

Lasing of *trans*-stilbene and its methyl derivatives

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Lasing properties and photostability of *trans*-stilbene and its methyl derivatives were studied when pumping by an excimer XeCl laser radiation. It was shown that the photostability of the studied compounds depends on the pump radiation intensity: it improves as the radiation intensity increases. This fact can be explained by possible competition of the processes of photoisomerization and stimulated emission.

Introduction

The stilbene molecule is quite widely used when studying the reaction of photoisomerization. It is studied for several decades, and a valuable experimental material on it has been accumulated by now. It is characteristic of stilbene that the reaction of photoisomerization runs in both liquid and gaseous medium with a high rate in both directions.

It was shown¹ that the *cis* → *trans*-reaction completes for 0.3–2 ps in liquid media, while the *trans* → *cis*-reaction takes 100 ps (Ref. 2). In the former case the reaction practically has no a barrier, while in the latter one the molecule has to overcome a low (~3.5 kcal/mol) barrier.^{1,2}

The main destruction channels of the S_1 state of *trans*-stilbene are radiationless deactivation into the S_0 state without changes in the molecular geometry and without isomerization (rotation of phenyl rings about the ethylene chain), which results in formation of *cis*-stilbene in the S_0 state.

Radiative deactivation of the excited state of *trans*-stilbene is too unlikely. The quantum yield of the fluorescence of *trans*-stilbene in solutions at a room temperature is 3–8% depending on the experimental conditions,^{1,3,4} while the fluorescence lifetime is about 100 ps (Ref. 4).

Having such physical properties, it can hardly be expected that *trans*-stilbene is capable of lasing. However, this capability manifests itself in the case of pumping by an excimer XeCl laser radiation.

In this paper we study lasing properties and photostability of ethanol solutions of *trans*-stilbene and its methyl derivatives. The set of molecules under study is given in Table 1.

Experiment

The lasing properties and photostability were studied using the setup, whose arrangement is shown in Fig. 1. The pump source was an excimer XeCl laser emitting at $\lambda = 308$ nm, the pulse duration at half maximum of 10 ns, and the mean pulse energy of 35 mJ. A cavity was formed by a cell side and a dielectric mirror with 80–90% reflection in the lasing region (350–370 nm).

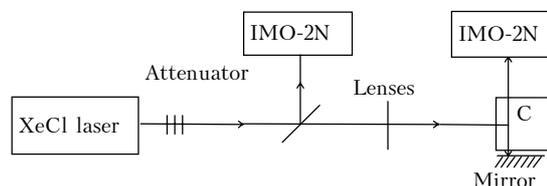


Fig. 1. Optical arrangement of the experimental setup; C denotes the cell with a solution.

To study the spectral properties of the molecules, we used a Specord-M40 spectrophotometer and a Hitachi 850 spectrofluorimeter.

Results and discussion

The spectral-luminescent properties of the studied compounds are given in Table 2. It is seen that the methyl substitution in various positions of methyl rings of *trans*-stilbene insignificantly influences the positions of absorption and fluorescence spectra. The radiative properties of all the compounds are also close. The values of the quantum yield of fluorescence (ϕ_{fl}) of the methyl derivatives listed in the table were obtained by the method described in Ref. 5. *Trans*-stilbene with the quantum yield of 5% was taken as a benchmark.⁴ Very weak fluorescence of these compounds indicates that the methyl groups are not an obstacle for photoisomerization of molecules.

Table 1. Studied compounds

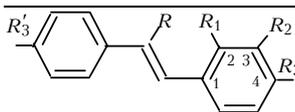
	R_1	R_2	R_3	R_3'	R
<i>trans</i> -stilbene	m	m	m	m	m
F - (2M)F	Cm ₃	m	m	m	m
F - (3M)F	m	Cm ₃	m	m	m
F - (4M)F	m	m	Cm ₃	m	m
F - (4M ₃)F	m	m	(Cm ₃) ₃	m	m
(4M)F - (2M)F	Cm ₃	m	m	Cm ₃	m
(4M)F - (3M)F	m	Cm ₃	m	Cm ₃	m
F - C(Cm ₃) = Cm - F	m	m	m	m	Cm ₃

Table 2. Spectral-luminescent properties of ethanol solutions of *trans*-stilbene and its methyl derivatives

