*Quantum Electronics* **35** (5) 415 – 418 (2005) 

PACS numbers: 42.65.An; 33.80.-b
DOI: 10.1070/QE2005v035n05ABEH003405

# Measurement of the two-photon absorption cross sections of dicyanomethylene-pyrans by the *z*-scan method

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***Abstract*. The two-photon absorption cross sections of three dicyanomethylene-pyrane DCM dyes excited by a femtosecond pulsed from a Ti : sapphire laser are measured by the open-aperture *z*-scan method. The experimental transmission curves are approximated by the corresponding model curves to give the two-photon absorption cross sections equal to $5.1 \times 10^3$ GM, $5.7 \times 10^3$ GM, and $8.4 \times 10^3$ GM for DCM, DCM-17, and DCM-doa, respectively (1 GM = $10^{-50}$ cm$^4$ s phot$^{-1}$ mol$^{-1}$).**

***Keywords***: *open-aperture z-scan method, two-photon absorption cross section of dyes, femtosecond pulses.*

## 1. Introduction

Laser technology advances during the last two decades resulted in the generation of light pulses of only a few femtoseconds in duration. An inherent feature of femtosecond pulses is their high peak power allowing the development of new directions in molecular optics based on the two-photon interaction of laser radiation with organic and biological molecules. This interaction is used in fluorescence two-photon microscopy [1], two-photon lithography [2], three-dimensional memory with two-photon data recording and reading [3], in optical limiters [4], etc. To induce two-photon processes, apart from pulses with high peak powers, materials with high two-photon absorption (TPA) cross sections at a certain wavelength are also required. The search for such materials and their synthesis are performed at many laboratories.

The TPA cross sections are most often determined by comparing the intensity of two-photon excited fluorescence of a substance under study with that of a substance with the known TPA cross section at a given wavelength, which is used as the reference [5, 6]. Such measurements are indirect but they have a high sensitivity.

Among the direct methods for measuring nonlinear optical properties of substances, in particular, TPA cross sections, the most popular is the *z*-scan method. This method was first proposed in [7, 8] for determining the value and sign of the nonlinear refractive index (closed-aperture *z*-scan) and measuring the nonlinear absorption coefficient (open-aperture *z*-scan). The method is based on the far-field measurement of a change in the exciting laser radiation transmitted through a sample depending on the sample position with respect to the focal point [9]. This method has a lower sensitivity compared to the reference method, but allows the measurement of the TPA cross sections for non-fluorescing substances. Thus, the *z*-scan method was used to measure TPA cross sections for some new asymmetric dyes (referred to as AF), for which record-high values were obtained: 11560 GM, 9700 GM, and 3900 GM for AF-50, AF-60, and AF-70, respectively [10] (1 GM = $10^{-50}$ cm$^4$ s phot$^{-1}$ mol$^{-1}$).

In this paper, we measured for the first time the coefficient of nonlinear absorption of radiation from a femtosecond Ti : sapphire laser for three dicyanomethylene-pyran dyes and calculated the corresponding TPA cross sections. It is shown that TPA cross sections of these dyes are comparable to those for AF dyes.

## 2. Samples and methods

We studied three dicyanomethylene-pyran dyes: DCM (Kodak), DCM-doa (Alpha-Akonis Research and Production Company, Dolgoprudnyi), and DCM-17 (donated by A.P. Lugovskoi, Minsk, Belarus) in 1-methyl,2-pyrollidone (MP) at a concentration of $10^{-2}$ M. Dyes of this type – efficient active media for tunable lasers, have a high quantum yield of fluorescence, a large Stokes shift (so that their absorption and fluorescence bands only weakly overlap), and are only weakly subjected to aggregation. This allows the use of dicyanomethylene-pyrans at high concentrations without reducing the fluorescence intensity, which is important for many practical applications. The long-wavelength absorption bands of these dyes in MP lie in the region between 450 and 520 nm (Fig. 2).

