

# Limitation of optical radiation power by organic molecules: II. Porphyrins and phthalocyanines

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**Abstract.** The nonlinear transmission of high-power 532-nm and 308-nm laser pulses of duration 7–13 ns by solutions of porphyrins and phthalocyanines and their metal complexes (13 compounds) is studied. The limitation of optical radiation at wavelengths 532 and 308 nm is studied depending on the laser radiation intensity, the solvent type, and the concentration of solutions. The effective cross sections for absorption of radiation by excited molecules are estimated. The induced short-lived absorption in the visible spectral region is studied in the range of hundreds of nanoseconds. The mechanisms of limitation of laser radiation are discussed.

**Keywords:** nonlinear transmission, induced absorption, porphyrins, phthalocyanines, ethyl acetate, chloroform, phototransformations, associates.

## 1. Introduction

The nonlinear-optical properties of organic molecules are widely used in the development of various devices, in particular, optical radiation limiters [1–4]. Few organic molecules have been studied in this respect to date, among them porphyrins and phthalocyanines should be noted. The properties of these molecules were extensively studied both for obtaining new fundamental knowledge and in connection with their applications in medicine [5, 6] and their use as optical radiation limiters [7–25]. It was found that porphyrins limit optical radiation due to reverse saturated absorption (RSA) in a broad spectral range. Porphyrins have a high quantum yield to triplet states [2, 5, 6], their triple–triplet absorption cross sections often greatly exceeding the ground-state absorption cross section [25]. The ability of porphyrins to limit optical radiation power was experimentally studied mainly in the visible region at

the 532-nm second-harmonic wavelength of a neodymium laser and at the 584-nm wavelength emitted by a dye laser [8]. It was found that the nonlinear-optical properties of porphyrins substantially depend both on the molecular structure and the intermolecular interaction (on the solvent type [24]).

Phthalocyanines have been also extensively studied. It was shown in Refs [11, 12] that metallophthalocyanines containing ‘heavy’ central atoms have enhanced absorption in the excited state, and the optical limitation of 532-nm nanosecond pulses in their solutions is related to the enhancement of intersystem crossing accompanied by the increase in the triplet-state population and induced triplet–triplet absorption. It was found that upon excitation by picosecond second-harmonic pulses from a neodymium laser, the ratio of excited-state and ground-state absorption cross sections for aluminium–chloride phthalocyanine [Al(Cl)Pc] was  $\sigma_{ex}/\sigma_{gr} = 10.5$ , while upon excitation by nanosecond pulses, this ratio was 20–50.

The studies of the influence of central atoms, paramagnetic groups, and heavy atoms of solvents on the ratio of these cross sections and the optical radiation limitation effect showed that this effect is related to triplet states of phthalocyanines. An obvious advantage of phthalocyanines is that their properties do not change in solid matrices, for example, in polymethyl methacrylate (PMMA). This is very important in the development of optical limiters with optimal parameters. Thus, it was shown [20] that the maximum attenuation (by a factor of 540) of 532-nm nanosecond laser pulses can be obtained with the help of three PMMA discs doped with In(Cl)(tretbutyl)Pc with a nonuniform concentration profile along the laser beam.

The limitation of optical radiation by porphyrins and phthalocyanines was investigated so far only in the visible spectral region. The aim of our paper is to study the possibility of using solutions of porphyrins and phthalocyanines for limiting radiation from a XeCl laser and the second-harmonic radiation from a neodymium laser and to analyse the proposed mechanisms of optical limitation.

## 2. Samples and methods

We studied tetraphenyl derivatives of porphyrin in complexes with different metals [MTPP, where M is Zn, Cu, Ni, Co, Eu, In(Cl), Al(Cl)], including free-base tetraphenylporphyrin H<sub>2</sub>TPP-1, free-base protoporphyrin IX (PP), and metallophthalocyanines [MPc, where M is In(Cl), Ni, Pd, Lu]. In the case of trivalent metals In and Al, a chlorine atom was bonded with them: M = In(Cl) and Al(Cl)

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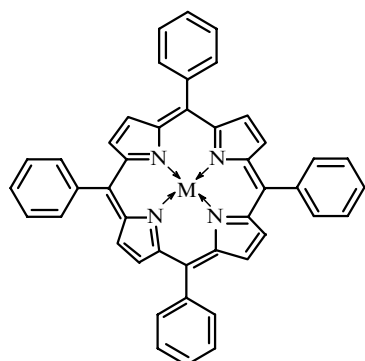
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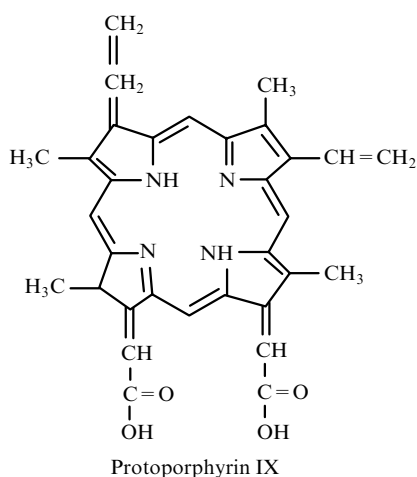
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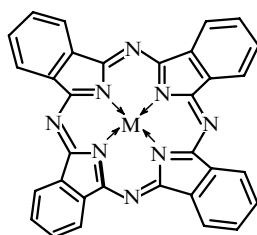
(Fig. 1). Chloroform, ethyl acetate, ethanol, and 3N aqueous solution of HCl (for PP) were used as solvents. The choice of solvents was determined on the one hand by the solubility of molecules and on the other by the necessity to simulate the intermolecular interactions of molecules imbedded then in films. Acidified solutions were used to determine the spectra of neutral and ionic forms of molecules.



