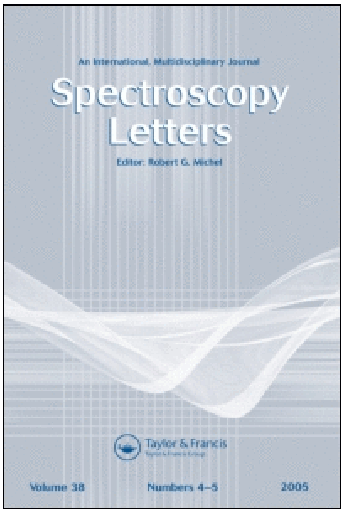

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LASER ACTION OF COMPLEX MOLECULES IN THE GAS PHASE

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For the past ten years interest in complex molecules as laser active media has been unflagging. This interest is brought about by the possibility to use a great number of complex organic compounds for achieving laser action, to obtain laser emission in different spectral regions and to tune the frequency of radiation over a wide range of frequencies employing a single active medium, as well as by the availability and low cost of many organic compounds.

The lasers in which complex molecules in the vapor phase are used as active media have essentially the same merits as the liquid phase lasers. In addition, low laser beam divergence may be expected when using gaseous medium since the latter is optically more homogeneous than a solution; also, if necessary, the active medium may be pumped through the cell with a high flow rate. The vapor spectra are in general blue-shifted with respect to the solution spectra; this makes it possible to obtain laser action at shorter wavelengths. The achievement of laser action of complex organic molecules in gas state signifies the introduction of a new research method for the study of practically free molecules, the interaction among which is reduced to a minimum.

Experimentally the creation of organic vapor lasers is more complicated than that of the liquid phase lasers. There are also essential differences and difficulties in performing the laser action of complex molecules in the vapor phase.

It is well-known that in rarefied vapor the excess (or deficiency) of vibrational energy, compared to equilibrium values, gained by molecules due to excitation process is conserved during the lifetime of excited molecules [I,2] . As a result, the fluorescence spectra, the quantum yield and fluorescence lifetime of vapor depend upon the frequency of the exciting radiation. On increasing the energy of the exciting quantum the diffuse fluorescence spectra become broadened, the diffuse-banded spectra also become broadened and they gradually lose their vibrational structure. At the same time the peaks of diffuse-banded fluorescence spectrum shift slightly to longer wavelengths whereas the position of diffuse spectra remains fixed. Therefore, in the vapor phase when high energies of exciting quanta are used molecular radiative transitions to higher, weakly populated vibrational levels of the ground state take place, which in general favours the attainment of inverted population. However, the probability of nonradiative transitions usually increases with the vibrational energy content of the excited molecules, which leads to decrease of fluorescence quantum yield and lifetime and lowers the ability of lasing. The radiationless transition probability can be affected by adding chemically inert foreign gases [1,3] . If vapor is excited by radiation the frequency of which is higher than inversion frequency, the radiationless transition probability decreases on the addition of foreign gas due to the transfer of excess of molecular vibrational energy from the excited molecules to foreign gas molecules (stabilization of excited molecules). If the exciting radiation frequency is lower than the frequency of inversion, the interaction of the excited molecules with the foreign gas molecules increases the vibrational energy content of excited molecules and as a result the radiationless transition probability rises. The foreign gas addition to the vapor will contribute also to more rapid attainment of equilibrium distribution over vibrational levels of molecules, which are coming into the ground state from the excited state. Increasing the temperature of vapor results in the broadening of the vibrational energy distribution of molecules in both the ground and excited electronic states. All the above must be taken into account when choosing the optimum conditions for obtaining the laser action of complex molecules in the gas phase.

The first organic vapor laser was created in 1973 [4] . The active medium of this laser was the 1,4-di-[2-(5-phenyloxazolyl)]-benzene (POPOP) vapor, stabilized by pentane. The pumping was performed with longitudinal geometry by second harmonic of ruby laser. The laser produced emission with the band maximum located at 398 nm and was operated in the temperature range 220-250°C.

