Absorption characteristics of Disperse Blue 1/dioxane solutions

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We have studied the absorption performance of the organic dye Disperse Blue 1 (DB1) in dioxane at different concentrations. Solutions were exposed to high intensities of CW laser radiation with the following wavelengths: 632.8 nm (He-Ne laser), 488, 496, and 514 nm (argon-ion laser). DB1 solutions showed optical limiting at high intensity of 632.8 nm laser radiation, which is very close to DB1 maximum absorption. Very dilute solution of the order of $\sim 10^{-4}$ M was enough to limit the transmitted power of the incident laser light by more than 90%. However, for other Ar-ion laser wavelengths, concentrations as high as 7.46×10^{-4} M were needed for the optical limiting characteristics to be observed.

Keywords: self-focusing and defocusing, polymers and organics, limiters, organic compounds and polymers.

1. Introduction

For the last two decades, absorption characterization of organic dyes and materials has been an active field of research due to growing needs in eye protection from intense laser exposure, as well as for protective applications in optical sensors [1]. The desired transmittance of such optical elements is inherently nonlinear, *i.e.*, the materials should be highly transparent at low input energies while the transmittance has to drop with increasing input energy. Fullerene materials have attracted attention for their potential optical limiting properties since the early days of their discovery in 1985 [2, 3]. TUTT and KOST studied the optical limiting of C_{60} and C_{70} solutions using 8-ns pulses of 532 nm laser light [3]. The strong absorption behaviour in these materials with saturation thresholds was found to be equal or lower than other materials reported to that date. The incorporation of noble metal nanoparticles in polymer matrices forms another promising field in the quest for efficient optical limiting materials. POREL *et al*. [4] have embedded silver and gold nanoparticles into poly(vinyl alcohol) films, which exhibited an appreciable linear transmission of ~89%, and showed a limiting threshold of ~0.7 J·cm^{-2}, at 800 nm Ti:sapphire laser (~100 fs).

Optical glasses form another appealing candidate class of photonic materials owing to their chemical and mechanical stability, as well as their ability to substitute

crystalline systems in many situations. Rai *et al*. [5] have studied the degenerate two-photon absorption (TPA) in a binary glass with composition TeO_2-PbO. They showed that the TPA coefficient, α_2, obtained with nanosecond laser pulses at 532 and 590 nm, increases when the relative amount of PbO is increased, and it reaches 12.6 cm/GW, which is comparable to or larger than the values reported for crystalline semiconductors and other recently reported glasses.

Semiconductor nanoparticles form another interesting class of promising materials. They have been under continuous scientific interest because of their unique quantum nature, which changes the material solid-state properties. Irimpan *et al*. studied the spectral and nonlinear optical properties of ZnO−CdS nanocomposites prepared by colloidal chemical synthesis, using nanosecond laser pulses from a tunable laser at the excitonic resonance and off-resonance wavelengths [6]. They observed that the nonlinear response is wavelength dependent, and switching from saturable absorption (SA) to reverse saturable absorption (RSA) for samples as the excitation wavelength changes from the excitonic resonance to off-resonance wavelengths.

In this work, we report the absorption behaviour of the organic dye Disperse Blue 1 (DB1) with dioxane to investigate the influence of CW laser power on its power limiting characteristics.

2. Experiment

2.1. Sample preparation

Disperse Blue 1 (DB1) was purchased from Acros Organics. Figure 1 shows the molecular structure of DB1 dye. Solutions of DB1 in dioxane were prepared by solving the 0.1 gm of DB1 in 20 ml of 1,4-dioxane, and stirred on a stirrer plate for two hours in a closed flask at room temperature. A series of different concentrations were prepared from this solution (Tab. 1) using very precise digital micropipettes (Transferpette Electronic, from Brand GMBH). The test cell used in this work was 10 mm thick quartz cell.

2.2. Experimental set-up and instrumentation

Several CW laser wavelengths obtained from an argon laser (543-MAP-A02, from Melles Griot), and a high power plane polarized Gaussian beam He-Ne laser (from
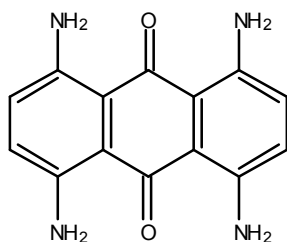

Fig. 1. Molecular structure of Disperse Blue 1 (DB1) dye.