Tetraphenylporphyrin + M [M: Zn, Ni, Co, Cu, Eu, Al(Cl), In(Cl)]



Protoporphyrin IX



Phthalocyanine + M [M: Ni, Pd, In(Cl), Lu].

**Figure 1.** Structural formulas of molecules studied.

Experimental setups used in the study are described in detail in Ref. [26]. Excitation was performed by  $\sim 20$ -mJ, 7-ns, 532-nm second-harmonic pulses from a Nd:YAG laser or  $\sim 40$ -mJ, 13-ns, 308-nm pulses from a XeCl laser. The laser power density was varied from low values up to  $300 \text{ MW cm}^{-2}$ , the pump geometry was the same for both lasers: the cell thickness was  $l = 0.5 \text{ cm}$ , laser radiation was focused to a spot of diameter  $0.1 \text{ cm}$ , the concentrations of molecules were chosen so that the initial transmission  $T_0$  at the laser wavelength was 80 %, 70 %, and 50 %. Each value

of  $T_W$  ( $T_W$  is the transmission of solution for the laser power density equal to  $W$ ) was determined as average over three–four measurements. The relative error  $\Delta T_m/T_m$  did not exceed 3 % and was caused by the systematic error of a KTP-2 power meter equal to  $\Delta E/E = 1.5 \%$ .

Phototransformations of solutions exposed to high-power laser radiation were determined both by measuring a change in their absorption for a fixed excitation intensity and by recording the stationary absorption spectra of irradiated solutions with a Specord M40 spectrophotometer.

In some cases, we measured the short-lived absorption spectra in the visible region in the range of hundreds of nanoseconds and estimated the lifetimes of absorbing entities; excitation was performed by a XeCl laser and the spectra were probed by the radiation of a spark in xenon [27]. The short-lived transient (induced) absorption spectra were measured with an error of 20 % (optical density) and 30 % (temporal parameters).

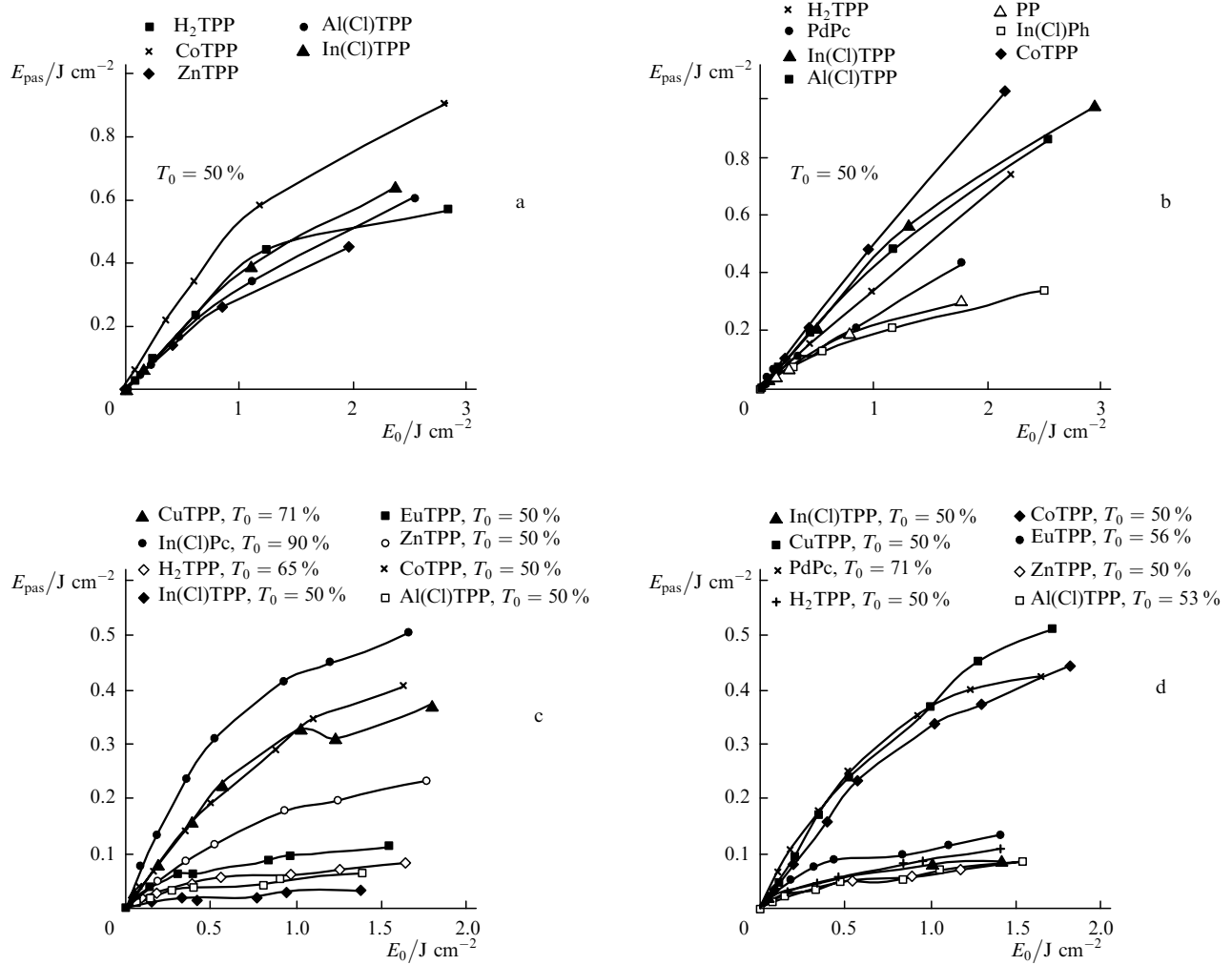
The optical limitation produced by solutions was characterised by the radiation limitation factor  $K_{\text{lim}} = T_0/T_W$ , where  $T_0$  is the linear transmission of the solution measured with a spectrophotometer.

