

# Experimental study of nonlinear absorption in polymethine dye solutions by the $z$ -scan method

V.A. Svetlichnyi

**Abstract.** The nonlinear absorption coefficients  $\beta$  and the ratios  $k$  of absorption cross sections in the ground and excited states are measured by the open-aperture  $z$ -scan method for three polymethine dyes excited by nanosecond 532-nm second-harmonic pulses of a Nd : YAG laser. The values of  $k$  measured for the 789, 842, and 823 dyes are 10, 11, and 11, respectively, and correlate with the limiting properties of these dyes.

**Keywords:** polymethine dyes,  $z$ -scan, nonlinear absorption.

## 1. Introduction

Among direct methods for measuring the nonlinear optical properties of substances, the  $z$ -scan method is most commonly used in the last years. This method was first proposed in [1, 2] for determining the value and sign of the nonlinear refractive index (closed-aperture  $z$ -scan) and the nonlinear absorption coefficient (open-aperture  $z$ -scan). The method is based on measuring the dependence of the far-field intensity of an exciting laser beam propagated through a sample on the sample position with respect to the focal plane of a lens. At present the  $z$ -scan method, along with flash photolysis, is widely used for determining the characteristics of various nonlinear processes: scattering, two-photon absorption, induced absorption, thermal defocusing, etc. [3–6].

The investigation of the dependence of nonlinear optical properties of organic molecules on a change in the population of electronic states is of great interest. One of the efficient mechanisms of the optical power limitation, when the absorption cross section from the lower excited singlet or triplet state of a molecule exceeds the absorption cross section from the ground state at the exciting wavelength, is reverse saturated absorption (RSA). In this case, the open-aperture  $z$ -scan method allows one to estimate the ratio  $k = \sigma_1/\sigma_0$  of cross sections for absorption from the excited and ground states at the exciting wavelength [7, 8].

In this paper, the open-aperture  $z$ -scan method was used to study the nonlinear optical properties of three poly-

methine dyes employed for the efficient limitation of the power of 532-nm nanosecond pulses [9, 10].

## 2. Theory

During the propagation of high-power laser radiation through a medium, the linear Lambert–Beer absorption law is violated and the transmission  $T$  of the medium begins to depend on the exciting radiation intensity  $I$ . In this case, the attenuation of the radiation intensity can be written in the form

$$\frac{dI}{dz} = -(\alpha_0 + \beta I)I, \quad (1)$$

where  $\alpha_0$  and  $\beta$  are the linear and nonlinear absorption coefficients, respectively.

The relation between  $\beta$  and parameters of the medium depends on the mechanisms of nonlinear absorption. For example, in the case of two-photon absorption, the coefficient  $\beta$  is related to the imaginary part of the third-order nonlinear susceptibility  $\chi^{(3)}$ . In turn,

$$\text{Im}\{\chi^{(3)}\} = \frac{n_0^2 \varepsilon_0 c \lambda \beta}{2\pi} \quad (2)$$

is related to the imaginary part of the second-order molecular hyperpolarisability  $\gamma$ :

$$\text{Im}\{\gamma\} = \frac{\text{Im}\{\chi^{(3)}\}}{f^4 C N_A}, \quad (3)$$

where  $n_0$  is the refractive index;  $\varepsilon_0$  is the dielectric constant;  $c$  is the speed of light;  $\lambda$  is the radiation wavelength;  $f = (n_0^2 + 2)/3$  is the Lorentz factor of the local field;  $C$  is the molar concentration; and  $N_A$  is Avogadro's number.

In the case of RSA, we are dealing with the redistribution of populations of the ground and excited states, and the coefficient  $\beta$  should depend on the exciting radiation intensity. Such dependence was observed, for example, in [7] and, as shown below, nonlinear absorption in a medium cannot be correctly estimated from  $\text{Im}\{\chi^{(3)}\}$  and  $\text{Im}\{\gamma\}$ .

In open-aperture  $z$ -scan experiments with thin samples, when only nonlinear absorption in the medium is studied, the dependence of the normalised transmission on the position  $z$  of a cell in the case of weak linear absorption and the Gaussian temporal profile of a beam is described by the expression [11]

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$$T(z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(1 + z^2/z_0^2)^m (m+1)^{3/2}} \simeq 1 - \frac{q_0(z)}{2\sqrt{2}}, \quad (4)$$

where

$$q_0(z) = \frac{\beta I L_{\text{eff}}}{1 + (z/z_0)^2}; \quad (5)$$

$z_0$  is the diffraction length of the beam;  $I$  is the radiation intensity incident on a sample;

$$L_{\text{eff}} = \frac{1 - \exp(-\alpha_0 L)}{\alpha_0} \quad (6)$$

is the effective sample length;  $\alpha_0$  is the linear absorption coefficient of the medium at the wavelength studied; and  $L$  is the sample thickness.

