

Thermo-optic nonlinearity of the laser dye LDS 867 under low power CW laser excitation

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Abstract. Thermally induced optical nonlinearity of the laser dye LDS 867 is studied in ethanol solution using the self phase modulation and closed aperture z-scan techniques, employing a continuous wave low power He-Ne laser beam for excitation. The nonlinear optical (NLO) coefficients are obtained by analyzing the z-scan curve on the basis of the thermal lens model. The dye exhibits a negative thermal nonlinearity which can be inferred from the occurrence of a pre-focal peak followed by a post-focal valley in the z-scan. The large nonlinear refractive index (n_2) measured at the excitation wavelength of 633nm reveals that the material is NLO active even at low excitation powers of less than 1 mW. Results indicate that LDS 867 is a promising material for optical power limiting applications.

1. Introduction

Absorptive and refractive nonlinearity of metal nanoparticles [1], organic dyes [2], polymers [3,4] and semiconductors [5] have been extensively studied using the z-scan technique, which is a sensitive tool for measuring the optical nonlinearity of materials. Laser dyes constitute an important group of organic molecules, and because of their intense and broad fluorescence emission spectra, they are becoming increasingly important in spectroscopy, holography, and biomedical applications.

In general, different types of optical nonlinearities can have response times extending from femtoseconds to milliseconds. Thermal nonlinearities are relatively slower, and can be induced by low power laser beams. The absorbed radiation can cause heating of the sample which leads to spatially varying temperature profiles. The temperature dependent induced refractive index leads to the creation of thermal lens as first observed by Gordon *et al* [6]. When a laser beam of intensity higher than a certain threshold value is incident on highly nonlinear materials, a far field diffraction ring pattern may become visible. This is caused by the thermally induced self phase modulation in the medium, and from the number of rings observed; the thermo optic nonlinear refractive index can be calculated [7].

Here we report the thermal nonlinearity measured in an ethanol solution of the laser dye LDS 867 excited by a low power (0.7 mW – 3.5 mW) He-Ne laser beam at 633 nm. The z-scan curve is numerically analyzed using both the Sheik-Bahae formalism and the Thermal Lens model, and the goodness of the resulting fits is compared. The value of nonlinear refractive index obtained numerically from closed aperture z-scan is confirmed from the number of self phase modulation rings observed.



2. Experimental details

Styryl dyes are widely used organic media with various applications in laser dyes [8], nonlinear optics [9], and dye sensitized solar cells [10]. Their derivatives are known for their light emitting properties and are useful in bio-labeling [11], optical recording [12] etc. The laser dye LDS867 belongs to the Styryl family. The UV-Visible absorption spectrum of LDS 867 in ethanol measured using a UV-Vis spectrometer (Lambda 35, Perkin-Elmer) exhibits a peak at 619 nm, with fairly good absorbance at the excitation wavelength of 633 nm (Figure 1).

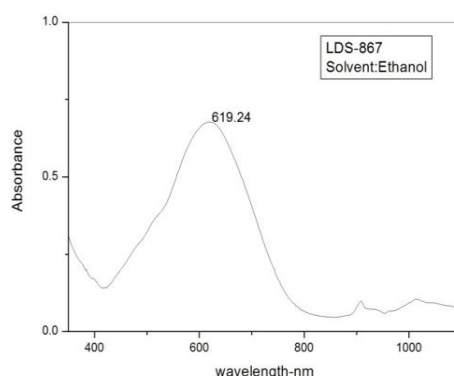


Figure 1: UV-Vis Absorption spectrum of LDS 867 measured in Ethanol.

For closed aperture z-scan measurements (Figure 2), the laser dye solution was prepared in ethanol with 10^{-4} M concentration, and then diluted further to get a linear transmittance of 45% at the probe laser wavelength of 633nm. The sample was taken in a 1 mm cuvette and is gradually translated along the axis of the Gaussian beam (TEM_{00} mode), which was focused to a spot size (ω_0) of $48\mu\text{m}$ using a 100 mm focal length convex lens. The power transmitted through the far field aperture (2mm diameter) is detected using a photodiode as a function of the sample position z (the focal point is taken as $z = 0$).