### 3. Results and discussion

Figure 2 shows the dependences of the transmitted energy density on the incident energy density of a XeCl laser and the second harmonic of a Nd:YAG laser for molecular solutions studied. One can see that all these dependences deviate from a linear dependence, i.e., the darkening of the solutions occurs, similarly to that observed in Refs [4, 7, 8]. The minimum transmission and energy density at which nonlinearity is observed strongly depend on the laser wavelength, a solvent, and the molecular structure.

The dependences of transmission on the pump power density presented in Fig. 3 show that transmission of light decreases in all solutions, the degree of darkening with increasing power density being dependent on the concentration (linear transmission  $T_0$ ) of the solution and the incident photon energy. One can see that the optical limitation increases with increasing concentration, the enhancement of this effect being different for different molecules. The threshold at which transmission begins to decrease, i.e., the optical limitation is observed is rather low, no more than  $10 \text{ MW cm}^{-2}$  ( $10\text{--}100 \text{ mJ cm}^{-2}$ ). The limitation factor  $K_{\text{lim}}$  for most molecules irradiated by 532-nm pulses was greater than that observed upon irradiation by 308-nm pulses of the same power. As a rule,  $K_{\text{lim}}$  had the highest value in chloroform. The values of  $K_{\text{lim}}$  and the effective excited-state absorption cross sections estimated for different molecules depending on the experimental conditions are presented in Tables 1 and 2.

The second harmonic of a Nd:YAG laser was most strongly attenuated in the In(Cl)TPP solution in chloroform with the initial transmission of 50 % ( $C = 2 \times 10^{-4} \text{ M}$ ), where the limitation factor was  $K_{\text{lim}} = 19$ . The limitation factors for In(Cl)TPP and Al(Cl)TPP in ethyl acetate were 9.2 and 10.6, respectively. MTPPs containing Ni, Co, and Cu attenuate the 532-nm and 308-nm radiation less efficiently than other molecules ( $K_{\text{lim}} \leq 2$ ). PdPc in ethanol and PP in ethyl acetate attenuate the 308-nm radiation more efficiently than the 532-nm radiation [ $K_{\text{lim}}(308) = 7$  and  $3.5$  compared to  $K_{\text{lim}}(532) = 2.4$  and  $1.3$ , respectively]. Radiation at both these wavelengths is quite efficiently limited by



**Figure 2.** Dependences of the transmitted energy density  $E_{\text{pas}}$  on the incident energy density  $E_0$  of the XeCl laser (a, b) and the second harmonic of the Nd:YAG laser (c, d) for H<sub>2</sub>TPP, CoTPP, ZnTPP, In(Cl)TPP, Al(Cl)TPP, CuTPP, EuTPP, In(Cl)Pc, PdPc, and PP in chloroform (a, c) and ethyl acetate (b, d) for different values of  $T_0$ .

the EuTPP solution in chloroform ( $K_{\text{lim}} \simeq 11$ ). However, in this case, phototransformations, which will be discussed below, play an important role.