For RSA,  $q_0$  is related to the excited-state absorption cross section  $\sigma_1$  by the expression [1]

$$q_0 = \frac{\alpha_0 \sigma_1 F_0 L_{\text{eff}}}{2h\nu}, \quad (7)$$

where  $F_0$  is the energy density.

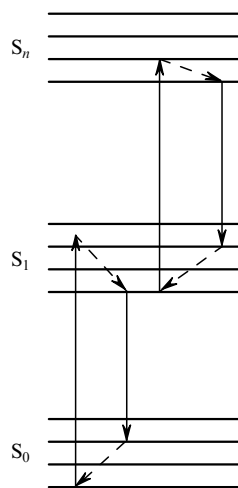
On the other hand, nonlinear absorption in solutions of organic compounds can be determined by solving a system of differential equations for populations of the energy levels of molecules [7, 9, 12].

Photoprocesses in polymethine dyes studied in the paper can be described by using a three-level scheme (Fig. 1):

$$\frac{dn_0}{dt} = -\frac{\sigma_0 I}{h\nu} n_0 + \frac{n_1}{\tau_{10}}, \quad (8)$$

$$\frac{dn_1}{dt} = \frac{\sigma_0 I}{h\nu} n_0 - \frac{\sigma_1 I}{h\nu} n_1 - \frac{n_1}{\tau_{10}}, \quad (9)$$

$$\frac{dn_2}{dt} = -\frac{\sigma_1 I}{h\nu} n_1 - \frac{n_2}{\tau_{21}}, \quad (10)$$



**Figure 1.** Three-level scheme describing photoprocesses in polymethine dyes excited by nanosecond pulses (only the most probable transitions are shown). The vertical arrows pointing up are the absorption of laser radiation from the ground  $S_0$  and lower  $S_1$  electronic singlet states, the arrows pointing down are nonradiative relaxation between electronic states, and the dashed arrows are vibration–rotation relaxation within an electronic state.

where  $n_0$ ,  $n_1$ , and  $n_2$  are populations of the  $S_0$ ,  $S_1$ , and  $S_n$  states.

We studied earlier in detail the luminescent and absorption properties of these molecules and obtained their excited-state absorption spectra in the visible region and dependences of the transmission  $T$  of their solutions on the incident radiation intensity  $I$  [9, 10]. Experimental dependences  $T(I)$  were approximated within the framework of a three-level scheme (by neglecting triplet states). Some data were obtained from quantum-chemical calculations (rate constants of transitions) and experiment (ground-state absorption cross sections). The absorption cross section  $\sigma_1$  is a fitting parameter. Polymethine dyes were described in [8, 12] also by using a three-level model, while in [8, 13] a five-level scheme was also used because the excited-state absorption anisotropy was found for these molecules and another system of excited singlet states was observed.

The decay of a laser pulse propagating through a medium, taking excited-state absorption into account, can be written in the form

$$\frac{\partial I}{\partial z} = -\alpha I = -(\sigma_0 n_0 + \sigma_1 n_1) I. \quad (11)$$

Expression (11) shows that the attenuation of the laser radiation intensity due to RSA is determined not by the absolute value of  $\sigma_1$  but by the ratio of absorption cross sections in the excited and ground states  $k = \sigma_1/\sigma_0$ .

Taking into account the system of equation (8)–(11), Eqn (11) can be solved numerically [9]. Here, we will use the quasi-stationary approximation because the relaxation times in the systems under study are  $10^{-12} - 10^{-9}$  s, which is much shorter than the laser pulse duration. In this case, the approximate solution of Eqn (11) can be written in the form [7]

$$\alpha(I, I_{\text{sat}}, k) = \alpha_0 \left(1 + \frac{I}{I_{\text{sat}}}\right)^{-1} \left(1 + k \frac{I}{I_{\text{sat}}}\right), \quad (12)$$

where  $I_{\text{sat}} = h\nu/(\sigma_0 \tau_{10})$  is the saturation intensity.

