M_3, M_4 — mirrors, PD — photodiode, Ph — photomultiplier, OS — oscilloscope, EDL — electrical delay line, L — cylindrical lens.

The wavelength of the probing beam were chosen in such a way that the absorption from ground state to excited singlet state could be neglected. The light intensity of this beam was kept in low level to prevent any additional changes in the physico-chemical properties of the solution due to the probing beam.

The investigated solution flowed continuously through the cuvette C' with a velocity of about 0.5 l/min. Repetition rate of the nitrogen lasers was 5 Hz.

As cw probing light source a HE—Ne laser (0.5 mW) was used (Fig. 1b). The intensity of the beam passing through the excited volume of the investigated solution was measured with a photomultiplier (Ph) and oscilloscope (OS).

The investigations were done for Uranine and Rhodamine 6G solutions in the concentration range of 10^{-2} M to 10^{-3} M. In order to distinguish different processes that take place in solutions, and that are dependent on the physico-chemi-

cal properties of the solvent, the following solvents were used: methanol, methanol with cyclooctatetraene (COT) as an effective triplet quencher [7], water, methanol + water (with different amount of the two components), and water with detergent (Triton X—100).

Results

In the course of the direct visual investigation it is perceptible, that the intensity, the direction, the divergence and the shape of probing beam considerably change increasing of the delay time.
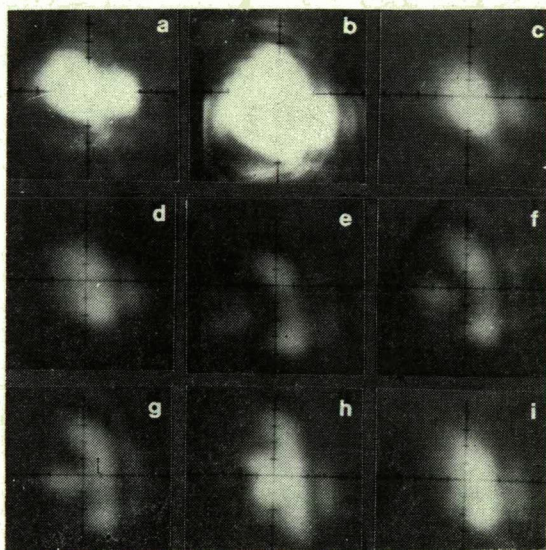

Fig. 2. Cross-section patterns of the probing beam for different delay times from exciting pulse. a — pure methanol, b-i — $5 \cdot 10^{-3}$ M Rhodamine 6G in methanol with several delay time: b — 0 ns, c — 50 ns, d — 90 ns, e — 150 ns, f — 210 ns, g — 300 ns, h — 430 ns, i — 5 µs.

The cross-section of the intensity pattern of probing pulses in a sequence of increasing delay times from 50 ns to 5 µs is shown in Fig. 2b-i. As shown is these patterns, the intensity distribution of the dye laser beam on the screen depends very much on the delay time, and there is no dependence, if the probing beam passes through the solvent only (Fig. 2a). The distortion of the original distribution becomes more pronounced when the concentration of the dye solution increases. The distortion of the beam depends on the solvent used, too. The intensity variation of the probing beam was similar in many parts of the total cross-section pattern (we separeted small area using a pinhole).

The results of intensity measurements versus delay time, using pulsed dye laser as probing light source are illustrated in Fig. 3. These curves have two minima in most

cases (broken lines). The first minimum appears in the range of 50—100 ns and the second minimum — the main minimum — in the range of 140—350 ns of the delay time. The first minimum is well pronounced for Uranine in methanol and the depth of these curves increases with increasing dye concentration $5 \cdot 10^{-3}$ through 10^{-2} M (Fig. 3c, d). The two minima could be measured for Rhodamine 6G in methanol only at high concentrations ($5 \cdot 10^{-3}$ M) (Fig. 3b).
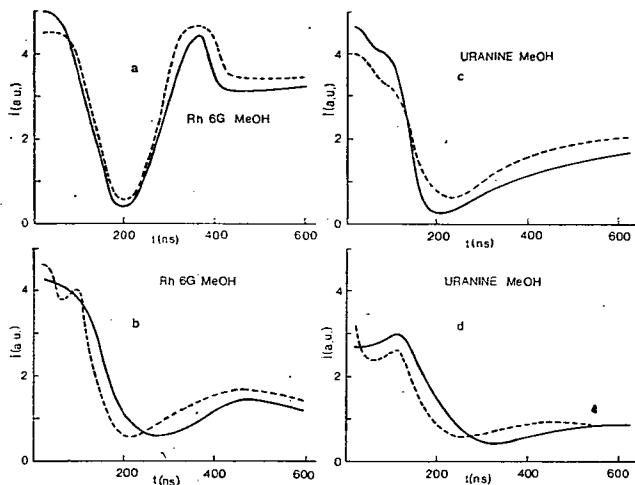

Fig. 3. Time dependence of the transparency of Rhodamine 6G (Rh 6G) in methanol (MeOH) — a — 10^{-3} M, b — $5 \cdot 10^{-3}$ M — and of Uranine in MeOH —c — $5 \cdot 10^{-3}$ M, d — 10^{-3} M. Broken line — without cyclooctatetraene (COT), solid line — with 2% COT.

An admixture of COT (2%, solid lines) to the solutions caused a shift of the second minimum towards the shorter delay times and a decrease of the first minimum. The second minimum was shifted towards longer delay times when the concentration of the solution increased.

