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Two-photon excitation of dyes in a polymer matrix by femtosecond pulses from a Ti : sapphire laser

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***Abstract*. Two-photon fluorescence was observed for 18 organic dyes in a polymethyl methacrylate (PMMA) matrix excited by a femtosecond Ti : sapphire laser. The product of the cross section for two-photon absorption by the quantum yield of fluorescence (two-photon fluorescence cross section) is estimated by comparing it with fluorescence of Rhodamine 6G in ethanol. Using this parameter, dyes are selected that exhibit the most intense fluorescence in PMMA and their concentrations in PMMA are optimised. Coumarin and rhodamine dyes in polymer matrices are proposed for using as visualisers of femtosecond radiation of a Ti : sapphire laser and as detectors in self-triggering systems.**

Keywords: *dyes, polymethyl methacrylate matrix, two-photon fluorescence spectrum and cross section.*

1. Introduction

Two-photon absorption (TPA) of laser radiation by organic molecules has been extensively studied by many research groups in the last decade. These studies are stimulated by the outlook for using two-photon interactions for the address delivery of radiation into an elementary volume to obtain the response in the form of specific physicochemical processes (nonlinear absorption, fluorescence, photoisomerisation, polymerisation, etc). A variety of practical applications of two-photon interactions were already proposed, including 3D optical memory [1, 2], 3D displays [3], stereolithography [4], optical limiters [5], fluorescence microscopy [6], and photodynamic diagnostics and therapy [7, 8]. Organic molecules with large TPA cross sections play a key role in all these applications.

Typical TPA cross sections of organic molecules are $10^{-48} - 10^{-50}$ cm^4 s phot^{-1} mol^{-1}, or 1 – 100 GM, where GM (Geppert – Mayer) is the TPA cross section unit equal to 10^{-50} cm^4 s phot^{-1} mol^{-1} [9]. When TPA is detected from fluorescence, it is convenient to use not the TPA cross section but its product by the quantum yield of fluorescence – the quantum yield of two-photon fluorescence (TPF) [10]. It is assumed in this case that the quantum yield of fluorescence upon one-photon excitation coincides with an accuracy of the factor 1/2 with that of two-photon fluorescence. It is obvious that, because the quantum yield of fluorescence is dimensionless, the TPF cross section can be also measured in GM.

Table 1 presents TPA and TPF cross sections for solutions of some dyes at the emission wavelengths of a Ti : sapphire laser measured by different researchers. N,N,N-tris[4-{2-(4-{5-[4(tert-butyl)phenol]-1,3,4-oxydiazole -2ol}-propyl}phenolamine (PPA) and Rhodamine B have the largest TPA cross sections: 309 GM at 802 nm and 210 GM at 840 nm, respectively. Note that the TPA cross section strongly depends on the wavelength. Some dyes have the maximum TPA cross section not at the doubled wavelength of the main absorption band but at the wavelength shifted to the blue by 150 – 200 nm [9]. The nature of this shift is not clear so far; however, the red shift was never observed for dyes. For this reason, dyes absorbing in different regions of the visible range can have close TPA and TPF cross sections at a certain excitation wavelength, for example, at the 800-nm emission wavelength of a Ti : sapphire laser.

Solid polymer matrices doped with organic dyes can be promising materials for two-photon technologies if they have sufficiently high TPA or TPF cross sections. However, at present the measurements of TPA and TPF cross sections for dyes in polymer matrices are scarce. The TPA cross sections have been measured only for a few dyes in polymer matrices [11, 12]. It was found that the TPA cross sections of the dyes in polymer matrices were several times lower than the cross sections of these dyes in solutions. Because this fact was not explained so far, the TPA cross sections of dyes in solutions cannot be used to estimate the cross section of these dyes in polymer matrices.

In this paper, we present the results of measurements of the TPF cross sections for 18 dyes in a PMMA matrix excited by a Ti : sapphire laser at 800 nm. We studied dyes absorbing light from the near-UV (Coumarin 151, $\lambda_{ab} = 370$ nm) to yellow spectral region (Rhodamine 101, $\lambda_{ab} = 580$ nm) at concentrations between 10^{-5} and 10^{-2} M (see Table 2).

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Table 1. TPA and TPF cross sections of organic dyes in solutions and matrices.