Later the laser action of POPOP vapor and the properties of laser emission were reported in papers [5-9] . The laser action was achieved also in I,4-di-[2-(5-n-totyloxazolyl)] -benzene [7] and dimethyl-POPOP [9] vapors. The problems of vapor laser action were treated theoretically [IO,II].

Mean free time Z^{-I} for collisions between the excited molecule and the foreign gas molecules must be far less than the lifetime of excited molecule for the removal of the vibrational energy excess from the latter to be effective. In the case of high volume densities of the pumping radiation U_p and emitted radiation U_{em} the lifetime of the excited molecule τ will be given by:

$$\tau^{-I} = k + B_pU_p + B_{em}U_{em}, \qquad (I)$$

where k is the rate of spontaneous depopulation of the excited state, B_pU_p and $B_{em}U_{em}$ are the rates of depopulation stimulated by radiation. When $k \gg B_pU_p + B_{em}U_{em}$ the lifetime does not depend on radiation density and when $k \ll B_pU_p + B_{em}U_{em}$ τ changes in inverse proportion to radiation density. Therefore, for the excited molecules to be stabilized effectively, pressures of the order of I atmosphere are insufficient at high exciting radiation densities.

If a chosen compound has a high gain and a sufficient vapor pressure can be obtained so that the exciting radiation is absorbed almost completely when passing through the active medium, then the laser action is observed at low pressures of foreign gases as well as in a pure vapor.

The POPOP and TOPOT vapor laser emission spectra [7] are shown in Fig. I. The longitudinal pumping with a ruby laser second harmonic was used. The vapors of these compounds without foreign gases at temperatures 270-300°C produce stimulated emission bands, the wavelengths of emission band maximum λ_{em} being 383 nm and 393 nm, respectively, and the half-widths being about 4 nm.

The laser emission bands shift to the long-wavelength side with increasing foreign gas pressure. When pentane pressure is 7 atm double-band emission spectrum (λ_{em} 383 and

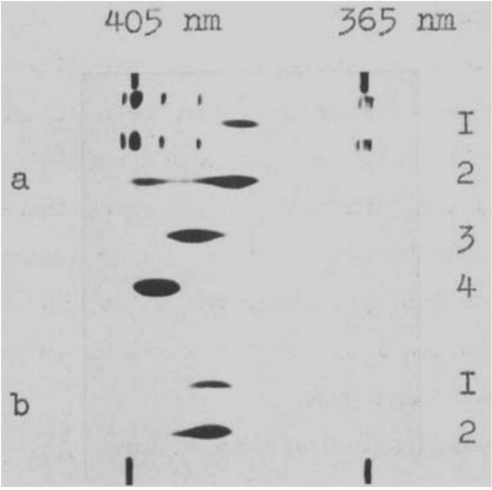

Figure I

Vapor laser emission spectra. a- POPOP: I - rarefied vapor (T=270°C, P=0.5 Torr); 2-4 - vapor stabilized by pentane (T=240°C: $C_{pentane}$ = I.3xIO^{20}(2), 6.0xIO^{20} (3) and 4.0x xIO^{2I}cm^{-3}(4). b - TOPOT: I - rarefied vapor (T-300°C, P=I.0 Torr), 2 - vapor stabilized by pentane (T=280°C), $C_{pentane}$ = 6.0xIO^{I9}cm^{-3}

403 nm) is observed (see Fig. Ia, Spectrum 2). When pentane concentration (C_f) is increased up to $4.10^{2I}cm^{-3}$, the wavelength of the emission band peak of POPOP increases from 383 to 400 nm, and λ_{em} of TOPOT changes from 393 to 404 nm with pentane concentration increasing up to $3.2.10^{2I}$ cm^{-3}. This can be explained by the fact that with increasing foreign gas pressure the absorption and fluorescence spectra of vapor and consequently the stimulated emission spectrum are red-shifted. Triplet absorption spectra which play an important role in the shaping of the POPOP and TOPOT vapor laser emission spectra as will be shown later, are strongly affected by the foreign gases as well [I2,I3] .

