Z-Scan measurements in Polyvinylpyrrolidone doped with 3- amino-7-dimethylamino-2-methyl phenazine azo dye

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Abstract:

Measurement calculations were carried out to determine the linear optical constants such as extinction coefficient, refractive index, average excitation energy and dispersion energy for the 3- amino-7-dimethylamino-2-methyl phenazine (Neutral red NR) doped Polyvinylpyrrolidone (PVP) film. Further the optical nonlinearities of Neutral Red : Polyvinylpyrrolidone solution have been investigated by Z-scan technique with CW laser at 657.2 nm The nonlinear refractive index and absorption coefficient are found to be in the order of - 1.91 $\times10^{-9}$cm^2/Watt , 1.13$\times10^{-5}$ cm/Watt, respectively .These results show that the ample has potential application in nonlinear optics.

Keyword: Optical properties, nonlinear refraction index, Z-scan, azo dye

1. Introduction

Nonlinear optical properties have been the subject of numerous investigations by both theoreticians and experimentalists in recent years especially due to the potential applications in optical signal processing and computing. Detailed investigations of linear and nonlinear optical coefficients enable to fabricate materials, appropriately designed at the molecular level for specific applications such as optoelectronic devices **[1,2]** .Knowledge of the optical constant of the materials (optical band gap and extinction coefficient) is vital to scrutinize the atomic structure, electronic band structure and electrical properties. The refractive index provides the information about the chemical bonding and electronic structure of the material.

This paper reports the linear optical constant of 3- amino-7-dimethylamino-2-methyl phenazine (NR) doped Polyvinylpyrrolidone (PVP) film through optical spectral analysis, also we investigated the nonlinear optical properties of NR:PVP solution by using Z-scan technique.

2. Preparation of sample and experimental method:

The molecular structure is shown in Fig. l. In our experiment, the host material is PVP and the ratio of NR in PVP by weight is 0.6 %. The NR doped PVP films were prepared as follows: NR and PVP are dissolved separately in distilled water, and then the solution of NR and that of PVP are mixed, heated (up to 50 ^{0}C) and stirred for 2 hrs; thus the mixed sols of NR and PVP were obtained. After the sols were filtrated, the films were prepared on a clean glass slide by the repeat-spin-coating method and dried at room temperature for 48 hrs. The thickness of the film is about 0.7 μm, and the film samples have good purity and uniform thickness.

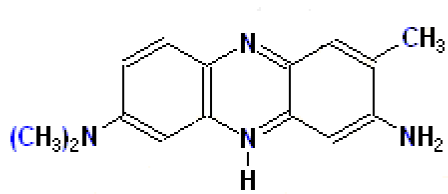
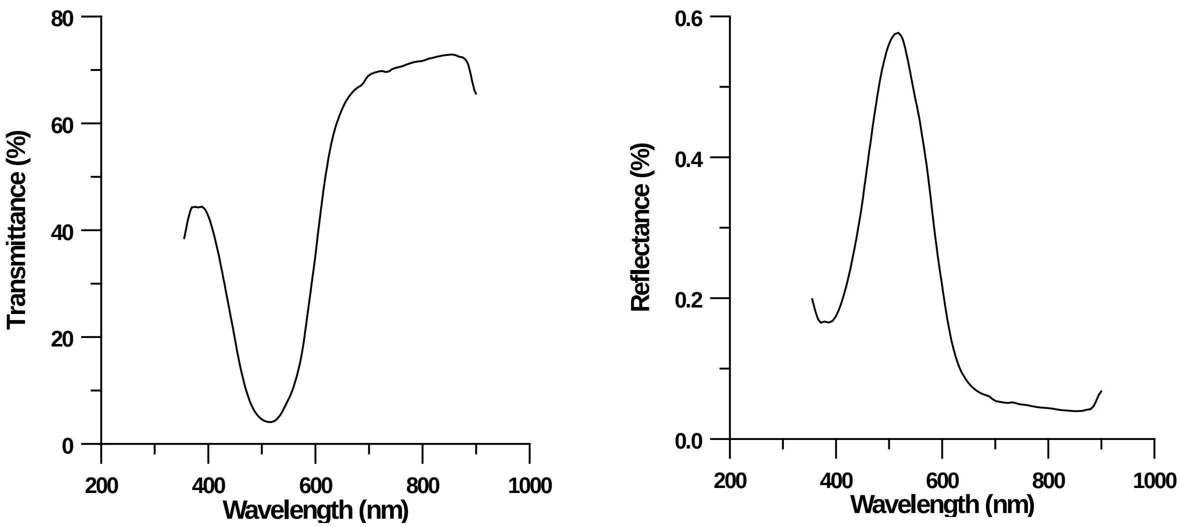