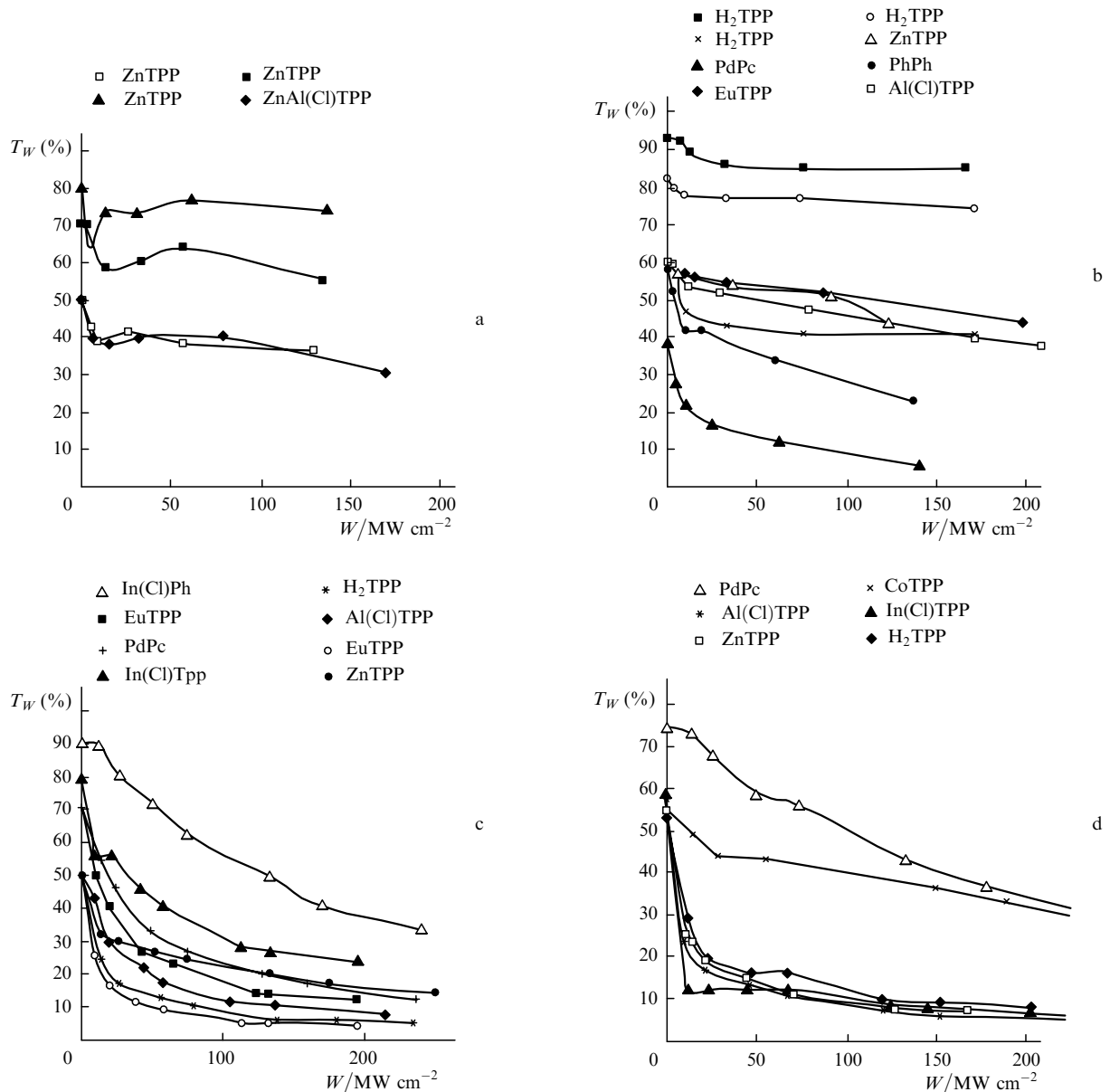
The threshold power density at which transmission no longer changes with increasing incident radiation power density also depends on the concentration and the molecule. For example, for H<sub>2</sub>TPP, saturation begins at  $W = 120 - 150 \text{ MW cm}^{-2}$  for the 532-nm radiation and at  $W = 50 - 70 \text{ MW cm}^{-2}$  for the 308-nm radiation (Fig. 3). Except free-base porphyrins, the saturation effect is observed in solution of ZnTPP, In(Cl)TPP, and Al(Cl)TPP. In many cases (for example, for PP in ethyl acetate, PdPc, CoTPP, CuTPP, etc.), no saturation is observed up to  $W = 250 \text{ MW cm}^{-2}$  (Figs 2 and 3). Our results agree qualitatively with results obtained in Ref. [8], where no saturation was observed in CuTPP sulfonate in gel matrix with increasing laser power density at 584 nm and  $K_{\text{lim}} \simeq 2$ , while the transmission of the 584-nm radiation in ZnTPP sulfonate saturated at  $W = 100 \text{ MW cm}^{-2}$  with  $K_{\text{lim}} = 6$ . This suggests that optical limitation mechanisms in CuTPP and ZnTPP are different.

