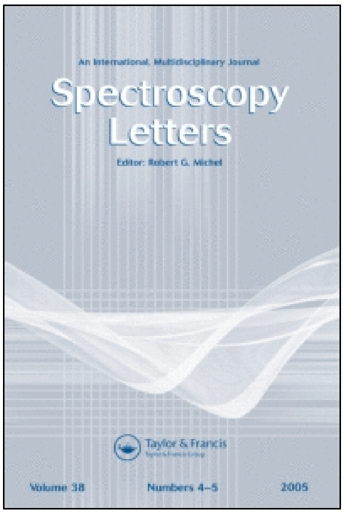

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M. V. Melishchuk[a]; E. A. Tikhonov[a]; M. T. Shpak[a]
[a] Academy of Sciences of the Ukrainian SSR, Institute of Physics, Kiev, USSR

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GENERATION OF STIMULATED EMISSION BY GREAT MOLECULES AT LOW TEMPERATURES

M.V.Melishchuk, E.A.Tikhonov, M.T.Shpak
Institute of Physics, Academy of Sciences of the
Ukrainian SSR, Kiev, USSR

Abstract: The paper outlines the principal features of the low temperature dye oscillation, primarily the polymethene dye laser. The key physical result is related to the nonhomogeneous broadening of the dye laser transitions at low temperatures. For the first time the nonambiguous experiments run to confirm reasonably the dependence of the fluorescence spectra of the polymethene dye solutions on the solvent, mean excitation frequency and linewidth.

The main feature of dye stimulated emission spectra at low temperatures is the occurence of many narrow lines specifying all the dyes. The origination of this quasiline structure is explained by the idea about the nonhomogeneous broadened transitions of dye solutions at low temperatures.

INTRODUCTION

The temperature region over which laser oscillation occurs on complex organic molecules ranges from 4.2 to 600^{0}K [I,2,3,4]. High temperatures at which the active media of dyes are in the gaseous state offer the challenge particularly for the lasers where the electric discharge was used instead of the optical pumping.

Low temperatures are sometimes the necessary condition for the oscillation threshold to be achieved (e.g. in semiconductor lasers). In dye lasers the temperature effect is multiform. The dye lasers at very low temperatures (below 77°K) seem not very promising in practice because high-quality and stable to optical damage matrices are difficult to obtain under these conditions. In this case the induced losses are very large what is especially undesirable for the cw oscillation. On the other hand, it may be of practical interest to use moderately low temperatures at which the dye solution becomes sufficienty viscous and yet optically homogeneous (respectively the quantum yield essentially increases, the photochemical bleaching is slowed down [5]). Operation under above conditions results in a higher efficiency of dye lasers, especially on polymethene dyes oscillating in the region 7000-I200 Å [6] . The successful use of dye lasers at low temperatures involves the detailed study of molecule spectroscopic characteristics. Below some original results on the spontaneous and stimulated emission from the polymethene dye solutions are presented within the temperature range 300-4.2°K.

SPECTRAL CHARACTERISTICS OF POLYMETHENE DYES AT LOW TEMPERATURES

The complex molecule model used in the oscillation theory is based on the idea of the homogeneously broadened transitions in the dye molecule and gives a valuable relation

