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Three-photon absorption of radiation from a Ti : sapphire laser by methylstyrylbenzene

Yu.P. Meshalkin, V.A. Svetlichnyi, N.N. Svetlichnaya, T.N. Kopylova

***Abstract*. It is shown that 2,2′-di-methylstyrylbenzene (bis-MSB) at a concentration of 10^{-3} M in 1-methyl-2-pyrrolidone can fluoresce at 420 nm upon excitation by a 708-nm femtosecond Ti : sapphire laser. The dependence of the fluorescence intensity on the excitation power proved to be cubic. The three-photon absorption cross section of bis-MSB was estimated as $(1.61 \pm 0.10) \times 10^{-79}$ cm^6 s^2 phot^{-2}. bis-MSB is recommended as a cubic standard to normalise laser powers in three-photon measurements.**

Keywords: *dyes, three-photon absorption, Ti : sapphire laser, cross section.*

1. Introduction

The possibility of simultaneous absorption of three IR photons by organic molecules accompanied by their transition to the excited state was first demonstrated by the example of a naphthalene crystal in 1964 [1]. Three-photon absorption was observed later in solutions of some organic molecules, molecular crystals, and semiconductors; however, this required in each case considerable efforts because three-photon absorption cross sections of most molecules were $10^{-82} - 10^{-79}$ cm^6 s^2 phot^{-2}. In most cases three-photon absorption was detected by three-photon-excited fluorescence measured with cooled photomultipliers [2, 3]. The main criterion confirming the three-photon nature of fluorescence was the cubic dependence of its intensity on the exciting radiation power [4].

Interest in three-photon absorption of laser radiation by organic molecules as a unique nonlinear phenomenon was initially related to its fundamental importance. However, later its practical applications such as optical limitation [5, 6] and multiphoton fluorescent microscopy [7] became of current interest. Certain efforts were devoted to the search for and synthesis of molecules with high three-photon absorption cross sections [6, 8]. However, the problem of 'mixing' of two-photon and three-photon absorption in organic molecules with broad absorption bands excited by broadband femtosecond pulses was not investigated.

We showed in this paper that the known laser dye 2,2′-di-methylstyrylbenzene (bis-MSB) with the absorption band at 355 nm excited by a femtosecond Ti : sapphire laser at a wavelength of 798 nm reveals real three-photon absorption (without contribution from two-photon absorption). The intensity of three-photon-excited fluorescence of methylstyrylbenzene (MSB) is sufficient for recording its spectrum with a photodiode linear array rather than with a cooled photomultiplier, as was done before in studies of other molecules with three-photon absorption. The solution of bis-MSB in 1-methyl-2-pyrrolidone (MP) can be used as a standard for calibrating lasers in three-photon absorption experiments.

2. Experimental

We studied solutions of bis-MSB (Eastman Kodak) in MP at a concentration of 10^{-3} M. MP was used as a solvent because it provided a high solubility of bis-MSB without a decrease in the fluorescence efficiency. We failed to obtain such a high concentration of the dye in other solvents. Bis-MSB in MP has a high molecular extinction $\varepsilon = 57700$ L cm^{-1} mol^{-1} at the 362-nm absorption maximum and a high quantum yield of fluorescence (0.90) in cyclohexane (at 416 nm) [9]. The structure of bis-MSB is presented in Fig. 1. This is polyene with a very rigid rod-like structure and the length of a molecule of $\sim$12 Å [10].

Multi-photon excitation of bis-MSB was performed by a FemtoMed Ti : sapphire laser (Tekhnoskan, Novosibirsk) pumped by an INVERsia Ar-5-150 argon laser (Inversiya, Novosibirsk). The Ti : sapphire laser pumped by 6 W of single-mode all-line cw radiation from the argon laser generated 798-nm, 50-fs pulses with a pulse repetition rate of 89 MHz.

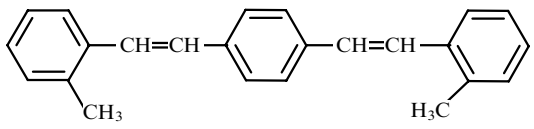

Figure 1. Structure of 2,2′-di-methylstyrylbenzene (bis-MSB).

