

LASER EMISSION OF HYDROGEN-BOND COMPLEXES  
OF 7-DIETHYLAMINO-4-METHYLCOUMARIN

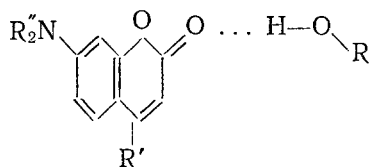
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UDC 621.375.8:535.37:  
541.571.9

Intra- and intermolecular relaxation processes have a significant influence on the threshold, energy, and spectral characteristics of lasers based on complicated organic compounds. These processes include, for example, complexation and, in particular, the formation of complexes with hydrogen bonds in an excited state. In the case of phthalimides, it was shown in [1-4] that the use of polar solvents, as well as mixtures of polar and nonpolar solvents, makes it possible to significantly expand the tuning range of the lasing wavelengths by forming excited associates of the organoluminophor with a polar solvent or a polar addition. The laser emission of 3-methoxybenzanthrone observed in [5] in a toluene-acetic acid system is caused, in our opinion, by the formation of complexes with hydrogen bonds. In the present work we studied the influence of the formation of hydrogen-bond complexes of 7-diethylamino-4-methylcoumarin (coumarin I) on the laser emission of its solutions.

In the work we used 7-diethylamino-4-methylcoumarin graded for use in quantum electronics and chemically pure or pure solvents, which were purified according to standard methods. The correction of the spectra and the determination of the fluorescence quantum yields were carried out, according to [6], with the use of a solution of quinine in a 0.1 N H<sub>2</sub>SO<sub>4</sub> solution as a standard ( $\Phi_f = 0.54$ ), the accuracy of a determination of  $\Phi_f$  being about 10%. The fluorescence lifetimes were measured by phase fluorometry of an SLM 4800S subnanosecond spectrofluorometer, the accuracy of a measurement being 0.1 nsec. The measurement of the lasing characteristics was carried out with laser excitation by the second harmonic of a ruby laser, and the lasing spectra were recorded by a spectrograph. The concentration of the solutions of coumarin I was  $\sim 2.5 \cdot 10^{-5}$  M for the luminescence-spectrophotometric measurements and  $2 \cdot 10^{-3}$  M for the lasing measurements.

Table 1 presents the luminescence-spectrophotometric characteristics of coumarin I in various solvents. From it it is seen that both the absorption spectrum and the luminescence spectrum of coumarin I in proton-donor solvents are shifted toward longer wavelengths in comparison to the spectra in aprotic solvents, the magnitude of this shift being greater than might have been expected only on the basis of the change in the polarity of the medium (this is seen, for example, by comparing the values of  $\lambda_{\text{abs}}^{\text{max}}$  and  $\lambda_{\text{fl}}^{\text{max}}$  for acetone and 1-propanol, for acetonitrile and ethylene glycol, and for ethyl acetate and acetic acid, for which the values of  $\epsilon$  are close). This may be attributed to the fact that complexes form in proton-donor solvents with a hydrogen bond between the coumarin and the solvent of the type



A similar conclusion was drawn in [7, 8] on the basis of the correlation of the values of  $\nu_{\text{abs}}^{\text{max}}$  and  $\nu_{\text{fl}}^{\text{max}}$  of coumarin I and other aminocoumarins with the Kamlet-Taft solvatochromic characteristics of the solvent. On the basis of picosecond measurements of the fluorescence spectra, Shapiro and Winn [9] showed that, in the case of coumarin 102 in alcohols, a hydrogen-bond complex forms in an excited state. In the case of coumarin I, a final conclusion as to whether the complex forms in the ground state or in an excited state cannot be drawn on the basis of our data.

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 40, No. 1, pp. 52-58, January, 1984. Original article submitted June 28, 1982; revised August 2, 1983.

TABLE 1. Wavelengths of the Maxima in the Absorption and Fluorescence Spectra, Quantum Yields, Fluorescence Lifetimes, and Values of  $\sigma_e(\lambda_{fl}^{max})$  for Coumarin I in Various Solvents