In our case (RSA in the singlet-state channel),  $k$  is the ratio of absorption cross sections for the  $S_1 \rightarrow S_m$  and  $S_0 \rightarrow S_n$  transitions at the 532-nm second harmonic of a Nd : YAG laser. For  $k > 1$ , the transmission of light in the medium should decrease with increasing the excitation intensity.

By definition, the absorption coefficient of a medium is

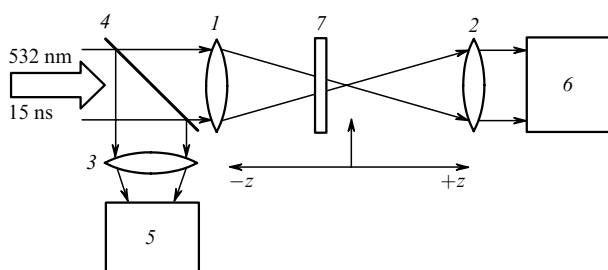
$$\alpha(I, I_{\text{sat}}, k) = -\frac{\ln T}{L}, \quad (13)$$

where  $T$  is the normalised transmission determined from experiments. By substituting (13) into (12), we can determine  $k$  and  $\sigma_1$ .

### 3. Experimental

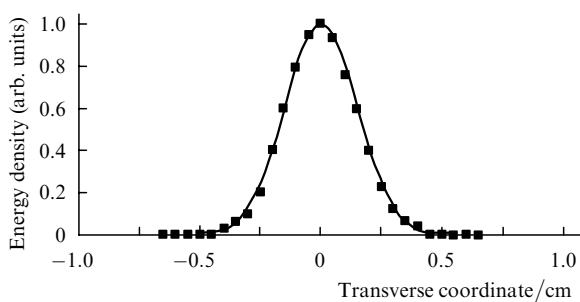
Figure 2 shows the experimental scheme for measuring nonlinear absorption by the  $z$ -scan method. Dye solutions were excited by the 532-nm, 15-ns, 0.07–1-mJ second-harmonic Gaussian pulses from a Nd:YAG laser with a pulse repetition rate of 1–10 Hz.

Because the spatial profile of a beam is important in  $z$ -scan experiments, we measured the radiation energy density



**Figure 2.** Scheme of the open-aperture  $z$ -scan setup: (1–3) spherical lenses with  $F = 12$  cm; (4) beamsplitter; (5) pyroelectric ED-100A detector; (6) KTP-2 calorimeter; (7) dye cell.

in the beam cross section (Fig. 3). For the unfocused beam, measurements were performed by two methods: the cut-off aperture method and by scanning the beam cross section with a fire of diameter 0.125 mm. One can see from Fig. 3 that the spatial profile is Gaussian. Radiation was focused with a spherical lens with the a focal distance of 12 cm. The optical system was assumed linear and aberration-free, i.e., a Gaussian beam was not distorted. The waist radius in the focal plane was estimated to be 33  $\mu\text{m}$  by the method described in [14].



**Figure 3.** Transverse distribution of the energy density in an unfocused pulsed laser beam; squares are experimental values; the solid curve is the Gaussian distribution  $\exp[-2(r/\omega)^2]$  with  $\omega = 0.3$  cm.

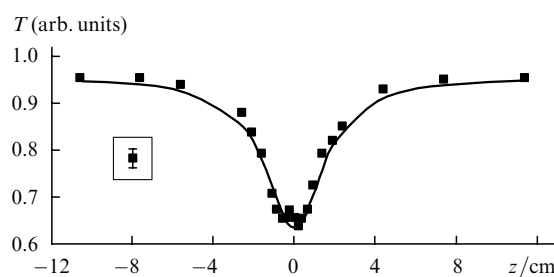
Dye solutions were studied in a 1-mm silica cell, which could be displaced along the optical axis with a step of 0.2 mm. The radiation intensity transmitted through the cell was measured with a precision KTP-2 microcalorimeter, which was calibrated with a pyroelectric ED-100A detector (Gentec EO). The input aperture of the KTP-2 calorimeter (20 mm) exceeded the diameter of the incident radiation beam approximately by a factor of five. A large distance to the detector, a low concentration of dyes and a low quantum yield of fluorescence ( $\sim 0.15$ ) [9] excluded the influence of the fluorescence signal on the calorimeter readings. For the maximum excitation intensity (in focus), the contribution of the dye emission was less than 0.1 %, which allowed us not to use selective optical filters in front of a detector of radiation transmitted through the dye solution. To control the incident laser energy, a part of incident laser radiation was deflected to a pyroelectric ED-100A detector by means of a beamsplitter placed in front of a focusing lens. The normalised ratio of the incident and transmitted laser energy at different positions of the dye cell with respect to the lens focus was equal to the transmission  $T(z)$ . In addition, the transmission in the cell with a solvent (ethanol) was

measured both upon linear excitation (with a spectrophotometer) and laser excitation – by the  $z$ -scan method. This allowed us to take into account reflection from the cell walls and nonlinear absorption in a dye.