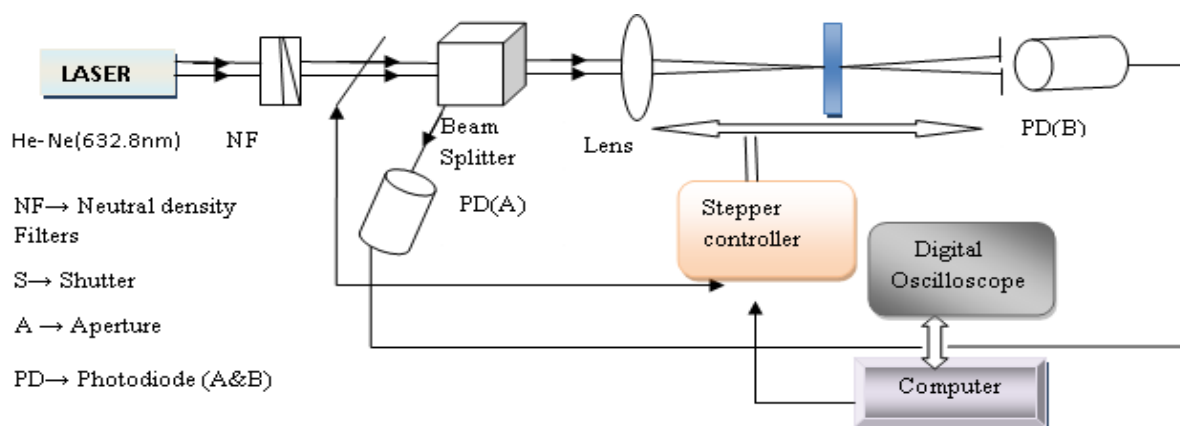


Figure 2: The closed aperture z-scan setup.

For the self phase modulation (SPM) measurements the far field aperture was removed and the beam was observed on a white screen. When the laser beam intensity is higher than a certain

threshold value, SPM rings are obtained as a far field diffraction pattern. We found that SPM rings occur when the incident He-Ne laser beam has a power of more than 3.5 mW. The images of the SPM rings were recorded using a CCD camera.

3. Results and discussion

The peak - valley transmittance curve obtained from the z-scan experiment is analyzed using two well known formalisms. According to the Sheik-Bahae Formalism (SBF) [13], the normalized transmittance $T_N^{SBF}(z)$ in the far field for a cubic nonlinearity and small phase shift $\Delta\phi$ is given by the equation,

$$T_N^{SBF}(z) \cong 1 + \Delta\phi \frac{4x}{(1+x^2)(9+x^2)} \quad (1)$$

where x is the dimensionless sample position given by z/z_0 , where z_0 is the Rayleigh range. In the Thermal Lens Model (TLM), the light absorbed is converted into heat with a Gaussian radial distribution, and due to the resulting spatial refractive index modification the material behaves as a thermal lens. Steady state is reached at $t \gg t_c$ where t_c is the thermal-diffusion time. In TLM the normalized transmittance $T_N^{TLM}(z)$ is related to nonlinear phase shift θ as [14],

$$T_N^{TLM}(z) \cong \frac{1}{1 + \theta \frac{2x}{1+x^2} + \theta^2 \frac{1}{1+x^2}} \quad (2)$$

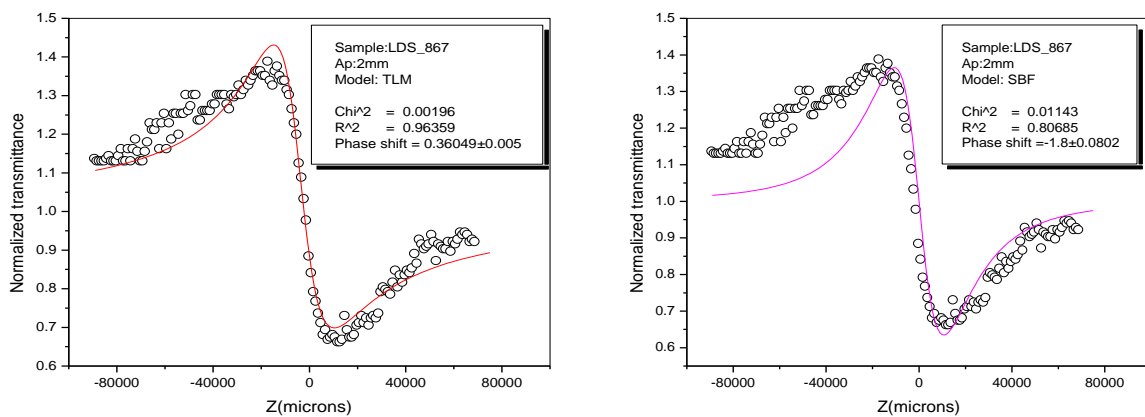


Figure 3: Measured closed aperture z-scan curve, with the data fitted to TLM (left) and SBF (right) respectively.

The experimentally obtained closed aperture z-scan curves are fitted with both models, and we found that TLM gives a better numerical fit to the measured data. For Equation 1 to be valid under SBF the condition $\Delta\phi \ll 1$ has to be satisfied, but in the present case the on axis phase shift is 1.8.