Solvent	$\epsilon$	$\lambda_{abs}^{max}$ , nm	$\lambda_{fl}^{max}$ , nm	$\Phi_f$	$\tau_f$ , nsec	$\sigma_e^{max}$ , $10^{-16}$ , cm <sup>2</sup>
Aprotic:						
Hexane	1,89	348	392	0,76	2,2	1,15
Toluene	2,38	360	410	0,57	2,7	0,63
Dioxane	2,21	363	412	0,66	2,9	0,75
Diethyl ether	4,34	360	409			
Ethyl acetate	6,02	360	415	0,69	2,9	0,85
Acetone	20,7	369	427	0,66	3,1	0,84
Acetonitrile	36,7	371	434	0,83	3,2	1,08
Dimethylformamide	36,7	375	441	0,46		
Protic:						
Acetic acid	6,19	380	448	0,46	1,95	0,92
2-Ethoxyethanol		374	446	0,56		
2-Propanol	18,3	375	441			
1-Propanol	20,1	376	446	0,73	3,4	0,90
Ethanol	24,3	377	448	0,65	2,85	0,98
Methanol	32,6	376	453	0,37	1,95	0,88
Ethylene glycol	37,7	383	459	0,375		
Formamide	110	382	455			
Water	78,5	380	471	0,043		

TABLE 2. Wavelength of the Maximum Half-Width of the Lasing Spectrum, and Lasing Efficiency of Coumarin I in Various Solvents

Solvent	$\lambda_{las}^{max}$ , nm	$\Delta\lambda$ , nm	$\eta$ , %
Hexane	Not generated		—
Toluene	414	4,4	1,2
Dioxane	418,8	7	3,3
Diethyl ether	413	5	1,7
Ethyl acetate	417	7,0	3,3
	457	10,7	
Acetonitrile	450	4,2	9,3
2-propanol	452	5,1	14,0
1-Propanol	455	5,8	14,9
Ethanol	458	6,7	16,6
Methanol	461	5,6	16,1
Ethylene glycol	469	7,4	15,4
Formamide	464	6,6	13,5

Table 2 presents the spectral and energy characteristics of the laser emission of coumarin I in various solvents. From the table it is seen that the lasing efficiency of coumarin I in the solvents capable of forming hydrogen-bond complexes with it is higher than in the solvents in which such complexes do not form, even despite the fact that the fluorescence quantum yield in the protic solvents is generally lower than in the aprotic solvents.

As follows from the theory in [10], the gain of the active medium (and, therefore, the radiant flux of the emission) of a laser is primarily dependent on the value of the stimulated-emission cross section  $\sigma_e$ , which is proportional to  $\lambda^4$ . However, as is seen from Table 1, these changes in  $\sigma_e$  are relatively small (the error in the determination of  $\sigma_e$  amounts to 15%).

Thus, the observed increase in the lasing efficiency upon the transition from aprotic solvents to protic is related mainly to something other than the changes in  $\sigma_e$ . The loss coefficient of the resonator in our experiments was also weakly dependent on the wavelength in the spectral range of interest to us. Therefore, the most likely cause of the increase in the lasing efficiency upon the transition to protic solvents may be the change in the relative positions of the fluorescence and induced singlet-singlet and (or) triplet-triplet absorption spectra or the change in the population of the triplet state.

For a more detailed investigation of the complexation mechanism, we studied the fluorescence of coumarin I in nonpolar solvents (toluene, hexane, ether, etc.) upon the addition

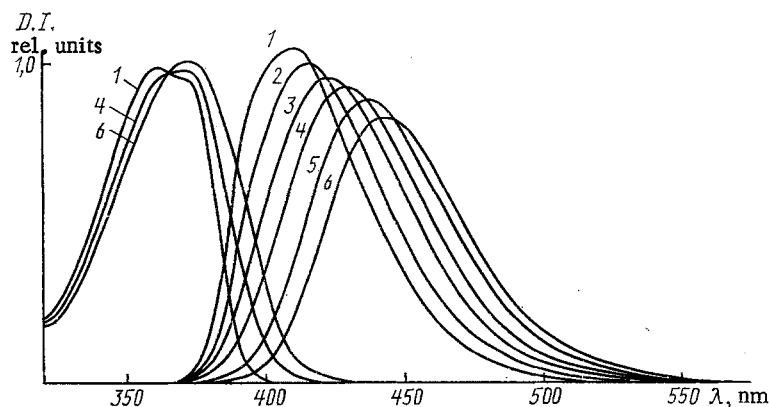
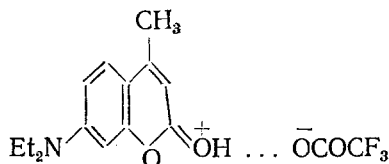


Fig. 1. Absorption and fluorescence spectra of coumarin I in toluene at various concentrations of the proton donor, viz., acetic acid: 0 (1), 0.14 (2), 0.52 (3), 1.16 (4), 3.5 (5), and 7 M (6). Excitation at the isobestic point.

