

Laser action in complex molecules in the gas phase

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The studies are reviewed on a new type of lasers whose active medium consists of vapors of complex organic compounds. We first present the fundamental facts of the spectroscopy of free complex molecules. Then we analyze the potentialities of gaseous media based on complex molecules for amplifying and generating radiation. A list is compiled of complex organic compounds that give laser action in the vapor, and also criteria are formulated for seeking new ones. The properties (spectral composition, frequency retuning, efficiency, divergence, polarization) of the radiation generated by vapors are examined in detail. Special attention is paid to the effect on the characteristics of lasers of added chemically inactive gases, the introduction of which into the vapor of the active molecules does not alter the advantages of the gaseous medium, and considerably improves the fundamental characteristics of the radiation being generated. We show that lasers based on vapors of organic compounds are an important instrument for studying complex molecules.

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1. INTRODUCTION

Laser action in complex molecules in the gas phase was first reported in 1973.¹ The active medium was the vapor of 1,4-di[2-(5-phenyloxazolyl)]-benzene (POPOP) stabilized with an added gas, for which pentane was used. The radiation of the second harmonic of a ruby laser was used for pumping. The possibility of obtaining laser action based on complex organic compounds in the gas phase had been previously discussed in Ref. 2.

In 1974 Refs. 3–7 were published, which reported laser action with optical pumping in vapors of POPOP, 1,4-di[2-(5-*p*-tolylloxazolyl)]-benzene (TOPOT), and dimethyl-POPOP, and which studied certain properties of the generated radiation.

A considerable number of papers have appeared up to now on the theoretical study of the lasing capability of vapors of complex molecules, on the search for new classes of complex organic compounds that lase in the gas phase, and on studying the properties of the generated radiation. The aim of this article is to review the results accumulated in this field.

In their nature, the vapors of complex molecules as an active laser medium are closest of all to solutions of organic compounds (dyes), in which laser action has been obtained by Sorokin and Lankard,⁸ and by Stepanov, Rubinov, and Mostovnikov.⁹

Complex molecules in the vapor and in solution have broad luminescence and absorption bands. Therefore frequency retuning of the generated radiation over a considerable interval and the use of various sources of

optical radiation for pumping are characteristic of both types of lasers. Owing to the broad set of active organic compounds, one can easily obtain laser action in various regions of the spectrum. An advantage of these types of lasers of no small importance is the low cost and availability of many organic compounds.

Moreover, the vapors of complex molecules possess a number of specific properties. The spectral-luminescence characteristics of complex molecules in the gas phase (they will be discussed in Sec. 2) differ substantially from the analogous characteristics of condensed media. Therefore they also differ in their laser characteristics.

The spectra of vapors are usually shifted toward the ultraviolet with respect to the spectra of solutions. This enables one to obtain laser action at different, shorter wavelengths. By using lasers based on vapors of complex molecules, one can generally penetrate into the shorter-wavelength ultraviolet region in which the solvents themselves absorb. A feature of gas lasers of no small importance is the high optical homogeneity of the active medium, whereby the generated beam has relatively small divergence. The low density of the gaseous medium enables one to circulate it through the active zone of the laser at a high rate.

In order to convert complex organic compounds into the gas phase, one must heat them under vacuum conditions to temperatures of 450–650 K. An extra heating of the molecules arises with high-power pumping, and this leads to an increased radiationless loss of molecules from the excited electron state, and in a number of cases—to thermal and photochemical decomposition

of the active medium. An added gas was used in the very first laser based on vapors of complex molecules to diminish these negative phenomena.¹

Up to now, pumping in lasers based on vapors of complex molecules has been carried out with sources of optical radiation. The gaseous medium enables one to pump in a discharge also with an electron beam, i.e., to realize direct conversion of electrical energy into light energy. Intensive searches are currently being conducted along this line.

2. SPECTRAL-LUMINESCENCE CHARACTERISTICS OF FREE COMPLEX MOLECULES

A characteristic feature of complex molecules as polyatomic dynamic structure is not only the aggregate of many electron and vibrational states, but also the strong coupling of the vibrations with each other and their interaction with the electron and rotational motions. On the one hand, this leads to a high efficiency of conversion of light by complex molecules, and on the other hand, to a smearing of the line structure of their electron-vibrational-rotational (electron) spectra. They become diffuse or continuous. Therefore the employment of methods developed in the spectroscopy of simple molecules for analyzing the emission and absorption spectra of complex molecules offers only highly limited information on their energetics and structure.

In the twenties Vavilov¹⁰ began to develop new spectral-luminescence methods for studying complex molecules of dyes in solution. Subsequently he proposed using the spectra of the quantum yield and duration and polarization of luminescence to describe their properties, in addition to the luminescence and absorption spectra. These concepts and the discovery by Terenin¹¹ of the nature of the metastable state enabled the establishment of a number of general laws of conversion of light energy by solutions of complex organic compounds, in particular, the independence of the luminescence, quantum yield, and duration of luminescence spectra of condensed media of the wavelength λ_{exc} of the exciting radiation. These laws arise from the strong interaction of the complex molecules with the molecules of the medium. Owing to the intermolecular interactions, an equilibrium distribution of the excited molecules over the vibrational levels determined by the temperature T of the medium is established within the lifetime of the complex molecules in the excited state, independently of the energy of the quanta that they have absorbed. The spectral-luminescence characteristics of condensed media are averaged and lose many of their individual features. The medium impedes the separation of the intermolecular and intramolecular interactions, and it transforms the system of electron levels.

Studies of the luminescence of polyatomic molecules in the gas phase, where they practically do not interact with one another, were started by Terenin and Neporent in the thirties. The status of the problem up to 1936 was reflected in a paper by Terenin.¹² The role of the vibrational energy in the luminescence of the vapors of complex molecules has been treated in a review by

Neporent and Stepanov.¹³ A monograph¹⁴ has been devoted to the spectroscopy of free complex molecules.

In rarefied gases and vapors (the time of free flight of the molecules being greater than the lifetime of the excited state), the excited molecules exist in the free state and do not interact with the environment. The excess or deficit of vibrational energy (with respect to the equilibrium state) that arises in the molecules in the process of absorption of a light quantum is conserved in it during its lifetime in the excited state. This leads to a strong dependence of the spectra of fluorescence, quantum yield, duration of the excited state, and other characteristics of the molecules in the gas phase on the energy $h\nu$ of the absorbed quanta. The spectral-luminescence characteristics of free complex molecules are more individual, and they bear important information on the structure and energetics of these molecules.

Figure 1 shows the fluorescence spectra of vapors of anthracene, POPOP, and 3,6-diaminophthalimide for different wavelengths λ_{exc} of the exciting radiation. As the energy of the exciting quantum increases, a spectrum with a marked vibrational structure undergoes considerable changes. The maximum of the spectrum shifts toward longer wavelengths, the half-width increases, and the vibrational structure is smeared out. Structureless (continuous) fluorescence spectra only broaden as λ_{exc} decreases.

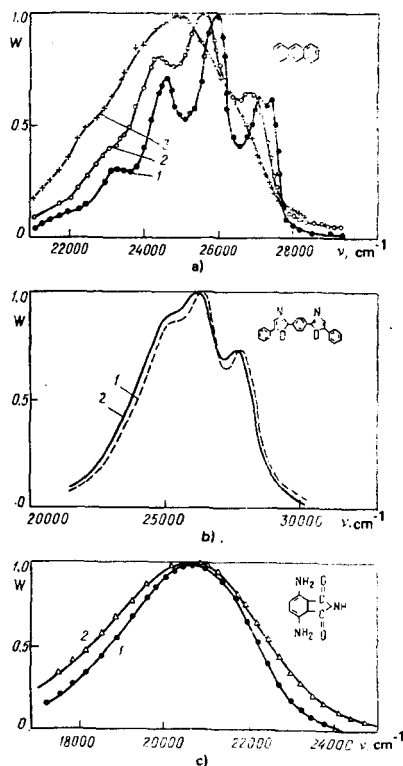


FIG. 1. Fluorescence spectra of vapors as functions of the wavelength λ_{exc} of the exciting radiation. a) anthracene¹⁴ (1 - λ_{exc} = 365, 2 - 313, 3 - 248 nm; $T = 503$ K, $p = 0.05$ Torr); b) POPOP²¹ (1 - λ_{exc} = 334, 2 - 296 nm; $T = 458$ K, $p = 0.02$ Torr); c) 3,6-diaminophthalimide¹⁴ (1 - λ_{exc} = 436, 2 - 265 nm; $T = 538$ K, $p = 0.05$ Torr).

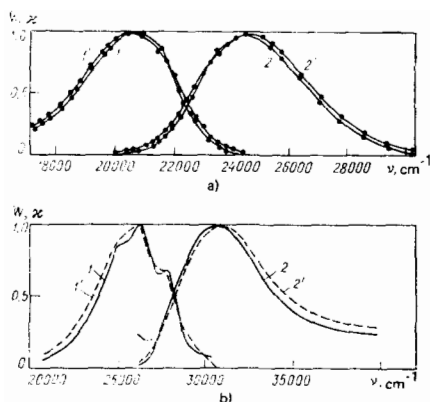


FIG. 2. Fluorescence (1 and 1') and absorption (2 and 2') spectra as functions of the temperature T of the vapors. a) 3,6-diaminophthalimide¹⁴ (1 and 2 - $T=563$, 1' and 2' - 653 K; 1 and 1' - $\lambda_{exc}=436$ nm); b) POPOP²¹ (1 - $T=458$, 1' - 733 , 2 - 573 , 2' - 673 K; 1 and 1' - $\lambda_{exc}=334$ nm).

Analogous deformations of the fluorescence and absorption spectra of vapors are observed with varying temperature (Fig. 2).

