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A Comparative Study of C_{60}, Pthalocyanine, and Porphyrin for Optical Limiting Over the Visible Region

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The Z-scan studies on C_{60}, pthalocyanine and porphyrin are reported to find their suitability as optical limiters over the visible region from 450 to 750 nm. The experiments are carried out using a nanosecond OPO laser. The excited state absorption cross-sections are calculated from the observed data and a comparison has been made between these three systems.

Introduction

Optical limiters are devices that strongly attenuate optical beams at high intensities while exhibiting high transmittance at low intensities. Such devices are required for the protection of human eye and optical sensors from intense laser fields. There is an intense search for materials exhibiting such properties. The development of these materials is based on various mechanisms such as nonlinear absorption and refraction in semiconductors[1], optical breakdown-induced scattering in carbon particle suspensions[2], thermal refractive beam spreading[3] and excited state absorption[4] (for a complete review of mechanisms responsible for optical limiting, *see* article by L.W.Tutt *et al.*[5]). Recent studies show very high performance excited state absorption (ESA) or reverse saturable absorption (RSA), behavior in C_{60} (Ref. 6), porphyrins[7], and pthalocyanines[8]. All the systems have higher excited state cross-sections (σ_{ex}) at 532 nm and show RSA behavior. Excitation with ns laser pulses leads to an enhanced RSA (σ_{ex}^{eff}) due to intersystem crossing and the involvement of triplet states T_1 to T_n absorption. Earlier reports on RSA are mostly using a single wavelength, i.e. 532 nm or 600 nm. We report here the excited state absorption cross-section for C_{60}, pthalocyanine, and porphyrin using Z-scan[9] experiment over the visible region. Z-scan is a single beam technique in which a laser beam is tightly focused and the sample is translated across the focal plane. Open aperture Z-scans, where the total energy transmitted through the sample is collected by a detector, are used to monitor the normalized transmittance vs position of the sample with respect to the focal plane. The sample position is related to the intensity and fluence.

The fundamental requirement for optical power limiting is that the system must exhibit fluence dependent RSA[10]. C_{60}, pthalocyanine, and porphyrin possess a larger excited state cross-section than the ground state absorption cross-section and hence they are suitable candidates for limiting applications.

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Materials and Methods

In the Z-scan studies, we employed a commercial OPO (MOPO, laser by Spectra Physics) pumped by the third harmonic (355 nm) from the Quanta Ray Nd:YAG laser with a repetition rate of 10 Hz and tunable in the range 380-1000nm. The pulse duration of the laser was 6 ns and an aperture of 1.4 mm was used at the output of the MOPO laser to obtain a smooth profile in the far field of the Z- scan studies. The energy after the aperture was varied from 0.2 to

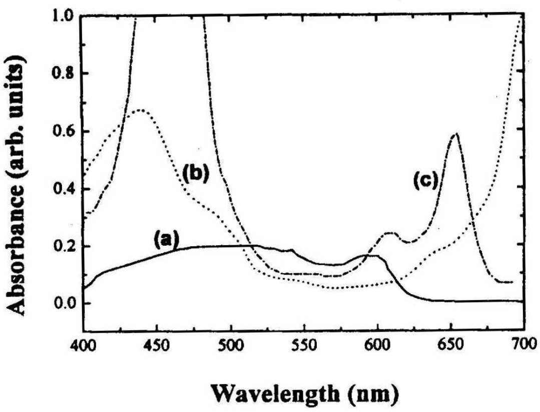

Fig. 1 — Linear absorption spectrum of (a) C_{60} (toluene), (b) Pthalocyanine (H_2SO_4), and (c) Porphyrin (THF) solutions

2.0 mJ/pulse, depending on the wavelength. The focal length of the lens used in the Z-scan experimental setup was 50 mm. 1 mm glass cuvettes were used for the solutions.

