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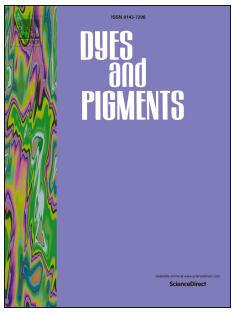

Peculiarities of the nonlinear optical absorption of Methylene blue and Thionine in different solvents

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Peculiarities of the nonlinear optical absorption of Methylene blue and Thionine in different solvents

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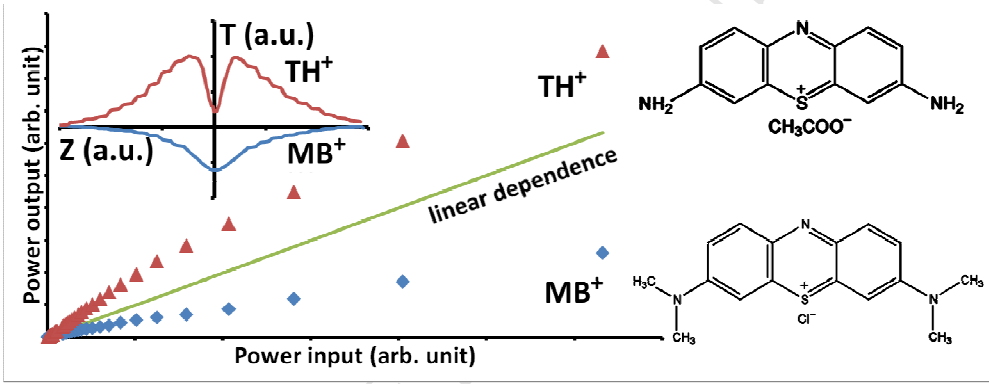
The saturated and reverse saturated absorption, as well as two-photon absorption, of two thiazine cationic dyes [Methylene blue (MB^+) and Thionine (TH^+)] were measured at the wavelengths of 532 nm using 10 nanosecond pulses. The concurrence of saturated absorption and two-photon absorption was analyzed in the case of aqueous and ethanol solutions of TH^+ dye in the range of 10^{-4} - 10^{-3} M concentrations. The reverse saturated absorption of the ethanol and aqueous solutions of MB^+ dye was observed. The nonlinear optical processes were fitted to the model of absorption allowing definition of the saturated intensities, reverse saturated, and two-photon absorption coefficients. It has been established that dimerization of MB^+ and TH^+ dyes plays a negative role in the processes of nonlinear absorption of 532 nm laser pulses. In this case, reverse saturation absorption for solutions containing predominantly MB^+ monomers provides an effective power limitation.



1. Introduction

At present, the physicochemical properties of thiazine dyes are being actively studied. Particular attention is paid to the photophysics and photochemistry of cationic dyes, Methylene Blue (MB^+) and Thionine (TH^+). The structural formulas of these thiazine dyes are shown in Fig. 1. These dyes are interesting from the point of view of creating photosensitizers of singlet oxygen, photobactericidal, and photocatalytic systems [1-6].

In particular, the molecules of MB^+ and TH^+ have some peculiar spectral properties. They absorb light in the 550 - 680 nm region [1, 7-10]. They also demonstrate a low-lying triplet state (0.3 - 0.4 eV below the first excited singlet state [11, 12], and an appreciable level of triplet yields for MB^+ and TH^+ of 0.4-0.5 [13-17]. At relatively low intensities of the exciting radiation, these dyes are able to transform into a colorless leuco-form ($MB^+ + H^+ + 2e^- \rightarrow MBH$), particularly through protonation from the triplet state and the attachment of electrons [1, 15, 18-20]. The dimers of these dyes have other properties and play a negative role in the photosensitization of singlet oxygen. To diminish such processes and enhance the unique photosensitizing properties of MB^+ and TH^+, attempts are made to interface them with semiconductor quantum dots and metal nanoparticles [21 - 23].

In most cases laser radiation was used for the probe experiments of these dyes. This requires a detailed analysis of the response caused by the action of pulsed laser radiation. The linear absorption properties for these dyes are the most studied. At the same time, there are practically no systematic studies of the optical nonlinearities of MB^+ and TH^+ molecules. In particular, there are no data on the processes determining such nonlinear optical response as nonlinear absorption. One of the attempts to analyze nonlinear optical properties was carried out for the molecules TH^+ associated with colloid quantum dots Ag_2S using 40 ps pulses at the wavelengths of 1064 nm and 532 nm [24]. However, in those studies the Ag_2S quantum dots served as reference samples.

In this paper, we report the studies of the nonlinear absorptive characteristics of some cationic organic thiazine dyes in aqueous and ethanol solution using 10 ns pulses at the wavelength of 532 nm (Methylene blue and Thionine). We analyze the two-photon absorption (TPA), the saturated absorption (SA), and the reverse saturated absorption (RSA) of these dyes. We also demonstrate the RSA in the case of MB^+ and the concurrence of SA and TPA in the case of TH^+