T a b l e 1. The investigated concentrations, with the appropriate laser lines that have been used in this work.

Concentration [M]	Wavelength [nm]	Laser source
3.73×10^{-5}		
7.46×10^{-5}		
1.12×10^{-4}		
1.49×10^{-4}	632.8	He-Ne
1.86×10^{-4}		
3.73×10^{-4}		
7.46×10^{-4}	632.8	He-Ne
	488, 496, 514	Ar$^+$

Coherent), were used in this work. Table 1 summarizes the prepared concentrations and the laser wavelengths that have been used with each solution.

A UV–visible spectrophotometer (Photodiode Array Photospectrometer (PDA) Specord S100, from Analytik Jena) was used to record the UV–visible absorption spectra of DB1 liquid samples. The optical setup used for transmittance measurements is shown in Fig. 2.
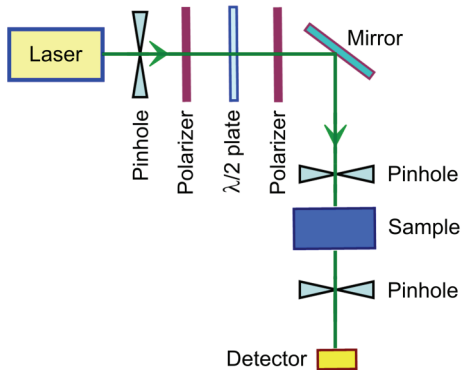

Fig. 2. The experimental set-up used for investigating the absorption characteristics.

An attenuator assembly (crossed Glan polarizers, and a $\lambda/2$ wave plate) was used to control the incident power on the sample, which kept the size of the laser beam unchanged as well. The laser beam was kept unfocussed, so that a beam of actual size as similar as much to real conditions in the lab was used. This procedure is useful for the fabrication of eye safe goggles and other protecting materials against laser radiation. On the other hand, the absence of lens focusing assembly that is usually used to increase the sample irradiance removes the side effect of lens imperfection. Lab-Master Ultima Coherent power meter was used to measure the incident and transmitted power of the laser beam. However, this experimental condition was at the expense of the sample irradiance.

3. Results

Figure 3 shows the dye spectra as a function of solution concentrations. The absorption increases as the dye concentration does, and a saturation effect starts to appear at the concentration of 4.1×10^{-4} M. This figure shows as well the irradiation laser wavelengths relative to the absorption maxima. The inset of Fig. 3 shows the optical density of the prepared solutions at the irradiation wavelengths, from which the studied concentrations were chosen.
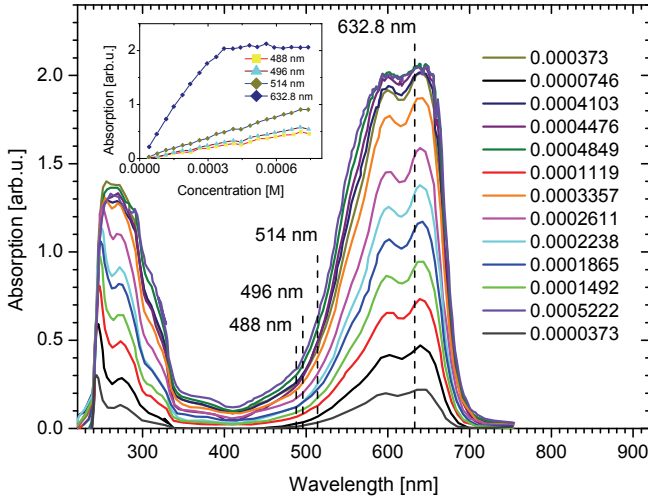

Fig. 3. UV–visible absorption spectra of DB1/dioxane solutions at different concentrations. The inset figure shows the plot of optical density at 488, 496, 514, and 632.8 nm versus concentration.

It is clear that the absorption of the samples follows the linearity of Beer–Lambert law for the argon laser wavelengths, as well as for the He-Ne laser wavelength, except for the highest concentration used. The effective extinction coefficient of the DB1/dioxane solution was estimated from the slope of the linear least-squares fits of the linear parts of the plots that are shown in the inset of Fig. 3, and are summarized in Tab. 2.