Dye	Solvent, matrix	Concentration/M	Wavelength/nm	τ_p/fs	TPA cross section/GM	TPF cross section/GM	References
Fura-2	Water	10^{-4}	700	100	–	11	[9]
DAPI	Methanol	10^{-4}	700	100	–	0.16 ± 0.05	[13]
Dansyl	Water	10^{-4}	700	100	–	0.72 ± 0.2	[13]
Indo-1	Water	10^{-4}	700	100	12 ± 4	4.5 ± 1.3	[13]
Rhodamine B	Methanol	10^{-4}	840	100	210 ± 55		[13]
	Ethanol	3.8×10^{-5}	802	1200	150*	–	[16]
Rhodamine 6G	Water	11×10^{-5}	700	100	140**	–	[15]
	Methanol	3.3×10^{-5}	802	1200	134*	–	[16]
Rhodamine 123	DMF	0.01	800	127	80 ± 5		[14]
Fluorescein	Water	8×10^{-5}	782	100	38 ± 9.7		[13]
	Water	14.5×10^{-6}	800	100	36**		[15]
	Buffer	10^{-6}	800	180	54		[17]
Bis-MSB	Cyclohexane	10^{-4}	690	100	6.3 ± 1.8	6.0 ± 1.8	[18]
Coumarin 138	DMF	0.01	800	127	10 ± 1		[14]
Coumarin 153	DMF	0.01	800	127	47 ± 2		[14]
Coumarin 307	Ethanol	6×10^{-3}	800	127	65 ± 4		[14]
	Methanol	10^{-4}	776	100	–	19 ± 5.5	[13]
Cascade blue	Water	10^{-4}	750	100	–	2.1 ± 0.6	[13]
Lucifer yellow	Water	10^{-4}	860	100	–	0.95 ± 0.3	[13]
Bodipy	Water	10^{-4}	920	100	–	17 ± 4.9	[13]
DiI	Methanol	10^{-4}	700	100	–	95 ± 28	[16]
APS	DMF	0.1	800	127	110 ± 6		[14]
	Methanol	2.6×10^{-4}	802	1200	60.6*		[16]
PPA	DCM	6.8×10^{-5}	802	1200	309*		[16]
DEDC	Trichloromethane	5×10^{-4}	800	120	29.5		[18]
AF-50	Benzene	4×10^{-4}	800	8×10^6	1.94×10^4		[19]
	PMMA	5×10^{-3}	760	200	658		[11]

Notes: APS: 4-[(hydroxy)-N-(methyl)aminophenol]-(6-hydroxy) stilbene; AF 50: N,N-diphenyl-7[2-(4-pyridinyl(ester-99-di-n-decyl fluorene-2-amine; Bis MSB: para-bis(O-methyl-sterol) benzene; Bodipy: 4,4-difluoro-1,3,5,7,8-pentomethyl-4-bora-3a,4a-diazoindocene-2,6-disulfo acid; Dansyl: 5-dimethylaminonaphthalene; DAPI: 4',6-diamido-2-phenylindole; DEDC: 7-diethyl-3'-(2'-benzoimidazole) coumarin; DiI: 1,1-dioctadecyl-3,3,3'3'-tetramethylindocarbocyanine; PPA: N,N,N-tris [4-{2-(4-{5-[4-(tert-butyl) phenol]-1,3,4-oxydiazole-2ol}-1-propyl} phenolamine.
*relative measurement error is ±15 %; **relative measurement error is ±30 %.

2. Experimental

We studied PMMA samples doped with laser dyes exhibiting intense fluorescence. Rectangular parallelepiped samples were cut from cylindrical PMMA rods. The end and side faces of the parallelepipeds were then polished. The TPA cross sections of the dyes were measured using a standard solution of Rhodamine 6G in ethanol (1.9×10^{-5} M) in a polystyrene cell.

The optical scheme of our setup is shown in Fig. 1. Radiation from a Ti : sapphire laser was focused through an OS-11 filter (to suppress radiation from an argon laser) on a sample by a lens with the focal length 6 cm. Fluorescence emitted through the side face of a sample was coupled via an optical fibre into an optical spectrum analyser.

A femtosecond FEMoS Ti : sapphire laser (Tekhnoskan, Novosibirsk) was pumped by an Ar-5-150 argon laser (Inversiya, Novosibirsk). The Ti : sapphire laser pumped by all blue – green lines (6.0 – 7.0 W) from the argon laser emitted 40 – 50-fs phase-locked pulses with an average power of 300 – 400 mW.