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The average output power of a Ti : sapphire laser without amplification was 300 – 450 mW, both in the cw and femtosecond regimes. The output power of the laser was measured with a four-probe LP-905 calorimeter power meter (Tekhnoskan).

The average radiation power was varied without changing the pulse duration by using a Glan prism. Radiation of the Ti : sapphire laser propagated through the Glan prism and was focused by a long-focus lens ($F = 120$ mm) into a 1-cm quartz cell with a sample.

Upon multiphoton excitation, the diameter of the focal spot is important. It was measured by using a fibre of diameter 125 μm for coupling radiation to an Angstrem optical analyser (Novosibirsk). The optical analyser was based on an ILX511A Sony linear photodiode array (2048 pixels) without cooling. The fibre was mounted on a two-coordinate automated stage (scanning along the cross-section diameter in the beam plane was performed over one coordinate, and a single displacement of the fibre with respect to the focal spot was performed along another coordinate). The laser-beam profiles for the femtosecond and cw regimes in the plane separated from the focal plane by 3 cm are presented in Fig. 2.

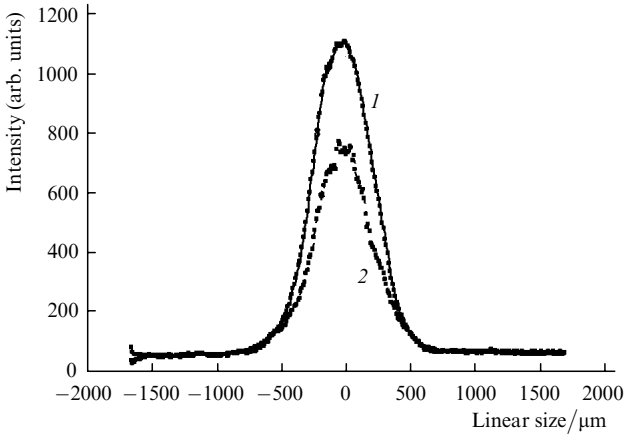

Figure 2. Gaussian profiles of the laser beam in a plane located at a distance of 3 cm from the focal plane in the femtosecond (*1*) and cw (*2*) regimes.

The beam waist radius was calculated from the expression

$$\omega^2 = \omega_0^2\left[1 + \left(\frac{\lambda z}{\pi\omega_0^2}\right)^2\right], \qquad (1)$$

where ω is the beam radius at the $1/e^2$ level in a plane located at a distance of z from the focal plane, which was an order of magnitude larger than the input aperture of the detector. The radius of the focal spot in the beam waist calculated from (1) was 16 μm.

Fluorescence was detected at an angle of 90° to exciting radiation through a fibre connected to the optical analyser.

3. Results and discussion

Figure 3 shows the absorption spectrum of bis-MSB in MP and its fluorescence spectrum upon one-photon excitation by the fourth harmonic of a Nd : YAG laser at 266 nm. The maximum of the absorption spectrum of bis-MSB is at

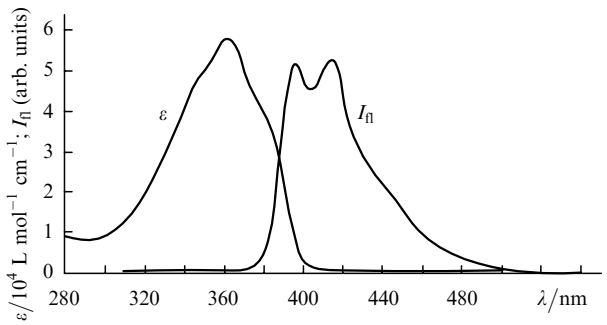

Figure 3. Absorption (ε) and fluorescence (I_{fl}) spectra of bis-MSB in MP.

350 nm, while absorption at the wavelength of the Ti : sapphire laser is negligible.

The fluorescence spectrum of bis-MSB in MP has a structure with the main maximum at 420 nm.

Figure 4 presents the fluorescence spectrum of bis-MSB observed upon multiphoton excitation by the femtosecond Ti : sapphire laser at 798 nm. The maximum of this nonlinear fluorescence spectrum is shifted to the red (to ~440 nm). However, the spectrum was recorded with large noise, which complicates the measurement of the fluorescence intensity at the maximum. Nevertheless, it is obvious that the noise component has a much higher frequency. The spectra were processed using digital filtration and the Fourier transform. Figure 5 shows multiphoton fluorescence spectra after filtration for different rotation angles of a polariser.