When transmission of radiation in solutions saturated with increasing laser power density [In(Cl)TPP, Al(Cl)TPP, etc., Fig. 3], the excited centres had the absorption coefficient  $K^* = \varepsilon^* C^* = \sigma^* n^*$  that was higher than the ground-

state absorption coefficient and did not change with increasing pump power. Here,  $n^* = n\varphi$  is the concentration of the excited centres having the effective absorption cross section  $\sigma^*$ ;  $n$  is the initial concentration of molecules in solution (in  $\text{cm}^{-3}$ );  $\varphi$  is the yield of excited centres;  $C^* = C_0\varphi$  and  $\varepsilon^*$  are the concentration (M) and the decimal extinction coefficient for the excited centres, respectively; and  $C_0$  is the initial concentration (M) of molecules. By assuming that the yield is constant and close to unity ( $\varphi \leq 1$ ), we estimated from Fig. 3 the effective absorption cross sections for absorbing entities formed in solutions by using the expression presented in Ref. [28]:

$$\sigma^* \geq 0.38 \times 10^{-20} \varepsilon^* = 0.38 \times 10^{-20} [\lg(1/T_w)] / C_0 l. \quad (1)$$

One can see from the data presented in Tables 1 and 2 that the quantitative estimate confirms our assumption that the darkening of solutions is mainly caused by the formation of one entity during the excitation pulse. Despite the fact that the initial concentrations differ from each other by several times ( $T_0 = 50\%$  or  $90\%$ ), the effective cross sections of the intermediate centres are the same within the measurement error ( $\sim 10\%$ ). The effective cross sections of excited molecules are greater by a factor of 4–12 than the



**Figure 3.** Dependences of the transmission of radiation from the XeCl laser (a, b) and second harmonic of the Nd:YAG laser (c, d) on the laser power density for H<sub>2</sub>TPP, ZnTPP, Al(Cl)TPP, EuTPP, In(Cl)TPP, In(Cl)Pc, PdPc, CoTPP, and PP in chloroform (a, c) and ethyl acetate (b, d).

ground-state absorption cross sections, and this excess correlates with  $K_{lim}$  (Tables 1 and 2). In the case of excitation by a XeCl laser, absorption saturation was observed only for H<sub>2</sub>TPP in ethyl acetate (Fig. 3b), and  $\sigma^*(308) = 4.5 \times 10^{-17}$  cm<sup>2</sup> in contrast to the value  $\sigma_{01}(308) = 3.3 \times 10^{-17}$  cm<sup>2</sup>, also in accordance with a lower value of  $K_{lim}(308)$  compared to  $K_{lim}(532)$  for this molecule (1.6 and 7.1, respectively) (Table 1). As for the nature of the induced absorption, it is probably related to the triplet-triplet absorption. This agrees with the effect of ‘heavy’ atom located at the centre of the molecule or contained in the solvent. The value of  $K_{lim}$  increases in the presence of this atom due to the enhancement of intersystem crossing and the increase in the yield of triplet molecules (cf. the values of  $K_{lim}$  for the same values of  $T_0$  and  $W$  for H<sub>2</sub>TPP and In(Cl)TPP in Tables 1 and 2. For example,  $K_{lim}(532) = 7.1$  and 9.2 for this molecules, respectively, in ethyl acetate for  $T_0 = 50\%$  and  $W = 200$  MW cm<sup>-2</sup>, while in chloroform having three ‘heavy’ atoms,  $K_{lim}(532) = 9.2$

and 19, respectively, for these molecules for close values of  $T_0$  and  $W$ ).

Note that molecules, for which absorption saturation depends on the laser radiation power density, exhibit intense induced absorption, which we measured in the time interval 100–700 ns after the onset of excitation (Fig. 4). The maximum of induced absorption of these molecules shifted to the red compared to the Soret band. The estimate of the lifetime of induced absorption by the method proposed in Ref. [27] showed that absorption at the maximum of the spectrum first increases [ $\tau_{grow} = 100$  ns for In(Cl)TPP and 300 ns for H<sub>2</sub>TPP and Al(Cl)TPP]. The decay time of this absorption is of the order of 1  $\mu$ s for In(Cl)TPP and more than 2  $\mu$ s for H<sub>2</sub>TPP and Al(Cl)TPP. It follows from these data that the solutions of H<sub>2</sub>TPP, In(Cl)TPP, and Al(Cl)TPP will attenuate laser radiation not only in the nanosecond but also microsecond range virtually within the entire visible region. The induced absorption of these molecules, as follows from the rise and decay times observed

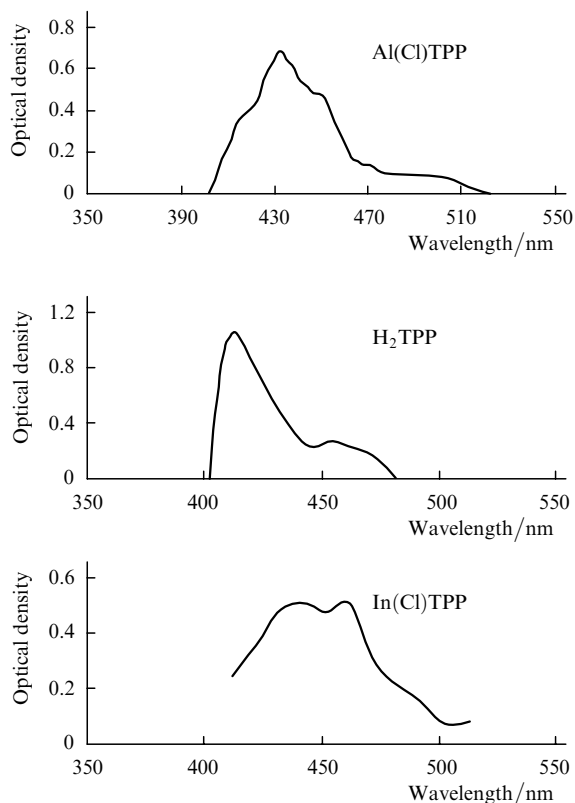
**Table 1.** Radiation limitation factors for a 308-nm XeCl laser and the 532-nm second harmonic of a neodymium laser and the effective absorption cross sections at 532 nm for the ground state [ $\sigma_{01}(532)$ ] and excited state [ $\sigma^*(532)$ ] of solutions of porphyrins and phthalocyanines in ethyl acetate as functions of the initial transmission  $T_0$  and laser radiation power density  $W$ .