$$\sigma_a(\nu) = \sigma_e(\nu)\, exp\, \frac{\nu-\nu_0}{\kappa T} \tag{I}$$

where $\sigma_a(\nu)$, $\sigma_e(\nu)$ are the absorption and emission cross-sections, ν_0 is the pure electron transition frequency in cm^{-I}, κT is the thermal motion energy [7,8] . This relation holds true also for the inhomogeneously broadened transitions provided the energy distribution of centres is of an equilibrium type [9]. Inhomogeneous broadening in the spectra of complex molecules with the constant dipole moment (merocyanine, phtalimide) originates from the spread of the dipole moment orientations with respect to the direction of the local field resulted from the solvent molecules. For polymethene dyes, the orientational interaction energy is negligible as compared to that of Van der Waals interaction [IO] , and it is the disordered liquid structure that is responsible for the spectral inhomogeneity. At room temperatures, even in such viscous solvents as glycerol, ethylene glycol, the equilibrium molecule distribution can be set in during the lifetime of the excited electron state. This results in a good agreement between the oscillation characteristics and the theory based on the relation (I). As the temperature is lowered the relaxation processes in the liquid get essentially slowed down, the absorption and fluorescence spectra become statically inhomogeneous. The long-wavelength band halfwidth of the absorption spectra is largely caused by statistical properties of the glassy solvent rather than by the intramolecular processes, and for one of polymethene dyes (e.g. cryptocyanine) it can range from 250 cm^{-I} in propanol to 600 cm^{-I} in glycerol [II] .Under these conditions it is impossible to extrapolate the ideas of the homogeneously broadened transitions for the description of the oscillation processes at low temperatures.

The fluorescence spectra studies at 4.2°K showed that the shape and halfwidth of the long-wavelength bands are essentially dependent on the spectral width and wavelength of the exciting radiation. FIG. I shows the long-wavelength absorption spectrum (dotted curve) and relevant fluorescence bands (curve I-I2) of the 3-3'-diethyl-9,II,I3 (penta-I",3",5"-triethyl)-thiathiazolinotricarbocyanine iodide, excited at the different parts of the absorption spectrum by the quasimonochromatic light with the line width 5 nm.

It is seen from FIG.I that under excitation at the short wavelength edge the fluorescence spectrum is wide and has the structure. The increase of the excitation wavelength results in an intensity redistribution in favour of one maximum, the band gets narrower and shifts towards longer waves. The narrowest band with the halfwidth $\simeq$I80 cm^{-I} was observed under excitation at the long-wavelength edge of the absorption band. With the temperature rise, the spectral dependence on the exciting wavelength becomes weaker and at room temperature it vanishes. Similar dependences were observed for all the polymethene dyes presented in the table.

The results obtained are well agreed with the assumption of the inhomogeneously broadened transitions for the polymethene dye solutions at low temperatures. Indeed, the fluorescence spectrum is wide and has the structure which is believed to be associated with the overlapping of the spectra from individual

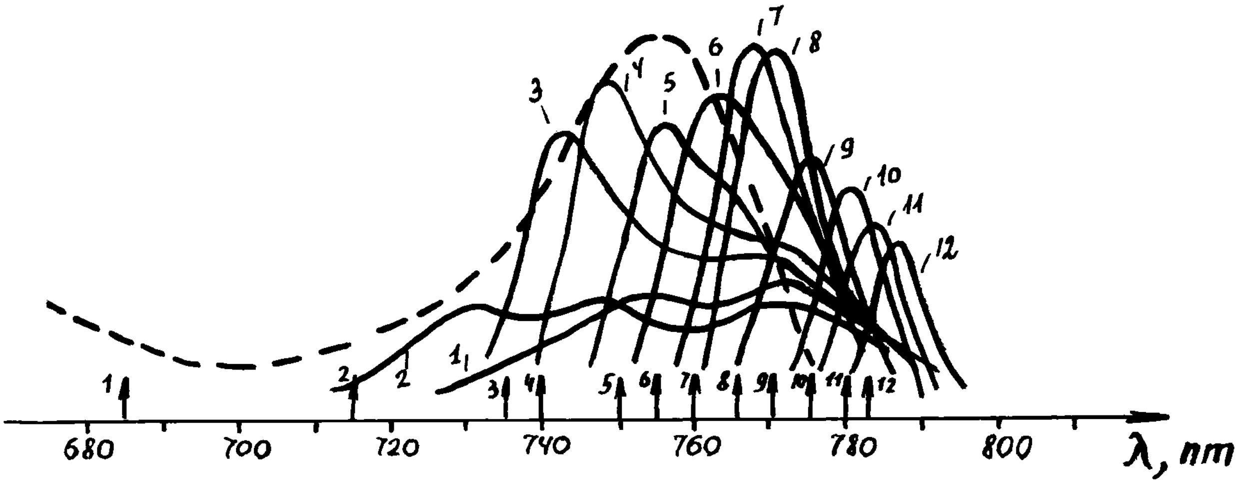

FIG. I

The absorption and fluorescence spectra of the polymethene dye-I (see table) at T=4.2^{o}K. The exciting light wavelengths are shown by arrows.