Fig. 1 Molecular structure of neutral red dye molecule

3. Result and discussion

3.1 Linear optical properties

Figs. 2-a and b show the transmittance and reflectance spectra of the NR doped PVP film. As seen in the figures, the direct electronic transitions from π to π^* orbitals in the 300-450 nm range results in an intense band called the Soret band, which gives the absorption edge in NR doped PVP film **[3].** The other band of the NR doped PVP film is the Q-band, which appears in the region between 550 and 750nm.



(a) **(b)**

Fig .2. The transmittance and reflectance spectra of the samples.

For understanding the interaction of light with matter, it is very essential to study the refractive index and the extinction coefficient .The reflectance spectrum was used to calculate the refractive index of the NR doped PVP film. The refractive index can be determined from the following relation **[4]:**

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad \text{.................(1)}$$

where k is the extinction coefficient and was calculated using $k = \alpha\lambda / 4\pi$. Figs. 3-a and b show the real and imaginary parts of the refractive index of the NR doped PVP film. It is seen that the refractive index n changes with wavelength and shows peak. In the region between 550 and 750 nm a Q band was observed .There is a little variation in the position of peaks and the magnitude of the peaks is greater. A normal dispersion was observed at λ < 500nm as well as anomalous dispersion at , λ > 500 nm.

Based on the single-oscillator model, Wemple- DiDomenico **[5]** is a semi-empirical dispertion relation to for determine the refractive index n at photon energy $h\upsilon$ can be written as follows:

$$n^2 = 1 + \frac{E_d E_0}{E_0^2 - (h\upsilon)^2} \text{ .... } \mathbf{(2)}$$

Where h is the Planck constant, ν is the frequency, E_o is the average excitation energy for electronic transitions and E_d is the dispersion energy which is the measure of the average strength of inter-band optical transitions or the oscillator strength.

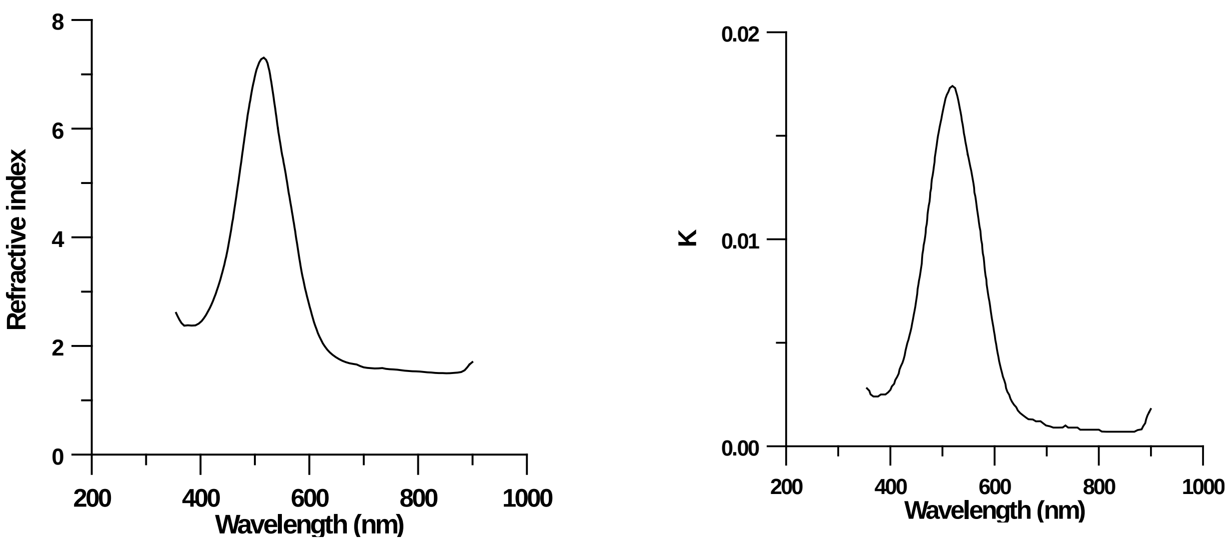
The M_{-1} and M_{-3} moments of the optical spectra can be obtained from the relationship.

$$E_0^2 = \frac{M_{-1}}{M_{-3}}, E_d^2 = \frac{M_{-1}^3}{M_{-3}} \text{ .... } \mathbf{(3)}$$

The M_{-1} and M_{-3} moments were calculated using the above equations and are given in table l. The M_{-1} and M_{-3} moments changed due to the formation coordination of complex. It is found that M_{-1} values decrease with atomic number of metal ion in the compounds .Whereas M_{-3} moments do not indicate any certain trend.