Molecule	$T_0(532)$ (%)	$T_0(308)$ (%)	$W(532)/$ MW cm <sup>-2</sup>	$W(308)/$ MW cm <sup>-2</sup>	$\sigma_{01}(532)/$ 10 <sup>-17</sup> cm <sup>2</sup>	$\sigma^*(532)/$ 10 <sup>-17</sup> cm <sup>2</sup>	$K_{lim}(532)$ = $T_0/T_W$	$K_{lim}(308)$ = $T_0/T_W$
H <sub>2</sub> TPP	80	79	200	150	2.3	9	2.9	1.1
	70	70	200	150	–	8.5	5.0	1.3
	50	51	150	150	–	–	7.1	1.6
	–	–	200	–	–	8.5	7.1	–
In(Cl)TPP	80	80	200	200	0.76	5.2	3.6	1.2
	70	70	200	200	–	4.7	5.8	1.2
	55	50	200	200	–	4.6	9.2	1.4
Al(Cl)TPP	80	80	200	200	0.95	6.3	3.2	1.3
	70	70	200	200	–	5.6	5.8	1.4
	53	50	200	200	–	5.8	11	1.7
ZnTPP	80	80	200	150	1.5	–	2.1	1.3
	70	70	200	150	–	7.1	4.1	1.4
	50	50	200	150	–	5.6	8.3	1.4
EuTPP	56	56	200	150	–	–	5.6	1.5
NiTPP	63	59	200	150	–	–	1.2	1.3
CuTPP	50	50	200	200	–	–	1.5	1.4
CoTPP	51	50	200	150	–	–	1.8	1.1
	17	–	200	–	–	–	2.8	–
PP <sup>1)</sup>	62	49	200	150	–	–	1.3	3.5
In(Cl)Pc	–	50	–	150	–	–	–	3.3
NiPc <sup>2)</sup>	–	60	–	150	–	–	–	1.5
PdPc <sup>2)</sup>	71	49	200	150	–	–	2.4	2
	–	35	–	150	–	–	–	7

Notes: <sup>1)</sup> 3N HCl solution; <sup>2)</sup> ethanol solution.**Table 2.** Radiation limitation factors for a 308-nm XeCl laser and the 532-nm second harmonic of a neodymium laser and the effective absorption cross sections at 532 nm for the ground state [ $\sigma_{01}(532)$ ] and excited state [ $\sigma^*(532)$ ] of solutions of porphyrins and phthalocyanines in chloroform as functions of the initial transmission  $T_0$  and laser radiation power density  $W$ .

Molecule	$T_0(532)$ (%)	$T_0(308)$ (%)	$W(532)/$ MW cm <sup>-2</sup>	$W(308)/$ MW cm <sup>-2</sup>	$\sigma_{01}(532)/$ 10 <sup>-17</sup> cm <sup>2</sup>	$\sigma^*(532)/$ 10 <sup>-17</sup> cm <sup>2</sup>	$K_{lim}(532)$ = $T_0/T_W$	$K_{lim}(308)$ = $T_0/T_W$
In(Cl)TPP	86	80	200	170	0.9	11	7.6	1.3
	77	70	200	170	–	–	13	1.2
	54	50	200	170	–	–	19	1.6
Al(Cl)TPP	80	80	200	170	1.2	–	2.1	1.3
	70	70	200	170	–	17	4	1.2
	50	50	200	170	–	16	6.7	1.8
H <sub>2</sub> TPP	80	80	250	170	2	–	4.2	1.5
	70	70	250	170	–	12	6.2	1.6
	50	50	250	170	–	9.7	9.2	2.2
EuTPP	86	80	200	150	1.1	–	3.4	1.7
	77	70	200	150	–	5.9	5.7	5.8
	54	50	200	150	–	–	11	11
ZnTPP	50	50	200	150	–	–	3.1	2.2
	–	–	250	–	–	–	3.6	–
CoTPP	50	70	200	170	–	–	1.7	2
NiTPP	50	70	200	170	–	–	1.4	2.1
CuTPP	50	70	200	170	–	–	2	1.8
	–	–	250	–	–	–	2.3	–
Lu(Pc) <sub>2</sub>	77	–	200	–	–	–	3.2	–
PdPc	80	–	200	–	–	–	3.8	–
	–	–	250	–	–	–	3.8	–
	70	–	200	–	–	–	5.2	–
	–	–	250	–	–	–	5.7	–
In(Cl)Pc	90	–	200	–	–	–	2.5	–
	–	–	250	–	–	–	2.8	–