The changes in laser emission when gradually passing from solution to rarefied vapors have been investigated and the temperature dependence data have been obtained [7] . Fig.2 gives TOPOT laser emission spectra in different states of aggregation. The conditions under which these spectra have been obtained and the wavelength of laser emission band peaks are presented in Table I. Saturated solutions and vapors were used. The reflection indices of the resonator mirrors for λ=400 nm were 93 and 97%.

With increased solution temperature λ_{em} shifts slightly to shorter wavelength and at T=I03°C the laser emission becomes double-banded. The two bands of laser emission are observed also when passing from solution to vapor near the critical point. The difference of laser emission band frequencies is approximately equal to 400 cm^{-I} that does not correspond to vibrational structure of TOPOT stimulated emission spectrum. Only one band of laser emission is observed

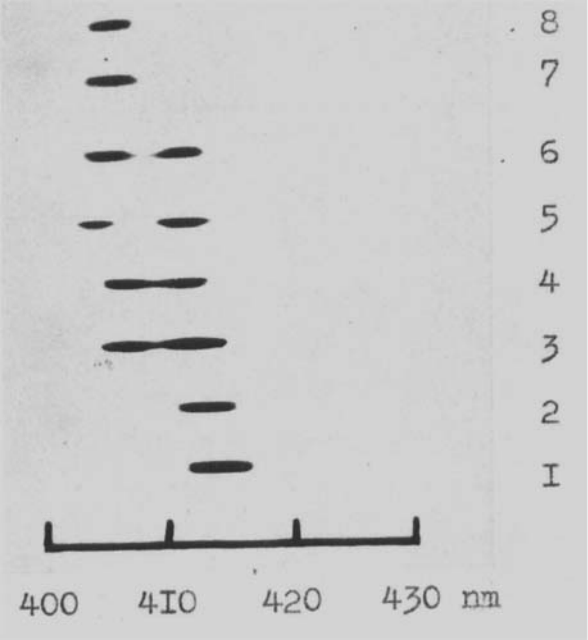

Figure 2

Laser emission spectra of TOPOT in solution and in vapor. I - 8 correspond to item Nos. of spectra given in Table I.

(see Fig.2, spectra 7 and 8) if the cavity Q-factor is reduced. Lowering of the pumping power results in more rapid drop of the intensity of the long-wavelength band in the two-banded emission spectrum. Near the threshold the emission becomes single-banded. The rarefied vapors and those with the relatively slight pentane concentration (4.5 atm) produce laser emission with a single band (Fig.Ib). The position of the maximum of vapor laser emission band is practically temperature independent.

TABLE I

Wavelengths of the Laser Emission Band Maxima of TOPOT

No. of spectrum in Fig.2	T, °C	State of aggregation	C_f, cm^{-3}	λ_{em}, nm
1	18	Solution	$5.3x10^{21}$	414
2	53	- " -		413
3	103	- " -		406; 412
4	154			405.5; 411
5	205	Vapor	$3.2x10^{21}$	404; 412
6	255	- " -	$3.2x10^{21}$	404; 412
7[a]	255	- " -	$3.2x10^{21}$	405.5
8[b]	255	- " -	$3.2x10^{21}$	405
	280	- " -	$6.0x10^{19}$	393
	300	- " -	0	393

a) one resonator mirror is absent

b) the both mirrors are absent

According to estimates made in paper [14] the triplet-triplet molar absorptivity $\mathcal{H}^T$ of the vapor in the T-T absorption maximum (λ =400 nm) at T=330°C is 1250 l·mole^{-1}·cm^{-1} (POPOP) and 1200 l·mole^{-1}·cm^{-1} (TOPOT). The molar absorptivity $\mathcal{H}^S$ for vapor S-S absorption of these substances is equal to 49000 and 48000 l·mole^{-1}·cm^{-1}, respectively.