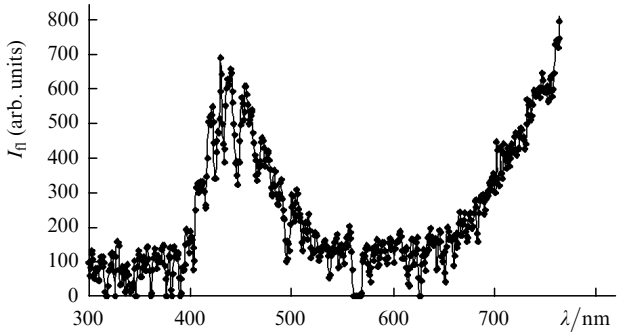

Figure 4. Fluorescence spectrum of bis-MSB excited by a Ti : sapphire laser at ~800 nm.

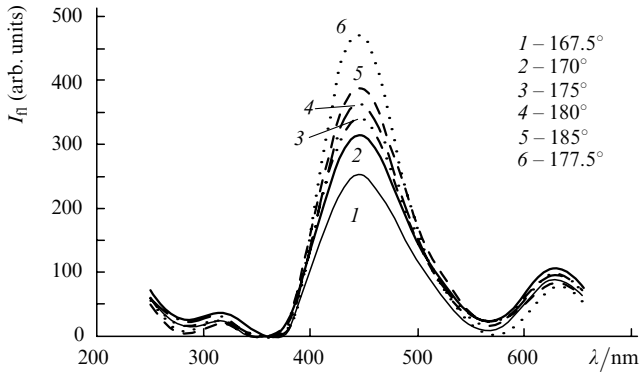

Figure 5. Fluorescence spectra of bis-MSB excited by a Ti : sapphire laser at ~800 nm after digital filtration at different rotation angles of a polariser.

To elucidate the excitation mechanism of fluorescence, we studied the dependence of the fluorescence intensity on the excitation intensity. This dependence for multiphoton processes should satisfy the expression [7]

$$F^{(n)} = \gamma\eta\delta^{(n)}\left[\frac{1}{\Delta t}\int_0^{\Delta t}\int_0^{\infty} I_{ex}^n(r,t')C(r,t')\mathrm{d}r\mathrm{d}t'\right], \qquad (2)$$

where $F^{(n)}$ is the multiphoton fluorescence intensity; η is the quantum yield of fluorescence; γ is the instrumental coefficient characterising a fraction of collected fluorescence; $\delta^{(n)}$ is the multiphoton absorption cross section; I_{ex} is the excitation intensity; C is the number of molecules per unit volume; r is the radius of the focal spot on the object; Δt is the laser pulse duration; and n is the process order.

In the general case of excitation of homogeneous dye solutions by a focused laser pulse with Gaussian temporal and spatial profiles, the fluorescence intensity can be described by the expressions

$$F^{(2)} = \frac{1}{2}\eta\gamma C n_0 I_{ex}^2\delta^{(2)}, \qquad (3)$$

upon two-photon excitation and

$$F^{(3)} = \frac{1}{3}\eta\gamma C n_0 I_{ex}^3\delta^{(3)}, \qquad (4)$$

upon three-photon excitation, where n_0 is the refractive index of the sample (below we will use the refractive index of solvent).

Two-photon absorption of bis-MSB was investigated in detail already in 1986 [11]. In fact, it was the first organic compound for which the two-photon absorption cross section was measured in a broad wavelength range from 537 to 694 nm. The maximum two-photon absorption cross section of bis-MSB equal to 6.9×10^{-48} cm^4 s phot^{-1} mol^{-1} was observed at 585 nm. In the late 1980s this compound had the highest two-photon absorption cross section and was widely used as a standard in measurements of the absorption cross sections of organic and biological molecules by the fluorescent method. Due to an ideal quadratic dependence of its fluorescence on the excitation intensity, bis-MSB was used as a standard to normalise the laser radiation power in two-photon absorption measurements [11].