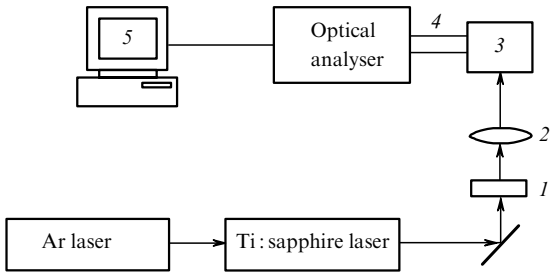

Figure 1. Optical scheme for measuring the TPF cross sections of dyes in polymer matrices: (*1*) OS-11 filter; (*2*) lens ($F = 6$ cm); (*3*) sample; (*4*) optical fibre; (*5*) PC.

The duration of femtosecond pulses was measured with a FS-PS optical autocorrelator (Tekhnoskan, Novosibirsk) based on a scanning Michelson interferometer.

The fluorescence and laser emission spectra were measured with an Angstrem optical spectrum analyser (Angstrem, Novosibirsk) in the spectral range from 350 to 950 nm with the energy sensitivity of 1 pJ. Such a high sensitivity of the

spectrum analyser was provided by a Toshiba TCD 1201 linear photodiode array with an enlarged working area (14×200 μm), which was cooled by a thermoelectric Peltier cooler. After the measurement of the TPF spectra of dyes in PMMA with exposures 10, 30, and 50 ms, the fluorescence spectra of Rhodamine 6G in ethanol were measured using the same exposures. The geometry of excitation and collection of fluorescence was the same. Fig. 2 shows the dependences of the total fluorescence energy on the exposure time for azocoumarin (AC1F) in PMMA and Rhodamine 6G in ethanol measured in the intervals 10 – 350 ms and 10 – 100 ms, respectively. The linear dependences observed both for a sample and a standard allow us to average the results of measurement of the TPF cross sections over all the three above exposures.

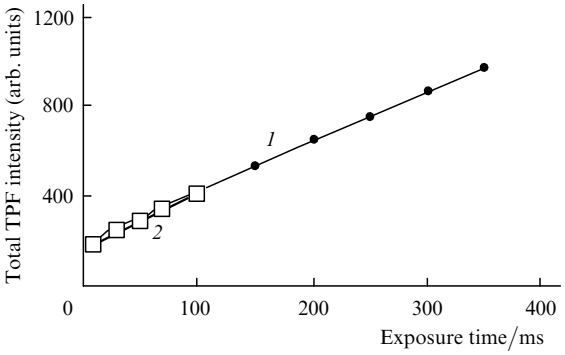

Figure 2. Dependence of the total TPF intensity of the AC1F dye in PMMA (10^{-3} M) (*1*) and Rhodamine 6G in ethanol (*2*) on the exposure time.

3. Results and discussion

Phase locking was achieved in the femtosecond FEMoS laser by moving the second prism in a two-prism compressor mounted on a moveable holder. The generation of femtosecond pulses is characterised by a sharp broadening of the emission spectrum of the laser, which can be detected with the optical analyser (Fig. 3).

The laser generated 3 – 4-nJ femtosecond pulses with a pulse repetition rate of 88 – 100 MHz and an average power of 300 – 400 mW. The peak power of 30 – 60-fs pulses achieved 50 – 130 kW, which is sufficient for excitation of two-photon fluorescence of dyes even without focusing of

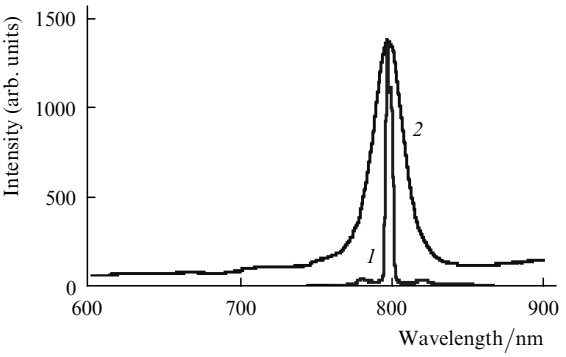

Figure 3. Emission spectra of the Ti : sapphire laser in the cw regime (*1*) and in the regime of generation of phase-locked femtosecond pulses (*2*).

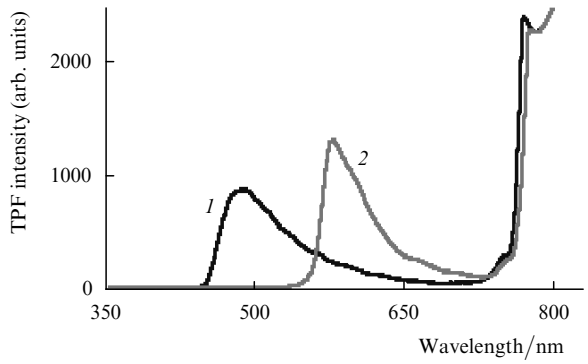

Figure 4. TPF spectra of Coumarin 30 (*1*) and Rhodamine 11B (*2*) in PMMA recorded at the exposure time 30 ms.

incident radiation. As a result, we observed a trace caused by the TPF of dyes in PMMA. When the incident radiation was focused, the trace was most bright in the caustic waist. Depending on the dye, the maximum of the fluorescence spectrum can lie in any part of the visible spectral region, which is optimal for visualisation problems. Fig. 4 shows the TPF spectra of Coumarin 30 and Rhodamine 11B in PMMA.