TABLE

Dyes	Name	Absorpt. peak(nm) (ethanol solution)
I	3-3'-diethyl-9,II,I3 (penta-I",3",5"-triethyl) -thiathiazolinotricarbocyanin iodide	705
II	3-3'-diethyl-9,II,I3 (penta-I",3",5"-triethyl) -thiatricarbocyanin iodide	750
III	I-I'-dimethylindotricarbocyanin iodide	750
IV	triscyanine perchlorate	706
V	I-I'-dimethylaminobenzyltrimethyncyanine perchlorate	695
VI	cryptocyanine iodide	7I5

centers since the shortwavelength edge of the absorption band is due to the contribution from all kinds of centers. Towards longer waves the number of centers involved in absorption decreases resulting in a narrowing of the fluorescence band under study. Due to the excitation of the long-wavelength absorption band edge by the quasimonochromatic radiation one can distinguish one kind of centers and estimate approximately the homogeneous width of the fluorescence spectrum of the long-wavelength band. At 4.2^{o}K the fluorescence band halfwidth from a single center in the pure electron transition region is found to be ≃ I80 cm^{-I} which is 3 to 4 times less than the absorption spectrum halfwidth. At room temperature the homogeneous and inhomogeneous widths are comparable and equal to 500-600 cm^{-I}. From the temperature dependence of the single center spectrum halfwidth it was found that in the low temperature region ($T < T_g$, where T_g is the temperature at which the solvent viscosity reaches IO^{II} poises) the fluorescence spectrum from the sample excited by the monochromatic light at the absorption band long-wavelength edge is described fairly well by the vibronic spectra theory for the impurity centers in the matrice [I2] . At temperatures higher than T_g, the band broadening gets more rapidly than it is predicted by the theory. This result agrees with the above statement that in the liquid phase of solutions the excited molecules can undergo a partial or complete redistribution during the excited state lifetime according to the local field spread in the matrice. That is why many kinds of centers contribute to the fluorescence. Therefore, the inhomogeneous spectrum broadening at room temperature can be detected only by the picosecond laser spectroscopy methods while the study of the "hole burning" for the polymethene dyes in the nanosecond range yielded no expected results. [I3] . Previously received results on some polymethene dye solutions (300^oK, nanosecond time interval) can be interpreted as the Rayleigh scattering effects. [I4, I5]

PECULIARITIES OF STIMULATED EMISSION OF DYES AT LOW TEMPERATURES

The polymethene dyes (Table) in such alcohol solvents as glycerol, diethylene glycol, propanol, ethanol, were investigated. The active media length utilized was I.5-2 cm. For each solvent the cooling conditions were empirically chosen so that the optically transparent matrices could be formed at all temperatures studied. Longitudinal pumping was performed by the single-mode ruby laser. The dye laser operated in the superluminiscence regime.

According to the temperature change of the oscillation spectra we have two particular temperature ranges: I) from $T=300^{\circ}K$ to $T=T_g$; 2) from $T=T_g$ to $T=4.2^{\circ}K$.

