



Two-parametric scaling law and figures of merit of excited-state absorption of organic dyes



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ABSTRACT

Sequential theoretical analysis of the excited-state absorption of organic dyes is carried out. It is established that the transmission dependence on laser radiation intensity of optical elements activated by organic dyes is described by the scaling law. It contains two parameters (the critical intensity and the contrast parameter) which are figures of merit of the excited state absorption of dye. Requirements to experimental conditions needed for correctly determination of figures of merit of the excited-state absorption efficiency of organic dyes are formulated. It is shown that there is a good agreement between experimental data of the sample transmission dependence on laser radiation intensity with the result of its calculation based on the scaling law. Figures of merit for several organic dyes are obtained.

1. Introduction

The excited-state absorption (ESA) attracts considerable attention in literature [1–19] since there is a great practical interest in the development of nonlinear optical elements for quantum electronics. In particular, a large number of works have a goal to develop a passive optical limiter based on ESA of organic dyes which are apparently the most promising materials for this application in the visible and infrared wavelength region of laser radiation and in the domain of ps – ns pulsewidths [1]. The most active investigations carry out with dyes of phthalocyanine (Pc) series [1–17] which have good thermal stability, high photo-stability, fast non-linear optical susceptibility and high value of relaxation rate to the ground state. Attractive feature of organic dyes consist in numerous capabilities of their modification. In the phthalocyanine dye, for example, it is possible to change the central cation in the macro-cycle of molecule [7], the axial ligand [8–10] and peripheral substitutions of molecule [10,11]. Chemical modification of dye leads to a change of photo-physical properties including ESA of molecule. It enables to optimize the molecular structure by molecular engineering methods for a purpose of getting the dye with needed properties. In order to resolve the problem of molecular structure optimization, it is necessary to have clear understanding of the relationship between the ESA efficiency and the molecular structure. It is clear that there is no way to reveal a correlation between structure of the molecule and its ESA properties without the determination of

physically-based figures of merit of ESA.

There are a number of attempts to suggest the characteristics of the ESA efficiency. Some results of these works are summarized in the review [10] where are collected different figures of merit suggested earlier. It is shown in the paper [10] that there is no united point of view on figures of merit of ESA; it is extremely onerous or even impossibly to compare results presented in different articles since they are represented in terms of different figures of merit.

The crucial drawback of suggested figures of merit of ESA is that all of them, as we know, have no theoretical ground. They have only phenomenological origin and, in some cases, connect with the experimental procedure (for instance, the Z-scan method) using by authors. It is clear that characteristics suggested without any substantiation cannot correctly characterize ESA and what is more they may contradict each other. For example, the ratio σ_{ex}/σ_g (where σ_{ex} and σ_g are excited and ground state absorption cross sections respectively) was introduced in the paper [7] as the figure of merit of ESA efficiency. There is shown [4,7] that this parameter is a good one as the ESA figure of merit in a series of dyes such as PcPb, PcZn, PcSi and PcSn and some others. At the same time, it is shown in the paper [8] that this parameter badly characterizes the ESA efficiency of the XPcIn series (where X is the axial ligand such as Cl, Br or I). The authors of this work assumed that in the capacity of the characteristic of the ESA efficiency should take the value of the difference of excited and ground-state absorption cross sections, that is, $\sigma_{ex} - \sigma_g$.

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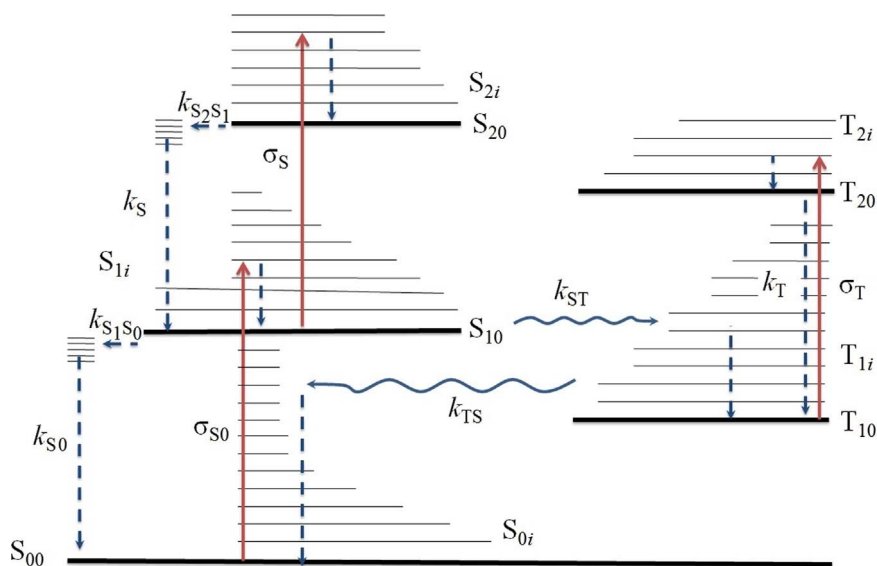


Fig. 1. Diagram of energy states in the organic dye and transitions between them. Radiative transitions are indicated by solid lines. Internal conversions and vibration transitions are depicted by dotted straight lines. Intercombinative conversions are depicted by wavy lines. σ_{S0} , σ_S and σ_T are absorption cross sections, k_{S0} , k_S and k_T are internal conversion rates, k_{ST} and k_{TS} are intercombinative rates.