Using mixed methanol + water solvent the second minimum decreased and was shifted towards the shorter delay times when the amount of water increased (Fig. 4), especially for Rhodamine 6G solution (circles).

The results of intensity measurements (using continuous laser as probing light source) versus time are shown in Fig. 5. When the solvent was methanol, the same trends were observed for both Uranine and Rhodamine 6G (Fig. 5a, b), *i.e.* the curves showed two maxima. But when the solvent was $H_2O + $ Triton X—100, the curve had only one maximum and the intensity change was less (Fig. 5c). The duration of this effect was 20—30 ms.

In our experimental conditions there were no measurable changes in the probing pulse intensity versus time neither in small (50—500 ns), nor longer (10—100 ms) time intervals after the primary exciting pulse when pure solvent was filled only into the cuvette.
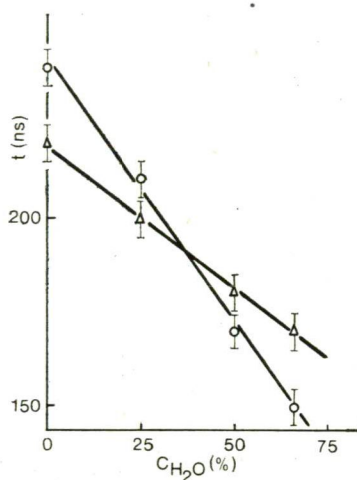
Fig. 4. Dependence of transparency minimum on the water (H_2O) concentration for mixed solutions (methanol + water). — o — o — 5 · 10^{-3} M Rhodamine 6G, — △ — △ — 5 · 10^{-3} M Uranine.
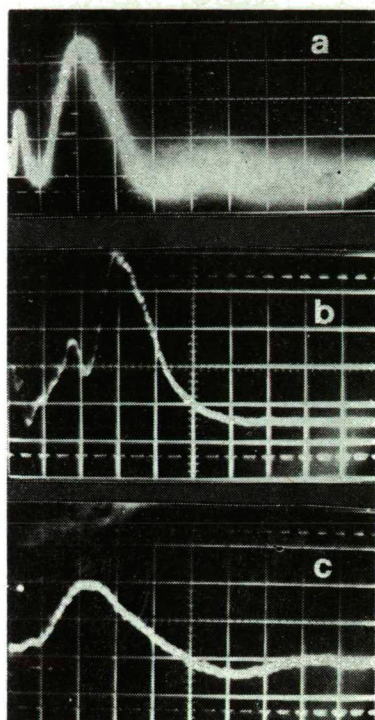

Fig. 5. Intensity of the He-Ne laser as probing light source versus time. a — 5 · 10^{-3} M Rhodamine 6G in methanol, b — 5 · 10^{-3} M Uranine in methanol, c — 5 · 10^{-3} M Rhodamine 6G in water with Triton X-100. The oscilloscope time scale is 5 ms/div.

Discussion

Taking into account that no change in transparency could be measured for pure solvents one has to conclude that the observed effect has its origin in the dye molecules that absorb the energy of the light pulses (of a nitrogen laser). The value of the transparency change depended, however, on the solvent and was much smaller in water solutions than in methanol.

The complicated behaviour of the time dependence after the primary excitation indicated that several processes, with different time constant, could take place, e.g. the minima, shown in Fig. 3. seemed to indicate among others *triplet-triplet absorption* in dye molecules [5, 6]. This is supported by the fact that the first minimum is much more pronounced in Uranine solution, where the triplet-triplet absorption is higher than in Rhodamine 6G solution. A further support is provided by the observation that COT admixture to the solution caused a shift of the second minimum towards the longer delay times, because of decreasing of the triplet population.

In microsecond delay time intervals the solution transparency increased slowly and did not reach its original value even in 15 μs. This slow change can be attributed to the *photochemical instability* of the solution that was caused by intense nitrogen laser irradiation.

The observations with He-Ne laser (Fig. 5) suggest that the main contribution to the transparency change is due to *thermal processes* connected with the transfer of excess excitation energy from dye molecules to solvent. (This excess energy is proportional to the difference between the energy of absorbed and emitted photons. This energy leads to a time-dependent local temperature difference between luminescence centre and mean temperature of solution.) The heat capacity of water is much higher than that of methanol and, therefore, any temperature inhomogeneity due to energy transfer is small in water as compared to that in methanol. In conclusion one can suppose that the long-duration change is caused by dispersion of the probing beam on refraction inhomogeneity arising as a result of thermal effects [2].

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References

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РАЗВИТИЕ ПО ВРЕМЕНИ ПРОЗРАЧНОСТИ РАСТВОРОВ В ЛАЗЕРАХ НА КРАСИТЕЛЕ ПОСЛЕ ИНТЕНСИВНОГО ВОЗБУЖДЕНИЯ АЗОТНЫМ ЛАЗЕРОМ

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Поведение по времени прозрачности растворов в лазерах на красителе возбуждённых интенсивным импульсом азотного лазера показывает сложный комплексный характер в наносекундном и миллисекундном диапозонах. Это развитие по времени вероятно является результатом разных внутри- и межмолекулярных процессов. Главным составляющим этих процессов можно предполагать термический процесс в течение которого происходит передача избытка возбуждающей энергии от возбуждённых молекул к молекулам растворов.