The experimental scheme for the *z*-scan measurement of nonlinear absorption is shown in Fig. 3. Excitation is performed by a femtosecond FemtoMed Ti : sapphire laser (Tekhnoskan, Novosibirsk) emitting 790-nm, 100-fs pulses with a pulse repetition rate of 90 MHz and an average power of 300 ± 10 mW. This laser was pumped by an argon

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Received 18 January 2005
*Kvantovaya Elektronika* **35** (5) 415 – 418 (2005)
Translated by M.N. Sapozhnikov

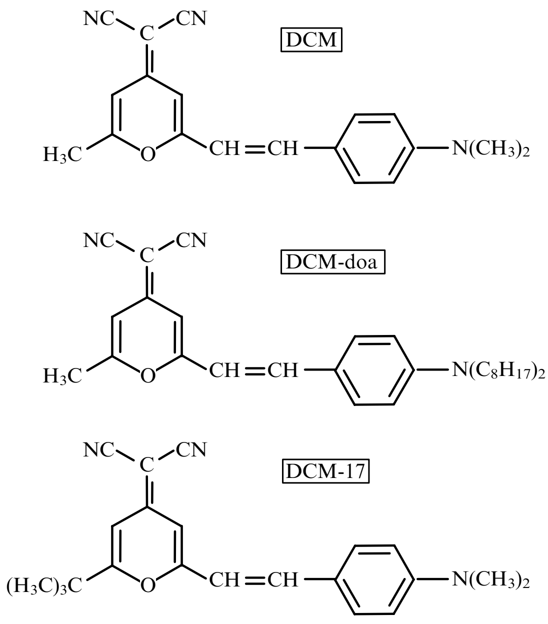


**Figure 1.** Structural formulas of the dye studied in the paper.

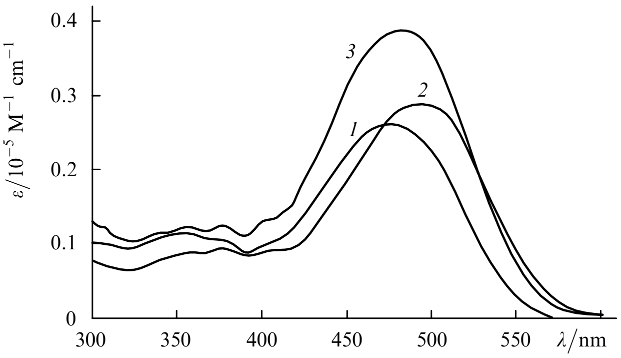


**Figure 2.** Absorption spectra of dicyanomethylene-pyran substituents DCM (*1*), DCM-doa (*2*), and DCM-17 (*3*) in MP.

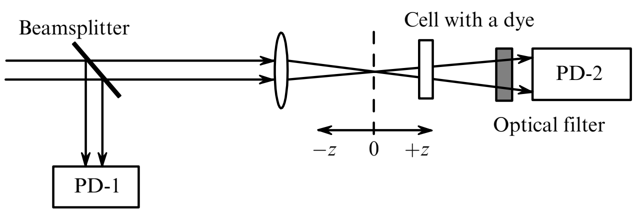


**Figure 3.** Scheme of $z$-scan measurements.

laser (INVERsia Ar-5-15, manufactured by Inversia, Novosibirsk).

Laser radiation was focused by a spherical lens with a focal distance of 12 cm. The dye solution was studied in a 1-mm quartz cell which could be displaced along the optical axis $z$. The average radiation power transmitted through the cell was measured with a photodetector PD-2 (PD-24 photodiode) located at a distance of 22 cm from the focal point. The input aperture of PD-2 (12 mm) exceeded the laser-beam diameter approximately by a factor of four. To provide the operation of the photodiode in a linear regime, the dye florescence and exciting radiation were suppressed with the help of neutral optical filters. A photodetector PD-1 (PD-24 photodiode) was used to control the intensity of radiation incident on the cell. The normalised intensity ratio of output signals from photodetectors PD-2 and PD-1 was equal to the transmission $T_z$ of the solution obtained for different positions of the cell with respect to the lens focus. Photodetectors PD-1 and PD-2 were calibrated by using a calorimetric power meter. Output signals from the photodetectors were fed to a memory board and computer-processed.

The dye solutions studied in the paper do not exhibit linear absorption at the wavelength of a Ti : sapphire laser. As the excitation intensity was increased by focusing the pump radiation in the solution, nonlinear TPA appeared. The nonlinear absorption coefficient $\beta$ and the TPA cross section $\sigma_2$ can be calculated from the dependence of the transmission of laser radiation on the position of the cell with solution with respect to the lens focus [8].