Compound	λ_{ab}^1 , nm	$\frac{\epsilon_1}{l}$, mol-cm	λ_{ab}^2 , nm	$\frac{\epsilon_2}{l}$, mol-cm	λ_{fl} , nm	φ_{fl}
<i>trans</i> -stilbene	294	26900	307.6	26000	348	0.05 (Ref. 4)
F-(2M)F	297.6	23500	–	–	358	0.06
F-(3M)F	296.7	28400	308.6	27450	350	0.07
F-(4M)F	298.5	30200	311.5	29700	355.5	0.09
(4M)F-(2M)F	302	24400	–	–	363	0.05
F-(4M ₃)F	301.2	31200	313.4	31400	354	0.06
F-C(Cm ₃) = Cm-F	274.7	18800	–	–	–	0.0

The introduction of the methyl group in the ethylene link (compound F – C(CH₃) = CH – F) results in a significant shift of the absorption spectrum toward shorter waves and in the disappearance of the radiative properties. This compound is likely in the *cis*-configuration. This statement is supported by similar properties of this molecule and *cis*-stilbene: close positions of the maxima of absorption bands (274 and 277 nm, respectively⁶) and by the absence of fluorescence.

All the studied compounds, except for F – C(CH₃) = CH – F, are capable of lasing when pumped with an excimer XeCl laser. The lasing characteristics are given in Table 3.

Table 3. Lasing properties of ethanol solutions of *trans*-stilbene and its methyl derivatives (C = 5·10⁻³ mol/liter)

Compound	λ_{las} , nm	η_{max} , %	K_{308} , cm ⁻¹
<i>trans</i> -stilbene	348	4.1	128
F-(2M)F	358.6	5.5	102
F-(3M)F	351.4	4.8	138
F-(4M)F	355	4.5	141
F-(4M ₃)F	355.5	3.2	156
(4M)F-(2M)F	363	1.7	113
(4M)F-(3M)F	357	2.9	143

Trans-stilbene and its methyl derivatives generate laser radiation under rather rigorous conditions. Lasing occurs at a high concentration with the absorption coefficient at $\lambda = 308$ nm being 100 cm⁻¹ and higher. Under these conditions lasing evolves in a very narrow area near the cell walls. The threshold level of the pump power density achieves ~10 MW/cm², what is far higher than that for paraterphenyl generating in the same spectral region.

The lasing by *trans*-stilbene at so short lifetime and so low quantum yield of fluorescence is not a trivial fact and to be explained it requires additional data. References 7 and 8 can be a key in addressing this problem. Their main outcome is in the following. The molecules of *trans*-stilbene and some simple derivatives were excited by picosecond laser pulses as they left the supersonic jet nozzle. The fluorescence decay time was measured as a function of the pump radiation wavelength, namely, the vibrational energy stored in

the *S*₁ state. It was found that the frequency of the transition 0–0 corresponds to 310.1 nm wavelength, and the height of the potential barrier of the *S*₁ state is ~1200 cm⁻¹ (Ref. 8). It was shown that fluorescence decays in about 2 ns when excited by the radiation at the frequencies which populate the lower vibrational levels of the state *S*₁, and it decays in 80 ps at the excitation above the potential barrier. If the vibrational energy roughly equal to the value of the potential barrier is stored in the state *S*₁, the decay curves have a biexponential character with pico- and nano-second components.

In our experiment, the excitation of *trans*-stilbene by the excimer laser radiation at $\lambda = 308$ nm creates just these conditions: the lowest vibrational levels of the state *S*₁ are populated. The high intensity and the steep leading edge of the pump pulse, as well as the high concentration of *trans*-stilbene lead to stimulated emission before the molecule has time to overcome the potential barrier due to the energy of thermal motion of the neighboring molecules and to transform into *cis*-stilbene.

The attempts to obtain lasing in the ethanol solution of *trans*-stilbene pumped by KrCl laser radiation at $\lambda = 222$ nm under similar conditions ($W_p \sim 30$ MW/cm², $\tau = 8$ ns, $C = 5$ mmol/l) failed.

It is worth noting that fluorescence excitation at the frequencies $\nu < \nu_{thr}$ does not change the quantum yield of the fluorescence. Under conditions of spontaneous emission, the reaction of photoisomerization prevails over emission regardless of the energy of the excitation quantum. Under lasing conditions described above, the process of stimulated emission and the reaction of photoisomerization are the processes that compete.

Along with the lasing properties, we studied the photostability of *trans*-stilbene and its derivatives. Ethanol solutions with the concentration of 0.5 mmol/l were exposed to XeCl laser radiation of different intensity (unfocused beam $S = 0.8 \times 2.8$ cm, focused beam $S = 0.15 \times 0.9$ cm, and focused beam with the intensity halved by a neutral density filter). The absorption spectra were recorded before and after the exposure to laser radiation. The number of phototransformed molecules (N_{ph}) per unit volume was calculated by the change in the optical density of the solution in the long-wave band, and the quantum yield of photodecay was estimated by the equation

$$\gamma = N_{ph}/N^*,$$

where N^* is the number of light quanta absorbed in the solution of a unit volume.

