

Spectral-luminescent properties of laser dyes in silica gel-matrix

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Spectral-luminescent properties of laser dyes (coumarine 102 and dimethylaminosubstituted 4-pyridylphenyloxazole) in solid tetraethoxysilane matrix are studied. Peculiarities in interaction of organic molecules with silanol groups of gel-matrix in the ground and excited states are considered by comparing spectral characteristics of solid and liquid samples.

Introduction

Successful application of tunable organic lasers is now retarded by some inconvenience in their use due to cumbersome gas transport systems, fluctuations of fluid flows, evaporation and fire hazard of solvents, etc. The feasibility of using solid active media (SAM) based on organic compounds makes tunable lasers more compact and safe and allow their accelerated implementation in practice.

Till recently this problem was not solved both because of impossibility to make laser-purity polymers and the lack of a mechanism of dye interaction with polymers, what led to the lower, as compared with solutions, lasing efficiency and, especially, the shorter service life due to irreversible phototransformation of laser dyes in polymers.¹

Nowadays the considerable progress is achieved in obtaining SAM based on polymethylmethacrylate (PMMA) with embedded organic compounds. Pumping of such matrices with rhodamine and phenalemine dyes into their longwave absorption band (the second harmonic of an Nd:YAG laser and copper vapor laser) yields the efficiency and service life close to those for solutions.²⁻⁴ Nevertheless, at excitation of polymer SAM by a XeCl laser, which is a universal source for most organic compounds fluorescing in the near UV and visible blue-green regions, some problems arise which prevent their application. In particular, PMMA characteristic absorption starts from 350 nm, that is, a part of the pump radiation is lost for matrix heating, what inevitably decreases the lasing efficiency and matrix stability. Another significant problem is the presence of residual amounts of radical-type photoinitiators of PMMA polymerization, what can worsen the lasing properties of polymer SAM at UV pumping.

Unlike this, the sol-gel method of obtaining solid matrices is not connected with radical photoinitiators, and their characteristic absorption starts, as a rule, from the wavelength less than 250 nm. Therefore, such matrices are promising for their use as SAM basis.

Therefore, in this work we studied the spectral-luminescent properties of two laser dyes embedded in tetraethoxysilane (TEOS) gel-matrix: coumarine 102 (C 102) and dimethylaminosubstituted 4-pyridylphenyloxazole (4PyPON(CH₃)₂), that emit in ethanol solutions at excitation by XeCl laser radiation.^{5,6}

Objects and methods of study

A silica inorganic gel-matrix with laser dyes was obtained by the sol-gel method described in detail in Ref. 7. The reaction mixture was tetraethoxysilane [Si(OC₂H₅)₄] in the water-ethanol mixture in the molar ratio 1:4:4 with addition of a minor amount of inorganic acid (HCl) that accelerated hydrolysis. Dye molecules were introduced into that mixture having passed the hydrolysis stage in the form of ethanol solution. At the last stage of polymerization, solid gel-matrices were formed and then dried in darkness in air at the room temperature. The dye molecules were contained in micropores of the polymer frame ≡Si-O-Si≡ covered by ≡Si-O-H groups.

Coumarine 102 was used as a laser dye; the ethanol solution of C 102 generates radiation in the region of 477 nm with the efficiency up to 33% when pumped by XeCl laser.⁵ Another dye was 4PyPON(CH₃)₂, for which the anomalous Stokes shift is observed in polar solvents, as well as the decrease of the quantum yield of fluorescence due to formation of the plane TICT conformation in the excited state. Lasing of 4PyPON(CH₃)₂ was obtained in hexane and ethanol in both cases within the fluorescence bands: 418 and 590 nm, respectively.⁶

The absorption spectra of solid samples were recorded with a Specord M40 spectrophotometer, and the fluorescence spectra were recorded with a Hitachi 850 spectrofluorimeter at different drying stages: after 10, 30, 90, and 200 days.