The dependence of the quantum yield γ of fluorescence of vapors on the frequency of the exciting radiation (quantum-yield spectrum) is illustrated by Fig. 3. As the energy of the quantum absorbed by the molecules increases, the fluorescence yield declines. The duration of luminescence τ of the vapors also varies approximately proportionally to γ . Increase in temperature is accompanied by an analogous variation in these spectral-luminescence characteristics of the vapors of complex molecules. We should note that the quantum yields of the vapors of a number of compounds attain high values in the long-wavelength excitation region.

The optical complexity of a molecule is determined mainly by the degree of interaction of the eigenvibrations participating in the electronic-vibrational transition with the other vibrations, which constitute the internal "heat reservoir". In complex molecules, complete redistribution of the vibrational energy occurs within the lifetime in the electronically excited state.¹⁵⁻¹⁷ Therefore free complex molecules are characterized

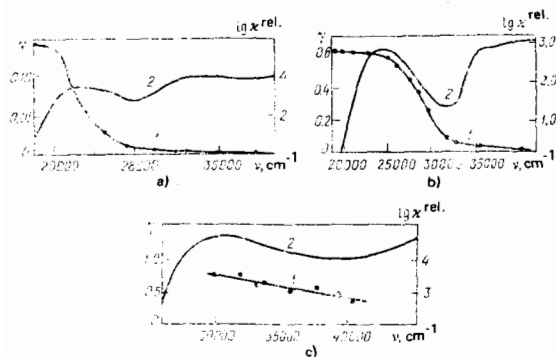


FIG. 3. Quantum yield (1) and absorption (2) spectra of vapors. a) 3,6-tetramethyldiaminophthalimide ($T=558$ K); b) 3,6-diaminophthalimide¹⁴ ($T=538$ K); c) POPOP²² (1 - $T=543$, 2 - 573 K). (In all three diagrams, right-hand scale of ordinates is: $\log \gamma_{rel.}$)

by the principle of equivalence of optical (frequency of the exciting light) and thermal (temperature) methods of varying the supply of vibrational energy¹⁸: the spectra of fluorescence, quantum yield, and duration of the excited state of complex molecules depend on the general supply of vibrational energy of the excited molecules, rather than on the method of introducing it. The establishment of this principle has enabled the development of optical methods of determining the vibrational heat capacity of excited molecules from quantum-yield spectra¹⁸ and from fluorescence spectra.^{19,20}

The decline in the quantum yield and duration of fluorescence of vapors with increasing supply of vibrational energy (increasing ν_{exc} and T) of excited molecules involves the increased probability of radiationless transitions.^{18,23-26,14} The quantum yield γ and the duration τ of luminescence are determined by the expressions

$$\gamma = \frac{A}{A+d}, \quad (1)$$

$$\tau = \frac{1}{A+d}. \quad (2)$$

Here A and d are the generalized probabilities of radiative and radiationless transitions, respectively. The generalized probability A practically does not depend on the supply of vibrational energy ΔE^* of the excited molecules. The probability d of radiationless transitions increases exponentially in most cases with increasing ΔE^* .^{18,23,24} These dependences differ when the molecules are excited in different electronic absorption bands.^{27,28,25,14}

One also encounters complex molecules for which γ and τ remain constant²⁹⁻³¹ with increasing ΔE^* , or even increase.³²⁻³⁵ This involves constancy or decline of the probability of radiationless transitions.^{34,35}

Two pathways of radiationless degradation of the energy of electronic excitation can occur for complex molecules: radiationless transition of singlet excited molecules to the triplet state (intercombination conversion), and direct radiationless transition of molecules from the singlet excited state to the ground state (internal conversion). It has recently been possible to elucidate the role of these channels in the radiationless degradation of absorbed energy in free complex molecules.³⁶⁻³⁹ For most molecules both intercombination and internal conversion take place. For example, in the phthalimides (γ and τ decline with increasing ΔE^*) the probability of intercombination conversion increases most rapidly with increasing supply of vibrational energy. In the case of anthracene vapors (γ and τ independent of ν_{exc} and T), the sole pathway of degradation of electronic energy is intercombination conversion, whose probability does not depend on the supply of vibrational energy of the excited molecules. In 9,10-dimethylantracene the increase in the quantum yield and the duration of fluorescence with increasing supply of vibrational energy of the singlet excited molecules arises from the fact that the probability of internal conversion declines more rapidly than that of intercombination conversion increases. In general, for all the studied free molecules except for anthracene, one observes an increase in the probability of intercombination conversion with increasing energy supply ΔE^* of the excited singlet mole-

cules. Yet the probability of internal conversion can either increase or decrease.

We can see from what we have presented above how important it is to know the supply of vibrational energy of the excited molecules. A detailed analysis of the absorption process has shown⁴⁰⁻⁴² that the mean excess or deficit of vibrational energy (as compared with equilibrium) that arises in free molecules after absorbing the quantum $h\nu$ does not equal the difference $h\nu - h\nu_{el}$ ($h\nu_{el}$ is the energy of the pure electronic transition). This involves the fact that the statistical set (ensemble) of molecules which have a broad distribution of vibrational energies E of the ground state, participates in the absorption process and the Einstein coefficient for absorption $B(E, \nu)$ depends on E . Also, molecules whose energy is $E < h\nu_{el} - h\nu$ cannot participate in absorbing frequencies $\nu < \nu_{el}$. The mean electronic-vibrational energy actually acquired by the molecules in absorbing the quanta $h\nu$ has been called the effective excitation energy E_{eff}^* . It equals the difference between the mean electronic-vibrational energy \bar{E}_1^* of the molecules entering the excited state after absorbing the quanta $h\nu$ and the mean vibrational energy \bar{E} of the molecules in the ground state:

$$E_{eff}^* = \bar{E}_1^* - \bar{E}. \quad (3)$$

The difference between the effective excitation energy and the energy of the absorbed quantum

$$\Delta E' = E_{eff}^* - h\nu \quad (4)$$

has been called the selective energy, since it arises from the conversion, selective with respect to the energy E in the ground state, of molecules to the excited state upon absorbing the quanta $h\nu$. It has been found theoretically that the selective energy is

$$\Delta E' = -\frac{\partial}{\partial \frac{1}{kT}} \ln \kappa_\nu \quad (5)$$

Here κ_ν is the absorption coefficient, and k is the Boltzmann constant. Thus, if we know the dependence of the absorption spectra of free molecules on the temperature T , one can determine the selective energy $\Delta E'$ and find E_{eff}^* .

By studying the temperature-dependence of the fluorescence intensity $W(\nu_1)$ over the spectrum, one can gain information on the dependence of the mean energy of the fluorescing molecules $\bar{E}_a^*(\nu_1)$ on the frequency ν_1 in the fluorescence spectrum for different frequencies ν of the absorbed radiation⁴³:

$$-\frac{\partial}{\partial \frac{1}{kT}} \ln W(\nu_1) = \bar{E}_a^*(\nu_1) - \bar{E} - h\nu = \Delta E_a^*(\nu_1). \quad (6)$$

Here \bar{E} is the mean energy of the molecules in the ground state, which is independent of ν and ν_1 . By analogy with (3), the difference

$$\bar{E}_a^*(\nu_1) - \bar{E} = E_{a, eff}^*(\nu_1) \quad (7)$$

has been called the effective excitation energy of the molecules that emit fluorescence at the frequency ν_1 .

Figure 4 shows the spectra of the effective excitation energy E_{eff}^* and the effective excitation energy $E_{a, eff}^*(\nu_1)$

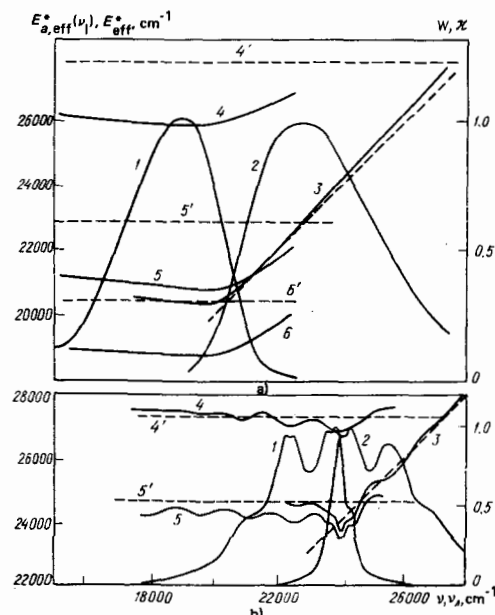


FIG. 4. Effective-energy spectra.¹⁴ a) 3,6-tetramethyldiaminophthalimide (1 - fluorescence spectrum, 2 - absorption spectrum, 3 - effective excitation energy E_{eff}^* of the molecules emitting fluorescence for respectively $\lambda_{exc} = 365, 436, \text{ and } 546 \text{ nm}$); b) perylene (1 - fluorescence spectrum, 2 - absorption spectrum, 3 - effective excitation energy E_{eff}^* of the molecules emitting fluorescence respectively for $\lambda_{exc} = 365 \text{ and } 436 \text{ nm}$). The dotted lines 4', 5', and 6' correspond to the values of E_{eff}^* for the chosen λ_{exc} .

of the fluorescing molecules for vapors of 3,6-tetramethyldiaminophthalimide and perylene. The difference between the effective excitation energy E_{eff}^* and the effective excitation energy $E_{a, eff}^*$ of the fluorescing molecules at a given frequency of exciting radiation arises from the degree of dependence of the radiative and radiationless transitions of the excited molecules on its supply of vibrational energy.

The selective- and effective-energy spectra that have been introduced in spectroscopy supplement the luminescence and absorption spectra and enable one to extract important information on the energetics of complex molecules. In particular, an analysis of them indicates that E_{eff}^* is practically constant in the anti-Stokes excitation region, and differs considerably from the energy $h\nu$ of the absorbed quantum, and that the wings of the electronic absorption and fluorescence bands stem from optical transitions preferentially of the high-energy ("hot") molecules. By analyzing the selective-energy spectra one can draw conclusions concerning the number of electronic-vibrational bands in a complex absorption spectrum and find the frequencies of the pure electronic transitions.^{42,43} For electronic levels above the first excited level, this proves to be the only method. Selective-energy spectra have been calculated theoretically in Refs. 44 and 45.

Up to now we have been treating the spectral-luminescence properties of rarefied vapors (sometimes one uses the term "pure vapors"). If one mixes the vapor of

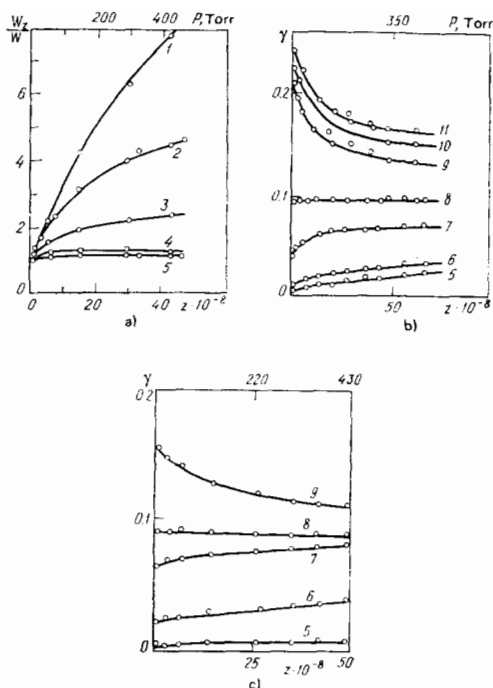


FIG. 5. Effect of pentane on the fluorescence of vapors. 1 - $\lambda_{exc} = 253$, 2 - 265, 3 - 280, 4 - 302, 5 - 313, 6 - 365, 7 - 405, 8 - 436, 9 - 492, 10 - 520, 11 - 546 nm. a) β -naphthylamine¹⁵ (vapor pressure $p = 0.53$ Torr; $T = 423$ K); b) 3,6-tetramethyldiaminophthalimide ($p = 0.59$ Torr, $T = 516$ K); c) 3-dimethylamino-6-aminophthalimide¹⁴ ($p = 0.54$ Torr, $T = 503$ K), z - number of collisions per second of excited molecules with pentane molecules, P - pentane pressure, W_z - the same in the presence of the added gas, γ - absolute values of the quantum yield.

the complex molecules with various chemically inactive added¹⁾ gases at different pressures, one can vary the nature and intensity of the action on the complex molecules within broad limits. That is, one can model the effect of the medium and study the intermolecular interactions. The studies along this line have led to the discovery of the phenomenon of stabilization-labilization of electronically excited polyatomic molecules.^{46, 15, 47, 48}

The interaction of the complex molecules with the added gases enhances the fluorescence excited by radiation having a frequency ν_{exc} greater (curves 1-7 in Fig. 5) than the inversion frequency ν_{inv} . The opposite relationship between these frequencies weakens the fluorescence (curves 9-11). If the excitation is performed with $\nu_{exc} = \nu_{inv}$, the added gas exerts no influence on the fluorescence of the vapor (curve 8). It has been proved that the enhancement of fluorescence involves stabilization (increased stability) of the electronically excited molecules owing to transfer from them to the added molecules of the excess supply of vibrational energy. This diminishes the probability d of radiationless deactivation of the electronically excited molecules. The weakening of fluorescence is due to labilization (decreased stability) of the excited molecules as a

¹⁾Sometimes one uses the term "buffer gas" instead of "added gas". In the spectroscopy of atoms and simple molecules, a buffer gas plays a different role. Therefore it is more correct in the spectroscopy of complex molecules to employ the specially introduced term "added gas".

results of reverse energy transfer, which increases the probability of radiationless deactivation. The inversion frequency is the frequency for which no change in the supply of vibrational energy of the molecules occurs upon excitation. Thus the possibility has been opened up of controlling the degree of stability of the excited state of complex molecules.

Analysis of the stabilization-labilization phenomenon has enabled the development of methods of determining such important characteristics of molecules as the inversion frequency ν_{inv} , the mean amount of vibrational energy ΔE_1^* transferred in a single collision of an excited molecule with a molecule of the added gas, and the accommodation coefficient α , which characterizes the degree of approximation of the system of colliding particles to an equilibrium distribution of vibrational energy among them.

As an example, Table I gives the results of determining ΔE_1^* and α with allowance for the differences in the long-wavelength region between the exciting quantum $h\nu$ and the effective excitation energy E_{eff}^* . For the β -naphthylamine molecule only the stabilization region has been studied. Therefore all the values of ΔE_1^* are positive. In the case of 3,6-tetramethyldiaminophthalimide ($\nu_{inv} = 22950$ cm^{-1}), the negative values of ΔE_1^* correspond to the labilization region, and they characterize the transfer of vibrational energy to the electronically excited molecule from a molecule of the added gas. The table illustrates the dependence of the amount ΔE_1^* of transferred energy and the accommodation coefficient α on the frequency of the radiation exciting the fluorescence, i.e., on the supply of vibrational energy of the molecule being excited, and also on the type of molecule of the added gas. It has turned out that transfer of an excess of vibrational energy ($\nu_{exc} > \nu_{inv}$) by the electronically excited molecule to a molecule of the added gas occurs more efficiently than a compensation of a deficit in it ($\nu_{exc} < \nu_{inv}$). As $|\Delta E^*|$ increases and

TABLE I. Mean amount of vibrational energy ΔE_1^* (in cm^{-1}) transferred in collisions of excited molecules with molecules of added gases, and the accommodation coefficient α .

Added gas	$\lambda_{exc} = 312.9$ nm	302.2	280.4	265.2	253.7	
	$\nu_{exc} = 31930$ cm^{-1}	33890	35600	37680	39400	
	$\Delta E^* = 2730$ cm^{-1}					
	ΔE_1^*	α	ΔE_1^*	α	ΔE_1^*	
β-naphthylamine						
He ($T = 423$ K)	—	—	—	30	0.04	
H ₂ ($T = 423$ K)	—	—	—	30	0.03	
D ₂ ($T = 438$ K)	—	—	—	90	0.06	
N ₂ ($T = 423$ K)	—	—	50	0.07	90	
CO ₂ ($T = 423$ K)	—	—	120	0.12	430	
NH ₃ ($T = 423$ K)	20	0.05	50	0.09	750	
NH ₂ ($T = 423$ K)	20	0.05	50	0.10	160	
CHCl ₃ ($T = 423$ K)	160	0.16	150	0.17	300	
C ₆ H ₁₂ ($T = 423$ K)	60	0.06	120	0.08	1150	
C ₆ H ₁₂ ($T = 463$ K)	50	0.05	100	0.07	330	
C ₆ H ₆ ($T = 423$ K)	—	—	—	300	0.17	
				1150	0.52	
				3000	1.15	
Added gas	$\lambda_{exc} = 520$ nm	492	436	405	365	
	$\nu_{exc} = 20400$ cm^{-1}	20500	22950	24600	27400	
	$\Delta E^* = 2350$ cm^{-1}		0	1750	4460	
	ΔE_1^*	α	ΔE_1^*	α	ΔE_1^*	
3,6-tetramethyldiaminophthalimide						
N ₂ ($T = 516$ K)	-16	0.10	-24	0.15	0	
NH ₃ ($T = 516$ K)	-65	0.26	-75	0.29	0	
C ₆ H ₁₂ ($T = 516$ K)	-135	0.18	-100	0.13	0	
C ₆ H ₁₂ ($T = 608$ K)	-65	0.09	-160	0.21	0	
					40	
					80	
					350	
					400	
					1000	
					950	

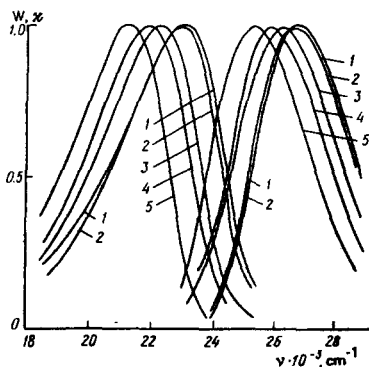


FIG. 6. Fluorescence and absorption spectra of 3-methylaminophthalimide at different ether concentrations and temperatures⁵¹ (the conditions under which the spectra 1-5 were obtained are given in Table II).

the interacting molecules become more complex, the amount $|\Delta E_1^*|$ of energy transferred and the accommodation coefficient α increase, but according to different laws in each electronic absorption band.

Evidently, in treating the degree of approximation of the colliding particles to thermal equilibrium, one must take into account the contribution of the different degrees of freedom (vibrational, rotational, and translational). This problem has been discussed in Refs. 15, 27, 48-51 and in the reviews of Refs. 52-54. The dependence of the effectiveness of the collisions on the mass and degree of complexity of the molecules of the added gas have been studied in Refs. 49-51, 55-57.

The correctness of the interpretation of the phenomenon of stabilization-labilization is confirmed by studies of the effect of added gases on the spectrum^{48, 49, 58-60} and duration⁶¹⁻⁶³ of fluorescence of vapors of complex molecules.

The effect on fluorescence spectra of singlet and triplet absorption of added gases has been studied^{64, 51, 65, 66} as their pressures were varied over broad ranges (from the gas phase through the critical state to the liquid). At low pressures of the added gas, the nature of the variation of the fluorescence^{48, 14} and triplet absorption^{67, 68} spectra corresponds to the direction of energy exchange between the complex molecules and the molecules of the added gas. As the pressure increases, the

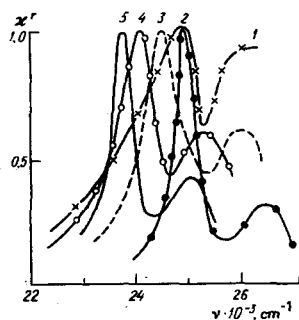


FIG. 7. Triplet-absorption spectra of anthracene at different concentrations of the added medium⁶⁶ (the conditions under which the spectra 1-5 were obtained are given in Table II).

TABLE II.

Compound	Curve in Figs. 6 and 7	State of aggregation	T, K	Added medium	Concentration of the added medium, $C \times 10^{-10}, \text{cm}^{-3}$
3-methylaminophthalimide	1	Vapor	493	—	0
	2	»	493	Ether	0.7
	3	»	493	»	19.5
	4	Liquid	443	»	39.5
	5	»	293	»	58.0
Anthracene	1	Vapor	453	—	0
	2	»	453	Pentane	0.1
	3	»	533	Hexane	3.0
	4	»	533	»	31.0
	5	Liquid	293	»	46.0

added gas begins to act as a continually coupled thermal reservoir that averages all the properties of the molecules that depend on their supply of vibrational energy. Moreover, the internal field of the medium exerts an effect on the complex molecules and shifts the electronic levels. Consequently the fluorescence,^{51, 66} singlet-absorption,^{51, 166} and triplet-absorption^{65, 66} spectra are shifted to longer wavelengths. Transition through the critical state of the added substance is not accompanied by any special features in the variation of the spectra (Figs. 6 and 7; Table II).

Important information on free complex molecules is conveyed by the spectra of temperatures $T^*(\nu_{exc})$ of excited molecules obtained in Refs. 69, 59, and 70. Besides confirming the validity of the conclusion of complete intramolecular redistribution of vibrational energy, these studies have proposed other methods of determining the inversion frequencies and the vibrational heat capacity of the excited molecules.

3. LASING CAPABILITY

One usually understands lasing capability to mean the capability of a material with a certain relationship of concentration (occupancies) of electronic states to amplify light in a certain range of wavelengths, and to generate stimulated radiation when the appropriate conditions have been met.

The problem of lasing capability has been under development already for more than twenty years. It has been discussed in the reviews of Refs. 71-74. In the pumping of the complex molecules whose level diagram is shown in Fig. 8, owing to the occupation of the excited singlet (n_3) and triplet (n_2) states, the effective light-absorption cross section σ_{eff} is expressed in terms of the transition cross-sections σ_{ij} between the states i and j by the relationship⁷⁵:

$$n\sigma_{eff} = n_1(\sigma_{13} + \sigma_{12}) - n_2(\sigma_{21} - \sigma_{24}) - n_3(\sigma_{31} - \sigma_{36}), \quad (7')$$

Here $n = n_1 + n_2 + n_3$ is the total concentration of molecules of the active material. Equation (7') directly implies that amplification ($\sigma_{eff} < 0$) will be absent in materials for which $\sigma_{21} \leq \sigma_{24}$ and $\sigma_{31} \leq \sigma_{36}$. Since the cross-sections σ_{21} and σ_{12} characterize forbidden intercombination optical transitions, under ordinary conditions they are small in comparison with the rest of the cross-sections of allowed transitions entering into (7'). Thus the decisive relationship for the existence of lasing capability of the material is that between the quantities

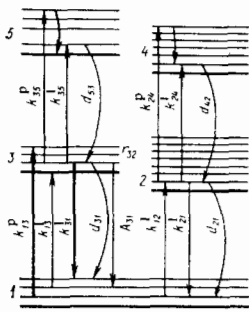


FIG. 8. Diagram of transitions between electronic-vibrational levels of a complex molecule. 1, 3, 5 – singlet states; 2, 4 – triplet states; the $k_{ij}^n = \sigma_{ij}^n N^n$ are the probabilities of stimulated transitions between the states i and j with the cross-section σ_{ij}^n under the action of the pump radiation ($n=p$) or laser action ($n=1$) with the photon flux densities N^n ; d_{ij} is the probability of radiationless spontaneous transitions, and A_{ij} that of radiative spontaneous transitions.

σ_{31} and σ_{35} . If $\sigma_{31} \leq \sigma_{35}$ throughout the region of stimulated emission (fluorescence), then $\sigma_{\text{eff}} > 0$, and the material is incapable of laser action.⁷⁵

We can write the condition for the existence of amplification $\sigma_{\text{eff}} < 0$, employing (7'), in the form:

$$\frac{n_1}{n_3} \sigma_{13} - \frac{n_2}{n_3} \sigma_{24} < \sigma_{21} - \sigma_{35}. \quad (8)$$

Equation (8) implies that not only the condition $\sigma_{31} - \sigma_{35} > 0$ is necessary for obtaining amplification, but also a certain relationship between the occupancies of the states and the cross-sections for absorption of the radiation. It is difficult to satisfy the condition (8) for small n_3 . In addition to the trivial conditions of weak pumping, this can involve a high rate of radiationless decay of the excited state (low quantum yield of fluorescence), high occupancies of the triplet state (n_2), and also large cross-sections for absorption from the ground state or the triplet state. In the region of the stimulated-emission spectrum, the large cross-sections σ_{13} correspond to the region of the short-wavelength tail of the fluorescence spectrum. The interval of wavelengths in which (8) is satisfied is the amplification region.

Figure 9 shows the results of an experimental determination of the amplification region for vapors of POPOP pumped with a nitrogen laser of power 0.4 MW in terms of the amplification of the intrinsic fluo-

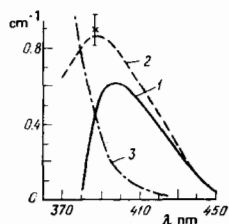


FIG. 9. Wavelength-dependence of the overall amplification (1), the amplification without absorption losses from the ground state (2), and of absorption from the ground state (3) in POPOP vapor at 618 K.

rescence.⁷⁶ As we see from the diagram, the amplification region extends from 380 to 450 nm. Absorption by molecules in the ground state causes the amplification to decline sharply in the short-wavelength region. External losses introduced by impurities, by the optical elements, or in other ways, narrow down the amplification region. Formally, in order to take the external losses into account, one adds the term $\sigma_{\text{loss}} \cdot n/n_3$ to the left-hand side of (8). The amplification region is the outer bound of the frequency-tuning region of the laser.

In order to determine the amplification region of the active medium of a vapor laser, a method has been developed of unsaturated laser action in a highly selective resonator having reflectors in the form of stacks of thin quartz plates. In it the low-intensity laser action practically does not diminish the amplification, but its line spectrum marks the region of amplification and thus facilitates singling it out distinctly.⁷⁷

The rapid increase in the vibrational energy during pumping and laser action of the laser substantially alters in time such spectral characteristics as the probabilities of radiationless conversion, the cross-sections of stimulated transitions, the probabilities of photo-decay, the efficiency of energy exchange in collisions, etc. The role of each of the listed quantities is thereby altered during the laser process. The essential features of the gas phase have required the development of appropriate theoretical models for studying the processes occurring in the active medium, and for prediction of the properties and features of the laser action. In rarefied vapors, in which the time between collisions of molecules of the active material exceeds the duration of the pump pulse, and the molecules maintain their supply of vibrational energy during this time, the equations of balance of occupancies must reflect the successive accumulation of vibrational energy owing to intramolecular radiationless degradation of the energy of the absorbed pump quanta $h\nu_p$ and laser quanta $h\nu_l$ and the differences between these quantities. Taking this into account enables one to calculate not only the dynamics of laser action, but also separately the dynamics of occupation of the singlet excited and the triplet states, and also the time-dependence of the mean supply of vibrational energy in each of these states⁷⁸:

$$\left. \begin{aligned} \frac{dn_1^{k,m}}{dt} &= (A_{31} + \sigma_{31}^1 N^1) n_3^{k,m-1} - \sigma_{13}^p N^p n_1^{k,m}, \\ \frac{dn_2^{k,m}}{dt} &= \sigma_{13}^p N^p n_1^{k,m} - (\sigma_{35}^1 N^1 + \sigma_{31}^1 N^1 + A_{31} + r^{k,m}) n_2^{k,m} - \sigma_{35}^1 N^1 n_3^{k-1,m}, \\ \frac{dn_3}{dt} &= \sum_{k,m} r^{k,m} n_2^{k,m}, \quad n_1 = \sum_{k,m} n_1^{k,m}, \quad n_3 = \sum_{k,m} n_3^{k,m}, \\ n_1 + n_2 + n_3 &= n, \quad k, m = 0, 1, 2, 3, \dots \end{aligned} \right\} \quad (9)$$

Here $r^{k,m}$ is the probability of $S^* \rightarrow T$ conversion of a molecule, in which k pumping photons are radiationlessly scattered, and which has completed m "absorption-emission" cycles that have increased its supply of vibrational energy by $E^{k,m} = kh\nu_p + mh(\nu_p - \nu_l)$. In the absence of internal conversion, one can find the probability $r^{k,m}$ of interconversion from the dependence of

the quantum yield on the supply of vibrational energy (temperature of the excited molecules $T^* = T + E^{h,m}/C_{\text{vib}}$, where C_{vib} is the heat capacity⁷⁸:

$$r^{h,m} = \frac{A_{31}(1-\gamma(T^*))}{\gamma(T^*)}$$

The equations (9), when supplemented by the known equations of balance of laser-action photons, have made it possible to show,⁷⁸ for example a sharp increase in the probability of intercombination conversion of excited singlet molecules in laser action in an active medium having the spectral parameters of POPOP vapor (Fig. 10). However, here the rate of accumulation of triplet molecules varies weakly, owing to the competing increase in stimulated radiative transitions. Characteristically, in the absence of laser action the probability of interconversion of the singlet excited state hardly varies. This specificity of the mechanism of laser action in rarefied vapors is explained by the sharp increase in the supply of vibrational energy of the singlet excited molecules.

If we supplement the model⁷⁸ that we have discussed by taking into account the dependence of the transition cross-sections, the heat capacity, and the internal conversion on the supply of vibrational energy as well as the induced absorption of the pump and light quenching, then we can describe most fully the process of amplification and laser action in rarefied vapors of complex organic compounds.

In simpler models of laser action in vapors, one takes into account only the fundamental feature of the active medium—the growth in the laser process of the supply of vibrational energy of the working molecules, and correspondingly, the increase in the probability of radiationless transitions,^{79,80} or decomposition of the active medium under the action of the pump and laser radiation.^{74,81,82} The action of an added stabilizing gas in the simple model of the active medium of the laser is introduced as an increase in the heat capacity of the active medium^{79,80} or as a more complex process of collisional exchange vibrational energy.⁸³ Despite the incompleteness of the proposed models, they have enabled elucidation of a number of characteristic features of lasers based on vapors of complex molecules.

For a correct estimate of the lasing capability and of the properties of the laser action, it is important to know the nature of the broadening of the spectrum.

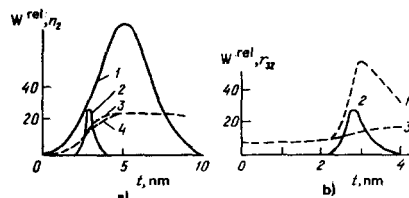


FIG. 10. Time-dependence for a given pump pulse (a, 1) of: a) the laser power (2), the occupancy of the triplet state in the presence of laser action (3) and without it (4); b) the laser power (2) and the probability of intercombination conversion of singlet excited molecules in the presence of laser action (1) and without it (3).

The broadening of the spectrum is a dynamic characteristic that depends on the relationship between the time constant τ_v of the optical process, e.g., the duration of fluorescence or the time interval between successive stimulated transitions of the molecule and the intermolecular τ'' and intramolecular τ' vibrational relaxation times. When $\tau' < \tau'' < \tau_v$, the spectrum in the vapor is broadened homogeneously. Since in a gas phase τ'' is determined by the number z of collisions per unit time, the region of homogeneity of the spectrum is fixed by the condition $\tau_v z \gg 1$ (dense vapor).

One can estimate the inhomogeneity of broadening of the spectra of complex molecules in the gas phase for the conditions $\tau' < \tau_v < \tau''$ (rarefied vapor) by analyzing the selective-energy spectra (see Sec. 2).

However, the selective energy characterizes only the mean energy shift of the ensemble selected in the optical-transition process with respect to the original. An additional characteristic of the inhomogeneity of broadening is the ratio of the energy dispersion in the initial ensemble $\overline{\Delta E^2}$ and in the ensemble selected out in the optical process $\overline{\Delta E_0^2}$, which arises from (5):

$$\theta = \sqrt{\frac{\overline{\Delta E_0^2}}{\overline{\Delta E^2}}} = \sqrt{1 - \frac{1}{C_{\text{vib}}} \frac{u(\Delta E^2)}{uT}} \quad (10)$$

$$= \sqrt{\frac{\overline{\Delta E_0^2}}{\overline{\Delta E^{*2}}}} \sqrt{\frac{C_{\text{vib}}^*}{C_{\text{vib}}}} = \theta^* \sqrt{\frac{C_{\text{vib}}^*}{C_{\text{vib}}}}$$

Here C_{vib} and C_{vib}^* are the vibrational heat capacities of the molecules in the ground state and the excited state, $\overline{\Delta E_0^2}$, $\overline{\Delta E^{*2}}$, and $\overline{\Delta E_{\text{fl}}^2}$ are respectively the energy dispersions of the molecules being excited, of those existing in the excited singlet state, and of those leaving it while emitting fluorescence. The relationship (10) connects the ratio of dispersions of the initial and optically selected distributions in a transition with the absorption (θ) and with the fluorescence or with the stimulated emission (θ^*) under the assumption that a universal relationship is satisfied between the absorption and emission spectra.¹⁴ Since the heat capacities of complex polyatomic molecules in the ground and excited states are practically identical, we have $\theta = \theta^*$. It was found from the experimental data for perylene that $\theta = 0.99$ in the region of the spectrum where $\Delta E'/E \leq 6\%$; for 3,6-tetramethyldiaminophthalimide in the region where $\Delta E'/E \leq 2.5\%$, we have $\theta = 0.99$. For POPOP at the maximum of the absorption band we have $\theta = 0.87$.

Thus inhomogeneity of broadening of the spectra of complex molecules in the gas phase is distinctly manifested, but its degree is not great. The rather high homogeneity of the stimulated-emission spectrum of POPOP vapor has been also shown by direct experiment⁷⁶ (see Sec. 5).

For ultrashort optical processes, e.g., picosecond and subpicosecond pumping or stimulated emission, conditions can be created in which the intramolecular-relaxation time proves to be greater than the time τ_v ($\tau_v < \tau' < \tau''$). Under these conditions, in which the intramolecular redistribution of vibrational energy cannot be completed, the spectra of complex molecules must in many ways approach in nature those of simple

molecules, i.e., must be more strongly inhomogeneously broadened.

In vapors between collisions, the molecules rotate according to the laws of free rotation, in which the energy and the total rotational angular momentum of the molecules are conserved. When an ensemble of free molecules interacts with an anisotropic optical excitation, orientational optically induced anisotropy will arise in it. This anisotropy can be manifested in anisotropic emission (polarized radiation) and absorption (dichroism) by the vapors of complex molecules.⁸⁴⁻⁸⁸

A theoretical analysis of the relaxation of induced anisotropy conducted in the rigid-molecular-top approximation has shown that the induced anisotropy for free excited molecules declines in a time of the order of several rotation periods to a steady-state value that persists until collisional reorientation.⁸⁴⁻⁸⁶ The fast phase of orientational relaxation is significant only for picosecond time intervals. Hence, under conditions of nanosecond lifetimes of the excited state, the anisotropy is governed by its steady-state, collisionless component. The dichroism of the cross-section for stimulated transition of an excited molecule D_0 caused by this collisionless component in the simplest case of a rigid symmetric top is associated with the anisotropy parameter of the moment of inertia tensor $\kappa = 1 - (I_z/I_x)$ (I_z and I_x are the components of the moment-of-inertia tensor parallel and perpendicular to the axis of the top) by the relationship⁸⁴:

$$D_0^{-1} = \frac{1}{3} + \frac{4\kappa^2}{3 \left[(\kappa-3)(8\kappa-9) - 3(9-\delta\kappa)(1-\kappa) \frac{\text{arctanh } \sqrt{\kappa}}{\sqrt{\kappa}} \right]} \times \frac{1}{\left\{ (d_{00}^2(\beta))^2 + \delta(\kappa) \sum_{\lambda_1, \lambda_2, \dots} (d_{\lambda_1 \lambda_2}^2(\beta))^2 \right\}} \quad (11)$$

Here $d_{\lambda_1 \lambda_2}^2(\beta)$ is the real component of the Wigner function, $\delta(\kappa)$ is a delta function, and β is the angle between the axis of the top and the direction of the transition dipole moment. The magnitude of the steady-state component of the dichroism of the transition cross-section for a rigid asymmetric top lies within the range from 9 to 14% and depends on the form of the ellipsoid of inertia of the molecule and the orientation of the dipole moments of the transitions involving absorption and emission with respect to one another and to the ellipsoid of inertia.^{86, 87} Thus, first, the amplification coefficient in rarefied vapors is dichroic, and second, owing to the difference in the general intramolecular orientations of the dipole moments of transitions involving excitation, emission, and induced absorption, the nature and magnitude of the anisotropy of amplification must vary in time in correspondence with the change in the dichroism of the cross-sections entering into the condition (7'). Collisional perturbations destroy the optically induced anisotropy and thereby also the induced dichroism of amplification. The dichroism of the transition cross-section for z collisions per second (D_z) and without collisions (D_0) are connected by the relationship⁸⁸

$$D_z = \frac{D_0}{1 + \left(1 - \frac{D_0}{3}\right) \tau z s} \quad (12)$$

Here s is the probability that a collision will destroy the anisotropy, which is close to unity for large molecules.

Thus, inhomogeneous broadening owing to orientational optically induced anisotropy must exist in vapors of complex molecules. The results of studying the polarization properties of the generated radiation are discussed in Sec. 5.

4. ACTIVE GAS-PHASE MEDIA

When one is selecting complex organic materials to obtain laser action in the gas phase, a number of evident requirements must be satisfied in addition to the conditions presented in Sec. 3. The materials must be sufficiently volatile that the concentration of the vapors amounts to 10^{16} – 10^{18} cm⁻³ at temperatures not exceeding the thermal-stability limit (600–800 K). Volatility is low in compounds that form specific intermolecular bonds like the hydrogen bond in the solid or liquid state. Volatility of organic compounds declines with increasing molecular weight. Therefore the search for materials having a molecular weight above 400 that yield a concentration of pure vapor necessary for laser action is a difficult problem. Employment of added gases facilitates solving this problem. They not only diminish the supply of vibrational energy of the excited molecules owing to stabilization (see Sec. 2), i.e., decrease the overheating of the excited molecules, but also, at very high pressures (tens of atmospheres), they increase the concentration of the active vapor.⁸⁹ Of course, the added gases must not absorb the pump or laser radiation. One must strive to keep the temperature of the vapor low, not only to avoid thermal decomposition of the molecules, but also to increase the quantum yield, since in most cases γ declines with increasing T (see Sec. 2). Employment of added gases enables one to obtain laser action in vapors at temperatures 50–100° lower, and also laser action from materials in the gas phase whose pure vapors do not lase.

Since laser action requires considerable power densities of the pump radiation, the molecules in vapors, just as in solution, must be photochemically stable.

Existence of laser action in a given compound in solution is far from implying its ability to lase in the gas phase. In going to the gas phase, lasing capability is lost in all materials when it is due to specific interactions with the solvent (ionic forms, complexes, solvates, etc.). Transition to the gas phase, even of materials that lase most effectively in neutral solvents, can lead to loss of lasing capability. The converse is also true. This arises from the difference in spectral characteristics (stimulated emission spectra, singlet and triplet absorption spectra) in the two states of aggregation.

When the requirements listed above for obtaining laser action are satisfied, the spectral characteristics of the vapor must satisfy the lasing condition (8).

According to the literature data, more than 200 organic compounds have been examined for the exis-

TABLE III. Active materials of vapor lasers.

Compound	λ_1^{\max} , nm	Reference
1. 2-(<i>p</i> -methoxyphenyl)-benzoxazole (<i>p</i> -methoxy-PBO)	333.5; 344	91
2. <i>p</i> -terphenyl	335; 345	91
3. 1,4-di-[1-(4-ethylphenyl)]-benzene (<i>p,p'</i> -diethyl- <i>p</i> -terphenyl)	335.5; 342.5	92
4. 2-(<i>p</i> -butoxyphenyl)-benzoxazole (<i>p</i> -butoxy-PBO)	337.5; 351.5	92
5. 2-phenylbenzoxazole (PBO)	338; 340	91
6. 2-(<i>p</i> -hexadecyloxyphenyl)-benzoxazole (<i>p</i> -hexadecyloxy-PBO)	339; 355	92
7. 2-(<i>p</i> -tolyl)-benzoxazole (<i>p</i> -methyl-PBO)	340	91
8. 1,4-di(<i>p</i> -phenylethynyl)-benzene (PEBEP)	349.5	92
9. 2-biphenylbenzoxazole (<i>p</i> -phenyl-PBO)	350.2; 351.4	91
10. 2,5-diphenylfuran (PPF)	356	93
11. 2-(<i>p</i> -dimethylaminophenyl)-benzoxazole (<i>p</i> -dimethylamino-PBO)	357.6	91
12. 2-(α -naphthyl)-benzoxazole (α -NBO)	362.4	94
13. <i>p</i> -quaterphenyl	364	95
14. 2-(<i>p</i> -methoxyphenyl)-5-(<i>p</i> -carboxyphenyl)-1,3,4-oxadiazole	367	95
15. 2-phenyl-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole	369	95
16. β -dinaphthyleneoxide	370	94
17. 2,5-diphenyloxazole (PPO)	370	94
18. 2-(<i>p</i> -methoxyphenyl)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole	371; 383	95
19. 2-biphenyl-5-(<i>p</i> -dimethylaminophenyl)-1,3,4-oxadiazole	376; 388	95
20. 1,4-di(2-benzoxazolyl)-benzene (BOPOB)	378	98
21. 2-(<i>p</i> -biphenyl)-5-phenyloxazole (BPO)	382	98
22. 2,5-di(<i>p</i> -dimethylaminophenyl)-1,3,4-oxadiazole	382; 394	95
23. 2,5-di(<i>p</i> -aminophenyl)-1,3,4-oxadiazole	383; 397	95
24. 2-(<i>p</i> -methoxyphenyl)-5-(phthalanhydrido)-oxadiazole	385; 409	95
25. 1,4-di[(5-methyl)-benzoxazol-2'-yl]-benzene (dimethyl-BOPOB)	386	97
26. 2,5-biphenyloxazole (BBO)	390	97
27. 2-(α -naphthyl)-5-phenyloxazole (α -NPO)	391	95
28. 2-(<i>p</i> -dimethylaminophenyl)-5-(<i>p</i> -carboxyphenyl)-1,3,4-oxadiazole	393	95
29. 1,4-di[2-(5- <i>p</i> -tolylloxazolyl)]-benzene (TOPOP)	393	4
30. 2-biphenyl-5-(<i>p</i> -naphthyl)-oxazole (BNO)	395	94
31. 1,4-di[2-(5-phenyloxazolyl)]-benzene (POPOP)	398	1
32. 2,5-di[5-(<i>tert</i> -butyl)-2-benzoxazolyl]-thiophene (BBOT)	407	94
33. 1,4-di[2-(4-methyl-5-phenyloxazolyl)]-benzene (dimethyl-POPOP)	410	5
34. 1,2-di[2-(5-phenyloxazolyl)]-ethylene (BOEOB)	423	94
35. 1,4-di[2-(5- <i>p</i> -aminophenylloxazolyl)]-benzene (diamino-POPOP)	425	94
36. perylene	430	98
37. 9,9'-dianthryl-4,4'-di(xylyl-3''A'')	441	94
38. 1,4-di(1-phenyl-5'-(2,4-dimethoxyphenyl)- Δ^2 -pyrazolonyl-3')-benzene	457	94
39. 1,2-dimethyl-3-phenylimidazotriazine (imitrine 3)	471	99
40. coumarin 153	481	100
41. 7-diethylamino-3-(2'-benzoxazolyl)-coumarin	506	100
42. Diisobutyl 3,9-perylene-dicarboxylate (defectol)	518	94
43. 3-(2'-benzothiazolyl)-7-diethylaminocoumarin (coumarin 6)	520	100
44. 3-(2'-benzimidazolyl)-7-diethylaminocoumarin (coumarin 7)	520	99
45. 1,2-dimethyl-3,4-diphenylimidazotriazine (imitrine 9)	526	101
46. 3-[2-(<i>N</i> -methyl)-benzimidazolyl]-7-diethylaminocoumarin	526	93
47. 1,8-naphthylene-1',2'-benzimidazole	540	94
48. Benz[<i>f</i>] fluoranthene oxide	542	94
49. 3,6-diamino- <i>N</i> -methylphthalimide		
50. 3,6-diaminophthalimide	520-570	102
51. 3,6-dimonomethylamino- <i>N</i> -methylphthalimide		
52. 3,6-tetramethyldiamino- <i>N</i> -methylphthalimide		
53. 1,2-di(5-methyl-2-benzoxazolyl)-ethylene	-	97
54. 1,2-di(2-benzoxazolyl)-ethylene	-	97

tence of laser action in the gas phase. More than 50 substances proved to be capable of lasing in the vapor. Pumping was carried out with second-harmonic radiation of a ruby laser ($\lambda_p = 347$ nm), a nitrogen laser ($\lambda_p = 337$ nm), the third and fourth harmonics of a neodymium laser ($\lambda_p = 357$ nm and 266 nm), and the radiation of an excimer laser ($\lambda_p = 308$ nm). The tunable radiation of lasers based on solutions of complex organic compounds was also used for pumping the vapors. Laser action in vapors has recently been obtained with lamp pumping.⁹⁰

Table III gives the names of materials that lase in the gas phase, the wavelengths of the maxima of the generated bands λ_1^{\max} , and the literature sources in which the laser action was reported. Sometimes one observes two-band laser action. The compounds are arranged in order of increasing λ_1^{\max} of the short-wavelength band. In a number of cases laser action was obtained upon mixing an added gas with the vapors.

Upon examining the structural features of the compounds presented in Table III, we note the absence of polyenes and polymethines and molecules related to

them in chain structure, owing to the nonrigidity of the structure. Substances that lase in the gas phase are either polycyclic condensed nuclei with or without substituents (perylene, coumarins, naphthylenebenzimidazoles, phthalimides, imidazotriazines, etc.) or most often chains made of mono- or bicyclic units of the type of benzene, oxazole, oxadiazole, furan, benzoxazole, benzimidazole, thiophene, etc.

We see from Table III that the region of wavelengths now covered by vapor lasers stretches from 333 to 570 nm, with the greater number of compounds lasing in the ultraviolet.

As compared with solutions, the lasing region is restricted on the long-wavelength side. This arises from the fact that, as a rule, displacement of a spectrum to longer wavelengths involves enlarging the system of conjugated π -electrons, making the molecule more complex, and increasing its molecular weight. The fraction of these compounds lightest in molecular weight (for a given chain of conjugated π -electrons) has a nonrigid structure and fluorescences in the vapor with a low quantum yield. Rotational isomers can also occur that are not capable of laser action. Compounds with a rigid structure that fluoresce in the long-wavelength region usually have very high molecular weights, provided that the fluorescence capability does not arise from specific intermolecular interactions.

Varied points of view have been expressed on progressing into the shorter-wavelength region of the spectrum using vapor lasers. Thus, the conclusion has been drawn¹⁰³ that it is impossible to obtain laser action in complex molecules in the region of wavelengths shorter than 300 nm. This was based on an analysis of oscillator strengths of transitions with absorption from the ground and first excited singlet states theoretically calculated for a group of the simplest diaryls and condensed bicyclic compounds: biphenyl, bipyridyls, benzimidazole, indazole, etc. The converse conclusion¹⁰⁴ has been drawn from theoretical calculations of the spectral-luminescence characteristics of benzoxazoles.

5. PROPERTIES OF THE GENERATED RADIATION

An important property of lasers based on complex molecules is the tunability of the generated radiation over a broad frequency range. For example, the wavelength λ of the radiation generated by lasers based on vapors of POPOP⁷⁶ and TOPOT⁷⁷ can be tuned over

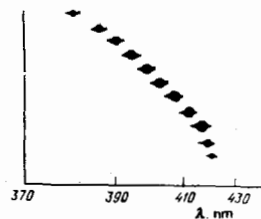


FIG. 11. Tuning of the wavelength of the radiation generated by a TOPOT-vapor laser by using a diffraction grating.

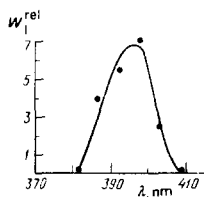


FIG. 12. Dependence of the laser power of a POPOP-vapor laser on the wavelength when tuned with a diffraction grating.⁷⁶

ranges respectively of 25 and 40 nm with a diffraction grating serving as one of the mirrors of the resonator (Figs. 11, 12). The output power of the laser declines at the edges of the tuning region. At the maximum of the curve, the output power of a POPOP vapor laser in a 1-nm band amounts to 90% of that of the broad-band laser action obtained upon replacing the diffraction grating with a nonselective mirror. This high degree of spectral concentration confirms the conclusion drawn from analyzing the selective-energy spectra that the inhomogeneity of broadening of the spectra of free complex molecules is slight (see Sec. 3).

Laser action has been obtained in POPOP vapor with pentane as the added gas ($C = 10^{19} - 4 \times 10^{21} \text{ cm}^{-3}$) by using distributed feedback (DF).¹⁰⁵ In this case the spatially periodic grating was of resonance phase-amplitude type.¹⁰⁶ The DF-laser enabled tuning the wavelength of the generated radiation over a range of about 50 nm by varying the angle of incidence of the pump beam on a prism serving as one of the walls of the cuvette. A change in the concentration of the added gas is accompanied by a shift in the tuning region. The spectral width of the laser radiation is close to the width of the pump line.

One can tune the frequency of the radiation of a laser based on vapors of complex molecules by varying the pressure of the added gas.^{4, 6, 107} Figure 13 shows the laser spectra of vapors of POPOP and TOPOT. The second harmonic of a ruby laser in the longitudinal variant was used as the pump. The vapors of these

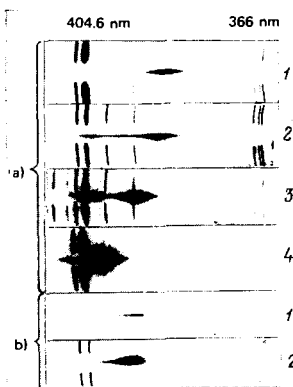


FIG. 13. Emission spectra generated by vapors.⁴ a) POPOP (1 - rarefield vapors, $T = 543 \text{ K}$, $p = 0.5 \text{ Torr}$; 2-4 - vapor with pentane, $T = 513 \text{ K}$, 2 - $C = 1.3 \times 10^{20}$, 3 - 6×10^{20} , 4 - $4 \times 10^{21} \text{ cm}^{-3}$); b) TOPOT (1 - rarefield vapor, $T = 573 \text{ K}$, $p = 1.0 \text{ Torr}$, 2 - vapor with pentane, $T = 553 \text{ K}$, $C = 6 \times 10^{19} \text{ cm}^{-3}$).

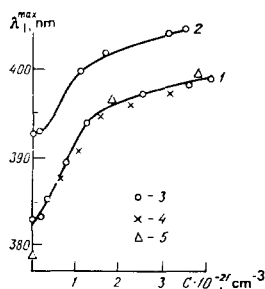


FIG. 14. Dependence of the wavelength of the maximum of the laser band on the concentration C of pentane for vapors of POPOP (curve 1, $T = 513 \text{ K}$) and TOPOT (curve 2, $T = 528 \text{ K}$). 3 - excitation with nanosecond pulses; 4 - the same with picosecond pulses; 5 - wavelength of the maximum of the 0-1 band of the fluorescence spectrum (POPOP).

materials without an added gas at temperatures 513-573 K generate bands with peak wavelengths λ_1^{max} of respectively 383 and 393 nm, with a half-width of about 4 nm. A shift of the bands to longer wavelengths occurs with increasing concentration (pressure) of the added gas. When the pressure of pentane is 7 atm, one observes (Fig. 13a, spectrum 2) two-band laser action in POPOP ($\lambda_1^{\text{max}} = 383$ and 403 nm). The long-wavelength displacement of the bands involves the fact that the absorption and fluorescence spectra, and hence also the stimulated-emission spectra, are shifted to longer wavelengths with increasing pressure of the added gas (see Sec. 2, Fig. 6). The shift of λ_1^{max} into the long-wavelength region has been traced⁴ as the active medium was gradually changed from the rarefied vapor through the critical state into the solution.

Figure 14 illustrates the shift of the peaks of the laser bands of POPOP and TOPOT and of the band of the 0-1 fluorescence spectrum of POPOP as a function of the concentration of pentane. A parallel red shift in these bands occurs with increasing concentration of the added gas. Apparently the maxima of the band do not coincide for the rarefied vapors, owing to the difference in the temperatures of the vapors at which the laser and fluorescence spectra were obtained.

The data discussed above pertain to laser action of nanosecond duration. In Ref. 108 picosecond laser action was obtained for the first time in vapors of complex molecules. Studies have shown^{109, 110} that the picosecond laser spectra undergo an analogous red shift with increasing concentration of the added gas (see Fig. 14). In the case of fluorescence or laser action of nanosecond duration, the excited molecules undergo collisions of the order of hundreds within their lifetime, even at pressures of the added gas of 10 atm. If the red shift of the laser spectra of nanosecond duration involves the collisional interaction of the added gas with the active molecules, it should not have been observed in laser spectra of picosecond duration. This implies that, at high pressures of the added gas, intermolecular interactions involving perturbation of the electronic state of the active molecules can be realized in a time less than 20 ps. That is, starting at pressures of the added gas of the order of several atmo-

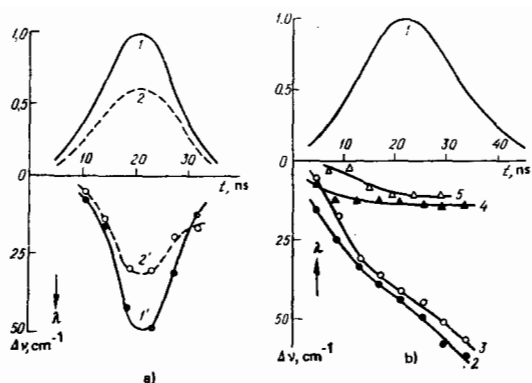


FIG. 15. Time-dependence of: a) the laser power (1, 2) and the frequency shift of the maximum of the laser spectrum (1', 2') of POPOP vapor for a maximum pump power density of ~ 30 (1, 1') and ~ 17 MW/cm² (2, 2'); b) laser power (1) and frequency shift of the maximum of the laser spectrum for solutions of POPOP in hexane (2), pentane (3), toluene (4), and dimethylformamide (5).¹¹²

spheres, the active molecules exist under a quasistatic influence of the medium.

Considerable influence is exerted on the position and shape of the spectrum of the generated radiation by the spectrum of the triplet state, which gives rise to losses selective in frequency. The interrelation of these spectra has been studied in Refs. 65 and 66.

The duration of the laser pulse lies close to that of a nanosecond pump pulse,³ whereas with pump durations of tens of nanoseconds the laser pulse proves to be considerably shorter than the pump pulse.^{5, 112} This is also confirmed by the theoretical calculations^{78, 79} (see Fig. 10). This mainly involves an increase in the internal losses due to the triplet state, with decline in the concentration of singlet molecules owing to interconversion caused by the accumulation of an excess of vibrational energy in the molecules.^{74, 78, 79, 112} Stabilization by the added gas substantially prolongs the duration of laser action.^{79, 111} For example, the upper limit of duration of laser action in POPOP vapor is 93 ns, and 105 ns in TOPOT vapor.⁷⁴

The time development of the pulse has been studied in Ref. 112. In contrast to the POPOP-solution laser, the radiation frequency of which increases monotonically during laser action owing to relaxation effects¹¹³⁻¹¹⁵ (Fig. 15b), in the POPOP-vapor laser one observes a

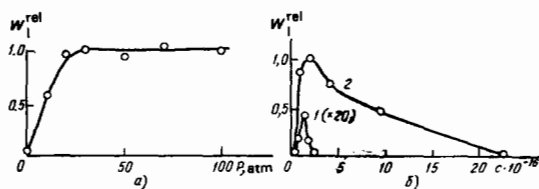


FIG. 16. Dependence of the power of the radiation generated in TOPOT vapor: on the pentane pressure P (a), and on the intrinsic concentration of the vapor (b) at a pentane concentration $C=0$ (1) and $C=1.2 \times 10^{21}$ cm⁻³ (2). $T=573$ K (a and b, 2), 623 K (b, 1).¹¹⁶

frequency shift that is practically the mirror image of the laser pulse (Fig. 15a). The amplitude of the reversible displacement depends on the pump power, while the instant of maximal shift coincides with an accuracy up to 2 ns with the maximum of the laser pulse. At the attained levels of laser field density in the resonator, the observed spectral kinetics in POPOP vapor is explained by the dependence of the amplification contour on the excess vibrational energy of the radiating molecules and the variation in the concentration of active centers.

The laser power in vapors substantially increases with increasing P of the added gas, and the threshold declines (Fig. 16).¹¹⁶ The data presented in the diagram were obtained with longitudinal pumping of the vapor with the second harmonic of a ruby laser. We see from Fig. 16a that the stabilizing action of the added gas saturates at a pentane pressure of about 20 atm, which corresponds to a time between collisions of tens of picoseconds. At this pressure the active medium is still almost 20 times less dense than the solution. This enables one to reduce by the thermo-optical losses by an order of magnitude with a high efficiency of laser action. The lowering of the laser threshold by adding pentane at 50 atm (Fig. 16b) considerably extends the range of concentrations of TOPOT at which one can obtain laser action.