The dependence of the quantum yield of phototransformations on the pump radiation intensity is shown in Fig. 2. The results demonstrate that the higher is the power density of the pump radiation, the higher is the photostability of the studied compounds. This is likely to be explained by the fact that the part of stimulated emission of molecules is higher at a

higher intensity of the pump radiation. In this case the molecule has time to emit a light quantum before transition to *cis*-stilbene. The lowest quantum yield of *trans*-stilbene photodecay was equal to $2 \cdot 10^{-2}$; it corresponded to the case that the solution was under the lasing conditions. In the absence of a cavity and at about 30-fold intensity attenuation the quantum yield of the photodecay increases by an order of magnitude.

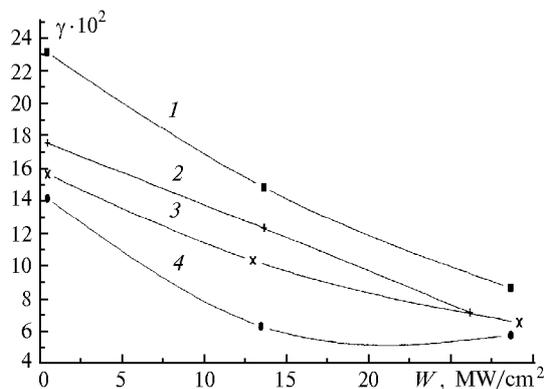


Fig. 2. Quantum yield of the photodecay vs. intensity of XeCl laser radiation: F-(2M)F (1), *trans*-stilbene (2), F-(3M)F (3), and F-(4M)F (4).

As regarding the nature of photoproducts, the main photoproduct is likely the *cis*-stilbene, whose absorption band's maximum lies in the region of 277 nm (Ref. 5). Actually, along with the decrease in the intensity of the *trans*-stilbene absorption band, in the process of illumination, deformation of the short-wave wing of the band is observed with the growth of absorption (Fig. 3). Since *cis*-stilbene formed in the process can absorb the long-wave radiation at 308 nm by the long-wave wing of the band, it also must be subject to phototransformation. The main products in this case can be *trans*-stilbene and dihydrophenanthrene.² The latter, in its turn, oxidizes to phenanthrene in the presence of atmospheric oxygen.²

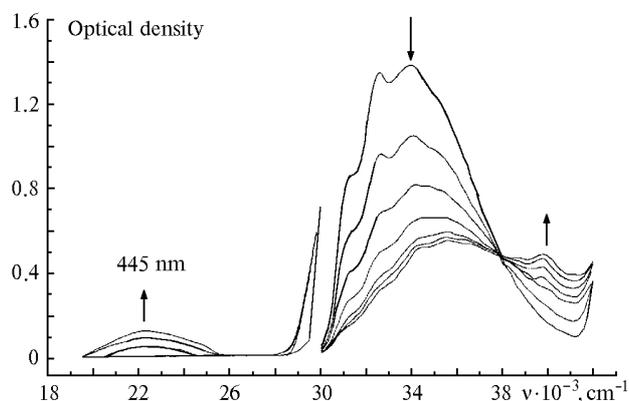


Fig. 3. Change of absorption spectrum of ethanol solution of *trans*-stilbene under exposure to XeCl laser radiation.

Dihydrophenanthrene absorbs the shorter waves as compared with the *trans*-stilbene, and phenanthrene absorption terminates in the region of 28000 cm^{-1} . Nevertheless, the band with $\lambda = 454 \text{ nm}$ (22000 cm^{-1}) appears behind the long-wave absorption band of *trans*-stilbene in the process of illumination. It is difficult to judge on the nature of this photoproduct, but probably it is tetraphenylcyclobutane – the product of *trans*-stilbene dimerization, which is also formed with the participation of the excited state.⁹

Conclusion

Thus, we have demonstrated the possibility of obtaining the lasing effect in *trans*-stilbene solutions. The main condition for lasing to occur is likely the excitation of molecules to the almost zero vibrational level of the state S_1 . At a high density of the exciting radiation and high concentration of the compounds with no vibrational energy stored in the state S_1 , the process of stimulated emission competes with the reaction of isomerization.

Methyl substitution only slightly affects the spectral-luminescent and lasing properties of the substance and its photostability. Consequently, it has no significant inhibiting effect on the reaction of photoisomerization.

The stronger factor affecting the rate of phototransformations of molecules is creation of the conditions, under which the radiative process and photoisomerization become competing processes, that is, the conditions of stimulated emission.

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