of proton donors, viz., acetic acid or trifluoroacetic acid; typical results are presented in Fig. 1. When the concentration of the proton donor is increased, the absorption spectra of coumarin I show a shift of the maximum to longer wavelengths, which is characteristic of hydrogen-bond complexes formed with the participation of a carbonyl group. The absorption spectra have a pronounced isobestic point. The fluorescence spectra show a continuous shift of the fluorescence maximum to longer wavelengths as the concentration of the proton donor is increased. The continuous nature of this shift may be attributed to the overlapping of the fluorescence spectra of the original form and the hydrogen-bond complex, as well as the increasing contribution of specific interactions. In the range of accuracy of the measurements, the fluorescence quantum yield remains practically unchanged.

In the case of the stronger donor trifluoroacetic acid (TFA)\* at low concentrations, the formation of a hydrogen-bond complex is also observed. At high concentrations of the acid (~0.1 M) protonation of coumarin I at the amino group, which results in a characteristic shift to shorter wavelengths in the absorption spectrum, occurs. In this case, the fluorescence spectrum shows a new band with a maximum at 480-490 nm, which may be assigned to the ion pair



The formation of the hydrogen-bond complex and the ion pair in the case of TFA is accompanied by a significant decrease in the fluorescence quantum yield. Deactivation is apparently observed in pure solvents: As the proton-donor ability of the solvent increases, the fluorescence quantum yield decreases. Jones et al. [7] believe that this is due to a change in the conformation of the molecule in the excited state, which produces a state with intramolecular charge transfer that is stabilized in polar solvents and characterized by low values of  $k_f$ . Such a mechanism is especially characteristic of aminocoumarins containing electron-acceptor substituents. In the case of coumarin I, the deactivation mechanism has not yet been conclusively established.

Figures 2 and 3 present the spectral and energy output characteristics of the laser emission of coumarin I in mixed solvents. An increase in the concentration of the proton donor in the mixture results in an increase in the lasting efficiency and displacement of the emission maximum toward longer wavelengths. Two-band lasing is observed at a definite concentration of the proton donor. It is noteworthy that the fluorescence spectrum in this case contains only one maximum (see Fig. 1). It is interesting that in ethyl acetate two-band lasing is observed even in the absence of additions of a proton donor in a thoroughly purified solvent.

\*In the case of TFA, the situation is complicated by the presence of an irreversible dark reaction of coumarin I with TFA; therefore, the measurements were carried out directly after the preparation of the solvent.

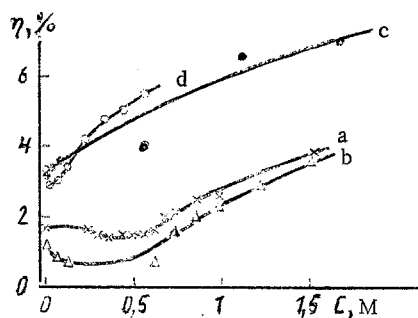


Fig. 2

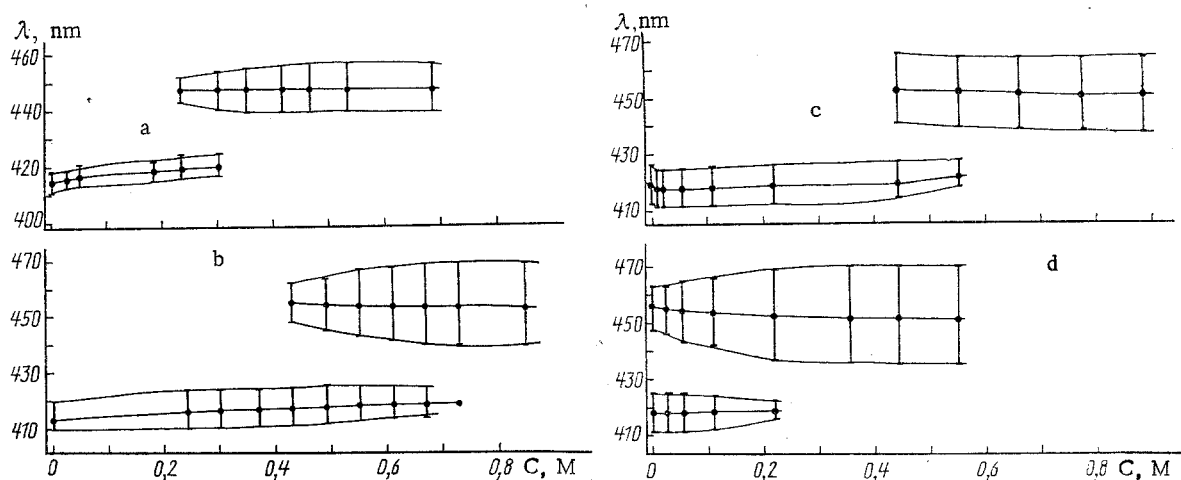


Fig. 3

Fig. 2. Dependence of the lasing efficiency of comarin I on the concentration of the proton donor in the following systems: toluene-acetic acid (a), diethyl ether-acetic acid (b), dioxane-water (c), and ethyl acetate-water (d).

