



## Two-photon absorption of Crystal Violet in solutions: Analysis of the solvent effect and aggregation process based on linear and nonlinear absorption spectra



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### ABSTRACT

We report on the aggregation and solvent effects on one-photon absorption (1PA) and two-photon absorption (2PA) spectra of Crystal Violet (CV) chromophore, which is a model octupolar molecule. In the case of the 1PA spectra we have measured the aggregation thresholds for three highly polar solvents (*N,N*-dimethylformamide, dimethyl sulfoxide and propylene carbonate) and for water solvent as a reference. The 2PA spectra have been measured above the aggregation threshold for all selected solvents, however, the measurements at concentrations below the aggregation threshold were unsuccessful. In all cases the observed solvent effect is noticeable. On the other hand, this effect is not always consistent with the solvent polarity scale. The obtained results indicate that CV in the selected solvents aggregates in the form of sandwich-type dimers.

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### 1. Introduction

Solvatochromism, defined as a shift of the maximum, and also often change of the shape or intensity, of UV–Vis absorption bands is a well known phenomenon. In the case of one-photon absorption (1PA) this phenomenon is generally well understood and has been comprehensively described both experimentally and theoretically [1]. However, the solvent effects on the simultaneous absorption of two photons by a single molecule (two-photon absorption (2PA) process) are still not fully understood nor described. Despite the growing amount of available reports concerning this issue [2–31], the systematic investigations of model chromophore systems are still valuable and deliver important data enabling analysis of solvent effects on the 2PA spectra.

In this study we report on the aggregation effects on 2PA of Crystal Violet (CV) measured in polar solvents. CV belongs to the family of triphenylmethane dyes and is a model octupolar molecule (see Fig. 1) that, in spite of its small size, exhibits a relatively substantial nonlinearity [32–37]. A variety of possible applications in different areas like the textile industry, medical sciences and biotechnology have been indicated. In particular, CV is used as a germicide and disinfectant [38,39], for bacterial and DNA staining [40] as well as in photodynamic therapy as a photosensitizer [41,42].

Characteristic features of CV are its relatively high  $D_3$  symmetry [36] and a clearly separated linear absorption band that in many solvents exhibits two maxima. It has been shown by Campo et al. that the electronic and geometrical structure of CV can be defined as a superposition of three dipolar molecules rotated by  $0^\circ$ ,  $120^\circ$  and  $240^\circ$  angles [34]. Hence, its electronic properties are a reflection of three conjugated charge transfer (CT) processes from dimethylamine donors, through phenyl rings to the positively charged carbon atom acting as an acceptor [34–36]. Based on the crystallographic data as well as quantum chemistry calculations it has been determined that the CV molecule can be characterized as a three bladed propeller shape, however the blades are deflected from the plane by  $30^\circ$  [34,36,43]. A characteristic double-maximum linear absorption band was also thoroughly investigated. Initially, this feature was explained by either the vibronic structure of the excited state resulting from the stretching vibration of the phenyl ring–nitrogen system [44] or the occurrence of two overlapping electronic transitions [45]. Also the hypothesis that CV can simultaneously exist in two forms having  $D_3$  and  $C_2$  symmetry was investigated. In the second case one of the phenyl rings to be rotated in the opposite direction in relation to the remaining two [46,47]. However this hypothesis was rejected by Zyss et al. [36] Those authors stated that the symmetry is broken in the excited state, which was later confirmed by Campo et al. [34].

Another important feature of CV is its tendency to aggregation [48–50]. Stork et al. investigated CV aggregation process in water and reported that this effect influences the shape and intensity of

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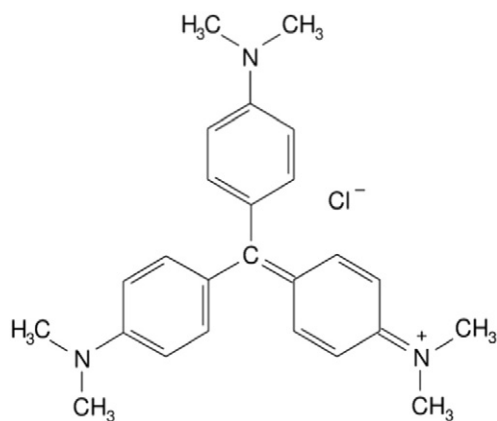


Fig. 1. Crystal Violet structure.

the main linear absorption band [49]. Oliveira et al. reported on the aggregation effect in solvents of low and medium polarity [50]. In the solvents of low polarity they have observed formation of ion pairs and a red shift of the maximum of main absorption band. In the case of aqueous solution hydrogen bonds creation and a blue shift of the absorption band was reported. Regarding the medium polarity solvents the aggregation effect was minor and was observed only for very high concentrations [50].

All above mentioned features of CV make it a very interesting model system for the investigations of the influence of solvent and aggregation effects on the 2PA spectra. In this study we focus on the aggregation effect on the 2PA cross section of CV in a series of polar aprotic solvents. The 2PA cross sections were measured with femtosecond (fs) laser pulses using the Z-scan measurement technique. The relation between the aggregation and solvent effects in the 1PA and 2PA spectra is considered. To the best of our knowledge no systematic Z-scan measurements of the 2PA spectra of CV have been published to date. A Z-scan measurement of the nonlinear refractive index exists in the literature, but it has been performed with a cw laser at a wavelength corresponding to strong one-photon absorption (632.8 nm) and therefore is related mostly to thermal effects [51]. On the other hand, the available scientific reports regarding the nonlinear optical processes such as two-photon absorption and second-harmonic generation were obtained *via* the two-photon induced fluorescence (TPEF) [32,33] and hyper-Rayleigh scattering (HRS) [33,34] techniques, respectively. Therefore, the motivation for this study was to extend the current knowledge about the two-photon, solvent and aggregation effects occurring in this chromophore.