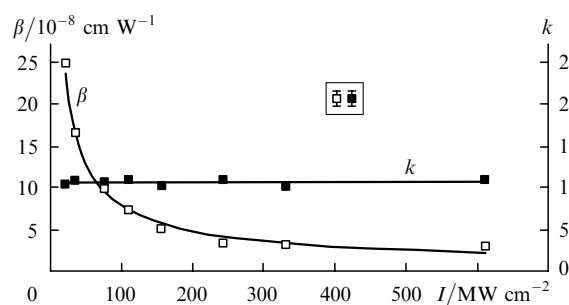
#### 4. Results

Figure 4 shows transmission measured for the ethanol solution of the PD 823 polymethine dye by the open-aperture  $z$ -scan method with a pulse energy of 0.35 mJ, corresponding to the excitation intensity in the focal plane ( $z = 0$ ) of 610  $\text{MW cm}^{-2}$ . By measuring nonlinear transmission at different excitation intensities, we obtained the dependence of the nonlinear absorption coefficient  $\beta$ , calculated by (4), on the radiation intensity  $I$  (Fig. 5). The value of  $\beta$  depends on the radiation intensity because it is related to a change in the population of molecular states. The absorption cross section  $\sigma_1$ , calculated taking (7) into account, also depends on the incident radiation intensity. Note that  $\sigma_1$  is a spectroscopic constant of a substance. The absorption cross section  $\sigma_1$  can be changed only when the exciting field strength is much higher than that of intramolecular fields, which is not achieved in  $z$ -scan experiments with nanosecond and picosecond pulses. Therefore, the absorption cross section cannot be correctly estimated by this method. This is explained first of all by the fact that expressions (1)–(7) neglect the redistribution of electronic-state populations upon high-power laser excitation.

Note nevertheless that the nonlinearity of organic molecules caused by RSA was estimated in the literature in terms of the nonlinear susceptibility  $\text{Im}\{\chi^{(3)}\}$  and hyper-



**Figure 4.** Transmission measured for the PD 823 dye solution by the open-aperture  $z$ -scan method upon excitation by 0.35-mJ nanosecond pulses; squares are experimental values; the solid curve is the best fit by using the three-level RSA model.



**Figure 5.** Dependences of the nonlinear absorption coefficient  $\beta$  and the ratio  $k$  of the excited- and ground-state absorption cross sections for the PD 823 dye on the excitation intensity.

polarisability  $\text{Im}\{\gamma\}$ , and the excited-state absorption cross section was estimated from expressions (1)–(7), in particular, for comparing the nonlinear properties of series of molecules with similar structures [7, 15].

In this paper, the ratio  $k$  of absorption cross sections in the excited and ground states of polymethine dyes was calculated from expressions (1)–(13). The results are presented in Table 1, where the measured values of the absorption coefficient  $\beta$  and, for comparison, the data for the DCM-620 solution [(dicyanomethylene)-pyran derivative], which is used, as polymethine dyes, to limit the radiation power at 532 nm [9] are also given.

The experimental dependence of transmission by the PD 823 dye solution on the cell position with respect to the focal plane of the lens in Fig. 4 is fitted by the solid curve taking (12) and (13) into account, where the intensity corresponds to the intensity of a focused Gaussian beam. The beam waist radius used in the simulation was 35 mm, in good agreement with its experimental value.

The correctness of the description of photoprocesses used in the paper is confirmed by the independence of the absorption cross section  $\sigma_1$  (or the parameter  $k$ ) on the excitation intensity (Fig. 5). Note that this dependence was plotted by using the lifetime  $\tau_{10}$  of the  $S_1$  state as a fitting parameter, whose preliminary value was taken from quantum-chemical calculations [10].