Fig. 3. Spectral range of the laser emission of coumarin I in mixed solvents for various concentrations of the proton donor: a) toluene-acetic acid; b) diethyl ether-acetic acid; c) dioxane-water; d) ethyl acetate-water. [The maximum and the limits of the range of laser emission along the base (~1% from the maximum) as a function of the concentration of the proton donor are shown in the figure.]

A similar situation was observed for the lasing of 4-amino-N-methylphthalimide and several other phthalimides in various solvents and binary mixtures of solvents [1-4], in which a) the existence of excited complexes of the phthalimide with the polar addition was demonstrated [2, 11], b) an increase in the energy (or a decrease in the threshold) of the emission in polar solvents was observed, despite the decrease in the fluorescence quantum yield [1, 3], c) two-band lasing was observed in a definite range of concentrations of the polar addition with one band in the fluorescence spectrum, and, d) the absence of lasing was observed in a definite portion of the spectrum regardless of the type of solvent and addition. It should be stressed that the presence of two types of luminescent centers does not necessarily result in the appearance of two bands in the lasing spectrum, and if the fluorescence spectra of these centers are similar, one band should be observed in the lasing spectrum [12].

In the case of phthalimides, all the aforementioned phenomena were attributed to the presence of induced absorption in the region of luminescence, whose spectrum is shifted only slightly when the solvent is altered [13, 14]. In the case of coumarin I, the phenomenon of two-band lasing and the other effects are probably also attributed to the presence of bands of induced singlet-singlet and (or) triplet-triplet absorption which overlap the fluorescence spectrum. From the literature it is known that in the T-T absorption spectrum of coumarin I in ethanol, whose fundamental maximum is shifted toward a longer wavelength in comparison to

the fluorescence spectrum, there is a small maximum at  $\sim 430$  nm ( $\sigma_{T-T} = 1.6 \cdot 10^{-17}$  cm<sup>2</sup>), and the T-T absorption minimum is located at 460 nm [15]. Simple evaluations [10] show that the T-T absorption should result in disruption of the lasing when  $t_{ex} \geq \sigma_e / \sigma_{T-T} \cdot k_{S-T}$ . If it is assumed that the rate constant for intersystem crossing  $k_{S-T}$  is equal to  $(1 - \phi_f) / \tau_f$ , this gives a value of  $\sim 47$  nsec, which is commensurate with the duration of the exciting flash (25 nsec). In addition, the value of  $k_{S-T}$  may be dependent on the solvent [for example, in toluene  $(1 - \phi_f) / \tau_f$  is 1.3 times high and in methanol it is 2.6 times higher than in ethanol]. Thus, the T-T absorption is probably the reason for the two-band lasing and the increase in the lasing efficiency upon complexation (as a consequence of the shift of the fluorescence spectrum relative to the T-T absorption spectrum). Apparently, a definite role may also be played by the  $S_1 \rightarrow S_n$  absorption; however, the  $S_1 \rightarrow S_n$  absorption spectrum of coumarin I is presently unknown. The lasing spectra of the structurally similar compounds 7-diethylamino-4-trifluoromethylcoumarin in dioxane-ethanol mixtures [16] and coumarin 102 in toluene-acetic acid mixtures do not show two bands.

From the work carried out it is seen that in solutions of 7-diethylamino-4-methylcoumarin in protic solvents and in aprotic solvents with an addition of a proton donor, hydrogen-bond complexes involving the carbonyl group of the coumarin molecule form in the ground and excited states. Despite the fact that the fluorescence quantum yield of 7-diethylamino-4-methylcoumarin in protic solvents is generally lower than in aprotic solvents, the lasing efficiency of the complexes is significantly higher, and the spectral range of the laser emission is broader. The lower threshold for the laser emission of the hydrogen-bond complexes is apparently related to the alteration of the relative positions of the fluorescence and triplet-triplet or singlet-singlet absorption spectra.

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