The absorbance of solutions of DB1 at all used wavelengths was also in line with Beer–Lambert law: $I = I_0 \exp(-\varepsilon c L)$, where I_0, I, ε, c and L are the incident energy,

T a b l e 2. The estimated effective extinction coefficients of the DB1/dioxane solutions at the laser lines used.

Wavelength [nm]	Effective extinction coefficient [$M^{-1}cm^{-1}$]	Linear least-squares fit R^2
488	666.47	0.9939
496	804.33	0.9951
514	1278	0.9965
632.8	6466.2	0.9937

the output energy, the extinction coefficient, the sample concentration and the sample path length, respectively. For example, the inset in Fig. 3 shows that a linear relationship exists between the absorption and the concentrations measured at all laser wavelengths that have been used in this study. An exceptional result was noticed for the 632.8 nm laser line at high concentrations, at which Beer−Lambert law was no longer linear. These results demonstrate that dye molecules were homogeneously dispersed in dioxane [7].

We have measured the laser spot size behind the sample at different concentrations by using the knife-edge technique, and it was found to be 1.24 mm. Figure 4 shows the results of the transmission measurements in DB1 dissolved in dioxane with the concentrations stated in Tab. 1 as a function of incident laser power. At low incident powers, the output power varies linearly with input power. The linear transmittance obeyed Beer−Lambert law. At high input intensity, sample transmission starts to deviate away from the linearity behaviour. This fashion was observed for all laser wavelengths that have been used, and for all dye concentrations, except for the very dilute one at 3.73×10^{-5} M for 632.8 nm laser line, which was not clear enough whether the plot has a beginning of a plateau or not, due to the limitation of our laser power. It was noticeable that the plateau at which the optical limiting takes place is dependent on the laser wavelength for a constant concentration of 7.46×10^{-4} M. Looking at Figs. 3 and 4, one can see clearly that the more the irradiation wavelength is close to the maximum absorption wavelength, the less power of the laser is transmitted. In other words, the optical limiting effect occurs at lower irradiation intensity at wavelengths close to the maximum absorption peak. On the other hand, He-Ne laser line at 632.8 nm resides very close to the maximum absorption wavelength, so that samples were
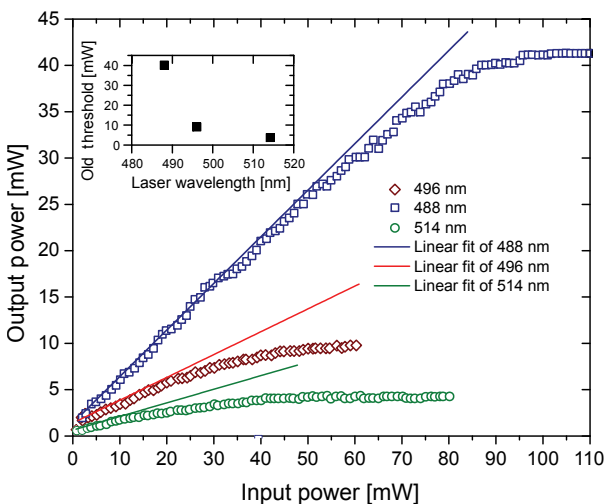

Fig. 4. Transmitted laser power as a function of incident laser power at Ar-laser lines: 488, 496, and 514 nm. The straight lines are the linear fit for each plot. The inset figure shows the power threshold at which the power limiting took place. The sample concentration was 7.46×10^{-4} M.
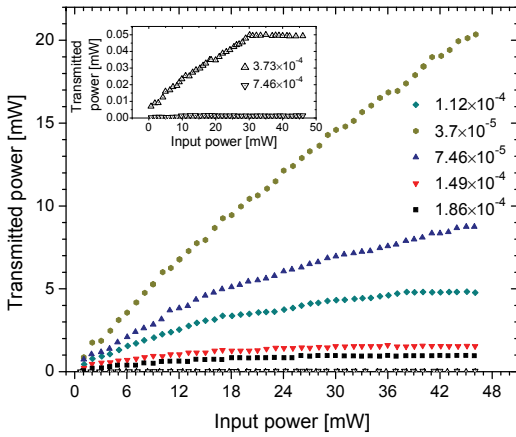
Fig. 5. Transmitted laser power as a function incident laser power at 632.8 nm at different dye concentrations. The inset figure shows this behaviour at the highest two concentrations.