C_{60} (> 99% pure) was brought from Strem Chemicals, USA and dissolved in toluene to make ~ 10^{-4} – 10^{-3} *M* solutions. CuPc pthalocyanine was dissolved in sulphuric acid (10^{-4} *M*) and porphyrin was dissolved in THF (10^{-3} *M*). The absorption spectra of C_{60}, pthalocyanine, and porphyrin are shown in Fig.1. Open aperture Z-scans were obtained in the region covering from 450 to 730 nm wavelengths.

Results and Discussion

The results indicate that RSA and SA behavior occur at different regions for each system. To our knowledge this is the first report of a comparative study of these three important optical limiters showing the dispersion behavior and also being carried out at identical conditions. The results indicate that porphyrin is most suitable for the optical limiting in the region 500 – 600 nm; pthalocyanine suitable in the region 475 – 680 nm and C_{60} in the region 430 – 650 nm. From the data observed, the open aperture Z-scans, the transmittance, *T* was fitted for the case of RSA behavior[11] to Eq. (1)

$$T = \frac{\ln\left[1 + \left(\frac{q_0}{1+x^2}\right)\right]}{\left(\frac{q_0}{1+x^2}\right)} \quad ...(1)$$

where $q_0 = \sigma_{ex}^{eff}\, \alpha F_0 L_{eff}/2 h\omega$ and $x = z/z_0$

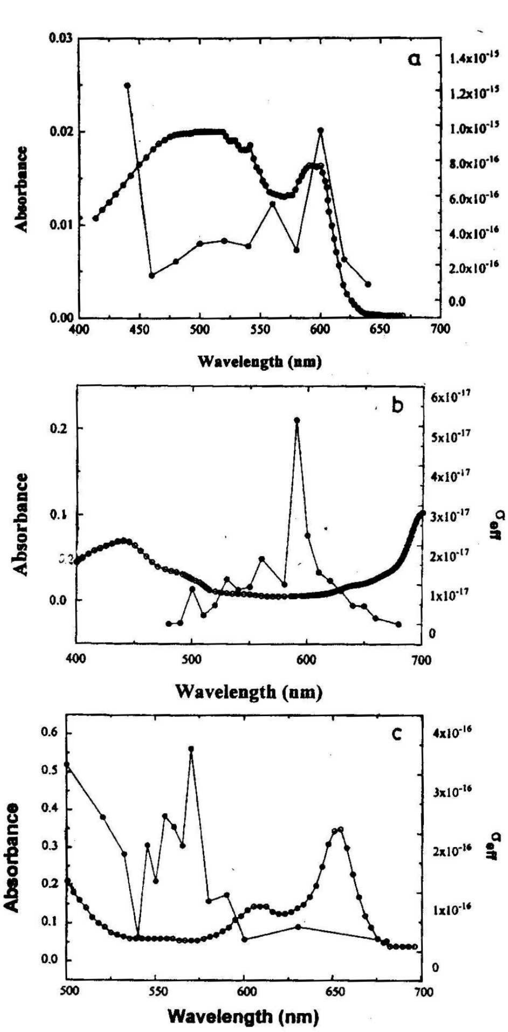

Fig. 2 — Effective excited state absorption cross-section values as a function of the wavelengths for (a) C_{60} (toluene), (b) Pthalocyanine (H_2SO_4), and (c) Porphyrin (THF) solutions. The linear absorption spectrum (open circles) is also shown in the figure.

σ_{ex}^{eff} is the effective excited state cross-section, which for the given laser pulse duration of 6 ns, contains contribution from both the singlet and triplet states, assuming that the intersystem crossing takes place within the duration of 6ns. Here, (α is the linear absorption coefficient, F_0 is the fluence, L_{eff} is the effective length of the sample $[(1-\exp(-\alpha l)]/(\alpha')$, and