When the laser operated in a cw regime, the TPF of dyes in PMMA was not observed. Therefore, the lasing regime can be visualised by the presence of absence of the TPF trace. By detecting the TPF of a dye in a polymer matrix with a sensitive photodiode, one can easily detect the femtosecond regime of a Ti : sapphire laser and use this detector in self-triggering systems.

The fluorescence intensity of the dye depends first of all on the TPF cross section and the quantum yield of fluorescence.

We measured the TPF cross section of dyes in PMMA at the emission wavelength of the Ti : sapphire laser by comparing the TPF intensity of samples with that of a standard for the same exposure times. The cross section was calculated from the expression

$$\delta_x \eta_x = \frac{\delta_{et} \eta_{et} C_{et} I_{fl\,x}}{C_x I_{fl\,et}},$$

where C_x and C_{et} are the dye concentrations in the sample and standard, respectively; $I_{fl\,x}$ and $I_{fl\,et}$ are the TPF intensities of the sample and standard, respectively; η_{et} is the quantum yield of fluorescence of Rhodamine 6G in ethanol (0.94 [20]); and δ_{et} is the TPF cross section of Rhodamine 6G in ethanol at a wavelength of 800 nm (40 GM [13]). The results of measurements are presented in Table 2. All the measurements were performed by exciting fluorescence by 50-fs pulses with an average power of 300 mW.

In the blue spectral range, coumarin 30 has the highest TPF cross section, while azocoumarin AC1F has the lowest cross section.

In the green – yellow spectral range, Rhodamine 11B has the highest TPF cross section. This dye can be recommended for as a visualiser of the femtosecond regime in a Ti : sapphire laser. Pyrromethene 546 fluorescing in this spectral range has a low TPF cross section.

Dyes fluorescing in the red spectral region ($\lambda_{fl} > 600$ nm) cannot be used as visualisers of femtosecond laser radiation

Table 2. TPF cross section of dyes* in PMMA.

Dye	Concentration/M	λ_{abs}/nm	λ_{fl}/nm	TPF cross section/GM
LD490	5×10^{-3}	370	452	2.24 ± 0.72
Coumarin 151	5×10^{-3}	370	469	1.79 ± 0.01
AC1F	10^{-2}	380	474	1.15 ± 0.18
Coumarin 307	5×10^{-3}	390	474	3.23 ± 0.15
Coumarin 547	5×10^{-3}	400	494	2.61 ± 0.14
Coumarin 314	5.4×10^{-3}	400	487	2.14 ± 0.20
Coumarin 314T	5.4×10^{-3}	400	483	2.76 ± 0.40
Coumarin 522	5×10^{-3}	400	492	3.39 ± 0.41
Coumarin 30	10^{-3}	400	487	12.3 ± 1.14
Coumarin 7	10^{-3}	425	509	6.48 ± 0.43
Coumarin 6	5×10^{-3}	435	524	2.35 ± 0.22
Coumarin 153	5×10^{-3}	415	510	2.53 ± 0.14
Coumarin 525	2.5×10^{-3}	425	532	4.00 ± 0.24
Pyrromethene 546	5×10^{-3}	460	543	0.36 ± 0.08
Rhodamine 11B	10^{-3}	530	580	38.66 ± 5.22
Phenalemine 512	3.9×10^{-3}	550	609	0.40 ± 0.06
P220	2.5×10^{-3}	580	643	4.29 ± 0.23
Rhodamine 101	2.3×10^{-3}	580	660	2.76 ± 0.21

Notes: *LD490, AC1FLD490 and AC1F are coumarin derivatives; P220 is the stilbene substitute.

because the trace of their fluorescence is masked by the scattered red laser line. In addition, the sensitivity of the dye in the red spectral region is lower than that in the yellow–green region.

The TPF cross sections of the dyes in PMMA measured in this paper make it possible to compare the intensity of TPF in different samples. At the same time, it is necessary to elucidate the mechanism of the decrease in the TPF intensity of dyes in matrices compared to that in solutions.

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