absorbing this line more efficiently than other laser lines. Figure 5 shows the absorption behaviour of different dye concentrations. The absorption responses of the low concentration solutions are generally much weaker than those of more concentrated solutions, while high concentrated solution exhibits strong absorption. This indicates that the number density of dye molecules in the laser beam is the main factor affecting the clamped level [8]. From the threshold intensity (at which the plateau appears) for absorption for each sample, it can be seen that the optical power limiting threshold is inversely proportional to the concentration. Moreover, the data shows that as the concentration increases, a reduction in linear transmittance as well as the clamping level is observed. The observed results confirm previous findings that the concentration effect is rather determinant [3]. Figure 6 shows both the maximum transmitted laser power and threshold values as a function of dye concentration for the laser line of 632.8 nm. The behaviour of both plots follows an exponential decay as the dye
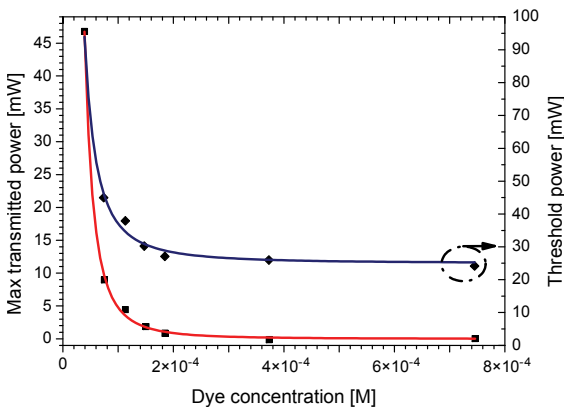

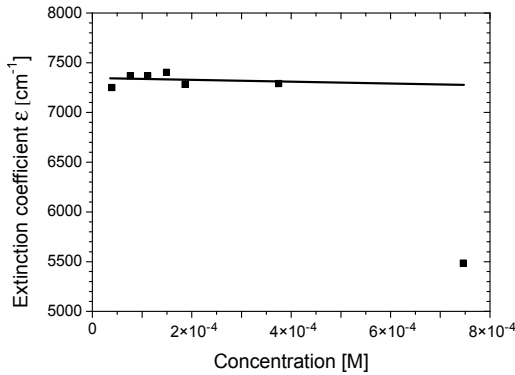Fig. 6. Maximum transmitted and threshold powers at 632.8 nm as a function of dye concentration.

Fig. 7. A plot of the extinction coefficient versus dye concentration at 632.8 nm laser irradiation.

concentration increases. At higher concentrations, the samples reach a saturation state, at which no further decrease in the transmitted laser power is observed. Figure 7 shows the calculated extinction coefficient ε, by taking the logarithm of both sides of Beer–Lambert law and solve for ε; then substituting the relevant experimental data in the resulting equation:

$$\varepsilon = \frac{\log(I_0 / I)}{cL}$$

and plotting ε against c [9]. This figure shows that the extinction coefficient values at 632.8 nm laser line obey Beer–Lambert law, except for the highest concentration value, at which the linear relationship is no longer valid.

Several mechanisms have been proposed for power limiting, including two-photon absorption (TPA), free-carrier absorption (FCA) associated with TPA, reverse-saturable absorption (RSA) using a five-energy-level model, self-focusing/defocusing, thermal blooming, and nonlinear scattering [10, 11]. Our absorption measurements show the participation of both mechanisms: RSA and nonlinear refraction. The RSA contribution is expected from the nonlinear behaviour of the measured output power as a function of the input power. BINDHU *et al*. showed that in the case of pure RSA, the incident laser power I_0 and the transmitted laser power I obey the relation [12],