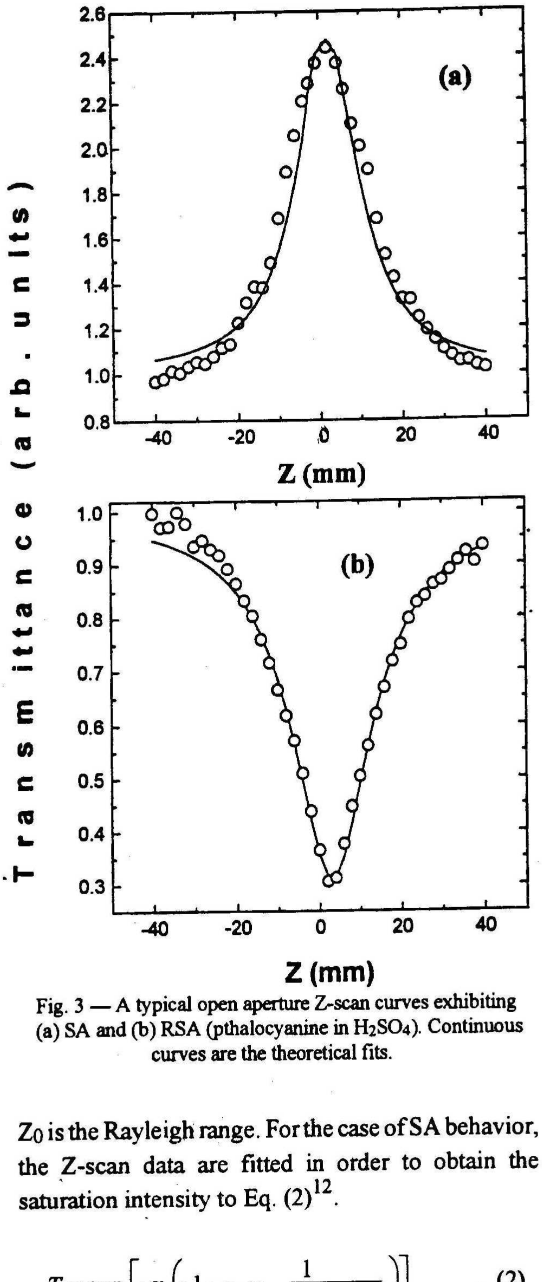

Fig. 3 — A typical open aperture Z-scan curves exhibiting (a) SA and (b) RSA (pthalocyanine in H_2SO_4). Continuous curves are the theoretical fits.

Z_0 is the Rayleigh range. For the case of SA behavior, the Z-scan data are fitted in order to obtain the saturation intensity to Eq. (2)[12].

$$T = \exp\left[\cdot \alpha \left(\cdot 1 - \frac{1}{1 + \frac{I_0}{I_0(1+x^2)}}\right)\right] \quad ...(2)$$

The results obtained for the σ_{ex}^{eff} are plotted in Fig. 2 for (a) C_{60}, (b) pthalocyanine, and (c) porphyrin. The values obtained for σ_{ex}^{eff} at 532 nm match very well with the values reported earlier for the materials. The typical curves obtained for the RSA and SA behaviors are shown in Fig. 3. The figure also shows the theoretical fit (solid line). In the regions (Fig. 2) where the RSA data are not given, the materials show SA behavior for the laser powers used in the experiments (0.2 to 2 mJ per pulse). Since the present studies were confined to the RSA behavior of the materials, these regions where the material showed RSA, are only shown in the figure.

A comparison of the respective absorption spectra indicates that the excited state absorption cross-sections are high where the absorbance, is low for one photon absorption (ground state absorption) and in the regions where there is high absorbance one sees SA behavior. From the above experimental data it is quite clear that an optical limiter over the entire visible region is possible only with a suitable combination of all the materials — C_{60}, pthalocyanine, and porphyrin. Fig.3 shows the typical curves obtained for the RSA and SA behaviors. The figure also shows the theoretical fit. We have thus presented our results on the dispersion characteristics of the RSA and SA behaviors of C_{60}, pthalocyanine, and porphyrin in solution state. The results show the most suitable region for the RSA behavior for each system.

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