I) Temperature Range from $T=300^{\circ}K$ to $T=T_g$. Within this range the spectra show the shift of the mean generation frequency with no change in the spectrum width and also the lowering of the oscillation threshold, as the solution gets cooler. In different solvents these peculiarities are displayed in different ways.

a) Glycerol. As the temperature is lowered from $300^{\circ}K$ to $190^{\circ}K$ the mean oscillation wavelength shifts towards shorter waves almost without the oscillation threshold change. The shift magnitude is different for a variety of dyes and weakly depends on the optical density of solution. For instance, for the dye I (see Table) the shift is found to be $\simeq 40$ Å, for the dye III - 90 Å. With the further solution cooling the spectrum shows no shift. The oscillation spectrum of the dye I at different temperatures $T > T_g$ is shown in FIG. 2.

b) Dyethelene glycol. At temperatures ranging from $300^{\circ}K$ to $270^{\circ}K$ the dye I shows a shift of the mean oscillation wavelength towards longer waves with a simultaneous lowering of the threshold (approximately three times); in the range $270^{\circ}K$ to $180^{\circ}K$ the spectrum shifts towards short waves involving no change of the threshold and with further cooling shows no shift.

c)Ethanol. Over the whole temperature range we have the shift towards longer waves with a simultaneous lowering of the thres-

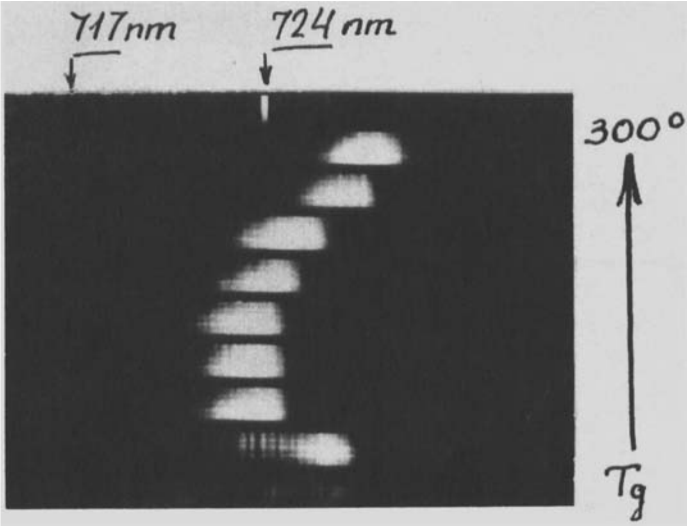

FIG. 2

hold pumping power by an order of magnitude. The shift is more rapid in the high temperature region and is saturated near $T=T_g$. The temperature dependence of the mean oscillation wavelength for the dye I in different solvents are plotted in FIG. 3. The qualitative explanation of these shifts is as follows: the oscillation spectrum shift towards short wavelengths correlates with that in the fluorescence spectrum within the same temperature range. The long-wavelength shift is due to non-stationary processes in generation atudied at room temperature in Ref. [I6] . For ethanol as a solvent, more favourable conditions are created since at lower temperature the solution quantum yield becomes significantly larger. This results in an essential lowering of the oscillation threshold and, since all the spectra have been obtained at the same pumping power,

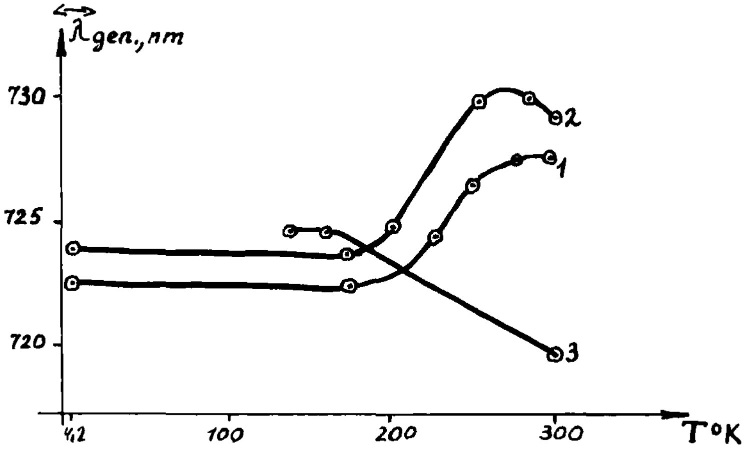

FIG. 3

each spectrum corresponds to the appropriate excess of pumping over the threshold (e.g. at 300°K $J_p=J_{thr}$, at 180°K $J_p=10\,J_{thr}$). This interpretation agrees with the curve dependence in FIG. 3 vs the solvent viscosity at room temperature. In viscous solvents the increase of quantum yield is not large therefore the temperature shift of the fluorescence spectrum contributes mainly to the oscillation spectrum behaviour. For nonviscous solvents, in the temperature range with the largest increase of the quantum yield the shift due to the nonstationary inversion of population in the dye molecules dominates over the temperature shift of the fluorescence spectrum.

