

Study of two-photon excitation spectra of organic compounds absorbing in the UV region

V.A. Babenko, A.A. Sychev

Abstract. A method is proposed for recording two-photon excitation (TPE) spectra of organic compounds with the help of picosecond pulses from a dye laser tunable in the range from 550 to 640 nm. The TPE spectra are obtained for organic scintillators and drugs: paraterphenyl in liquid and solid phases, stilbene single crystal and Streptocid powder, having a one-photon absorption band in the region from 270 to 350 nm. It is shown that the vibronic structure in the TPE spectra of these compounds is independent of their aggregate state and is an individual characteristic of each of the compounds.

Keywords: two-photon excitation, one-photon absorption, vibronic structure of spectra.

1. Introduction

Two-photon excitation (TPE) is one of the methods for pumping media that can be potentially used as active materials for UV lasers. Because TPE is a nonlinear process, such media can be efficiently pumped by ultrashort light pulses in the visible range. The wavelength of such lasers should be determined by the properties of the TPE spectrum of the medium, which substantially differs from known one-photon absorption (OPA) spectra. The difference between the TPE and OPA spectra is caused by the different selection rules for two-photon and one-photon transitions [1]. Therefore, TPE spectroscopy gives information on the vibronic states of molecules, which cannot be detected by the methods of OPA spectroscopy.

The aim of this paper is to develop the method for recording TPE spectra and to study these spectra in media absorbing in the UV spectral range between 270 and 350 nm.

2. Objects of investigation

We studied UV scintillators, which can be used as active laser materials, and also biological objects and drugs. Excitation was performed by picosecond laser pulses, which

have a high peak intensity achieving 10^{10} W cm⁻² along with a comparatively low energy. For this reason, the role of destructive thermal effects upon the interaction of such pulses with matter is insignificant, which is, for example, can be important in the studied of medical and biological objects. The TPE spectra were recorded by measuring the integrated intensity of the fluorescence band of objects by varying the excitation wavelength from a tunable laser.

3. Experimental setup

Ultrashort tunable light pulses were produced by a dye laser synchronously pumped by 30-ps second-harmonic pulses from a passively mode-locked Nd:YAG laser. The scheme of the laser setup is shown in Fig. 1. A dye laser assembled in a telescopic scheme was formed by mirrors (1–4) and 600 lines mm⁻¹ diffraction grating (5). The laser wavelength was tuned by rotating the grating. We used in the laser the alcohol solutions of rhodamine 6G, rhodamine C, and rhodamine 101 in longitudinally pumped 3-mm thick cell (7). The cell was placed near the focal waist of the laser beam. To redistribute laser radiation predominantly in one of the directions (in our case, clockwise), we used a telescopic scheme with lenses (8)

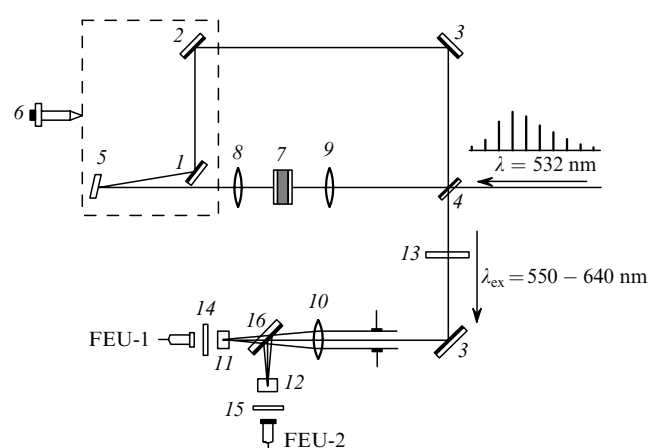


Figure 1. Scheme of the experimental setup: (1–4) dye laser mirrors; (5) 600 lines mm⁻¹ diffraction grating; (6) control screw for adjusting the resonator length; (7) cell with the dye solution; (8, 9, 10) lenses with focal lengths 100, 136, and 100 mm, respectively; (11) sample; (12) reference sample (ZnS10 glass); (13) optical filter suppressing pump radiation (532 nm); (14) optical filter selecting radiation in the region 330–380 nm; (15) optical filter selecting radiation in the region 380–430 nm; (16) beamsplitter; FEU-1 and FEU-2 are photomultipliers.

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and (9) having different focal distances. The lenses with the focal distances $f_8 = 100$ mm and $f_9 = 136$ mm proved to be optimal. In this case, we obtained the ratio of counter-propagating radiation intensities equal to 10, i.e., virtually unidirectional lasing was achieved.

Apart from a proper choice of the telescope parameters, the type and concentration of a dye, it was also necessary to control appropriately the total length of the laser resonator. This was performed by means of control screw (6) producing a parallel displacement of a laser unit on which the diffraction grating and mirrors (1) and (2) were mounted (Fig. 1). The dye laser emitted, as the pump laser, a train of ultrashort 30-ps pulses. The duration of pump and dye laser pulses was measured with an Agat streak camera with a time resolution of 2 ps.