$$\ln\left(\frac{I_0}{I}\right) = k(I_0 - I) + A_g$$

where k is a constant that depends on the absorption cross-sections and lifetimes of the ground, excited singlet and excited triplet states, and A_g is the ground-state absorbance (according to the five-energy-level model). The above equation says that the plot of $\ln(I_0/I)$ versus $(I_0 - I)$ should be a straight line with the slope k and the intercept A_g. Figures 8 and 9 show such representative plots for DB1 molecules for the concentration 7.46×10^{-4} M irradiated with the He-Ne laser (632.8 nm) and
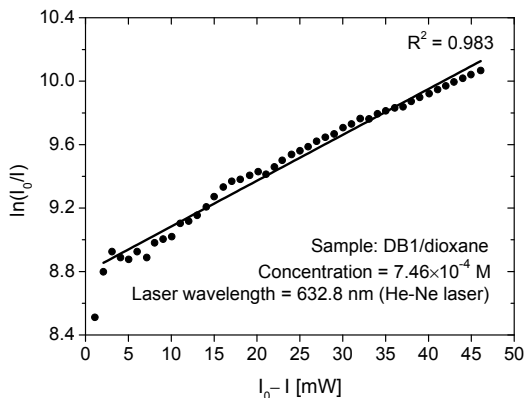
Fig. 8. A plot of $\ln(I_0/I)$ versus $(I_0 - I)$ for DB1/dioxane solution (irradiated with 632.8 nm laser line) showing approximate linearity.
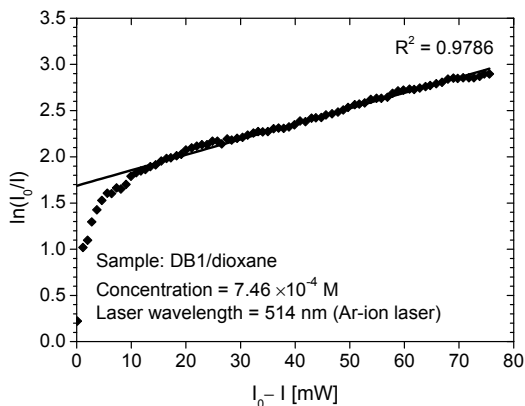

Fig. 9. A plot of $\ln(I_0/I)$ versus $(I_0 - I)$ for DB1/dioxane solution (irradiated with 514 nm laser line) showing approximate linearity.

the Ar-ion laser (514 nm), respectively. These plots appear almost linear in the practical power ranges of the lasers, which indicate that the RSA mechanism is not the only one that contributes to optical limiting behaviour of our samples. Similar plots were produced for other concentrations at all laser lines that have been used in this work.

The discrepancy of the measured transmitted power from the linear behaviour is related to the nonlinear absorption which, in turn, originated from the RSA mechanism in the chromophore. However, although RSA is a major contributor to the optical power limiting effect, it is speculated that nonlinear scattering plays an important role as well, which will be the subject of a separate investigation.

On a different note, the physical and chemical properties of organic molecules utilized in different scientific and technological applications can strongly depend on the properties of surrounding media [13–15]. For liquid solutions, the solvent plays a fundamental role in photo-physical processes, leading to the modification of

the ground and excited-state energies of the molecules. The interaction of solute with surrounding solvent leads to solvation effect, which refers to the reorientation of the solvent molecules around a solute molecule. The result of interaction of solute with solvent molecules depends on the nature of arising forces (specific, such as hydrogen bonding, and/or nonspecific, universal interactions) [15], which are determined by charge distribution and polarizability of the solvent and solute molecules. Considerable changes in the energy of solvated solute molecules may occur with changes in the solvent, especially in polar media [16−19]. For this reason, one should not exclude such important effect, and effect of the solvent nature on the absorption and optical limiting characteristics will be studied thoroughly in our future papers.

One last note should be mentioned here that we did not notice any signs of photobleaching due to using high laser intensities. This could be attributed to the RSA major contribution to the optical power limiting effect [10].

4. Conclusions

Absorption performance of the organic dye Disperse Blue 1 in dioxane was studied using a CW He-Ne laser at 632.8 nm as well as a CW argon-ion laser with 488, 496, and 514 nm. 3.70×10^{-5}, 7.46×10^{-5}, 1.12×10^{-4}, 1.49×10^{-4}, 1.86×10^{-4}, 3.73×10^{-4}, and 7.46×10^{-4} M solutions were prepared and exposed to high laser intensities at different laser wavelengths. DB1 showed considerable optical limiting at high laser light intensities. However, the best absorption effect was at 632.8 nm, which is very close to DB1 maximum absorption. At this wavelength, very dilute solution of the order of $\sim10^{-4}$ M was enough to limit the transmitted power of the incident laser light by more than 90%. However, for other Ar-ion laser wavelengths, concentrations as high as 7.46×10^{-4} M were needed to observe the absorption characteristics, which were clearer as the irradiation wavelength approached the maximum absorption wavelength of DB1 molecules.

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