Results

Figures 1 and 2 depict the absorption and fluorescence spectra of C 102 in the sol-gel matrix and in solutions of various acidity. It can be seen from Fig. 1 that just after preparation (10 days of drying) the absorption and fluorescence spectra of C 102 in the gel-matrix differ from the spectra of aqueous and ethanol solutions (curves 1 and 5). In place of the longwave absorption band with a peak nearby 26000 cm^{-1} (385 nm) in ethanol, which corresponds to intense fluorescence with a peak at 475 nm (Fig. 2, curve 6), the longwave absorption in the gel-matrix peaks nearby 23000 cm^{-1} (435 nm) and 20000 cm^{-1} (500 nm). As the drying becomes longer, the intensity in these bands redistributes into the longwave region (cp. curves 1–4 in Fig. 1). Besides, in the region of $25000\text{--}26000\text{ cm}^{-1}$ a peak arises, which was absent for the fresh matrices (curves 3 and 4 in Fig. 1). In the shortwave region, as the drying becomes longer, the absorption in the region of $30000\text{--}32000\text{ cm}^{-1}$ increases. In the last sample dried for 200 days, one more absorption band is formed nearby 18500 cm^{-1} (540 nm). At excitation into this band, fluorescence is observed nearby 600 nm (see Fig. 2).

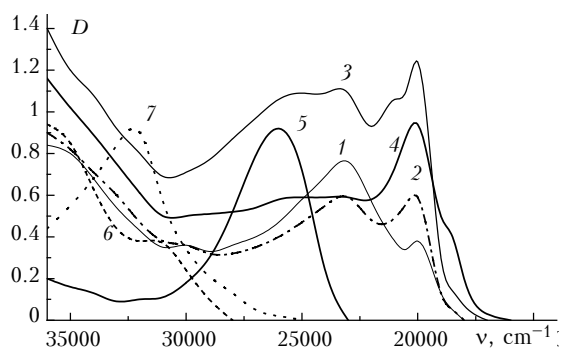


Fig. 1. Absorption spectra of C 102 in gel-matrix (1–4), in ethanol (neutral form) (5), in ethanol +40% H_2SO_4 (amino group cation) (6), in ethanol +90% H_2SO_4 (dication) (7), drying in darkness for 10 (1), 30 (2), 90 (3), and 200 days (4). $l = 0.15\text{ cm}$ (1, 2, 4) and $l = 0.4\text{ cm}$ (3).

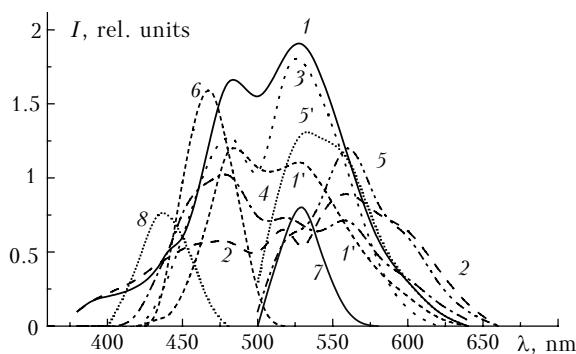


Fig. 2. Fluorescence spectra of C 102 in gel-matrix (1–5), ethanol (neutral form) (6), ethanol +5% H_2SO_4 (carbonyl group cation) (7), ethanol +90% H_2SO_4 (dication) (8), $\lambda_{\text{exc}} = 308\text{ nm}$ (1, 2, 6–8), 400 nm (1', 3, 4), 500 nm (5', 5). Drying for 10 (1', 1, 5'), 90 (3), and 200 days (2, 4, 5).

Fluorescence spectra of fresh gel-samples of C 102 at shortwave excitation ($\lambda_{\text{exc}} = 308\text{ nm}$, 32470 cm^{-1}) have three clearly seen bands: $\lambda_{\text{max}} = 390, 480,$ and 530 nm . The longwave band (curve 1 in Fig. 2) is the most intense among them. At excitation of this sample into the fundamental absorption band ($\lambda_{\text{exc}} = 400\text{ nm}$, 25000 cm^{-1}), fluorescence nearby 480 nm (curve 1') is the most intense, and at excitation into the longwave peak ($\lambda_{\text{exc}} = 500\text{ nm}$) a band near 560 nm is seen along with the band at 530 nm (curve 5'). As the time of drying increases, this band becomes dominant at both longwave and shortwave excitation (curves 2 and 5 in Fig. 2).

Our earlier studies have shown that the C 102 molecule in proton-donor solvents (ethanol with addition of mineral acids) can exist in the neutral and ionic forms.^{5,8} These forms are formed due to proton acceptance from the solvation sphere by proton-acceptor centers: nitrogen atoms of the amino group, oxygen atom of the carbonyl group, or by the both groups depending on the electronic state of the molecule and the state of the solvation sphere (curves 5–7 in Fig. 1 and curves 6–8 in Fig. 2).