Table 1. Fitting parameters for LDS 867

Power 0.75mW	SBF	TLM
Chi-Square Value	0.0114	0.0019
Good Fit		✓
Phase Shift	1.8	0.34

Table 2. Calculated nonlinear parameters

n_2	$1.12 \times 10^{-6} \text{ cm}^2 / \text{W}$
$\frac{\partial n}{\partial T}$	$5.141 \times 10^{-5} \text{ K}^{-1}$
$\chi_{therm}^{(3)}$	$4.6 \times 10^{-5} \text{ esu}$

The optical nonlinearity arises from the dependence of refractive index on temperature, defined by the thermo-optic coefficient $\frac{\partial n}{\partial T}$. The nonlinear refractive index n_2 is given by [15],

$$n_2^{th} = \frac{dn}{dt} \frac{\alpha \omega^2}{4\kappa} \quad (3)$$

where, α is the absorption coefficient, ω is the beam waist, and κ is the thermal conductivity. The nonlinear refractive index and thermo-optic coefficient are calculated and the thermal contribution to the third order susceptibility is estimated (Table 2). The z-scan curves show a pre-focal peak followed by a post-focal valley indicating a negative nonlinear refractive index, so that $\frac{\partial n}{\partial T}$ also is negative. We performed open aperture z-scans also by removing the far field aperture, but no absorptive nonlinearity could be measured at the low power levels employed.

In a medium exhibiting thermally induced refractive index changes, laser induced self phase modulation can give rise to far field ring pattern [16]. This effect can be analyzed using the Fraunhofer diffraction integral, and the nonlinear refractive index can be found out from the number of principal SPM rings as [7],

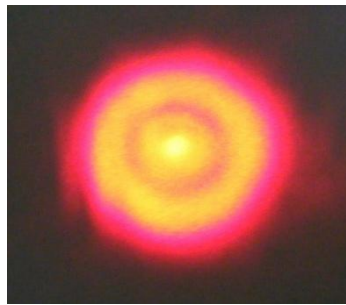


Figure 4: SPM rings observed in the far field.

$$n_2 = \frac{N\lambda}{Id} \quad (4)$$

where N is the number of SPM rings, I is the input intensity, and d is the cell thickness.

The SPM ring pattern in LDS 867-ethanol system shown in figure 4 was obtained above the threshold power of 3.5 mW. We calculated the thermal nonlinear refractive index as $0.94 \times 10^{-5} \text{ cm}^2/\text{W}$ in LDS 867 from SPM ring measurements. The occurrence of SPM rings and asymmetric nature of closed aperture z-scan curve confirms that the nonlinearity is of thermal origin.

4. Conclusion

Optical nonlinearity due to thermal effects in the laser dye LDS 867 in ethanol under low power cw laser illumination (0.7mW – 3.5mW) is studied using the techniques of closed aperture z-scan and spatial self phase modulation. The closed aperture z-scan curve is analyzed using two models (Sheik-Bahae formalism and Thermal lens model). Due to the high on-axis phase shift exhibited by LDS 867 under these conditions, the Thermal Lens model provides a better fit to the

experimental data. The calculated negative nonlinear refractive index and thermo-optic coefficient indicate that LDS 867 is a potential candidate for NLO applications.

5. References

1. He T, Wang C, Pan X and Wang Y 2009 *Phys Lett A* **373** 592
2. Sreekumar G, Louie Frobel P G, Muneera C I, Sathiyamoorthy K, Vijayan C and Mukherjee C 2009 *J. Opt. A: Pure Appl. Opt.* **11** 125204
3. Meyer R K, Benner R E, Vardeny Z V, Liess M, Ozaki M, Yoshino K, Ding Y and Barton T 1997 *Synth. Met.* **84** 549–550
4. Jang J I, Mani S, Ketterson J B, Lovera P and Redmond G 2009 *Appl. Phys. Lett.* **95**, 221906
5. Sreejaa R, Jobina Johna, Aneesha P M and Jayaraj M K 2010 *Opt Comm* **283**, 14
6. Gordon J P, Leite R C C, Moore R S, Porto S P S, and Whinnery J R 1965 *J. Appl. Phys.* **36**, 3
7. Binh L N, Dai X and Ja Y H 1989 *Appl. Phys. B* **49** 393-396.
8. Hoffnagle J, Roesch L Ph, Schlumpf N and Weis A 1982 *Opt Comm* **42** 267-268
9. Shettigar S, Umesh G, Poornesh P, Manjunatha K B and Asiri A M 2009 *Dyes Pigm.* **83** 207-210.
10. Dentani T, Ken-ichi Nagasaka, Funabiki K, Ji-Ye Jin, Yoshida T, Minoura H and Matsui M 2008 *Dyes Pigm.* **77** 59-69.
11. Moritz . R, Holzhauser C, Bohlander R P and Hans-Achim Wagenknecht 2012 *Chem. Eur. J* **18** 1299 – 1302
12. Chung-Chun Lee and Hu A H 2003 *Dyes Pigm* **59** 63-69
13. Sheik-Bahae M, Said A A, Tai- Huei Wei, David J Hagan and E W Van Stryland 1990 *Quantum Electron.* **26**, 760.
14. Carter C A and Harris J M 1984 *Appl. Opt.* **23** 3
15. Yu B, Zhu C, Gan F and Huang Y 1997 *Opt. Mater.* **7** 103-107.
16. Dabby F W, Gustafson T K, Whinnery J R and Kohanzadeh Y 1970 *Appl. Phys. Lett.* **16** 362-365.