## 2. Methodology

The CV dye as well as solvents were purchased from Sigma Aldrich and used as received. In our measurements a set of polar aprotic solvents were used, appropriate to dissolve a proper amount of the chromophore. We have chosen *N,N*-dimethylformamide (DMF), propylene carbonate (PC) and dimethyl sulfoxide (DMSO). In order to obtain the aggregation threshold values linear absorption spectra of CV in the selected solvents were measured in the concentration range from  $5.00 \cdot 10^{-6}$  to  $1.40 \cdot 10^{-2}$  mol/L. The one-photon measurements were performed using a Perkin Elmer spectrophotometer using cuvettes having different optical path lengths. Highly concentrated solutions (more than  $5.00 \cdot 10^{-4}$  mol/L) were measured using 10  $\mu$ m dismountable cuvettes. This kind of cuvettes consists of a base plate with a 10  $\mu$ m deep cavity and a flat coverslip. Lower concentration solutions were measured in the standard 1 mm and 10 mm cuvettes. The 2PA spectra of the CV dye were measured using the Z-scan technique [52,53]. Our measurement set-up and analysis methodology are described in detail elsewhere [13, 16,21,53]. In this section the most important principles and parameters

of used measurement system will be briefly recalled. An amplified femto-second Quantronix Integra Ti-sapphire laser together with the Palitra optical parametric amplifier (OPA) were used as a light source. The obtained pulses were of ca. 130 fs duration, at repetition rate of 1 kHz and the available wavelengths were in the range of 530–2000 nm. The OPA output beam was purified from the unwanted wavelength components and attenuated using the attached to the OPA wavelength separators as well as colour and density filters. The attenuation enabled to keep the light intensities at about 100 GW/cm<sup>2</sup> or below. The beam was then focused in order to obtain a beam waist in the 20–50  $\mu$ m range and directed on the 1 mm glass cuvette containing a sample solution. The cuvette was mounted on a computer-controlled travel stage (100 mm range). The movement range of the sample along the focused beam was typically from –25 to +25 mm or slightly shorter ( $\pm 20$  mm). After leaving the sample the laser beam was split in two parts – one monitored by a detector situated behind an aperture (closed aperture signal, CA) and the second one that was collected by a lens and fed to another photodiode (open aperture signal, OA). A third photodiode was used to collect the reference signal needed to account for the beam intensity fluctuations. For each wavelength the measurement set-up was adjusted and tested by a Z-scan measurement performed for a 4.66 mm thick silica plate. The light pulse energy was determined by the nonlinear phase shift generated by the silica plate, which was kept in the range of 0.5–1.5 rad. After adjusting the measurement system the pure solvent and sample were measured in identical cuvettes. The obtained data were analyzed using theoretical formalism developed by Sheik-Bahae [52,53] and the 2PA cross section ( $\sigma^{2PA}$ ) values were derived from the obtained nonlinear absorption data. The methodology was the same as that applied previously in a series of our studies on the 2PA solvatochromism of organic chromophores (see Refs. [13,16,21]).

## 3. Results and discussion

Measurements of 1PA and 2PA spectra of CV were performed in diluted and highly concentrated solutions, prepared using three polar solvents [*N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and propylene carbonate (PC)]. This set of solvents has been chosen after preliminary studies and ensured the possibility of obtaining the high concentration as well as stability of the CV solutions. These features are essential for 2PA measurements performed using the Z-scan technique. It must also be noticed that these solvents are very hygroscopic and the presence of water can modify their polarity, however in order to avoid this effect, a freshly bought and opened solvents were used. Solvent polarity is qualitatively defined by so-called polarity scales, which are usually constructed based on experimental measurements of 1PA spectra of carefully selected chromophores (polarity indicators) in different solvents [1,54,55]. The most popular polarity scale,  $E_T(30)$ , has been proposed by Christian Reichardt [1,54]. In our previous investigations of solvent effect on 1PA and 2PA spectra of *p*-nitroaniline (*p*NA), we have mentioned that in the  $E_T(30)$  scale PC is more polar than DMF and DMSO, whereas in the case of polarity scales proposed by Catalan, e.g., SPP, SdP and SP, the picture is opposite [21]. In the cited paper, it has been postulated that the Catalan scales provide more proper classification of this particular solvent than  $E_T(30)$  [21], which may not detecting the solvent's polarizability (see also discussion in Ref. [54]). Hence, in this paper the polarity of solvents as well as solvent effects on 2PA of CV will be characterized based on the SPP polarity scale, which, in our opinion, describes the solute-solvent interactions more precisely (see Table 1).

1PA spectra of diluted solutions of CV in the selected solvents is presented in Fig. 2 and quantified in Table 1. This spectrum is dominated by intense double-winged absorption band, which exhibits a very small positive solvatochromic shift ( $\lambda_{\max}^{1PA} = 594$  nm in PC, 598 nm in DMF and 602 nm in DMSO). It should be noticed here that the observation of small solvatochromic shift is related not only to the CV properties, but also to the necessity of choosing the solvents which polarity

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