These results show that some of the emission and absorption bands of C 102 in the silica gel-matrix coincide with the spectral characteristics of ionic forms, while others experience longwave shift, and new bands, absent in the absorption spectrum of solutions, arise.

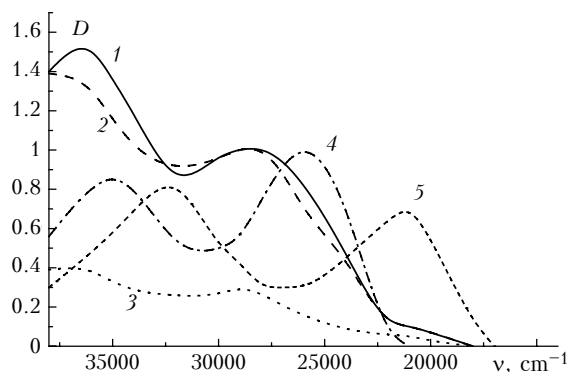


Fig. 3. Absorption spectra of $4\text{PyPON}(\text{CH}_3)_2$ in gel-matrix after 10 (1) and 90 days of drying (2), in water (3), in ethanol (4), in ethanol +5% H_2SO_4 (cation) (5), $l = 0.15\text{ cm}$ (1, 2) and 1 cm (3–5).

The absorption spectrum of $4\text{PyPON}(\text{CH}_3)_2$ in the TEOS matrix includes a wide band near 29000 cm^{-1} with an arm at 26000 cm^{-1} (curve 1 in Fig. 3) and a band with a peak nearby 36000 cm^{-1} , what qualitatively resembles the absorption spectrum of $4\text{PyPON}(\text{CH}_3)_2$ in neutral water (cp. curves 1 and 3 in Fig. 3). As the drying time increases, the absorption spectrum changes significantly less than in the case of C 102 (Figs. 1 and 3). The fluorescence spectrum of $4\text{PyPON}(\text{CH}_3)_2$ in the gel-matrix, as well as that of C 102, depends markedly on the drying time and λ_{exc} : just after preparation (10 days of drying) its fluorescence spectrum is close to the spectrum of $4\text{PyPON}(\text{CH}_3)_2$ in neutral water (curves 1 and 8 in Fig. 4). At excitation of the same

sample in the region of the longwave wing of the absorption band (curve 1 in Fig. 3) the peak of fluorescence shifts to 590 and 480 nm (curve 3 in Fig. 4). As the drying time increases up to 90 days, the fluorescence peak shifts to 410 nm, what coincides with fluorescence of the amino group cation (Fig. 4, curves 4 and 6). After 200 days of drying, fluorescence with $\lambda_{\max} = 480$ nm (coinciding with cation fluorescence) prevails, but emission near 590 nm, corresponding to the emission of nitrogen atom cation of pyridine cycle (curves 2, 6, 7 in Fig. 4), is still observed.

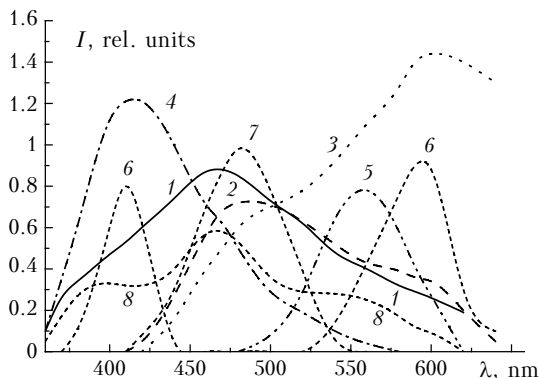


Fig. 4. Fluorescence spectra of 4PyPON(CH₃)₂ in gel-matrix after 10 (1, 3), 90 (4), and 200 days of drying (2), in ethanol (5), in ethanol +5% H₂SO₄ – frozen solid solution (cation) (6), in ethanol +80% H₂SO₄ (dication) (7), in water (8), $\lambda_{\text{exc}} = 330$ nm (1, 2, 4–8) and 400 nm (3).

Thus, for this molecule in the sol-gel-matrix, as well as for C 102, the neutral and ionic forms manifest themselves in the absorption and emission spectra.

Discussion

Analysis of these results show that molecules of laser dyes in silica gel-matrices are in dissimilar environment, what manifests itself in simultaneous existence of different forms.