2) Temperature Range from $T=T_g$ to $T=4.2$°K.

When approaching $T=T_g$ the oscillation band is markedly broadened, the oscillation threshold remains unchanged or increases. As a rule, the largest increase of the threshold occurs in more viscous solvents. The oscillation spectrum broadens quickly. In the narrow temperature region not higher than 20-30°K, the spectrum width is 3 to 4 times as large and a large broadening towards longer waves is seen. With the further lowering of temperature the oscillation band width is scarcely changed but the short-wavelength part of the spectrum diffuses near T_g and becomes narrow-line at 4.2°K (Fig. 4).

The frequency spacings from the excitation line remain constant in the same dye in different solvents and can serve as a dye characteristic. Simultaneously with the narrow-line structure, in the diffuse part of the spectrum sharp absorption bands are observed. The whole spectrum is somehow dependent on the solution optical density and the pumping power. For the optimal threshold of the optical density oscillation (d=4-5 for the pumping frequency) and the pumping power above the threshold, a diffuse background appears in the structural part of the spectrum. For the density above the optimal no structure can be observed. For the densities below optimal only the structural spectrum is

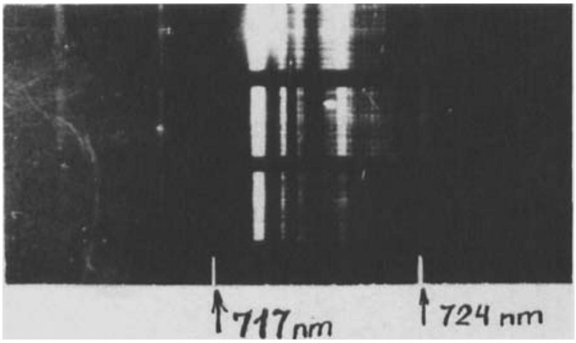

FIG. 4

Oscillation spectrum for the dye I solution (glycerol).

exhibited. When the solution density is optimal the number of lines increases near the diffuse part of the spectrum and in this region the spectrum is not reproduced for every pumping pulse. The shift of the excitation frequency by 4 cm^{-I} leads to a correspondent shift of lines.

General regul arities of the change in the oscillation spectra within the temperature range $T < T_g$ can be qualitatively explained from the comparison with the low temperature fluorescence spectra of the relevant dye solutions. As it was mentioned above, at $T < T_g$ the systems under study show inhomogeneous broadening and dependences of the curve shape and peak position on the exciting light wavelength. With the further temperature decrease, in the fluorescence spectra the crude structure is formed, whereas the oscillation spectra have the fine structure. The fluorescence spectrum from the dye IV in glycerol excited by the light with $\langle \lambda \rangle = 694$ nm and width 50 nm at 4.2^oK is pictured in FIG. 5. The stimulated emission spectrum obtained under the excitation by ruby laser is schematically shown.

The group of narrow bands of the dye oscillation spectrum is shown to lie in the region of fluorescence spectrum. To prove that the quasilines observed lie within the fluorescence spectrum this latter should be defined under conditions similar to those of excitation. They are difficult to be realized simultaneously. When the frequency condition was violated we succeeded to observe the fluorescence spectrum of the dye IV with the zero-phonon peaked traces on the general diffuse background. (FIG. 6).