4. Experimental method

The dye laser radiation tunable in the spectral range from 550 to 640 nm was split with beamsplitter (16) into two beams, each of them being focused by lens (10) ($f_{10} = 100$ mm). One of the beams was directed to sample under study (11) and another to reference sample (12). As a reference sample, a ZhS10 glass was used, which contained polycrystals of cadmium sulphide and had strong absorption in the UV spectral region but was transparent at wavelengths $\lambda \geq 400$ nm. Our preliminary studies have shown that the intensity of two-photon excited fluorescence of this glass in the spectral region from 380 to 430 nm is proportional to the square of the excitation intensity and is independent of the excitation frequency ($\lambda_{\text{ex}} = 550$ –640 nm) within the measurement error. This result agrees with data reported in paper [2], where the dependence of the two-photon cross section on the excitation frequency was determined in semiconductor CdS single crystals.

The fact that the intensity of two-photon excited fluorescence of the reference sample (ZhS10 glass) is independent of the excitation frequency in the spectral range from 550 to 640 nm allowed us to simplify substantially the method of recording the TPE spectra of organic compounds under study. The fluorescence of these compounds strongly depends on the excitation frequency, its intensity being quadratically dependent on the excitation intensity. In this connection we recorded the TPE spectra by measuring the ratio I of the fluorescence intensity of a sample under study to the fluorescence intensity of the reference sample by varying the excitation wavelength and intensity.

5. Experimental results

We studied the TPE spectra, representing the dependence of the integrated intensity of a fluorescence band on the excitation wavelength, for the following compounds absorbing in the UV spectral range: paraterphenyl in solutions and a solid phase and a stilbene single crystal, which are organic scintillators used as active laser materials, and also the well-known drug, Streptocid powder. The fluorescence spectra of these substances were studied earlier in our paper [3] upon picosecond excitation by the second harmonic of a Nd:YAG laser.

We investigated first the TPE spectra of paraterphenyl in toluene and orthodichlorobenzene. The concentration C of both solutions was 5 mg mL⁻¹. The paraterphenyl solution

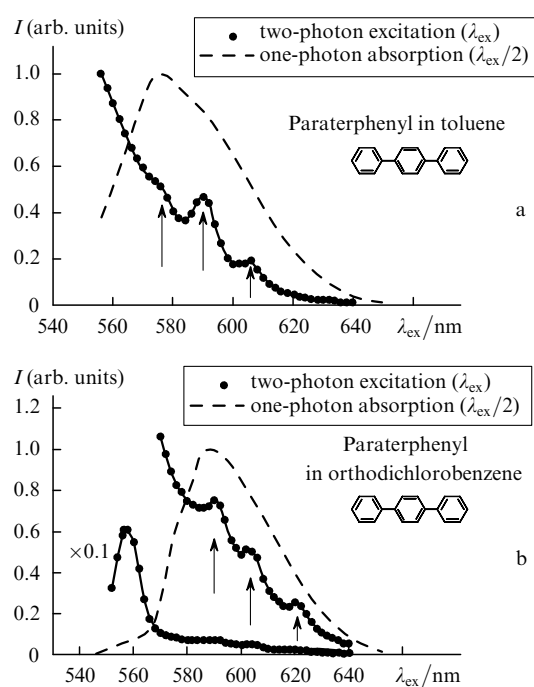


Figure 2. TPE (solid curve) and OPA (dashed curve) spectra of paraterphenyl solutions in toluene (a) and orthodichlorobenzene (b) at the concentration 5 mg mL⁻¹. Here and in Fig. 3, each point is the result of 32 measurements.

was studied in a 18-mm thick quartz cell placed in the focal waist of lens (10).

Figure 2 shows the TPE spectra of paraterphenyl solutions in toluene and orthodichlorobenzene and also the OPA spectra of these solutions in the UV region. Note that the corresponding wavelengths for the OPA spectra in the figure should be reduced by half.

In the case of paraterphenyl in toluene (Fig. 2a), the dependence of the quantity I normalised to unity, which characterises the TPE spectrum, decreases in the range 550–640 nm, showing a vibronic structure. One can see that the maximum of the TPE spectrum is shifted to the blue compared to the OPA maximum and lies beyond the lower boundary of the tuning range of the dye laser ($\lambda_{\text{ex}} = 550$ nm).

For the solution of paraterphenyl in orthodichlorobenzene (Fig. 2b), the situation is different. In this case, the absorption spectrum exhibits the bathochromic shift (red shift) because the refractive index of orthodichlorobenzene is higher than that of toluene. One can see from Fig. 2b that the doubled laser emission at $\lambda_{\text{ex}} = 550$ nm lies in the short-wavelength edge of the absorption band of paraterphenyl in orthodichlorobenzene. The TPE spectrum exhibits one distinct peak at 557 nm. The TPE intensity decreases with increasing wavelength, as in the case of paraterphenyl in toluene. A comparison of the TPE spectra of paraterphenyl in different solvents showed that all the characteristic properties of their vibronic structure indicated by the arrows in Figs 2a, b are mainly preserved in different solvents; however, the intensities of vibronic peaks noticeably change.