In the late 1990s, two-photon absorption studies came to be mainly performed by using a femtosecond Ti : sapphire laser. However, the two-photon absorption cross section of bis-MSB in the emission range of this laser drastically decreases from 4.5×10^{-50} (at 700 nm) and 10^{-50} (at 725 nm) down to 5×10^{-52} cm^4 s phot^{-1} mol^{-1} (at 780 nm) [12], and interest in the nonlinear optical properties of bis-MSB was lost.

Let us calculate the peak excitation intensity in terms of the average power

$$I_{ex} = \frac{\langle P\rangle}{hc\lambda_{ex}^{-1}\tau f\pi\omega_0^2}, \qquad (5)$$

where $\langle P\rangle$ is the average power of exciting radiation; ω_0 is the radius of the focused laser beam at the $1/e^2$ level; λ_{ex} is the excitation wavelength; τ is the laser pulse duration; f is the pulse repetition rate; and c is speed of light in vacuum.

By substituting expression (5) into (3) and (4), we can see that the intensity of three-photon-excited fluorescence is proportional to the cube of the average excitation power, whereas the intensity of two-photon-excited fluorescence is proportional to the square of the average excitation power.

Figure 6 shows the experimental dependence of the fluorescence intensity of bis-MSB on the average power of a femtosecond Ti : sapphire laser. One can see that this dependence is cubic with good accuracy, which demonstrates three-photon excitation of bis-MSB by the Ti : sapphire laser.

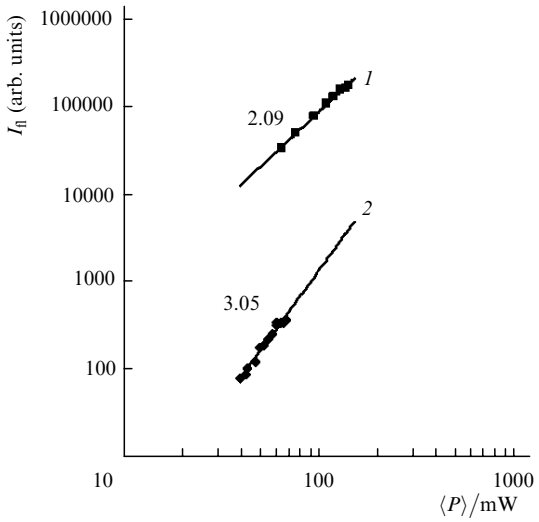

Figure 6. Dependences of the intensity of multiphoton fluorescence on the average excitation power for DCM (*1*) and bis-MSB (*2*).

In the case of 'mixing' of two-photon and three-photon processes, the fluorescence intensity should depend on the excitation power in a more complicated way. At low excitation powers, two-photon processes should dominate, and therefore the corresponding dependence at the logarithmic scale will have a slope equal to two. The probability of three-photon processes increases with increasing peak excitation power, and the slope of the dependence should tend to three.

We estimated the three-photon absorption cross section by the modified method of standard, comparing the intensities of two-photon-excited fluorescence of a standard (DCM dye in pyrrolidone at the concentration 10^{-2} M) and three-photon-excited fluorescence of bis-MSB in MP. Excitation was performed in both cases by the same Ti : sapphire laser with the same geometry of fluorescence collection. To make the intensities of multiphoton fluorescence of MSB and DCM approximately equal, the output power of the Ti : sapphire laser was substantially reduced in the latter case by a polariser. The peak intensity of laser radiation upon excitation of three-photon fluorescence of MSB was 21.6×10^{28} phot cm^{-2} s^{-1} (for $P = 340$ mW, $\tau = 10^{-13}$ s, and $f = 89$ MHz) and upon excitation of two-photon fluorescence of DCM, it was 1.64×10^{28} and 1.31×10^{28} phot cm^{-2} s^{-1}.

The three-photon absorption cross section was calculated by the expression obtained from (3) and (4), taking into account the excitation order:

$$\delta^{(3)}(\mathrm{MSB}) = \frac{3I_{ex}^2(\mathrm{DCM})F_{fl}^{(3)}(\mathrm{MSB})C_{\mathrm{DCM}}\eta(\mathrm{DCM})}{2I_{ex}^3(\mathrm{MSB})F_{fl}^{(2)}(\mathrm{DCM})C_{\mathrm{MCB}}\eta(\mathrm{MSB})}$$

$$\times \delta^{(2)}(\mathrm{DCM}), \quad (6)$$

where $\delta^{(2)}$ and $\delta^{(3)}$ are the two-photon and three-photon absorption cross sections of DCM and MSB, respectively.