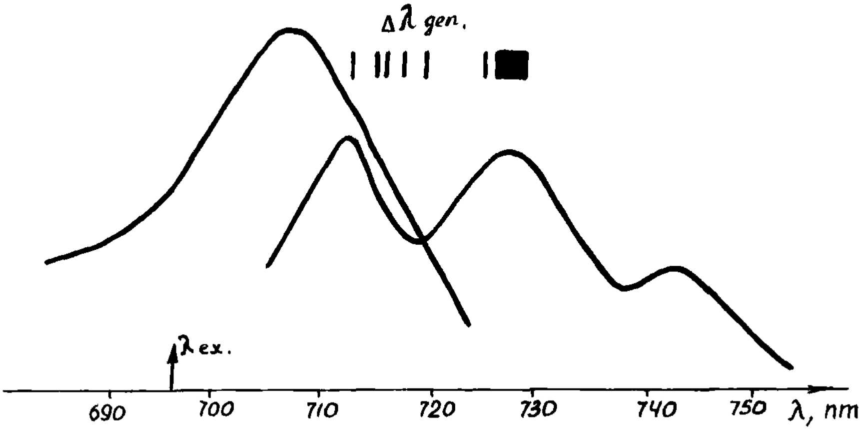

FIG. 5

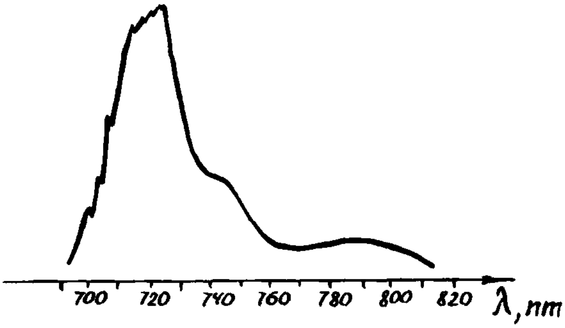

FIG. 6

It should be noted that this spectrum resulted from many centers since it has been obtained under excitation by He-Ne laser at the short wavelength slope of the absorption spectrum. When operating in the superluminiscence mode (or oscillation mode) the maximum enhancement of the dye solution in the region of these traces occurs resulting in the structural oscillation spectra.

Thus, inhomogeneous broadening of the absorption and fluorescence bands of the polymethene dye solutions exhibited in the low temperature region under the monochromatic excitation(probably also at 300^{0}K under picosecond pulse excitation) suggests the following interpretation for the narrow line structure:

I)Under excitation on the short wavelength absorption spectrum edge, the absorption is contributed from the groups of centers with the electronic and vibronic transitions at resonance with the exciting light frequency. Therefore, the structure in the stimulated emission spectra may be associated with discrete vibronic transitions in different kinds of centers. The spacings in the frequency scale between the excitation and oscillation lines correspond to the vibrational wave numbers of the ground state (in the case of excitation in the pure electronic transition region) or to their combination with the vibrational wave numbers of the excited electronic state (in the case of excitation in the vibronic transition region).

2) The shift of lines in the oscillation spectrum with the change of the excitation wavelength results from the inhomogeneous broadening of the absorption and fluorescence bands. Since the shift of the excitation frequency only by 4 cm^{-I} brings about the oscillation line shift it can be assumed that the homogeneously broadened fluorescence spectra have the fine structure due to the zero-phonon lines.

3) This nonreproduceability of some discrete lines in the oscillation spectra can be explained in terms of a competition between the oscillating modes existent in the lasers with in-

homogeneously broadened transitions of the active media.
The papers [I7, I8, I9, 20] studied also the stimulated emission spectra from the dye solutions at low temperatures where the fine structure is interpreted in terms of stimulated Raman scattering of the pumping light on the electronically excited dye molecules. However the principal criterion of the Raman scattering based on the relation between the excitation and scattering frequencies becomes ambiguous because of the inhomogeneous broadening. Other arguments favouring the essentially larger gain coefficient of the oscillation due to the stimulated fluorescence as compared to that of the resonance Raman scattering are given in Ref. [2I, 22] .

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