Table (1) The optical parameters of the NR doped PVP film

sample	E_0 (eV)	E_d(eV)	ε_∞	n(0)	S_0 (m^{-2})	M_{-1}(eV)	M_{-3} (eV)
NR doped PVP film	1.27	3.175	3.5	1.87	2.14×10^{13}	2.5	1.55



(a) **(b)**

Fig. 3. The real and imaginary parts of refractive index as a function of wavelength.

3.2 Nonlinear optical properties

The Nonlinear optical properties of organic molecules are being explored with great interest **[6-8]** .The Z-scan technique **[9,10]** is a simple and effective tool for determining the nonlinear properties and is being widely used in material characterization because it provides not only the magnitudes of real and imaginary part of nonlinear susceptibility ,but also the sign of the real part.

Organic materials exhibiting excellent third-order nonlinear optical (NLO) properties have stimulated great interest due to their potential applications including all-optical switching, optical limiting , signal processing ,ultra fast optical communications and ext **[11-13].** The current interest in organic nonlinear optical (NLO) materials is due to their potential application in various photonic technologies [14,15]. Many organic compounds that have nonlinear optical properties are known today. However, optimizing the optical and electro-optical behavior of these materials has been an area of intense experimental and theoretical research [16-18]. Organic materials with conjugated molecular systems possess large third order nonlinear susceptibility and ultra-fast response as a result of the delocalization of π-electron [19].

The schematic diagram of Z-scan technique is as shown in figure 4. By properly monitoring the transmittance change through a small aperture at the far field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus without placing an aperture at the detector (open aperture) one can measure the intensity dependent absorption of the sample. When both the methods (open and closed) are used in measurements of the ratio of signals determines the nonlinear refraction of the sample.

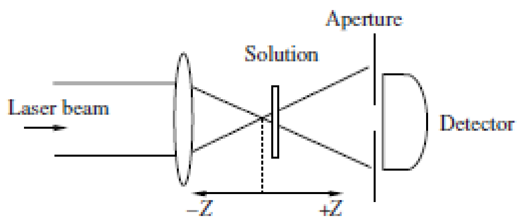


Fig. 4. Z - scan experimental setup.

A spatial distribution of the temperature in the surface is produced due to the localized absorption of a tightly focused beam propagation through the absorbing sample. Hence a spatial variation of the refractive index is produced which acts as a thermal lens resulting in the phase distortion of the propagating beam. The difference between normalized peak and valley transmittance ΔT_{P-V} can be measured by Z-scan technique. The peak to valley ΔT_{P-V} is linearly related to the on- axis phase distortion $\Delta\varphi_o$ of the radiation passed through the sample [18]. The relation is defined as,

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}\,|\Delta\varphi_\circ| \qquad \text{......................... (4)}$$

and

$$\Delta\varphi_o = k\, n_2 I_\circ\, L_{eff} \qquad \text{......................... (5)}$$

Where $S = 1-\exp(-2r_a/\omega_a)$ is the aperture linear transmittance with r_a denoting the aperture radius and ω_a denoting beam radius at the aperture in the linear region, $I_\circ$ is the intensity of the laser beam at focus $z=0$, $L_{eff} = (1-\exp(-\alpha_\circ L))/\alpha_\circ$ is the effective thickness of the sample (L is sample thickness), (α_o=0.279 cm^{-1}) is linear absorption coefficient of the NR:PVP solution and $k = 2\pi/\lambda$ is the wave number . The nonlinear refractive index n_2 can be obtained from equations 4 and 5, and the corresponding change in the refractive index $\boldsymbol{\Delta n = n_2 I_\circ}$.