As the two-photon absorption cross section of DCM upon femtosecond excitation, we used the cross section equal to 1.2×10^{-48} cm^4 s phot^{-1} mol^{-1} measured by us earlier. The quantum yield of fluorescence of DCM in MP measured by us was 0.85.

In two measurements performed at different excitation intensities of two-photon fluorescence of a standard, we obtained closed three-photon absorption cross sections for bis-MSB equal to 1.68×10^{-79} and 1.54×10^{-79} cm^6 s^2 phot^{-2}. The averaged value $(1.61 \pm 0.10) \times 10^{-79}$ cm^6 s^2 phot^{-2} corresponds to the three-photon absorption cross sections for some organic molecules ($10^{-82} - 10^{-79}$ cm^6 s^2 phot^{-2}) [13]) measured earlier and characterises MSB as a molecule with a rather high three-photon absorption cross section.

Let us use the two-photon (5×10^{-52} cm^4 s phot^{-1} mol^{-1}) and three-photon (1.6×10^{-79} cm^6 s^2 phot^{-2}) absorption cross sections to compare the intensities of two-photon and three-photon-excited fluorescence. We assume that the peak excitation power and the geometry of fluorescence collection are the same for different excitation mechanisms. The ratio of (4) and (3) for $I_{ex} = 21.6 \times 10^{28}$ phot cm^{-2} s^{-1} is

$$\frac{F^{(3)}}{F^{(2)}} = \frac{2}{3}\frac{I_{ex}\delta^{(3)}}{\delta^{(2)}} \approx 46. \quad (7)$$

Therefore, the expected intensity of three-photon-excited fluorescence is almost 50 times greater than that of two-photon-excited fluorescence. All this suggests that real three-photon absorption occurs in bis-MSB excited by a femtosecond Ti : sapphire laser, and this compound can be used as a standard in three-photon absorption studies.

Note at the same time that the three-photon absorption cross sections of derivatives of dimethylaminonaphthalene (5.2×10^{-77} cm^6 s^2 phot^{-2}) [5] and stilbazole ($10^{-78} - 10^{-76}$ cm^6 s^2 phot^{-2}) [6] measured recently are several orders of magnitude higher. However, these measurements were performed by the method of nonlinear absorption (the *z*-scan method), which, in our opinion, gives substantially higher cross sections compared to fluorescent methods.

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References

1. Singh S., Bradley L.T. *Phys. Rev. Lett.*, **12**, 612 (1964).
2. Gryczynski I., Malak H., Lakowicz J.R. *Biospectroscopy*, **2**, 9 (1996).
3. Shear J.B., Xu C., Webb W.W. *Photochem. Photobiol.*, **65**, 931 (1997).
4. Lakowicz J.R., Gryczynski I., in *Applied Fluorescence in Chemistry, Biology and Medicine*. Ed. by W. Rettig, B. Strehmel, S. Schader, H. Seifert (New York: Springer-Verlag, 1999) p. 136.
5. Bhavalkar J.D., He G.S., Prasad P.N. *Opt. Commun.*, **119**, 587 (1995).
6. Zhan C., Li D., Zhang D., et al. *Chem. Phys. Lett.*, **353**, 138 (2002).
7. Maiti S., Shear J.B., Williams R.M., Zipfel W.R., Webb W.W. *Science*, **275**, 530 (1997).
8. Ma W.B., Wu Y.Q., Han J.H., Gu D.H., Gan F.X. *Chem. Phys. Lett.*, **403**, 405 (2005).
9. Berlman I.B. *Handbook of Fluorescence Spectra of Aromatic Molecules* (New York: Acad. Press, 1971).
10. Sujatha J., Mishra A.K. *J. Photochim. Photobiol. A*, **101**, 245 (1996).
11. Kennedy S.M., Lytle F.T. *Anal. Chem.*, **58**, 2643 (1986).
12. Xu C., Webb W.W. *J. Opt. Soc. Am. B*, **13**, 481 (1996).
13. Penzkofer A., Falkenstein W. *Opt. Commun.*, **16**, 247 (1976).