in non-deoxygenated solutions, can be caused by the inverse absorption of light both by triplet and singlet molecules produced upon the interaction of porphyrins with oxygen dimoles, which were in turn formed via the triplet states of molecules accompanied by delayed fluorescence (see, for example, Ref. [29]). Although microsecond absorption requires a further investigation, it can be used to limit high-power microsecond laser pulses in the visible spectral range between 400 and 500 nm (Fig. 4).



**Figure 4.** Induced absorption spectra of Al(Cl)TPP, H<sub>2</sub>TPP, and In(Cl)TPP in ethyl acetate recorded 300 ns after the onset of excitation.

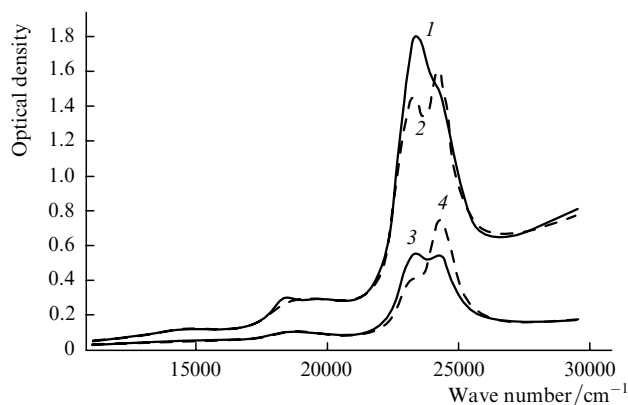
The second group of molecules (PdPc, CoTPP, PP, etc.) do not form any entity responsible for the transmission reduction, their transmission decreasing with increasing the laser power density up to 300 MW cm<sup>-2</sup>. When saturation is absent, the absorption coefficient increases with increasing pump power, which is probably explained by a change in the ratio of concentrations of several absorbing short-lived entities.

This can be explained by the fact that a part of excited molecules interact with each other during the laser pulse to produce strongly absorbing short-lived associates or ionic entities, whose concentration depends on the pump power density. The absence of induced absorption in the range of hundreds of nanoseconds in these solutions suggests that optical limitation is determined in this case by absorbing entities with nanosecond lifetimes, such as collision complexes, reversible ionic entities, etc.

Figure 5 demonstrates by the example of CoTPP that many porphyrins can form complexes in the ground and excited states. The shape of the absorption spectrum of CoTPP depends on its concentration. At the concentration of no more than 10<sup>-4</sup> M, along with the 24300-cm<sup>-1</sup> band,

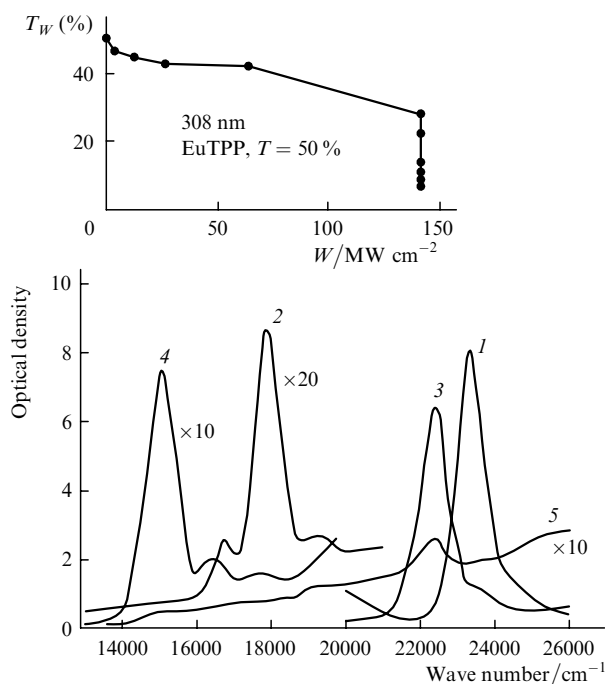
which dominates at concentrations above 10<sup>-4</sup> M, the maximum at 23400 cm<sup>-1</sup> is observed. Absorption in the long-wavelength region also changes correspondingly. This can be caused by a change in the structure of the CoTPP molecule due to the formation of associates or ionic entities.

Figure 5 also shows that after irradiation of these solutions by the second harmonic of the neodymium laser, the equilibrium between absorbing entities is displaced to one of them, suggesting selective excitation of different entities accompanied by a change in transmission. Such effects were observed in solutions of PP in ethyl acetate irradiated by the XeCl and neodymium lasers. Because the spectra of the PP dication in the 3N HCl solution differ from the spectra observed upon irradiation of PP in ethyl acetate, but change in this direction, this means that high-power laser radiation can produce in these solutions monocations, radicals, their associates, etc. In our case, the attenuation of pump radiation is related to a change in the ratio of concentrations of different entities, including ionic entities.