The aim of this paper is sequential theoretical analysis of the excited-state absorption of organic dyes and determination on the basis of this consideration well-grounded figures of merit which are completely characterized the excited-state absorption of dyes.

2. Theory

2.1. Model of excited state absorption and two-parametric scaling law

It is well known that ESA is caused by multi-step transitions. To describe ESA is used rate equations which take into account five energy states of the molecule shown in Fig. 1.

This five-level model has good experimental and theoretical grounds [10,11,17]. In the framework of this model is assumed that populations of S_{20} and T_{20} levels are negligible. Moreover it is supposed that vibrational relaxation takes place instantly and that luminescence of molecules is not taken into account since it is very weak for dyes exhibiting ESA. Besides the applicability domain of rate equations is limited by the condition $\tau_p \gg \tau_1$ (where τ_p and τ_1 are pulse-width and the transverse relaxation time of the molecule respectively). In typical case τ_1 is at about 100 fs for organic dyes. The exact value of τ_1 is depend on the selected dye. For this reason domain of applicability of theory based on rate equation is limited by inequality $\tau_p \gg 1$ ps or more. The analysis of interaction of fs laser radiation pulses with dye molecule should be based on the density matrix formalism.

The change of laser beam intensity I passing through the optically thin sample activated by an organic dye is given by the equation

$$\frac{dI(z)}{dz} = -\alpha(I)I(z) \quad (1)$$

where z is an axial coordinate in the direction of laser beam propagation, $\alpha(I)$ is the absorption coefficient. The solution of this equation has to satisfy the initial condition $I(z)|_{z=0} = I$, where I is the intensity on the front surface of the sample.

In the framework of the five-level model, the absorption coefficient is written down as

$$\alpha(I) = \sigma_{S0}n_{S0} + \sigma_S n_{S1} + \sigma_T n_{T1}, \quad (2)$$

where n_{S0} , n_{S1} and n_{T1} are populations of S_{00} , S_{10} and T_{10} levels respectively and σ_{S0} , σ_S and σ_T are absorption cross sections of transitions $S_{00} \rightarrow S_{10}$, $S_{10} \rightarrow S_{20}$ and $T_{10} \rightarrow T_{20}$ (see Fig. 1). In accordance

with the relationship (2), the absorption of organic dye depends on populations of molecular levels. So, the absorption is changed when levels populations are redistributed under the action of laser radiation and hence to determine the absorption coefficient, it is necessary to solve rate equations

$$\dot{n}_{S0} = -(I\hbar\omega)\sigma_{S0}n_{S0} + k_{S0}n_{S1} + k_{TS}n_{T1} \quad (3)$$

$$\dot{n}_{S1} = (I\hbar\omega)\sigma_{S0}n_{S0} - (I\hbar\omega)\sigma_S n_{S1} + k_S n_{S2} - k_{S0}n_{S1} - k_{ST}n_{S1} \quad (4)$$

$$\dot{n}_{S2} = (I\hbar\omega)\sigma_S n_{S1} - k_S n_{S2} \quad (5)$$

$$\dot{n}_{T1} = -(I\hbar\omega)\sigma_T n_{T1} - k_{TS}n_{T1} + k_T n_{T2} + k_{ST}n_{S1} \quad (6)$$

$$\dot{n}_{T2} = (I\hbar\omega)\sigma_T n_{T1} - k_T n_{T2} \quad (7)$$

where n_{S2} and n_{T2} are populations of S_{20} and T_{20} levels respectively, k_{S0} , k_S and k_T are internal conversion rates of S_{10} , S_{20} and T_{20} states, k_{ST} and k_{TS} are intercombinative rates of S_{10} and T_{10} states, ω is a frequency of laser radiation.

The solution of Eqs. (1)–(7) gives both sample transmission dependence on laser radiation intensity i.e. $T(I)$ and figures of merit of ESA of organic dyes. Populations of molecular levels according to rate equations are changed droningly during the action of laser radiation. Figures of merit are determined by the peak value of ESA which is realized when populations of energy levels S_{10} and T_{10} reach maximum. This takes place in the stationary state when populations of the molecular levels remains unchanged in time and the time derivatives of levels populations are equal to zero. In that case rate Eqs. (3)–(7) are algebraic and the populations of S_{00} , S_{10} , S_{20} , T_{10} and T_{20} levels are equal to:

$$n_{S0} = N\{1 + [1 + (k_{ST}/k_{TS})]I/I_{S0} + I^2/I_{S0}I_{ST}\} \quad (8)$$

$$n_{S1} = (I/I_{S0})n_{S0} \quad (9)$$

$$n_{T1} = (k_{ST}/k_{TS})n_{S1}, \quad (10)$$

$$n_{S2} = (I^2/I_S I_{S0})n_{S0}, \quad (11)$$

$$n_{T2} = (k_{ST}/k_{TS})(I^2/I_T I_{S0})n_{S0}, \quad (12)$$

where $I_{S0} = \hbar\omega(k_{S0} + k_{ST})/\sigma_{S0}$, $1/I_{ST} = 1/I_S + (k_{ST}/k_{TS}) \times 1/I_T$, $I_S = \hbar\omega k_S/\sigma_S$ and $I_T = \hbar\omega k_T/\sigma_T$, N is the concentration of the organic dye.

In conformity with relationships (8)–(10) the absorption coefficient (2) is given by

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