Fig.5.a shows the closed aperture (CA) Z-scan curve of NR: PVP solution. From the asymmetric curve there is obvious nonlinear absorption existing in the solution and the close transmittance is affected by the nonlinear refraction and absorption. In order to extract the pure nonlinear refraction part, we have computed the value of the closed aperture (CA) data by the open aperture (OA) data. Fig.5.c shows the resulting curve corresponding to pure nonlinear refraction. The sign and magnitude of $\boldsymbol{n_2}$ is determined from the relative position of the peak and the valley with $\boldsymbol{z}$ [20]. The normalized transmittance of pure nonlinear refraction is given by

$$T(z) = 1 + \frac{4x\Delta\varphi_o}{(x^2+9)(x^2+1)} \qquad \text{......................... (6)}$$

Where $x = z / z_o$, $z_o = \pi\omega_\circ^2 / \lambda$ is the diffraction length of the laser beam, and $\boldsymbol{\omega}_\circ$ is laser beam waist at the focal point.

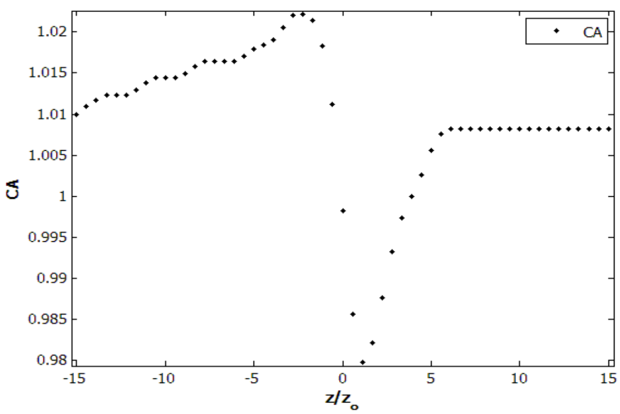
In the Z-scan measurement, the effective thickness of the sample was L_{eff} = 0.986 mm. The linear transmittance of the aperture was *S=0.39* and the optical intensity at the focus point is 5.09 *kWatt/cm^2*. From the theoretical fit results, the peak to valley ΔT_{P-V} indicates the negative sign of nonlinear refractive index, n_2 (self-defocusing) for the NR: PVP solution. The Z-scan signature for sample gives the value of the transmission for peak to valley (ΔT) is 0.033.

The nonlinear absorption coefficient $\beta(cm/W)$ is obtained from fitting performed on the experimental data of the open aperture measurement with the equation.

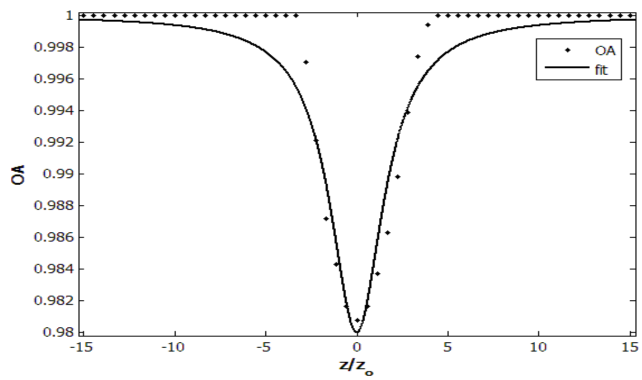
$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_o(z)]^m}{(m+1)^{3/2}} \qquad \textbf{For } |q_\circ(0)| < 1 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(7)}$$

Where $q_\circ(z) = \beta I_\circ L_{eff} / (1 + z^2 / z_o^2)$.

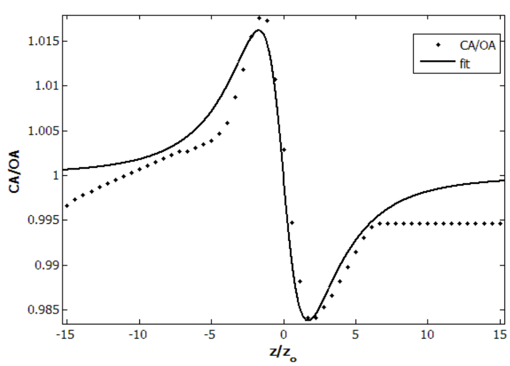
Fig.5.b shows the open aperture (S=1) Z-scan curve of sample. The enhanced transmission near the focus is indicative the for TPA process at high intensity (z = 0).



(a)



(b)



(c)

Fig. 5. Represent Z-scan experimental of NR :PVP solution (a) Close aperture (b) