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Excited state proton transfer dye lasers

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Abstract. Reactions of proton phototransfer in organic compounds and photochemical lasers based on these reactions are considered. A principle of operation of a photochemical laser is described. Selection criteria of acid-base systems to serve as active media in photochemical lasers are determined. A list of acid-base laser systems, conditions of their fabrication, and emission characteristics are collated. Specific losses in photochemical lasers are analysed. Methods of expanding the spectral range of tunable emission in the photochemical lasers are described.
The bibliography includes 134 references.

I. Introduction

Laser radiation is the emission of light upon transition of excited molecules to the ground electronic state. The emission of light is stimulated by an external electromagnetic field under the conditions of an optical resonator. The phenomenon of light amplification by the effect of stimulated radiation emission is called laser action, which stems from the abbreviation of the expression 'light amplification by stimulated emission of radiation'. Among numerous types of lasers used in the different fields of science and technology, those based on organic compounds (dyes) occupy a special place.[1] The advantages of the dye lasers over the others include the possibility of fine and continuous tuning of the laser radiation wavelength over a wide range (up to 100 nm), a high coefficient of emitted light amplification by the active medium, and the possibility of obtaining multiband radiation.[2] The latter is employed for the solution of a number of practically important problems (in particular, atmospheric probing, multipulse multicolour spectroscopy, *etc.*). Dye lasers are the main source of pico- and femtosecond pulses.[3] The possibility of achieving the femtosecond pulses is determined by the existence of highly effective amplification medium with a broad range of laser radiation tuning. A significant increase in the spectral range of tuning, up to 220 nm,[4] can be attained in the dye lasers with adiabatic photochemical reactions.

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A dye produces stimulated light emission in the spectral range of its fluorescence. The excited dye molecules may be generated in two ways: (1) as a result of direct excitation from the ground state through absorption of a photon or under electron impact; (2) as a result of an adiabatic photochemical reaction (photochemical laser). The regularities of radiation for the first type of dye laser are considered in numerous reviews and original papers.[5–11] The reactions of electron and proton phototransfer belong to the best studied adiabatic photochemical reactions of organic compounds.[12] The electron phototransfer reactions result in the formation of excited charge-transfer complexes (exciplexes).[13] The radiative transition in exciplexes is partially forbidden, therefore, the generation of laser radiation by the products of electron phototransfer reactions and, consequently, photochemical lasers based on these reactions are hardly probable.[14] The radiative transition in excited products of numerous proton phototransfer reactions is permitted.[15] These excited products are the potential generators of the laser radiation.

II. An operation scheme for a photochemical laser based on proton phototransfer reactions

Proton phototransfer reactions in organic compounds occur according to static and dynamic mechanisms. In the former case the reaction occurs 'instantaneously' in the excitation of a hydrogen-bonded complex of a proton donor with acceptor, which is formed in the ground state.

$$(A{-}H\cdots B) \longrightarrow (A{-}H\cdots B)^* \longrightarrow (A^- \cdots H{-}B^+)^* . \qquad (1)$$

In the latter case, the interaction between the excited molecule of an aromatic compound and a molecule of a base or acid is realised. Fluorophores that can participate in the acid-base interaction may be divided into two groups. Proton-donor fluorophores ArXH constitute the first group, their acidity being increased upon excitation. A reaction with a base B in the ground state occurs according to the scheme

$$ArXH^* + B \rightleftharpoons ArXH^- * + B^+ , \qquad (2)$$

$$ArXH^* \cdots B \rightleftharpoons ArXH^- * \cdots B^+ . \qquad (3)$$

The majority of compounds of this group possess an aromatic radical Ar bound by a single bond to the proton-donor group XH (X = O, S, NR, and NR_2^+).[16–19] The kinetic and thermodynamic parameters of reaction (2) and spectral-kinetic characteristics of the forms ArXH and ArX^- for the known laser acid-base systems are listed in Table 1.

Table 1. The spectral-luminescence characteristics of conjugated acid-base forms of dyes for photochemical lasers and the parameters of the intermolecular proton phototransfer reactions

$$AH^* + H_2O \xrightarrow{k} A^{-*} + H_3O^+$$

Laser dye	AH, A^-	λ_a /nm	ε /mol^{-1} litre cm^{-1}	λ_f /nm	φ_f (%)	τ /ns	k /mol^{-1} litre ns^{-1}	$pK_a^*-pK_a$	Ref.
2-Naphthol	AH	327 [a]	3.08 [a]	357 [a]	40 [b]	7.9	0.075 [c]	2.78 [d]	17
	A^-	345 [a]	1.78 [a]	418 [a]	57 [b]	9.0	46	−6.79	17
Potassium 7-hydroxy-naphthalene-1,3-disulfonate	AH	337	1.69 [e]	385	–	10.5	> 5 [c]	0.76 [d]	23
	AH	–	–	388	–	14.5	3.8 [c]	0.60 [d]	24
	A^-	359	3.38 [e]	470	–	15.5	< 200	−8.34	23
	A^-	389	–	458	–	26.2	16	−7.29	24
Sodium 8-hydroxypyrene-1,3,6-trisulfonate	AH	402 [f]	19.2 [f]	441	–	5.2	8.0 [c]	1.28 [d]	26
	AH	–	–	–	70	4.8	6.1 [c]	0.95 [d]	27
	A^-	453 [f]	18.2 [f]	510	85	5.3	115	–	26
	A^-	–	–	–	85	6.0	55	−6.45	27
Sodium 8-acetylaminopyrene-1,3,6-trisulfonate [g]	AH	371	28	443	–	4.0	1.48	6.9 [d]	19
	A^-	408	20	553	85	5.0	2.1×10^{-9} [c]	−7	19
1,3-Disulfo-7-naphthylammonium hydrogensulfate	AH	281	5.55	345	–	15	20 [c]	< −4.7 [d]	22
	A^-	350	3.96	450	84	14.7	$< 10^{-4}$	< −7.6	22

Note. Here and in Tables 2 and 3, the following designations are used: λ_a is the absorption spectrum maximum, λ_f is the fluorescence spectrum maximum, ε is the extinction coefficient for the absorption spectrum maximum, φ_f is the fluorescence quantum yield, τ is the fluorescence lifetime.
[a] From Ref. 20. [b] From Ref. 21. [c] Rate constant for a unimolecular tautomerisation reaction or a quasi-unimolecular reaction with the solvent (s^{-1}). [d] pK_a^*. [e] From Ref. 22. [f] From Ref. 25. [g] Reaction (2) with the OH^- ion.

Table 2. Spectral-luminescence characteristics of conjugated acid-base forms of dyes for the photochemical lasers and the parameters of proton intermolecular phototransfer reactions (4) in ethanol.

Laser dye	AH, A^-	λ_a /nm	ε /mol^{-1} litre cm^{-1}	λ_f /nm	φ_f (%)	τ /ns	Reagent	k /mol^{-1} litre ns^{-1}	$pK_a^*-pK_a$	Ref.
N-Phenylacridone	B	399	–	406	100	12	H_3O^+	7.4 [a]	2.05 [b]	33
	BH^+	427	–	450	–	–			2.92	33
3-Methoxybenzanthrone	B	445	24.3 [c]	547	57	7.8	H_3O^+	6.4 [a]	2.2 [b]	33
	BH^+	585	–	640	28	3.8			5.85	33
2,3,6,7-Tetrahydro-1*H*,5*H*-benzopyrano[6,7,8-*ij*]quinolizin-11-one	B	389 [d]	21.5 [d]	470	95	4.52	$EtOH_2^+$	4.33		35
	BH^+		–	533	40	–			5.51 [e]	35
9-Methyl-2,3,6,7-tetrahydro-1*H*,5*H*-benzopyrano-[6,7,8-*ij*]quinolizin-11-one	B	396 [d]	25.0 [d]	470	83	4.36	$EtOH_2^+$	3.56		35
	BH^+	–	–	530	47	5.45 [f]			5.14 [e]	35
5*H*-9-Diethylamino-5-imino-benzo[*a*]phenoxazine	B	510	–	605	–	1.85	EtOH	0.04 [g]	3	38
	BH^+	625	–	660 [h]	22 [i]	1.3 [h]			1.5 [j]	38
	BH^+	633	77.5	672	–	–				34
5-Phenyl-2-(4-pyridyl)-oxazole	B	322 [k]	24.5 [k]	400 [k]	46	2.12	AcOH	0.314	8.27 [l]	30
	BH^+	370 [k]	24.5 [k]	475 [k]	59				8.44 [e]	30
5-(4-Methoxyphenyl)-2-(4-pyridyl)oxazole	B	335 [k]	21.5 [k]	447 [k]	91	2.45	AcOH	0.501	8.78 [l]	30
	BH^+	399 [k]	21.0 [k]	550 [k]	64	3.08			10.04 [e]	30
5-Phenyl-2-(2-quinolyl)oxazole	B	350 [k]	21.5 [k]	423 [k]	61	1.89	AcOH	0.175	8.85 [l]	30
	BH^+	412 [k]	18.5 [k]	515 [k]	73	3.66			9.01 [e]	30
5-Phenyl-2-(4-quinolyl)-oxazole	B	350 [k]	18.5 [k]	437 [k]	63	1.87	AcOH	0.263	8.04 [l]	30
	BH^+	412 [k]	23.9 [k]	525 [k]	45	2.18			9.01 [e]	30
1,4-Bis(5-phenyloxazol-2-yl)benzene [n]	B	360	47.2 [m]	420	93 [m]	1.4 [m]	CF_3COOH	–		42
	BH^+	–	–	486	–	–			6.78 [l]	42
1,4-Bis[5-(4′-methylphenyl)-oxazol-2-yl]benzene [n]	B	362	51.1 [m]	430	93 [m]	1.5 [m]	CF_3COOH	–		42
	BH^+	–	–	500	–	–			6.83 [l]	42

[a] $k_1/(1 + k_{-1}\tau_0')$ from Ref. 32. [b] pK_a^*. [c] From Ref. 32. [d] From Ref. 34. [e] According to the Förster cycle [36] using the absorption spectra. [f] From Ref. 37. [g] Rate constant for a unimolecular tautomerisation reaction or a quasi-unimolecular reaction with the solvent (ns^{-1}). [h] Ion pair. [i] From Ref. 39. [j] pK^* for an equilibrium ion pair – complex with H-bond. [k] From Ref. 40. [l] According to the Förster cycle [36] using the fluorescence spectra. [m] In cyclohexane.[41] [n] In dioxane, reaction (5).

Proton-acceptor fluorophores constitute the second group, their basicity is increased upon excitation

$$B + HA \rightleftharpoons BH^{+} * + A^{-}, \quad (4)$$

$$B \cdots HA \rightleftharpoons BH^{+} * \cdots A^{-}. \quad (5)$$

In this type of base, the π-system is linked by a double bound to the proton-acceptor centre. The proton-acceptor centre can be exocyclic or endocyclic.

Aromatic carbonyl compounds (aldehydes and ketones) and their imine derivatives belong to the organic bases with an exocyclic proton-acceptor centre. Organic carbonyl compounds are weak bases.[28] Their basicity is increased in the excited state.[29] The protonation rate constants for aminocoumarins in the excited state in solution are close to the diffusion rates.[29] The rate constants for the protonation of pyridine and oxazole derivatives in the excited state by carboxylic acids are one or two orders of magnitude smaller than the rate constants for the diffusion-limited reactions, respectively.[30, 31] The photoprotonation of pyridine and oxazole derivatives occurs either according to the static [reaction (5)] or dynamic [reaction (4)] mechanism.[30, 31] The kinetic and thermodynamic parameters for the reactions (4) and (5) and spectral-kinetic characteristic of the forms B and BH^+ for the known laser acid-base systems are listed in Table 2.

Aromatic C-bases possess low basicity. These compounds are protonated in the ground state only in concentrated strong acids. The acid-base interaction in the excited state leads to quenching of the fluorescence. No excited products are generated in this reaction.[43, 44]

In numerous organic compounds, the proton-donor and proton-acceptor groups are linked by an intramolecular hydrogen bond.[45–48] The proton-donor and proton-acceptor ability of these reaction centres of the molecule is increased upon excitation of these compounds, which results in the intramolecular proton phototransfer. This type of reaction can be assigned to the stationary proton phototransfer. The kinetic and thermodynamic parameters for the reactions of intramolecular proton phototransfer as well as spectral-kinetic characteristics for the known laser systems of this type are listed in Table 3.

Table 3. Parameters of reactions of intramolecular proton phototransfer in dye molecules for photochemical lasers and spectral-luminescence characteristics of the initial form (N) and its tautomer (T).

Laser dye	Form	Solvent	λ_a /nm	ε /mol^{-1} litre cm^{-1}	λ_f /nm	φ_f (%)	τ /ns	$pK_a^* - pK_a$	Ref.
Sodium salicylate	N	EtOH	298	4.2	–	–	–	–	41
	T				405	27	26 [a]		41
Salicylamide	N	DMF	305	–	–	–	–	–	49
	T				438	27	2.6		49
3-Hydroxyflavone	N [b]	MeOH	344	16.35	405	–	1.24	−9.61 [c]	51
						–		4.08 [d]	51
	T				531	–	2.34	−12.3 [e]	51
	N [f]	Methyl-	–	25 [h]	410	–	–	–	50
	T [g]	cyclohexane			526	36	3		53
2,2′-Bipyridyl-3,3′-diol	N [i]	3-Methyl-	360 [j]	17.5 [j]	–	< 0.01	6.6 [a]	–	55
	T	pentane			513	31	3.2		54
2-(Benzimidazol-2-yl)phenol	N	Dioxane	333	28.0 [k]	350	–	–	−15.1 [e]	57
	T				468	65	4.2		57
	N	MeCN	331	22.1 [k]	354			−13.9 [e]	57
	T				463	55	3.7		57
	N	DMF	333	27.5 [k]	354	30	1.4	−13.9 [e]	57
	T				463	72	4.1		57
	N	MeOH	329	28.0 [k]	351	37	1.5	−8.0 [e]	57
	T				405	57	3.8		57
2-(Benzimidazol-2-yl)-	N	Dioxane	339	22.8 [k]	352	5	1.5	−16.7 [e]	57
4-methylphenol	T				489	65	4.5		57
2-(Benzimidazol-2-yl)-	N	MeCN	339	24.1 [k]	359	–	–	−14.5 [e]	57
4-fluorophenol	T				478	73	4.7		57
2-(Benzimidazol-2-yl)-	N	Dioxane	341	20.2 [k]	368	7	1.9	−17.4 [e]	57
4-methoxyphenol	T				530	48	4.2		57
2,5-Bis(benzimidazol-2-yl)-	N	"	345	34.0 [k]	358	6	2.0	−18.6 [e]	57
hydroquinone	T				525	39	3.4 [l]		57
	N	MeCN	342	19.6 [k]	369	6	1.8	−16.3 [e]	57
	T				517	18	3.4		57
	N	DMF	347	22.0 [k]	381	8	1.8	−15.1 [e]	57
	T				525	21	2.6		57
3,6-Bis(benzoxazol-2-yl)-	N [m]	MeTHF	381	24.7	445 [n]	35	–	−8.9 [e]	59
4-methoxyphenol	T				548	50	4.6		59
N-[2-(5-Phenyl-1,3,4-oxadiazol-	N	EtOH	312	12.5	330	–	–	−22.4 [e]	60
2-yl)phenyl]toluene-*p*-sulfamide	T				510	3	0.90		60

[a] Radiative lifetime of fluorescence. [b] Rate constant of proton phototransfer (k) > 8000 ns^{-1} (Ref. 50). [c] Deprotonation. [d] Protonation. [e] According to the Förster cycle [36] using the fluorescence spectra. [f] k = 4200 ns^{-1}. [g] k = 30 ns^{-1} in cyclohexane.[52] [h] In cyclohexane.[52] [i] k > 7000 ns^{-1}. [j] From Ref. 54. [k] From Ref. 56. [k] From Ref. 58. [m] k = 20 ns^{-1}. [n] For 1,4-dimethoxy-2,5-bis(benzoxazol-2-yl)benzene.

Intramolecular proton phototransfer reactions leading to species with effective fluorescence are wide-spread (see Tables 1 and 2). Compounds that give products with a high quantum yield of fluorescence of the intramolecular proton phototransfer product are scarce.[59, 61–64] The fluorescent reaction products of the proton phototransfer, as with usual fluorophores, under appropriate conditions can amplify the light passing through the solution.

In a number of studies that were performed over the period from 1960 to 1964, the possibility of the light amplification by the dye solutions has been demonstrated,[65] and the principles of generation of laser radiation (lasing) as a result of electron-vibrational singlet–singlet transitions in anthraquinone molecule have been discussed.[66] Certain theoretical calculations on lasing taking into account the vibrational structure of the electronic levels of dyes were carried out.[67, 68] The processes that occur in the excitation of complex molecules, including the processes of stimulated light emission, were analysed in detail.[69, 70] Slight amplification of light upon photoirradiation of a solution of perylene in benzene was detected in 1964.[71]

The lasing of organic compounds was first observed independently by two research groups.[72, 73] Chronologically, the first dye laser was created by Sorokin and Lankard[73] in 1966. Excitation of an ethanolic solution of phthalocyanine complex with aluminium chloride by the radiation of a ruby laser induced laser radiation resulting from electronic transitions in the organic ligand of the metallocomplex. Currently, dye lasing with a high conversion efficiency (71% for the Rhodamine 6G in EtOH[75] and 78% for the dye LKK-756 in MeCN[76]) can be obtained in a spectral range from 322 nm[74] to 1800 nm.[10] Arylazole, coumarin, xanthene, oxazine, and polymethine dyes are the most efficient laser dyes.[7] Active media for the dye lasers are liquid solutions of dyes,[1, 5] solid solutions in polymers,[77] and gaseous mixtures of dye vapour with buffer gases.[78]

A solution of an organic compound can generate laser radiation (lase) if its optical density $[-k_a(\nu)x]$ at some frequency ν is less than zero (negative absorption).[79]

$$\ln\left[\frac{I_0(\nu)}{I(\nu)}\right] = -k_a(\nu)x,$$

where $I_0(\nu)$ and $I(\nu)$ are the radiation flux intensities before and after the light has passed through the layer of a solution with a thickness x, $k_a(\nu)$ is an amplification coefficient of the medium.

In the simplest case of a two-level scheme, $k_a(\nu)$ is described by the equation

$$k_a(\nu) = \frac{h\nu}{\upsilon}\left[N_2 B_{21}(\nu) - N_1 B_{12}(\nu)\right],$$

where N_1 and N_2 are the population of the lower (1) and upper (2) levels, $B_{12}(\nu)$ and $B_{21}(\nu)$ are the probabilities of absorption and stimulated emission (Einstein's coefficients for induced transitions), respectively, υ is the velocity of light in the medium. More often, a cross-section of stimulated transition is used instead of $B(\nu)$

$$\sigma(\nu) = \frac{h\nu}{\upsilon} B(\nu)\ .$$

The Einstein coefficients, cross-sections of absorption and stimulated emission are the same, *i.e.*,

$$B_{12}(\nu) = B_{21}(\nu) \quad \text{and} \quad \sigma_{21}(\nu) = \sigma_{12}(\nu).$$

The condition for lasing

$$k_a(\nu) = N_2\sigma_{21}(\nu) - N_1\sigma_{12}(\nu) = \sigma_{21}(\nu)(N_2 - N_1) > 0$$

is fulfilled when $N_2 > N_1$, *i.e.*, in the presence in the system with an inverted (relative to thermal population) level population. This cannot be achieved in the two-level system with optical pumping. The currently known laser systems lase according to three- (1–3) and four-level (1–4) schemes (Fig. 1). Optical transitions occur between the levels 1–2 and 3–4. The system is excited from the lower vibrational sublevel of the main electronic state (level 1) to higher vibrational sublevels of the first excited electronic state (level 2). The lower laser level (level 4) consists of higher vibrational sublevels of the ground electronic state of the dye, the upper laser level (level 3) is a zero vibrational sublevel of the first excited electronic state. The transitions between the levels 2–3 and 4–1 are radiationless (the rate constant of these processes is $\sim 10^3$ ns^{-1}). They represent vibrational relaxation in the excited and ground electronic states, respectively. As the higher vibrational sublevels of the ground state are virtually unoccupied at room temperature, the concentration of excited molecules at the level 3 (N_3) exceeds that of molecules at the level 4 (N_4) upon excitation of the system even by light of relatively low power. In this case, an inverted population of the levels 3 and 4 is observed in the system ($N_3 > N_4$). An inverted population of the zero vibrational sublevels of the ground and excited states cannot be achieved. In addition to these processes, optical transitions from the level 3 to the highest singlet states of the molecule (level 5), intersystem transitions to the triplet state (level 6) and optical transitions from the level 6 to the highest triplet level of the molecule (level 7) as well as photochemical decay of the dye occur in the dye lasers. For the system that is described by this scheme the amplification coefficient is determined by the equation

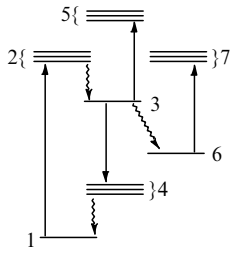


Figure 1. The energy level diagram of a laser dye molecule.

$$k_a(\nu) = N_2[\sigma_{34}(\nu) - \sigma_{35}(\nu)] - N_1\sigma_{12}(\nu) - N_6\sigma_{67}(\nu) - \sum_i N_{p_i}\sigma_{p_i}(\nu) - k_w(\nu), \qquad (6)$$

where the number in subscript indicates the number of the level, N_{p_i} is the population of levels, $\sigma_{p_i}(\nu)$ is the cross-section of absorption of photoproduct p_i at a frequency ν, $k_w(\nu)$ is the constant loss coefficient. Spectral criteria for the selection of a dye to produce efficient lasing have been formulated by Simonov[80] and Denisov and Uzhinov[81].

The idea of creating an inverted electronic state population as a result of the adiabatic reaction of organic compounds in excited state was suggested practically simultaneously by Derkacheva[82] and Kuz'min[83] (3 years before the appearance of the first dye laser[73]). It was assumed that photochemical reactions of dissociation, isomerisation, complexation, dimerisation, and polymerisation and redox processes can be adiabatic.[83] In the four-level scheme suggested,[82, 83] the ground and excited states of the initial form of the dye involved in the reaction correspond to levels 1 and 2 (see Fig. 1). The excited and ground state of the proton phototransfer product correspond to levels 3 and 4. In this case, the direct reaction in the excited state and the reverse reaction in the ground state play the roles of radiationless relaxation processes (transitions between the levels 2–3 and 4–1), respectively. The change in the equilibrium constant in the excited state compared to the ground state is crucial for lasing.

Derkacheva[82] has considered the mechanism of lasing of products of photoprotolytic reactions of phenols in water, which occur according to the following scheme.

$$\begin{array}{ccc} \mathrm{ROH^*} + \mathrm{H_2O} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{RO^{-}{*}} + \mathrm{H_3O^+} & & \\ & \Big\downarrow k_{34} & \\ \mathrm{ROH} + \mathrm{H_2O} \underset{k_{41}}{\overset{k_{14}}{\rightleftharpoons}} \mathrm{RO^-} + \mathrm{H_3O^+}. & & \end{array}$$

The value k_{34}^{-1} is the lifetime of the excited product of the photoreaction. It was considered [82, 83] that the attainment of an inverted population between the zero vibrational sublevels of the excited and the ground states of RO^- is a prerequisite for lasing. The difference in populations of these states under steady-state conditions is determined by the equation [82]

$$[\mathrm{RO^{-*}}] - [\mathrm{RO^-}] = [\mathrm{ROH}]\Big[\frac{\alpha k_{23}/k_{34}}{1 + k_{32}[\mathrm{H_3O^+}]/k_{34}} \times \times \Big(1 - \frac{1}{k_{41}[\mathrm{H_3O^+}]/k_{34}}\Big) - \frac{k_{14}}{k_{41}[\mathrm{H_3O^+}]}\Big],$$

where $\alpha = [\mathrm{ROH^*}]/[\mathrm{ROH}]$.

The following two conditions should be fulfilled to ensure an inverted population in the reaction product ($[\mathrm{RO^{-*}}] > [\mathrm{RO^-}]$): (1) $[\mathrm{H_3O^+}] > k_{34}/k_{41}$; (2) sufficiently intense excitation, which determines the value of α, as well as large value of k_{23}, which provides for the high formation rate of the excited molecules of the deprotonated form. In the case of acid dissociation of the excited 2-naphthol, the first condition is fulfilled at pH < 1.7 ($[\mathrm{H_3O^+}] >$ 0.02 mol litre^{-1}), and the second condition if sufficiently powerful excitation sources are employed.[82]

More recent studies have shown that the mechanism of lasing suggested earlier [82, 83] is invalid. Currently, it is believed that an inverted population between the zero vibrational sublevels of the excited state and the vibrational sublevels (excluding zero sublevel) of the dye ground state is the prerequisite for lasing in organic compounds.[79] This is also a prerequisite for the radiation of a photochemical laser. However, in this case the inverted population can also occur between the zero vibrational sublevels of the excited and ground states of the lasing species.

Due to spectral overlap of the stimulated emission of the components, the initial form influences significantly the emission by the photochemical reaction product, and *vice versa* the product influences the emission by the initial form. Thus, the properties of both components of an acid-base system determine the radiation characteristics of the photochemical laser. The energy diagram of the photochemical laser is a combination of 7-level schemes for the initial compound and the photoreaction product. In a general case, the diagram contains 14 levels (Fig. 2). The amplification coefficient of the active medium in such a laser is determined by the equation [22]

$$k_a(\nu) = N_3[\sigma_{31}(\nu) - \sigma_{35}(\nu)] - N_1\sigma_{12}(\nu) - N_6\sigma_{67}(\nu) + N_{3'}[\sigma_{3'1'}(\nu) - \sigma_{3'5'}(\nu)] - N_{1'}\sigma_{1'2'}(\nu) - N_{6'}\sigma_{6'7'}(\nu) - \sum_i N_{p_i}\sigma_{p_i}(\nu) - k_w(\nu), \quad (7)$$

where the quantities corresponding to the photoreaction product are primed.

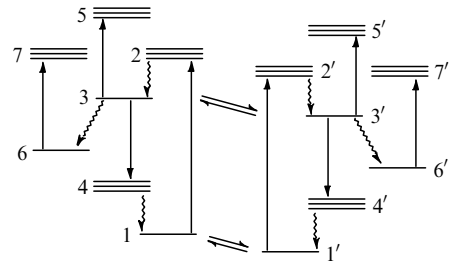


Figure 2. The energy level diagram of the components of a photochemical laser.

Analysis of the features of laser radiation of a system with an intermolecular proton transfer reaction at steady-state excitation [84] shows that the system is described by two pairs of electronic-vibrational levels for the initial form (1, 2) and the photoreaction product (1′, 2′), respectively; the transitions to the triplet levels are absent and the concentration of the reaction product in the ground state $N_{1'}$ is taken to be equal to zero.[84] When the intensity of excitation (I_e) is higher than the threshold for the photoreaction product (I'_t) and lower than the threshold for the initial form (I_t) and the laser radiation is generated only by the photoreaction product at a frequency ν', its radiation power is increased with the intensity of excitation up to the maximum value I'_{max} at $I_e = I_t$. On further increase in I_e, the passage of the system into a two-band generation mode occurs with frequencies ν' and ν:

$$I'(\nu') = I'_{max}(\nu') - \frac{\sigma_{2'1'}(\nu)}{\sigma_{2'1'}(\nu')} I(\nu),$$

$$I(\nu) = C(I_e - I_t),$$

$$I'_{max} = \frac{\sigma_{12}(\nu)(N - k_w(\nu')/\sigma_{2'1'}(\nu')) + k_w(\nu)}{k_w(\nu')\sigma_{21}(\nu)[1 + \exp(h(\nu' - \nu'_{00})/kT]} (k_{22'} - k_{22'}^{min}),$$

$$k_{22'}^{min} = \frac{k_{w'}(\nu')\sigma_{21}(\nu)k_{2'1'}}{\sigma_{2'1'}(\nu')},$$

where C is a coefficient, N is an analytical dye concentration, ν'_{00} is the frequency of the 0–0-transition in the reaction product, $k_{22'}^{min}$ is a minimum rate of the proton transfer reaction in the excited state, which provides the appearance of lasing of the product. The coefficient c is independent of pump power.

If fluorescence spectra of the initial form and the reaction product do not overlap at the frequencies of lasing ν and ν' [$\sigma_{21}(\nu') = \sigma_{2'1'}(\nu) = 0$], then the laser radiation power for the photoreaction product is independent of I_e if $I_e \geqslant I_t$. It was concluded [84] that I'_{max} is proportional to the rate constant for the proton transfer reaction in the excited state. If fluorescence spectra of the initial form and the product overlap at the frequency of lasing of the initial form [$\sigma_{21}(\nu') = 0$, $\sigma_{2'1'}(\nu) > 0$], then participation of the reaction product in the lasing of the initial form leads to an increase in amplification at the frequency of its lasing. For $I_e \geqslant I_t$, this leads to the situation, where the power of laser radiation at the frequency ν increases faster than in the previous case, but at the frequency ν' the power drops until the ceasing of generation at

$$I(\nu) = \frac{I'_{max}(\nu')\sigma_{2'1'}(\nu')}{\sigma_{2'1'}(\nu)}.$$

In other words, two thresholds (upper and lower) in the lasing of the photoreaction product should be observed for such a system. The range of I_e, where two-band laser radiation exists, is the wider the smaller $\sigma_{2'1'}(\nu)$ and the larger $k_{22'}$. Analysis of changes in the generated power of laser radiation at frequencies ν and ν' provided $N_{1'} > 0$ has shown [84] that at $I_e > I_t$ and $\sigma_{21}(\nu') = \sigma_{2'1'}(\nu) = 0$ the generation threshold at the frequency ν depends on the acidity of the medium due to absorption of the excitation radiation by the photoreaction product $N_{1'}\sigma_{1'2'}(\nu_p)I_p$. A limiting value for the ratio of the rate constants for the direct reaction in the excited state and the reverse reaction in the ground state exists

$$\frac{k_{22'}}{k_{1'1}} = \frac{a}{\sigma_{1'2'}(\nu)},$$

where coefficient a is independent of I_e. If this ratio is greater than the limiting value, the generation threshold for laser radiation of initial form becomes infinitely large.

Neglecting the terms that correspond to the absorption of light by the products of irreversible reactions of photodecay and constant losses in the resonator, Kasha and co-workers [53, 85–87] derived an expression similar to (7) for the change in the

amplification coefficient of a photochemical laser based on the reaction of intramolecular proton phototransfer of 3-hydroxyflavone in methylcyclohexane. In the approximation of a fast proton transfer reaction in the excited ($k_{3'3}^{-1} < 8$ ps) and ground states and neglecting the induced absorption $S_n \leftarrow S_1$ [$\sigma_{35}(\nu) = 0$], $T_n \leftarrow T_1$ [$\sigma_{67}(\nu) = 0$], $S_{n'} \leftarrow S_{1'}$ [$\sigma_{3'5'}(\nu) = 0$], and $T_{n'} \leftarrow T_{1'}$ [$\sigma_{6'7'}(\nu) = 0$], they obtained an amplification coefficient of the active medium equal to 10 cm^{-1} at an excitation power of 500 kW ($\lambda = 337$ nm) and dye concentration of 1.64 mmol $litre^{-1}$ (Ref. 53).

Radiation kinetics of a photochemical laser based on a binary mixture of dyes, 2-(biphenyl-4-yl)-6-phenylbenzoxazole and 2-(2-hydroxyphenyl)benzoxazole, was studied [58, 88] in the generation band of the first dye and a bifluorophore comprising these two dyes bound chemically. The solution of a direct kinetic problem to describe the radiation kinetics was attempted.[88] Using literature data on the optical properties of dyes, and experimental characteristics of the exciting radiation (308 nm) and optical resonator, and neglecting the light absorption by the singlet- and triplet-excited molecules, it was concluded [88] that the laser pulse duration of the first dye should be much smaller in the presence of the second dye. The results of calculation were in agreement with experiment. The laser pulse duration was 3.3 ns in the absence of the second dye and 80 ps in the presence of the second dye. It was assumed in the calculation [88] that the induced absorption in this system corresponds to absorption of a tautomer of the second dye in the ground state [$\sigma_{1'2'}(\nu) > 0$]. However, the induced absorption in 2-(2-hydroxyphenyl)benzoxazole was later assigned to $T_n \leftarrow T_1$ absorption of the dye [$\sigma_{67}(\nu)$].[89, 90]

The dynamics of lasing of the product of the intramolecular proton transfer in salicylamide and derivatives of 2-(2-hydroxyphenyl)benzoxazole in DMF [48] was described by the system of differential equations based on a previously employed model.[53, 85–88] It was assumed in the calculation that the rate constants for the direct proton transfer in singlet excited state of initial form ($k_{22'}$) and reverse proton transfer in triplet excited state ($k_{6'6}$) are equal to 10^{12} and 10^9 s^{-1}, respectively. Absorption by the excited singlet state [$\sigma_{35}(\nu) = \sigma_{3'5'}(\nu) = 0$] was neglected. The values calculated $\sigma_{1'2'}(\nu) = 8.0 \times 10^{-19} - 2.3 \times 10^{-17}$ cm^2 correlate linearly with a cross-section of stimulated emission of the tautomer at a frequency of the spectral maximum of lasing (this was estimated from the fluorescence spectrum). It was concluded [58] that the rate of reverse proton transfer in the ground state ($k_{1'1} = 1.50 \times 10^8$ s^{-1}) and light absorption by the reaction product in the ground state are the main factors determining lasing of the product of intramolecular proton phototransfer of 2-(2-hydroxyphenyl)benzoxazoles and salicylamide.

III. Selection criteria of acid-base systems for active media in photochemical lasers

The cross-section of stimulated emission (σ_{34}) is the main criterion, which determines the possibility of lasing by an organic compound on a certain frequency. The cross-section should exceed the threshold value estimated according to the following formula[11]

$$\sigma_{34}^{-1} = 8\pi n^2 c \nu_f^2 \Delta\nu_f \tau_r ,$$

where n is the refractive index of the medium, c is the velocity of light, τ_r is the radiative lifetime of fluorescence, ν_f and $\Delta\nu_f$ are the frequency of maximum and the peak halfwidth of the fluorescence spectrum, respectively.[80] Analysis of cross-sections of stimulated emission for the known laser dyes allows one to determine the threshold value σ_{34} for the existence of lasing in organic compounds as $\sigma_{34} > 5 \times 10^{-17}$ cm^2 (Ref. 91). Spectral criteria for the occurrence of lasing in organic compounds were suggested [81] taking account of the relation between the cross-section of stimulated emission and spectral characteristics of a laser dye. Quantum-chemical criteria for the occurrence of laser radiation in organic compounds were also formulated.[92, 93]

Along with cross-section σ_{34} the product of a photochemical reaction, thermodynamic and kinetic parameters of the reaction determine the efficiency of photochemical laser radiation. There are no rigorous quantitative criteria for the selection of lasing systems with proton phototransfer reactions. The following spectral-kinetic criteria for the selection of systems for the photochemical laser were suggested based on the analysis of the known laser systems with proton phototransfer reactions.[9, 15]

1. The initial compound (which absorbs light and in which the proton phototransfer reaction occurs) should absorb light strongly in excitation spectral range. The extinction coefficient should be greater than 10^4 litre mol^{-1} cm^{-1} at the excitation frequency.

2. The proton phototransfer reaction should be fast and efficient (*i.e.*, with low efficiency of competing radiationless deactivation processes). The rate constants for the intermolecular and intramolecular proton phototransfer should be greater than 10^8 litre mol^{-1} s^{-1} and 10^9 s^{-1}, respectively.

3. The product of the proton phototransfer reaction should possess intense fluorescence. The fluorescence quantum yield should be greater than 0.2.

4. The acid-base properties of the dye should be changed significantly ($\Delta pK_a > 1$) upon excitation to provide for the direct reaction of the proton transfer in the initial excited form of the dye and reverse reaction of the proton transfer in the product in the ground state.

5. The radiative transition in the product of the proton phototransfer reaction should possess a short radiative lifetime of fluorescence ($\tau_r < 10$ ns).

6. The rate of the reverse proton transfer reaction in the ground state should be significantly higher than the overall rate of the direct reaction of proton phototransfer in the excited state and the formation of the product of proton transfer in the ground state resulting from deactivation of the excited state.

7. The absorption spectra $S_n \leftarrow S_0$, $S_n \leftarrow S_1$ and $T_n \leftarrow T_1$ of the initial form of the dye and reaction product of proton phototransfer should possess minimum overlap with the fluorescence spectrum of the proton phototransfer product. The absorption coefficient at the frequency of lasing should not be higher than 0.01 cm^{-1}.

8. The steady-state concentration of molecules in the triplet state of the initial form of the dye and the proton phototransfer product should be low, which is ensured by a low rate constant for intersystem crossing from the S_1 state and a large rate constant for intersystem crossing from the T_1 state.

9. The initial form of the dye and the product of the proton phototransfer reaction should be photochemically stable.

The majority of dyes listed in Tables 1–3 fulfil the above-mentioned requirements. 2-Naphthol, potassium 7-hydroxynaphthalene-1,3-disulfonate, 1,3-disulfo-7-naphthylammonium hydrogensulfate, and sodium salicylate are the exceptions. The extinction coefficients for these compounds at the excitation wavelength are smaller than 10^4 litre mol^{-1} cm^{-1}. The radiative lifetime of fluorescence of the proton phototransfer products is greater than 10 ns. In spite of this, the reaction products of proton phototransfer of these compounds, except for the deprotonated form of 2-naphthol, lase. This is due to the fact that the numerical value of the criterion 5 permits selection of lasing dyes among all fluorophores. Aqueous 2-naphthol solution is also a useless laser system because the rate constant for the proton phototransfer for 2-naphthol in water is significantly smaller than 10^8 litre mol^{-1} cm^{-1}. The overlap of the absorption and fluorescence spectra will be the smaller the higher Stokes' shift of fluorescence. In the formation of the lasing form as a result of reaction in the excited state, Stokes' shift is increased significantly (see Tables 1–3).

IV. Acid-base laser systems

Schaefer [94] was the first to report in 1968 on a photochemical laser based on a product of intermolecular acid photodissociation reaction of sodium 8-acetylaminopyrene-1,3,6-trisulfonate. In the ground state in basic solution the dye exists in the form of a trianion. In the excited state, the trianion dissociates to form a tetraanion. In the excitation by a lamp the laser radiation in a neutral solution is observed for the trication and in a basic solution for the tetraanion. The laser radiation spectrum in basic solution is shifted to longer wavelengths by 125 nm compared to the spectrum in neutral solution. The duration of the radiation pulse in basic solution (1400 ns) is greater than in neutral solution (250 ns).[95]

Laser radiation was obtained in 1970 from an ethanolic solution of sodium salicylate upon laser-induced excitation.[96] The species that lased was not identified. However, the data then available and current data on fluorescence of sodium salicylate in ethanol allow assignment of this radiation to the product of intramolecular proton phototransfer to the oxygen of the carboxy group.[97] For the first time lasing of a product of intramolecular proton phototransfer and identification of a radiating species was reported [98] in a study of stimulated emission of 2-(2-tosylaminophenyl)-5-phenyl-1,3,4-oxadiazole and 2-(2-tosylaminophenyl)-benzoxazole in ethanol. The lasing species results from the intramolecular proton phototransfer from the nitrogen of the amino group of the phenyl ring to the nitrogen atoms of the oxadiazole and oxazole rings, respectively. The photochemical lasers known to date based on intermolecular and intramolecular reactions of proton phototransfer of organic compounds are listed in Tables 4 and 5.

Table 4. Characteristics of photochemical lasers based on intermolecular proton phototransfer reactions of organic compounds.

Reagents	c_1 /mmol litre^{-1}	c_2 /mol litre^{-1}	Solvent	Radiation range /nm	Laser efficiency (%)	Ref.
$ArOH^* + H_2O \longrightarrow ArO^{-*} + H_3O^+$						
Potassium 7-hydroxynaphthalene-1,3-disulfonate + H_2O	1	56	Water	475 [a]	–	99
	4.6	56	"	466 – 484 [b]	–	15
	4.6	56	Water, pH 5	460 – 490 [b]	–	22
Sodium 8-hydroxypyrene-1,3,6-trisulfonate + H_2O	0.2	56	Water	516 – 532 [c]	–	100
	0.02	56	Water, pH 5.6	520 [d] (2.9×10^{-16}, Ref. 2) [e]	–	101
7-Hydroxycoumarin + H_2O	5	44	EtOH, water (1:4)	460 [b]	10	102
	1	56	Water	457 [c]	–	103
7-Hydroxy-4-methylcoumarin + H_2O	5	44	EtOH, water (1:4)	460 [b]	7	102
	1	56	Water	430 – 485 [e]	–	104
	5	22	MeOH, water (3:2)	425 – 545 [a]	–	105
7-Hydroxy-4-trifluoromethyl-coumarin + H_2O	5	2.8	EtOH, water (19:1)	513 [b]	14.8	102
Ethyl 7-hydroxycoumarin-3-carboxylate + H_2O	–	56	Water	465 [c]	–	106
3-Cyano-7-hydroxy-4-methyl-coumarin + H_2O	2	28	EtOH, water (1:1)	450 – 510 [a]	–	107
$ArOH^* \cdots NAlk_nH_{3-n} \longrightarrow ArO^{-*} + H_{4-n}NAlk_n$						
7-Hydroxy-4-methylcoumarin + Et_3N	–	–	Toluene	415 [d]	–	108
7-Hydroxy-4-methylcoumarin + Et_2NH	–	–	"	470 – 480 [d]	–	108
$ArNHAc^* + B \longrightarrow ArNAc^{-*} + BH^+$						
Sodium 8-acetylaminopyrene-1,3,6-trisulfonate + NaOH	–	–	Water	566 – 574 [a, b]	–	95
$ArNH_3^+* + B \longrightarrow ArNH_2^* + BH^+$						
1,3-Disulfo-7-naphthylammonium hydrogensulfate + H_2O	19	56	Water, pH 1	450 – 484 [b]	–	22
	10	56	Water, pH 0.5	Blue radiation [c]	–	22
	10	56	Water	459 [c]	–	109
3,3-Dimethyl-2-(5-(7-R-3,3-dimethyl-2,3-dihydropyrrolo[2,3-*b*]-pyridinio-2-yliden)-penta-1,3-dienyl)-7R-2,3-dihydropyrrolo[2,3-*b*]pyridinium + OH^-	–	–	EtOH	730 [f]	10	110

Table 4 (continued).

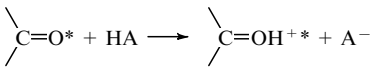
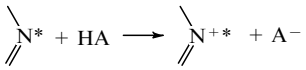
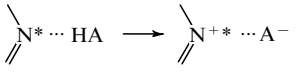
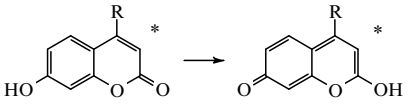
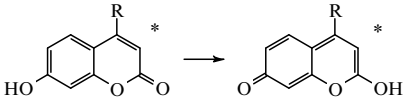
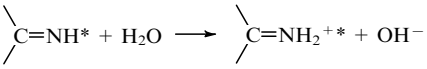
Reagents	c_1 /mmol litre^{-1}	c_2 /mol litre^{-1}	Solvent	Radiation range /nm	Laser efficiency (%)	Ref.
						
3-Methoxybenzanthrone + $HClO_4$	30	0.02	EtOH	540 – 660 [d]	–	111
3-Methoxybenzanthrone + AcOH	2.5	17.5	AcOH	563 – 586 606 – 627 [d]	– 0.9	33
7-Ethyl-4-methylcoumarin + HCl	1	–	EtOH	485 [a]	–	112
4,6-Dimethyl-7-methylamino-coumarin + HCl	1.5 –	– 0.1	" EtOH, water (24 : 1)	430 – 525 [a] 484 [c]	5 –	113 115
7-Ethylamino-4,6-dimethyl-coumarin + HCl	–	0.1	Ditto	487 [c]	–	114
2,3,6,7-Tetrahydro-1*H*,5*H*-benzo-pyrano[6,7,8-*ij*]quinolizin-11-one + H_2SO_4	2	0.2	"	474 – 548 [a]	4.8	115
9-Methyl-2,3,6,7-tetrahydro-1*H*,5*H*-benzopyrano[6,7,8-*ij*]quino-lizin-11-one + H_2SO_4	2	0.15	"	525 – 556 [a]	10	15
N-Phenylacridone + CF_3COOH	2.5	0.14	Toluene	472 [d]	0.2	33
3-Methoxybenzanthrone + CF_3COOH	2.5	0.13	"	611 – 641 [d]	2.5	33
						
5-Phenyl-2-(4-pyridyl)oxazole + AcOH	0.86 0.86 0.86 0.86 0.96	1.80 2.35 2.85 3.75 4.60	EtOH " " " "	506 – 520 [a] 512 – 522 [a] 510 – 520 [a] 505 – 517 [a] 501 – 515 [a]	0.4 0.6 1.0 2.0 2.6	116 116 116 116 116
5-(Methoxyphenyl)-2-(4-pyridyl)-oxazole + AcOH	0.70 0.70 0.70 0.70 0.70 0.70	0.92 1.62 2.26 2.68 3.69 4.57	" " " " " "	570 – 594 [a] 554 – 589 [a] 560 – 585 [a] 550 – 583 [a] 549 – 583 [a] 545 – 582 [a]	2.7 6.1 7.8 9.5 12 16	116 116 116 116 116 116
5-Phenyl-2-(2-quinolyl)-oxazole + AcOH	0.71	5.85	"	514 – 534 [a]	7.9	116
5-Phenyl-2-(4-quinolyl)-oxazole + AcOH	0.86	5.57	"	512 – 521 [a]	2.3	116
1,4-Bis(5-phenyloxazol-2-yl)benzene + $HClO_4$	0.4	–	MeCN	479 – 490 [a]	3.6	42
1,4-Bis(5-phenyloxazol-2-yl)benzene + CF_3COOH	0.4	–	CF_3COOH	460 – 476 [a]	17.0	42
1,4-Bis(5-sulfophenyloxazol-2-yl)-benzene + CF_3COOH	–	–	EtOH, water (3 : 1)	489 – 499 [a]	2.9	42
1,4-Bis(5-sulfophenyloxazol-2-yl)-benzene + $HClO_4$	–	–	Ditto	485-499 [a]	5.5	42
1,4-Bis(5-sulfophenyloxazol-2-yl)-benzene + H_2SO_4	–	–	Water	451 – 458 [a]	7.1	42
						
1,4-Bis(5-phenyloxazol-2-yl)benzene + CF_3COOH	0.4	–	Dioxane	476 – 491 [a]	14.2	42
1,4-Bis(5-*p*-tolyloxazol-2-yl)benzene + CF_3COOH	–	–	"	487 – 500 [a]	4.7	42

Table 4 (continued).

Reagents	c_1 /mmol litre^{-1}	c_2 /mol litre^{-1}	Solvent	Radiation range /nm	Laser efficiency (%)	Ref.
						
7-Hydroxycoumarin	5		EtOH, water 2.7% $HClO_4$	487 [b]	0.9	102
	–		EtOH, water (24 : 1)	408, 487 [b]	4.0	117
7-Hydroxy-4-methylcoumarin	5		MeOH, 0.37 N $HClO_4$ (3 : 2)	450 – 600 [a]	–	105
	5		EtOH, water 2.7% $HClO_4$	487 [b]	0.4	102
	–		EtOH, water (24 : 1)	400, 480 [b]	7.3	117
	1.8		EtOH	477 – 546 [a]	–	118
	–		EtOH, water (3 : 2)	437 – 544 [a]	–	119
7-Hydroxy-4-trifluorocoumarin	5		EtOH, water, 15% $HClO_4$	576 [b]	1.9	102
	–		EtOH, water (24 : 1)	530 [b]	10.7	117
	–		EtOH, water (1 : 1)	513 [b]	11.8	117
	0.75		Ditto	506 [c]	–	120
6-Glucosyl-7-hydroxy-coumarin	–		Water	440 – 490 [c]	–	121
3-Cyano-7-hydroxycoumarin	–		EtOH, water (7 : 3)	490 – 520 [c]	–	122
3-Cyano-7-hydroxy-4-methyl-coumarin	2		EtOH, water (9 : 1), 2.5 mM $HClO_4$	440 – 505 [a]	–	107
3-Cyano-7-hydroxy-4-trifluoro-methylcoumarin	–		EtOH, water (24 : 1)	543 [b]	12.6	117
	–		EtOH, water (1 : 1)	543 [b]	6.5	117
Two reactions simultaneously						
 ; $ArOH^* + H_2O \longrightarrow ArO^{-*} + H_3O^+$						
7-Hydroxy-4-methylcoumarin + H_2O	–	–	EtOH, water	370 – 530 [d]	–	123
7-Hydroxy-4-trifluoromethyl-coumarin + H_2O	5	–	EtOH, water (50%, 35%), 15% $HClO_4$	510 – 595 [b]	10	102
						
5*H*-9-Diethylamino-5-imino-benzo[*a*]phenoxazine + H_2O	0.14	3.3	EtOH, KOH (3 mmol litre^{-1})	610 – 715 [f]	–	38

Note. The following designations are adopted. c_1 and c_2 are concentrations of the first and second components, respectively.
Excitation source : [a] nitrogen laser (337 nm); [b] excimer laser (308 nm); [c] pulse lamp; [d] the second harmonic of a ruby laser (347.1 nm). [e] Cross-section of stimulated emission estimated according to the equation $\sigma_{34} = I_{1/2}\tau'$,[101] where $I_{1/2}$ is the intensity of light leading to half the fluorescence intensity, τ' was taken from Ref. 26. [f] The second harmonic of a YAG : Nd^{3+}-laser (532 nm).

Table 5. Characteristics of photochemical lasers based on intramolecular proton phototransfer reactions of organic compounds.

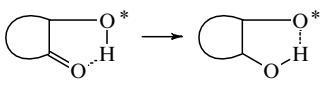
Reagent	c /mmol litre^{-1}	Solvent	Radiation range /nm	Laser efficiency (%)	Ref.
					
3-Hydroxyflavone	1.64	Methylcyclohexane	518 – 545[a]	1.2[b]	53
	1.64	Dioxane	535[a]	–	53
	3.0	MeCN	526[a]	–	124
	3.0	Acetone	526[a]	–	124

Table 5 (continued).

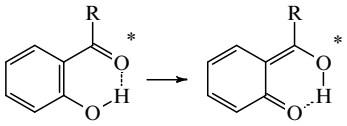
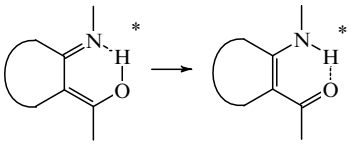
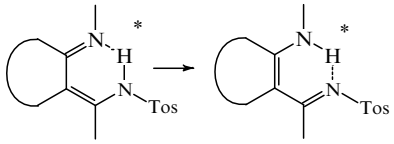
Reagent	c /mmol litre^{-1}	Solvent	Radiation range /nm	Laser efficiency (%)	Ref.
3,3′,4′,7-Tetrahydroxyflavone	2.0	Dioxane	544 – 570[a]	0.14[b]	124
					
Sodium salicylate	1	EtOH	395 – 417[a]	–	96
	1	Dioxane	390 – 411[c]	7	125
Salicylamide	1	DMF	439[c]	5	126
					
2-(Benzimidazol-2-yl)phenol	2.1	Dioxane	460 – 490[c]	14.5	56
	2.0	MeOH	450 – 480[c]	6.0	56
	1.9	EtOH	454 – 480[c]	3.0	56
	2.6	MeCN	459 – 489[c]	9.0	56
	1.9	DMF	463 – 495[c]	11.5	56
2-(Benzimidazol-2-yl)-4-methylphenol	1.2	Dioxane	475 – 522[a]	15.5	56
2-(Benzimidazol-2-yl)-4-fluorophenol	0.7	MeCN	465 – 510[a]	10	56
	1	Polymethylmethacrylate	487 – 499[a]	1	127
2-(Benzimidazol-2-yl)-4-methoxyphenol	1	Cyclohexane, Dioxane	509 – 537[a]	5.5	56
	1.4	"	514 – 552[a]	9.0	56
2,5-Bis(benzimidazol-2-yl)hydroquinone	1	Cyclohexane, Dioxane	509 – 542[a]	8.0	56
	1	MeCN	507 – 540[a]	10.0	56
	1.4	Dioxane	515 – 549[a]	13.5	56
	1.5	DMF	515 – 553[a]	7.0	56
Methyl 2-(2-hydroxyphenyl)benzimidazole-5(6)-carboxylate	0.5	Polymethylmethacrylate	489 – 499[a]	0.5	128
Methyl 2-(5-fluoro-2-hydroxyphenyl)-benzimidazole-5(6)-carboxylate	0.5	"	499 – 517[a]	1.8	128
Copolymer of allyl-2-(2-hydroxyphenyl)-benzimidazole-5(6)-carboxylate and methyl methacrylate	0.5	"	490 – 504[a]	1.4	128
Copolymer of allyl-2-(5-fluoro-2-hydroxyphenyl)benzimidazole-5(6)-carboxylate and methyl methacrylate	0.5	"	502 – 521[a]	11.3	128
3,6-Bis(benzoxazol-2-yl)hydroquinone	–	THF	650[a], 620 – 690[d]	–	129
4-Methoxy-3,6-bis(benzoxazol-2-yl)-phenol	–	"	615[a], 590-690[d]	–	129
3,6-Bis(benzoxazol-2-yl)pyrocatechol	–	"	560[a], 540 – 610[d]	–	129
2,2′-Bipyridyl-3,3′-diol	3	Dioxane	490 – 573[a]	12	130
		Benzene	495 – 567[a]	3	63
	εc = 20 cm^{-1}	Dioxane	494 – 567[a]	2	63
		Cyclohexane	492 – 572[a]	4	63
5-Methyl-2,2′-bipyridyl-3,3′-diol	3	Dioxane	503 – 564[a]	6.5	130
5,5′-Dimethyl-2,2′-bipyridyl-3,3′-diol	3	"	503 – 573[a]	7.2	130

Table 5 (continued).

Reagent	*c* /mmol litre^{-1}	Solvent	Radiation range /nm	Laser efficiency (%)	Ref.
					
N-[2-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenyl]toluene-*p*-sulfamide	–	EtOH	530 [a]	–	98
N-[2-(benzoxazol-2-yl)phenyl]toluene-*p*-sulfamide	–	"	530 [a]	–	98

Note. [a] Excitation by a nitrogen laser (337 nm). [b] The ratio of peak power to peak power of laser radiation of Rhodamine 6G. [c] Excitation by an excimer laser (308 nm). [d] Spectral range of amplification.

V. Losses in photochemical lasers

The efficiency of dye lasing is determined by the relationship between the light amplification and losses. The losses are classified as constant and induced losses. The former are the losses in the resonator and at the mirrors. In dye lasers overabsorption of the laser radiation by the dye in the ground state (for a photochemical laser, by the components of acid-base interaction) belong to the constant losses in addition to those mentioned above. The constant losses are time independent. The induced losses in dye lasers are related to the absorption of lasing by short-living intermediate species produced by the excitation light.

Induced losses in photochemical lasers unlike ordinary lasers may occur due to photoprotolytic reactions. Let us consider these induced losses.

1. Absorption of the laser radiation by the product of a photochemical reaction in the excited singlet [terms $N_3\sigma_{35}(\nu)$ and $N_{3'}\sigma_{3'5'}(\nu)$ in the equation (7)] and triplet [terms $N_6\sigma_{67}(\nu)$ and $N_{6'}\sigma_{6'7'}(\nu)$] states of the components of the acid-base interaction.

Acid-base systems with simultaneous lasing of the initial compound and the photoreaction product are the most valuable from the practical viewpoint. In the selective resonator of such a system, it is possible to attain laser radiation tuned over a wide spectral range, which exceeds the range of tuning for the individual components of the acid-base system. Lasing of the initial compound and the reaction product separately does not necessarily imply their simultaneous lasing. Thus 2-heteryloxazoles and their cations fluoresce efficiently and lase separately.[40] However, solutions with simultaneous efficient fluorescence of both the initial heteryloxazole and cation, do not lase at certain ratio of the components. As the concentration of a proton donor (acetic acid) in ethanolic solutions of 2-heteryloxazoles is increased, the quantum yields of fluorescence of the initial form are decreased, and a band of fluorescence of a protonated form resulting from the proton phototransfer appears in the longwave region of the spectrum,[30] and the efficiency of laser radiation of the initial form drops to zero at low concentrations of acetic acid. At certain concentrations, both forms do not lase. At higher acetic acid concentrations, the laser radiation of the photoreaction product appears and the efficiency of this radiation increases with the increase in the acid concentration.[116] Both the neutral and the protonated forms of 2-heteryloxazoles cause additional losses, which decrease stimulated emission by the corresponding conjugated acid-base form. For this reason, it is impossible to produce two-band laser radiation in solutions of 2-heteryloxazoles. The losses due to the neutral form in the lasing by the cations result from the $S_n \leftarrow S_1$ absorption of the neutral forms. The losses due to the cations in the lasing by the neutral forms, in addition to $S_n \leftarrow S_1$ absorption in the region of stimulated emission of the neutral forms, may result from slow dissociation of the cations in the ground state.[116]