The low values of triplet absorptivity $\mathcal{H}^T$ of POPOP and TOPOT vapor represent one of the main reasons which favoured observation of laser action for the first time in the vapors of this particular group of compounds. Since the spectra of triplet-triplet absorption of these compounds in vapors and solutions possess distinct vibrational structure and strongly overlap with the fluorescence spectra, the triplet absorption in some spectral regions at concentrations sufficient for laser action becomes a considerable loss source. The triplet absorption spectra together with the stimulated emission spectra, which practically coincide with the fluorescence spectra, define mainly the laser emission spectra as can be seen from Figs. 3 and 4. The emission band of rarefied POPOP vapor is observed in the fluorescence band main peak where the triplet absorption has a sharp minimum. Addition of hexane at high pressures leads to change of the relative position of the triplet absorption and fluorescence spectra. The peak of the most intensive triplet absorption band is now shifted to shorter wavelength with respect to the central fluorescence band maximum. As far as this T-T band is considerably narrower than the central fluorescence band the gain is sufficient for laser action in the frequency ranges located to the left and to the right from the triplet absorption peak and as a result the double-banded laser emission is observed. Increase in hexane pressure leads to further change in the mutual position of the spectra. The laser emission spectrum becomes single-banded, the emission band being located between the most intensive peaks in the fluorescence and triplet absorption spectra. The single emission band located between the fluorescence and triplet absorption band maxima is observed for POPOP solution in hexane. In this case the triplet absorption spectrum is also superimposed on the stimula-

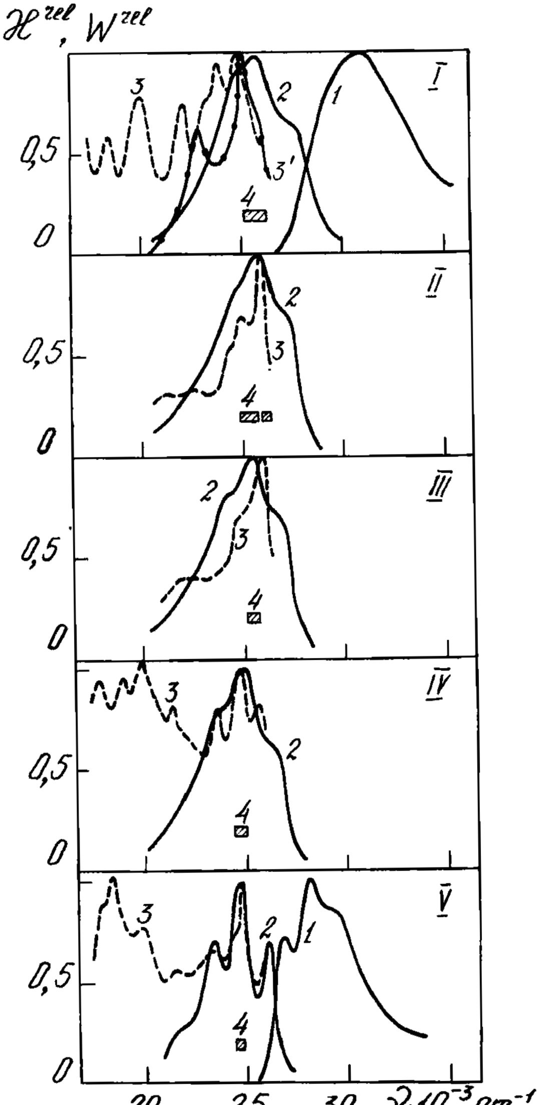

Figure 3

Spectra of singlet-singlet absorption (I), fluorescence (2), triplet-triplet absorption (3, 3′) and laser emission (4) of POPOP. The conditions of the experiments are presented in Table 2.