The shortening of the duration of laser action caused by the rapid accumulation of excess vibrational energy by the singlet molecules and the decline in power are the reason why the efficiency in pure vapors is small, as a rule not exceeding 10%.^{76, 81} In order to increase the efficiency of laser action in pure vapors, one can shorten the duration of the pump pulse to an interval of time in which the excess vibrational energy in the molecules is still not so large as to affect the characteristics of laser action. However, the energy of the generated radiation declines thereby.⁸⁰ Employment for stabilization of efficiently acting added gases and optimization of the pump wavelength, the resonator parameters, and the pump density have made possible an energy efficiency of POPOP-vapor lasers of 22.8%,¹¹⁷ for TOPOT 21.8%, and for coumarin-6 12%.¹¹⁸

Table IV¹¹⁷ enables us to compare the parameters of the POPOP-vapor laser with the addition of 35 atm of diethyl ether with those for solutions of POPOP diethyl ether and dioxane when pumped with the third and fourth harmonics of a neodymium laser. We see that the efficiency for the solutions is higher, and the laser thresholds for the vapor do not exceed those for the solutions. However, in the gas phase we observe a more rapid growth of the losses during the laser pulse. For the vapor, the power efficiency at the onset of the laser pulse exceeds by 14-90% the mean value, whereas for the solutions this increase is no more than 5%. The laser energy thresholds of the POPOP vapor laser are not correlated with the efficiency (Fig. 17). When one excites with $\lambda_p = 266$ nm, despite the low efficiency, the laser threshold is close to that with long-wavelength pumping. This is explained by a similarly low level of internal losses at the initial instant of laser

TABLE IV. Efficiency of laser action in POPOP.*

Working medium	T, K	$\sigma_{31}^p/\sigma_{35}^p$	$R_1, R_2, \%$	λ_{pump}, nm	$W_{thr}, MW/cm^2$	$\Delta\lambda_1, nm$	λ_1, nm	$W_{pump}^{max}, MW/cm^2$	Initial efficiency, %	Max. efficiency, %	Differential efficiency, %	Quantum efficiency, %
1. vapor 2. with ether	488	3.4	94; 94	355	0.18	389-408	394	3	8.2	7.2	7.6	8.4
	463	3.3	96; 31	355	0.65	384-415	388	5.4	12	11.4	12.5	13.7
	477	2.11	93; 7	355	1.5	391-403	396	6.7	28	22.8	31	33.4
	471	3.7	94; 94	266	1.8	394-399	396	5.6	11.5	11.7	1.3	2
	463	3.7	68; 4	355	1.0	—	—	5.6	2.5	1.7	2.3	3.5
6. Solution in dioxane	—	5.11	84; 4	355	0.5	415-421	418	10	40	38	41	47
7. Solution in ether	—	5.11	84; 4	355	0.5	418-416	412	5	31	50	53	61

*Here R_1 and R_2 are the reflection coefficients of the mirrors of the resonator, W_{thr} is the threshold pump power density, $\Delta\lambda_1$ is the width of the band of laser radiation, W_{pump}^{max} is the maximum pump power density, the initial efficiency is the power efficiency at the onset of the pump pulse, the mean efficiency is the ratio of the laser power to the pump power, the differential efficiency is the efficiency from the slope of the curves in Fig. 17, and the quantum efficiency is the integral efficiency of transformation of the number of absorbed pump photons into laser photons.

action, when an excess of vibrational energy has not yet been able to accumulate.

Besides the mean energy and quantum efficiencies, one can distinguish the power efficiency, the internal efficiency, the differential efficiency (efficiency defined by the slope), and various limiting efficiencies.^{74, 117} The upper limit on the efficiency of a laser is the quantum yield of stimulated emission. When account is taken of all the channels of loss of molecules from the excited singlet state and of the quantum yields of light quenching in absorption by singlet excited molecules of the pump radiation γ_{quench}^p and that of the laser action γ_{quench}^l we obtain

$$\text{Quantum efficiency} = \frac{\sigma_{31}^l - \sigma_{35}^l}{\sigma_{31}^l + \sigma_{35}^l \gamma_{quench}^l + \sigma_{35}^p \frac{N^p}{N^l} \gamma_{quench}^p + \sigma_{31}^p \frac{N^p}{N^l} + \frac{1}{\tau_3 N^l}} \quad (13)$$

When $1/\tau_3 N^l, \sigma_{31}^p (N^p/N^l), \sigma_{35}^p \gamma_{quench}^p (N^p/N^l) \ll \sigma_{31}^l$, then we have

$$\text{Quantum efficiency} = \frac{\sigma_{31}^l - \sigma_{35}^l}{\sigma_{31}^l + \sigma_{35}^l \gamma_{quench}^l} \quad (14)$$

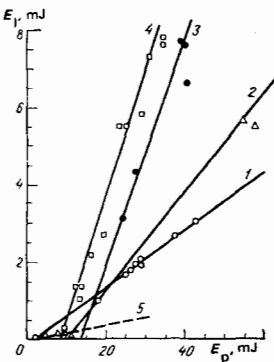


FIG. 17. Dependence of the laser energy E_l of POPOP vapor on the pump energy E_p .¹¹⁷ The numbers of curves 1, 2, 3, and 5 are the numbers of experiments in Table IV; curve 4 was obtained under the conditions of experiment 3 of Table IV, but with a power density increased by a factor of two.

When $\gamma_{quench}^l = 0$, this reduces to a known expression.⁷⁴

POPOP vapor shows intense light quenching, which is lowered by an added gas.^{119, 120} Since the ratio $\sigma_{35}^l/\sigma_{31}^l$ for POPOP vapor amounts to 0.8,^{111, 121, 80} then, according to (14), the quantum efficiency for $\gamma_{quench}^l = 0$ is 0.2, while the energy efficiency for $\lambda_p = 337$ nm, $\lambda_1 = 383$ nm is 0.17. If $\gamma_{quench}^l = 1$, then the quantum efficiency is 0.11, while the efficiency is 0.1, as has been observed for the pure vapor at low pressures of the added gas. In addition to stabilization, high pressures of added gases exert an appreciable influence on the spectral-luminescence characteristics of the material. Thus, ether vapor at 35 atm increases twofold the limiting amplification cross-section ($\sigma_{31} - \sigma_{35}$). According to (14), for $\gamma_{quench}^l = 0$, this yields a quantum efficiency of 0.47.¹¹⁷

The active medium of vapor lasers has an important advantage—greater homogeneity than a solution, with lower losses. The homogeneity of the active medium substantially reduces the divergence of the beam in vapor lasers.

Figure 18 shows the data on the dependence of the divergence of the laser beam on the pump density for lasers based on POPOP vapor and on its solution in toluene when pumped with a nitrogen laser with an energy of 50 mJ per pulse.¹²² The divergence of the radiation of the solution laser for the two bases of the resonator is higher and it increases with increasing pump power density, whereas it is constant for the vapor laser. Even at the threshold, the divergence in the solution laser is 2-3 times greater than in the vapor laser, and 4-6 times greater at a pump density of 170 MW/cm². At equal powers, the vapor laser has 10-30 times greater radiation density.

A laser model has been developed in which the active medium (mixture of POPOP and eicosane vapors is self-circulating in an "evaporation-condensation-evaporation" cycle.¹²² The pressure of eicosane in the optical part of the laser attained 600 Torr. Pumping was performed by a nitrogen laser ($\lambda_p = 337$ nm) of 1-MW power. At a pulse-repetition frequency of 10-30 Hz, the lasing power of this laser decline by half after 3×10^6 pulses.

Anisotropy of an ensemble of free excited molecules is manifested (see Sec. 3) in dichroism of the amplification coefficient. In the presence of dichroism of amplification, the threshold properties of the process of generation of stimulated emission involve differing survival of modes having different polarizations. This

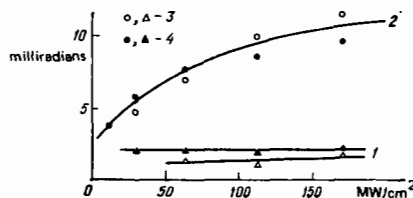


FIG. 18. Divergence of the radiation of a POPOP laser as a function of the pump power density.¹²² 1 - vapor, 2 - solution in toluene. Length of resonator = 20 (3) and 8 mm (4).

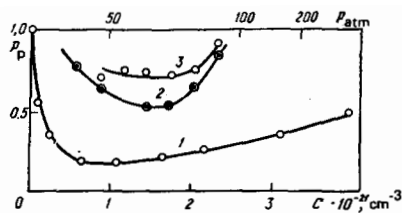


FIG. 19. Dependence of the degree of polarization of emission of nanosecond (1) and picosecond (2, 3) duration, generated in POPOP vapor, on the concentration of the added gas pentane. 1, 2 - concentration of POPOP = 2×10^{17} cm $^{-3}$, 3 - 7×10^{17} cm $^{-3}$, $T = 513$ K.

leads to enhancement of the selective action of the dichroism of the amplification coefficient, and the degree of polarization of the stimulated emission of gaseous active media can attain large values.^{84, 87, 110} Figure 19 shows the degree of polarization P_p of radiation generated by POPOP vapors with nanosecond (curve 1) and picosecond (curves 2 and 3) duration as a function of the concentration of the added gas pentane. The picosecond laser action was excited with a single pulse of linearly polarized radiation of the second harmonic of a ruby laser of duration about 20 ps, and the nanosecond laser action with a 2.5 ns pulse of linearly polarized radiation of a nitrogen laser. As the pentane pressure P was varied, the concentration of active centers remained constant. The degree of polarization P_p of pico- and nanosecond laser action depends strongly on the concentration C of pentane. The emission of nanosecond laser radiation in rarefied vapors has a maximum value $P_p = 1$ (see curve 1). Addition to the POPOP vapor of pentane at relatively low pressures strongly depolarizes the generated radiation. This is associated with impact disorientation of the active molecules. At large C , the degree of polarization begins to rise, perhaps owing to the increased viscosity of the medium. The fact that P_p for picosecond laser action exceeds that for nanosecond laser action is explained by the fact that the excited molecules interact for a shorter time with the surrounding medium in picosecond laser action. An increase in the POPOP concentration increases the degree of polarization of picosecond laser action (curve 3). This involves an increase in the dichroism of the amplification coefficient of the active medium.

Thus, study of the polarization of the radiation generated by vapors has made it possible to trace a continuous transition from depolarization due to impact disorientation of the active molecules to an increase in the degree of polarization at very high pressures of the extra gas owing to increased viscosity of the medium.

The review that we have presented implies that lasers based on complex molecules in the gas phase have a number of valuable properties. The obtaining of laser action in vapors of complex organic compounds has opened broad potentialities for studying the properties of free complex molecules and intermolecular interactions. Interest in these lasers is not weakening. There are grounds for expecting laser action in complex molecules with electrical excitation as well.

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