In the process of TEOS hydrolysis and the following polymerization and drying of gel-matrices, a porous solid silica frame is formed. The pore surface is covered by silanol $\equiv\text{Si}-\text{O}-\text{H}$ groups, whose number depends on pH of the initial solution and the gel-matrix drying temperature: at $\text{pH} > 7$ and increased temperature, the number of siloxane groups increases with respect to the number of silanol groups.⁹ Initially, the pores contain residual amount of organic solvents of the reaction mixture (mostly, water-ethanol medium), which evaporate at the following drying stages.^{7,9}

Therefore, the obtained results can be interpreted as follows. At the first stage of drying of a solid gel-matrix, 4PyPON(CH₃)₂ molecules are mostly in the water-ethanol medium of micropores (see Figs. 3 and 4). As the solvent evaporates and the pore size decreases, the dye molecule begins to interact with OH groups of the matrix in most proton-acceptor centers: nitrogen atoms of the amino group (cation with $\lambda_{\text{fl}} = 410$ nm, curves 4

and 6 in Fig. 4) and the pyridine cycle (cation with $\lambda_{\text{fl}} = 590$ nm, curves 3 and 6 in Fig. 4). At further drying, the dye molecule interacts with protons of the silanol $\equiv\text{Si}-\text{O}-\text{H}$ matrix by the both proton-acceptor centers, and thus a dication is mostly produced. The dication fluoresces in the region of 480 nm (Ref. 6) (Fig. 4, curves 2 and 7).

In the case of C 102, the similar pattern with formation of cation and dication forms characteristic of acidified solutions is observed (see Figs. 1 and 2). However, the pattern is complicated by the fact that the carbonyl group of C 102 in the acidified solution can be protonated only in the excited state (cation with $\lambda_{\text{fl}} = 530$ nm, curve 7 in Fig. 2), while nitrogen of amino group is more proton-acceptor center in solution in the ground state.⁸ In the TEOS gel-matrix, already at the first stage of drying, a new longwave band ($\lambda_{\text{max}} = 500$ nm, 20000 cm^{-1}) is present in absorption spectra in addition to the fundamental absorption band shifted to the longwave region. Its intensity increases with the increase of the drying time against the background of the decreasing intensity of the band nearby 23000 cm^{-1} (see Fig. 1). Excitation into this band yields fluorescence with the peaks at 530 and 560 nm with the following growth of the latter at the increase of the drying time (curves 5 and 5' in Fig. 2). This suggests that the silanol group of the TEOS gel-matrices interacts with the carbonyl group of C 102 with proton transfer to it not only in the excited state, but also in the ground state, and a band at 20000 cm^{-1} is formed as a result. Another peculiarity of the gel-matrix is that weak fluorescence of the C 102 amino group cation is also observed in this case ($\lambda_{\text{max}} \cong 390$ nm) unlike the acidified solution, in which such cation does not fluoresce because of the proton transfer from the amino group to the carbonyl group through the solvation sphere.⁸

We believe that nanometer-sized pores of the gel-matrix can favor formation of C 102 associations, just which have longer-wave spectra^{10,11} (in this case, 23000 cm^{-1} for the neutral form in absorption and 560 nm for the cation form in emission). At long drying, the pores decrease and the interaction with matrix increases, what shifts the equilibrium toward the ionic forms of both C 102 monomers and associations. The absorption band nearby 18500 cm^{-1} and the corresponding fluorescence at 600 nm at long drying may be caused by a new product of interaction with the gel-matrix. To check this hypothesis, further studies of phototransformations in solid samples are needed.

Conclusion

Thus, our studies have shown that this method of embedding laser dyes into the silica gel-matrix results in the simultaneous existence of molecules in both the neutral and ionic forms, what agrees with the results of Ref. 7 for the porphyrin molecules. At the first stages of drying, the dye molecules more intensely interact with the solvent left in pores. As it evaporates, interaction of

proton-acceptor centers with protons of the silanol matrix becomes dominant.

The gel-matrix significantly extends the lasing spectrum, and this opens new possibilities for obtaining lasers tunable in a wide range. However, excitation in such a sample "spreads" over different forms, quenching increases at energy transfer from one form to another, and the probability of population inversion at pumping of such elements decreases. Besides, in Ref. 5 it was shown that the cation forms of amino coumarines are less photostable as compared with the neutral forms, what is also unfavorable for SAM.

From analysis of the obtained results and the literature data, we can conclude that the proposed method of dye introduction into the gel-matrix allows a wide lasing spectrum to be obtained due to ionic, neutral, and associated forms of molecules and opens new ways for obtaining SAM based on gel-matrices.

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