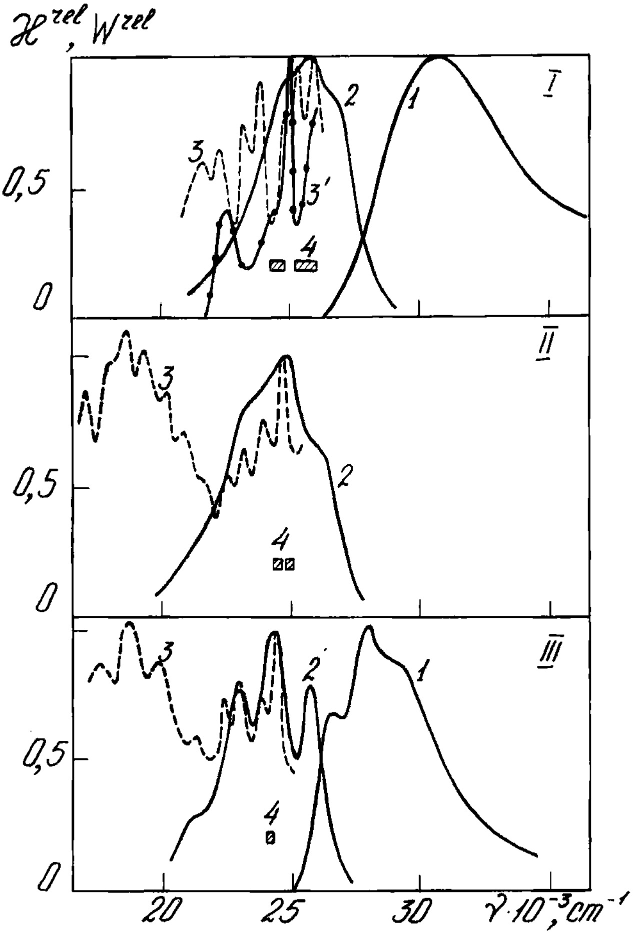

Figure 4

Spectra of singlet-singlet absorption (I), fluorescence (2), triplet-triplet absorption (3,3′) and laser emission (4) of TOPOT. The conditions of experiments are presented in Table 2.

ted emission spectrum, but the structure of the former is sharper. The emission band appears in the spectral range where sufficiently high intensity in the stimulated emission

TABLE 2

The Conditions of Obtaining Spectra are Shown in Fig. 3 and 4

Compound	Spectrum	State of aggregation	T, °C	foreign gas	foreign gas concentration	λ_{em}, nm
POPOP	I[a]	Vapor	320		0	390
	I		320	nitrogen, pentane	$7.4x10^{18}$	
	II		260	hexane	$3.0x10^{20}$	382, 395
	III		260	hexane	$7.5x10^{20}$	392
	IV		260	hexane	$3.0x10^{21}$	399.5
	V	Solution in hexane	20			408
TOPOT	I[a]	Vapor	330		0	390, 407
	I		330	pentane	$7.4x10^{18}$	
	II		260	pentane	$3.2x10^{21}$	404, 412
	III	Solution in pentane	20			414

a) the conditions of obtaining the triplet absorption spectra 3'.

spectrum is accompanied by low triplet-triplet absorption. Analogous results have been obtained for TOPOT (see Fig.4).

In general there is a satisfactory correlation between the spectra of laser emission, triplet absorption and stimulated emission of the compounds studied. The singlet-singlet absorption from high excited levels has not been measured. Since the correlation between the above-mentioned spectra takes place without allowing for the S-S absorption by excited molecules, it may be concluded that the latter does not influence essentially the laser emission spectra of the compounds investigated.

The pulse of vapor laser emission practically repeats the pumping pulse [6] . According to the estimates [8] the POPOP vapor gain is I cm^{-I}. The value of 0.6 cm^{-I} is obtained experimentally [9] . The output power of POPOP vapor laser with nitrogen laser transverse pumping [9] increases rapidly with increasing pumping power and approaches 30 kw at 400 kw pumping. The saturation is not observed and higher laser emission power is likely to be expected with the use of greater pumping power.

In the new type of lasers described the pumping is performed optically. The existence of laser action of complex organic molecules in the gas phase gives certain hope to create lasers on the basis of vapors of complex organic compounds which will effectively transform electric energy directly into the energy of light.

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