One can also see from Table 1 that the ratio of absorption cross sections in the ground and excited states correlates with the limiting ability of molecules defined by the attenuation coefficient

$$K_{100} = \frac{T_0}{T_{100}}, \quad (14)$$

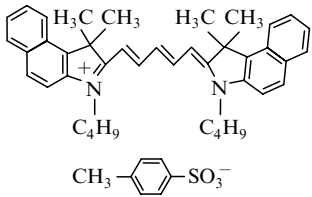
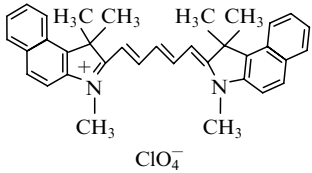
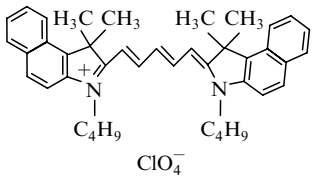
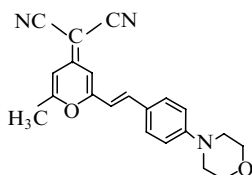
where  $T_0$  is the linear transmission (Table 1 presents the data for  $T_0 = 70\%$ ) and  $T_{100}$  is transmission for the exciting power density  $100 \text{ MW cm}^{-2}$ .

The values of  $k$  for all the polymethine dyes studied were 10–11 and the values of  $K_{100}$  were 6.5–7. For DCM-620, the value of  $k$  is considerably lower (3.5), which reduces the limiting ability of this molecule to  $K_{100} = 24$ . For polymethine molecules, which can be described by a three-level scheme, the parameter  $k$  is related only to singlet–singlet absorption. For the DCM-620 molecule, which is described in the general case by a five-level scheme, the parameter  $k$  is a generalised characteristic of the  $S_1 \rightarrow S_n$  singlet and  $T_1 \rightarrow T_n$  triplet absorptions.

## 5. Conclusions

The nonlinear optical properties of three polymethine dyes have been studied upon pulsed laser excitation. The ratio  $k$

**Table 1.** Spectral and nonlinear optical characteristics of molecules studied.

Molecule	Solvent	$\lambda_{ab}^{max}/$ nm	$\sigma_0^{max}/$ $10^{-16} \text{ cm}^2$	$\sigma_1/$ $10^{-18} \text{ cm}^2$ ( $\lambda = 532 \text{ nm}$ )	$\alpha_0/\text{cm}^{-1}$ ( $\lambda = 532 \text{ nm}$ )	$\beta/10^{-8}$ $\text{cm W}^{-1}$	$\tau_{10}/$ ns	$k = \sigma_{ex}/\sigma_0$ ( $\lambda = 532 \text{ nm}$ )	$K_{100}$
PD 842 	ethanol	687	$7.0 \pm 0.3$	$7.6 \pm 0.3$	$0.46 \pm 0.02$	$3.3 \pm 0.3^*$	0.7	$11 \pm 1.5$	7
PD 789 	ethanol	682	$7.2 \pm 0.3$	$8.7 \pm 0.3$	$0.53 \pm 0.03$	$3.3 \pm 0.3^*$	0.7	$10 \pm 1.2$	6.5
PD 823 	ethanol	687	$7.2 \pm 0.3$	$7.6 \pm 0.3$	$0.46 \pm 0.02$	$3.2 \pm 0.3^*$	0.7	$11 \pm 1.5$	7
DCM-620 	ethyl acetate	435	$0.99 \pm 0.05$	$2.5 \pm 0.1$	$1.5 \pm 0.2$	$6.7 \pm 0.7^{**}$	4	$3.5 \pm 0.4$	2.4

Note:  $K_{100}$  is the attenuation coefficient of the 532-nm, 6-ns pulses for the excitation intensity  $W \approx 100 \text{ MW cm}^{-2}$  [9]; \*  $610 \text{ MW cm}^{-2}$ ; and \*\*  $310 \text{ MW cm}^{-2}$ .

of the absorption cross sections of molecules in the excited and ground states has been measured. It has been shown that this ratio is related to the attenuation coefficient of the dyes. The cross-section ratio  $k$  for media used as optical limiters of the laser radiation power is a more important parameter than the excited-state absorption cross section  $\sigma_1$  because in the presence of intense ground-state absorption  $\sigma_0$  at a given wavelength the limiting properties of molecules can be absent [16].

The nonlinear absorption coefficient  $\beta$  of polymethine dyes has been determined, which, unlike the parameter  $k$  dependent on the spectral parameters of molecules (absorption cross sections), is determined by the excitation intensity because nonlinear absorption is related to a change in the population of electronic states of molecules.

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