**Figure 5.** Absorption spectra of CoTPP in ethyl acetate before (1, 3) and after (2, 4) irradiation by the second harmonic of the Nd:YAG laser for  $C = 3 \times 10^{-5}$  M,  $l = 1$  cm (1, 2) and  $C = 7 \times 10^{-5}$  M,  $l = 0.1$  cm (3, 4), the total specific absorbed energy  $E_{\text{abs}} = 30$  (2) and 50 mJ cm<sup>-3</sup> (4).

We observed a strong change in the absorption spectrum of the EuTPP solution in chloroform irradiated by the XeCl laser (Fig. 6). This result agrees with the data reported in Ref. [30], where it was shown that porphyrins in halogen-containing solvents undergo efficient phototransformations. In this case, the dependence of  $T_W$  on  $W$  for preliminary irradiated EuTPP solutions becomes steeper: after some dose of irradiation (up to 3 J cm<sup>-3</sup>) performed at the power density 140 MW cm<sup>-2</sup>, the value of  $K_{\text{lim}}$  increased from 1.8 to 8.3 (inset in Fig. 6), while at sufficiently high radiation doses ( $E_{\text{abs}} \sim 20$  J cm<sup>-3</sup>), the value of  $K_{\text{lim}}$  decreased due to a decrease in the concentration of molecules caused by phototransformations [curve (5) in Fig. 6]. The value  $K_{\text{lim}}(308) = 11$  presented in Table 2 was obtained taking into account the increase in  $T_0$  due to phototransformations. These results show that phototransformations of EuTPP in chloroform produced by high-power laser radiation substantially enhance attenuation (the study of the nature of these phototransformations is beyond the scope of this paper). Note that this effect was not observed in ethyl acetate. For this reason,  $K_{\text{lim}}(308) = 1.5$  for EuTPP (Table 1), which is close to  $K_{\text{lim}}(308) = 1.8$  for nonirradiated solutions in chloroform). Molecules In(Cl)TPP, Al(Cl)TPP,



**Figure 6.** Absorption spectra of EuTPP in chloroform before (1, 2) and after (3, 4, 5) irradiation by the XeCl laser for the total specific absorbed energy  $E_{\text{abs}} = 2$  (3, 4) and  $20 \text{ J cm}^{-3}$  (5). The inset shows the dependence of the transmission of radiation from the XeCl laser in the EuTPP solution in chloroform on the incident power density and its decrease at  $W = 140 \text{ MW cm}^{-2}$ .

and ZnTPP that produce strongest optical limitation did not exhibit noticeable phototransformations during transmission measurements.

Some oscillations of transmission observed in chloroform solutions at low pump powers (Fig. 3) should be studied separately. Although the absorption spectra of many molecules do not change substantially during transmission measurements, these oscillations can be caused by phototransformations, which are similar to those observed for EuTPP and can be partially reversible, as follows from our preliminary studies.

#### 4. Conclusions

We have shown that porphyrins and phthalocyanines studied in our paper are capable of limiting pulsed laser radiation in the visible and UV regions. The limitation factor  $K_{\text{lim}} = T_0/T_W$  is determined by the molecular structure, the initial concentration and the absorbing-layer thickness (increases with concentrations), the solvent, the power density, the wavelength and duration of a laser pulse.

The TPP derivatives attenuate more efficiently the second-harmonic radiation of a neodymium laser. In(Cl)TPP in chloroform has the highest limitation factor  $K_{\text{lim}} = 19$  for the power density equal to  $100\text{--}250 \text{ MW cm}^{-2}$ . Radiation of a XeCl laser was attenuated less efficiently. The best results were obtained for EuTPP in chloroform, PdPc in ethanol, and PP in ethyl acetate ( $K_{\text{lim}} = 11.2, 7, \text{ and } 3.5$ , respectively).

The measurements of induced absorption showed that  $\text{H}_2\text{TPP}$ , Al(Cl)TPP, and In(Cl)TPP in ethyl acetate can be

used as optical limiters of nanosecond and millisecond laser pulses in the visible region between 400 and 500 nm.

We assume that the limitation of laser radiation at 532 nm in  $\text{H}_2\text{TPP}$ , ZnTPP, Al(Cl)TPP, and In(Cl)TPP occurs due to inverse saturation upon transitions of molecules to triplet states, the effective absorption cross sections for these transitions exceeding the ground-state absorption cross section. In other cases, in the absence of absorption saturation with increasing laser radiation power density (PdPc, etc.), optical limitation can be caused by the efficient absorption of light by intermediate complexes or reversible photoproducts produced from excited molecules during a laser pulse.

The decrease in the limitation factor upon excitation of porphyrins by UV radiation from a 308-nm XeCl laser compared to excitation in the visible region can be explained by the decrease in the triplet-triplet absorption cross section at 308 nm and in the yield of triplet states. To elucidate this question, it is necessary to study the photophysical and photochemical properties of porphyrins upon UV excitation.

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