The accurate measurement of the waist radius of a laser beam in the focal plane is of fundamental importance in the $z$-scan method. It was measured in the following way. The transverse profile of the laser beam was measured at distances of 3 and 4 cm from the focal point by displacing a fibre of diameter 125 μm. The fibre was mounted on a computer-controlled scanning stage displaced over the beam cross section with a step of 10 μm (the profile of a femtosecond laser beam obtained in this way is shown in Fig. 4). The beam diameter was measured at the $1/e^2$ level and then, by using the expression for Gaussian beams, the waist radius in the focus was measured, which was found to be 16 μm.

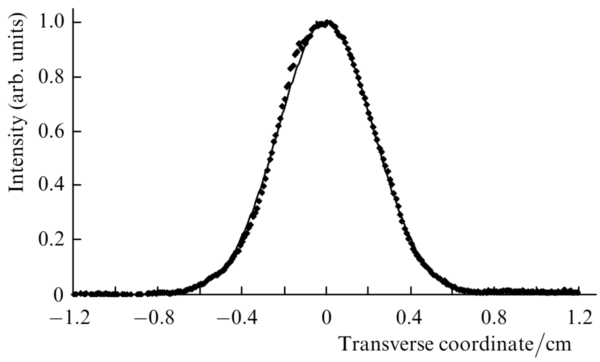


**Figure 4.** Laser-beam profile at a distance of 3 cm from the focal point.

To verify the two-photon nature of the interaction of Ti : sapphire laser radiation with dicyanomethylene-pyrans, we measured the dependences of the fluorescence intensity of these dyes on the laser radiation power, which proved to be close to quadratic. A typical example is presented in Fig. 5.

## 3. Results and discussion

The third-order nonlinear susceptibility $\chi^{(3)}$ in the case of TPA is

$$\chi^{(3)} = \chi_{\mathrm{R}}^{(3)} + \mathrm{i}\chi_{\mathrm{I}}^{(3)}. \tag{1}$$

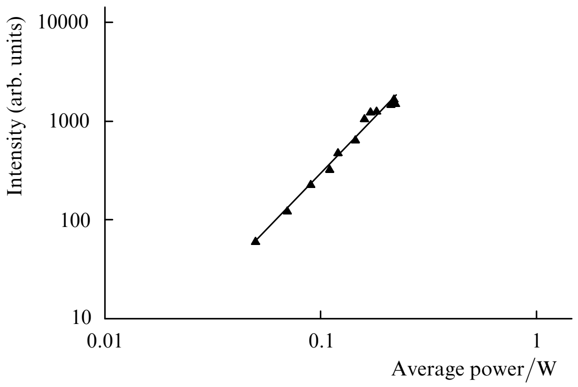


**Figure 5.** Dependence of the two-photon fluorescence intensity of DCM-doa on the exciting radiation power (the slope ratio of the straight line is 2.27).

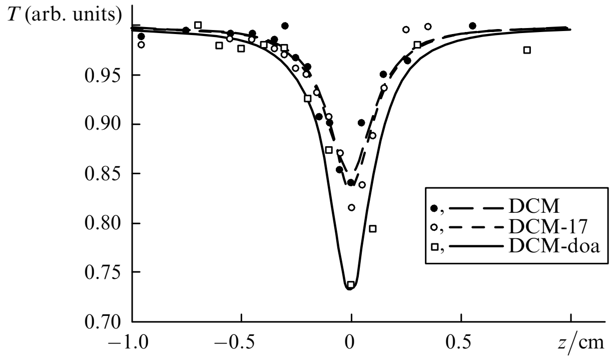


**Figure 6.** Dependences of the transmission $T$ in a cell with the DCM dyes on the cell position $z$ with respect to the focal point. The curves are approximations obtained by numerical simulation, points are the experiment.

Here, the imaginary part is related to the TPA coefficient $\beta$ by the expression

$$\chi_{\mathrm{I}}^{(3)} = \frac{n_0^2 \varepsilon_0 c^2}{\omega}\beta, \qquad (2)$$

where $n_0$ is the refractive index of a medium; $\varepsilon_0$ is the dielectric constant of vacuum; $c$ is the speed of light in vacuum; and $\omega$ is the exciting laser frequency.

In this case, the total absorption of the medium will be the sum of the linear absorption $\alpha$ and nonlinear TPA:

$$\alpha(I) = \alpha + \beta I, \qquad (3)$$

where $I$ is the incident radiation intensity.