2. Light absorption by decay products of a lasing species.

Reactions of electron photosplitting are typical of the aromatic compounds with the electron-donor group (OR, NR_2, O^-). The thus formed solvated electron has a broad absorption spectrum,[131] which can overlap with that of laser radiation of a photochemical laser. Thus flash lamp excitation of an aqueous solution of sodium 8-hydroxypyrene-1,3,6-trisulfonate (SHPTS) induced losses in the photochemical laser that are related to the absorption of the laser radiation from the deprotonated form of SHPTS by the hydrated electron produced from this excited form.[132] The light absorption by the hydrated electron leads to a decrease in the efficiency and narrows the lasing spectrum of SHPTS. In the laser excitation, the induced loses in this laser are small.[101] A decrease in the hydrated electron concentration due to its interaction with electron acceptors results in a decrease in these induced losses and an increase in the laser radiation efficiency of SHPTS in the lamp excitation.[132]

If the 7-aminonaphthalene-1,3-disulfonate dianion is formed in acidic solutions by the reaction of an acid photodissociated monoanion with the protonated amino group, the efficiency of the lasing upon pulse photoexcitation is considerably higher compared to that upon direct excitation from the ground state in neutral solutions.[22] This increase in efficiency is rationalised as a decrease in losses, due to the induced $T_n \leftarrow T_1$ absorption of light by the 7-aminonaphthalene-1,3-disulfonate dianion upon protonation of the amino group of the dianion triplet ($\sigma_{67} < \sigma_{6'7'}$) in acidic solutions and a decrease in losses, caused by the light absorption by the hydrated electron, as a result of the effective reaction of the electron with the proton.

VI. Tunable photochemical lasers

Systems with intermolecular relaxation processes that allow excitation of two or several different lasing species are promising for designing lasers tunable over a wide spectral range. This can be achieved in systems with electron energy transfer if both the donor and acceptor lase and in systems with fast reversible photochemical reactions provided both the initial species and the reaction product lase simultaneously.[9] Favourable relative disposition of the spectra of laser radiation of the components in binary systems with energy transfer and in systems with photoprotolytic reactions enables generation of laser radiation over a wide spectral range in a selective resonator.

The acid-base systems with simultaneous laser radiation of both photoprotolytic forms are few. In the majority of photo-

Table 6. Characteristics of photochemical lasers based on binary dye systems.

Binary dye system	c_1 /mmol litre^{-1}	c_2 /mmol litre^{-1}	$\lambda_1-\lambda_2$ or λ /nm
7-Hydroxy-4-methyl-coumarin [a] + sodium 8-hydroxypyrene-1,3,6-trisulfonate [a] in EtOH – water solution (3:7)	2.4	0	426 – 515
	2.4	0.15	440 – 523
	0	0.5	507 – 534
6-Glucosyl-7-hydroxy-coumarin [a] + sodium 8-hydroxypyrene-1,3,6-trisulfonate [a] in water	2.4	0	436 – 516
	2.4	0.15	441 – 527
	0	1.0	506 – 533
7-Diethylamino-4-methyl-coumarin [a] + sodium 8-hydroxypyrene-1,3,6-trisulfonate [a] in EtOH – water solution	1.6	0	450 – 510
	1.6	0.12	453 – 525
	0	0.7	510 – 535
1,4-Bis(5-phenyl-1-propionyl-Δ^2-pyrazolin-3-yl)benzene + 7-hydroxy-4-methyl-coumarin [a] in EtOH – water solution, (9:1), 0.05 mol litre^{-1} AcONa	0.5	0	404 – 418
	0.5	4	416 – 470
	0	2	429 – 497
1,4-Bis(5-phenyl-1-propionyl-Δ^2-pyrazolin-3-yl)benzene + 7-diethylamino-4-methyl-coumarin [b] in dioxane – water solution, (19:1)	0.5	0	405 – 417
	0.5	1	413 – 457
	0	2	435 – 473
3-Hydroxyflavone [a] + 1,1,4,4-tetraphenylbutadiene in methylcyclohexane	0	1.64	528 – 540
	3.5	1.64	509 – 540
	4.5	1.64	500 – 534
	4.5	1.24	496 – 528
	4.5	0	490 – 525
2-(Benzimidazol-2-yl)-4-methylphenol [a] + 2,5-bis-(benzimidazol-2-yl)hydroquinone [a] in dioxane	1.3	0	495
	1.2	0.1	502
	1.1	0.2	505
	0.9	0.4	509
	0.8	0.5	511
	0.7	0.6	515
	0.6	0.7	516
	0.4	0.9	519
	0.2	1.1	525
	0	1.3	527
2-(Benzimidazol-2-yl)-4-methylphenol [a] + 2,5-bis-(benzimidazol-2-yl)hydroquinone [a] in acetonitrile	2.6	0	474
	2.2	0.1	478
	2.0	0.3	488
	1.6	0.5	496
	1.3	0.5	503
	0.9	0.7	512
	0.4	0.9	520
	0	1.0	524

Note. The following designations are adopted: c_1 is the concentration of the first component of the binary dye system, c_2 is the concentration of the second component of the binary dye system, $\lambda_1-\lambda_2$ is the range of tuning of lasing, λ is the wavelength of spectral maximum of laser radiation. The data for the first five binary dye systems are taken from Ref. 134, for the next system from Ref. 133, and for the two last systems from Ref. 56. [a] The component that undergoes proton phototransfer reaction. [b] The component that forms a hydrogen-bond complex in the excited state.

chemical lasers (see Tables 4 and 5), stimulated light emission by the reaction product only is observed. This narrows substantially the possibility for creation of an increased range of tunable radiation in dye lasers. Binary mixtures were suggested to overcome this difficulty. In these mixtures, one or both components participate in photoprotolytic reactions.[133, 134] Realisation of a large Stokes' shift of fluorescence, due to adiabatic reactions of proton phototransfer allows the selection of binary solutions where the fluorescence band of one of the components lies in the spectral range between the absorption band and the fluorescence band of the second component. This allows one to create active media of lasers with an expanded range of the laser radiation tuning within the limits of the total luminescence band of the binary mixture components.

To increase substantially the tuning range of laser radiation in binary mixtures with photoprotolytic reactions it is necessary that first, the fluorescence bands are shifted relative to each other to make the total amplification band noticeably wider than the amplification bands of the individual components. Second, the energy transfer between components should not occur, that is, the absorption band of one component should not overlap with the fluorescence band of the other component. These requirements can be met if systems with a high Stokes' shift of fluorescence are used, *e.g.* systems with photoprotolytic reactions.[134] In coherent excitation, compounds should possess substantial absorption at the excitation wavelength. In lamp excitation the absorption spectra of the components should have minimum overlap to utilise efficiently the pump energy. For some binary mixtures of this type, broadening of the tuning range or shift of the maximum of laser radiation is observed at a certain ratio of the components (Table 6).

The spectrum of stimulated emission of 2,2′-bipyridyl-3,3′-diol in which intramolecular proton phototransfer occurs exhibits a blue shift in dioxane upon addition of 7-ethylamino-6-methyl-4-trifluoromethylcoumarin.[63] This effect depends on the relative concentration of the components. If spectra of laser radiation of components of a binary mixture are far removed from each other, the mutual influence of the components on the spectral position of their laser radiation is absent. The spectrum of stimulated emission of a mixture of 1,4-bis(2-methylstyryl)benzene (0.8×10^{-3} mol litre^{-1}) and 3-hydroxyflavone (3×10^{-3} mol litre^{-1}) which undergoes intramolecular proton phototransfer, exhibits two peaks at 420 and 535 nm in dioxane.[133] These maxima coincide with those of stimulated emission of the individual components in the same solvent and their relative intensities depend on the relative concentrations of the components. A similar picture is observed for a solution of 4,4′-diphenylstilbene (1.2×10^{-3} mol litre^{-1}) and 3-hydroxyflavone (1.64×10^{-3} mol litre^{-1}) in dioxane. Two maxima at 408 and 535 nm,[133] which correspond to the stimulated emission of individual components, are observed in the spectrum of stimulated emission of a mixture.

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