Figure 3 shows the TPE spectra of paraterphenyl, stilbene, and Streptocid in a solid phase. The Streptocid powder was prepared from a tablet. Paraterphenyl and Streptocid powders were studied in a 0.5-mm thick quartz

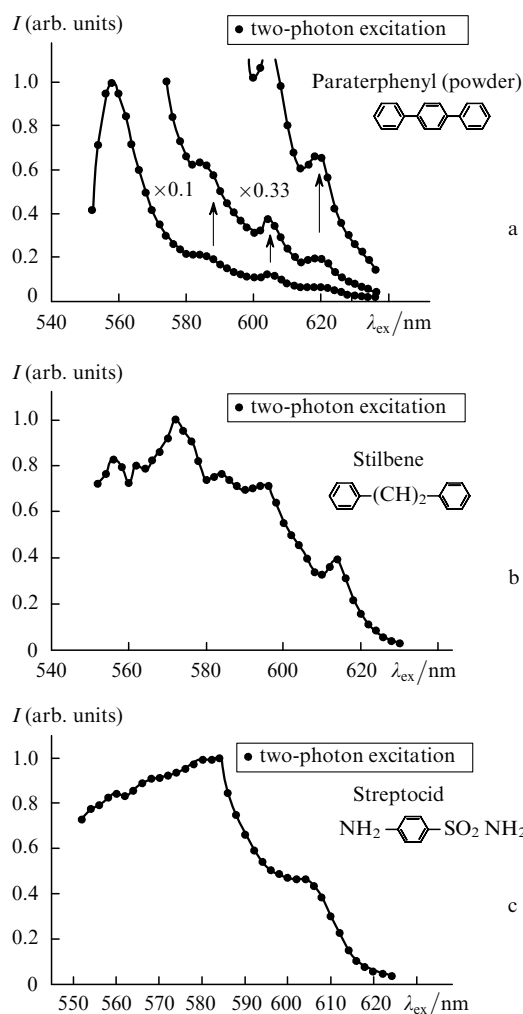


Figure 3. TPE spectra of paraterphenyl (a), stilbene (b), and Streptocid (c) in a solid phase.

cell. Stilbene was investigated in the form of a single crystal of thickness 0.7 mm. All the samples were placed in the focal region of lens (l_0) (Fig. 1). We have failed to obtain the OPA spectra in this case because thin films should be prepared for this purpose [4]. However, it is known that the characteristics of monomolecular layers of organic molecules deposited on a substrate can strongly depend on the substrate material and technology of preparation of monomolecular layers due to the aggregation of molecules on the substrate surface [4, 5]. Therefore, the absorption spectra of single crystals and monomolecular layers of organic molecules on substrates can be different. The recording of the OPA spectra of drug powders with amorphous fillers (in our case, Streptocid) is strongly complicated, and cannot be performed with the help of standard spectrophotometers.

At the same time, we can reliably record the TPE spectra of organic molecules in a solid state by using the method described above, as demonstrated in Fig. 3. The TPE spectra of these molecules exhibit the vibronic structure characterising the individual nature of each molecule. Note that the TPE spectra of paraterphenyl in orthodichlorobenzene (Fig. 2b) and of the paraterphenyl powder (Fig. 3a) are similar. One can see from these figures that the vibronic structure of the TPE spectrum is independent of the

aggregate state of paraterphenyl (solution or a solid) and is an individual molecular characteristic.

6. Conclusions

We have shown that the TPE spectra of a number of organic molecules absorbing in the UV region have a specific vibronic structure related to the molecular structure of these compounds. The characteristic properties of the TPE spectra of these molecules are the same in liquids and solids.

Note that because the exciting radiation lies within the transparency band of molecules absorbing in the UV region and can deeply penetrate to the substance under study, the TPE spectrum recorded in this way is an integral characteristic of the entire illuminated volume.

We have shown the TPE spectrum of paraterphenyl substantially differs from the OPA spectrum of this molecule (Fig. 2). This is probably explained by different selection rules for one-photon and two-photon transitions. Therefore, TPE spectroscopy can give additional information on the energy level diagram of organic molecules.

References

1. Bredikhin V.I., Galanin M.D., Genkin V.N. *Usp. Fiz. Nauk*, **110**, 3 (1973).
2. [doi](#) Penzkofer A., Falkenstein W., Kaiser W. *Appl. Phys. Lett.*, **28**, 319 (1976).
3. Babenko V.A., Verevkin Yu.Ya., Gorelik V.S., Mukhin I.S., Sychev A.A., Shcheglov V.A. *Kvantovaya Elektron.*, **20**, 1215 (1993) [*Quantum Electron.*, **23**, 1055 (1993)].
4. Blinov L.M. *Usp. Fiz. Nauk*, **155**, 443 (1988).
5. [doi](#) Dilella D.P., Barger W.R., Snow A.W., Smardzewski R.R. *Thin Sol. Films*, **133**, 207 (1985).