The normalised radiation energy transmitted through a sample obtained by the open-aperture $z$-scan method in the case of a Gaussian pulse is described by the expression [11]

$$T(z) = 1 - \frac{\beta I_0 L_{\mathrm{eff}}}{2\sqrt{2}} \frac{1}{1 + z^2/z_0^2}, \qquad (4)$$

where $z$ is the sample position with respect to the focal point; $I_0$ is the laser beam intensity at the focus ($z = 0$); $z_0$ is the diffraction length of the beam; $L_{\mathrm{eff}} = [1 - \exp(-\alpha L)]/\alpha$; and $L$ is the length of the medium.

In the Gaussian approximation, $z_0$ and the waist radius $w_0$ of the laser beam in the focus are related by the expression

$$z_0 = \frac{\pi w_0^2}{\lambda}, \qquad (5)$$

where $\lambda$ is the laser radiation wavelength.

Figure 6 shows the typical dependences of transmission in the cell with DCM dyes at a concentration of $10^{-2}$ M on the cell position with respect to the focal point. The intensity profiles of transmitted radiation are symmetric with respect to $z = 0$. The curves show approximations of the experimental data obtained by numerical simulations. This method was also used to measure the nonlinear absorption coefficient $\beta$ and the waist radius. The latter parameter, found with the help of approximating curves, is 17.64 μm, in good agreement with the experimental data.

Knowing the nonlinear absorption coefficient, we can calculate the TPA cross section [12],

$$\sigma_2 = \frac{h\omega\beta}{2\pi N}, \qquad (6)$$

where $N$ is the concentration of molecules in $\mathrm{cm}^3$ and $h\omega/2\pi$ is the exciting photon energy. The nonlinear absorption coefficients and TPA cross sections of the dyes are also presented in Table 1. Therefore, DCM dyes have high TPA cross sections at the wavelength of the Ti : sapphire laser, which are comparable to TPA cross sections for AF dyes [10], and can be used, for example, to visualise high-power IR radiation and femtosecond laser radiation [13], and also to obtain lasing upon two-photon pumping.

**Table 1.** Absorption, luminescent, and nonlinear parameters of dicyanomethylene-pyran substituents in MP at the 300-mW average laser radiation power.

| Dye | $\lambda_{\mathrm{ab}}$/nm | $\lambda_{\mathrm{fl}}$/nm | $\beta$/cm $\mathrm{GW}^{-1}$* | $T_0$ (arb. units)** | $\sigma_2/10^{-3}$ GM |
|---|---|---|---|---|---|
| DCM-doa | 495 | 644 | $2.0 \pm 0.2$ | 0.75 | $8.4 \pm 0.8$ |
| DCM | 474 | 640 | $1.22 \pm 0.16$ | 0.85 | $5.1 \pm 0.5$ |
| DCM-17 | 482 | 642 | $1.37 \pm 0.17$ | 0.83 | $5.7 \pm 0.6$ |
| AF-50 | 390 | 492 | 5.6 | – | 11.56 [10] |

Note: *At the concentration $10^{-2}$ M; **transmission in the focal plane of the lens ($z = 0$).

The $z$-scan method can be conveniently applied for measuring TPA cross sections for femtosecond radiation in the case of both fluorescing and non-fluorescing molecules. Because DCM dyes have a rather high quantum yield of fluorescence (up to 0.85 in MP), TPA cross sections can be measured upon excitation of these dyes by femtosecond pulses from a Ti : sapphire laser by the reference method. A comparison of the TPA cross sections measured by the direct ($z$-scan) and indirect (fluorescence) methods is of methodological interest because the data obtained by different methods for the same substances are substantially different. For example, the TPA cross section of rhodamine 6G measured by the fluorescence method upon femtosecond excitation at a wavelength of 800 nm is 134 GM, which is more than an order of magnitude higher than the value 12.8 GM obtained by the $z$-scan method [14]. According to our preliminary data, the fluorescence method gives lower values of TPA cross sections in the case of DCM dyes. A detailed comparison of the TPA cross sections of dicyanomethylene-pyrans measured by different methods will be the subject of our further investigations.

***Acknowledgements.*** This work was partially supported by the Russian Foundation for Basic Research (Grant No. 04-02-16515), the Ministry of Education and Science of the Russian Federation (Project Nos 15459 and 4175) and by the Joint BRHE Russian – American Program (Grant No. Y2-P-16-01).

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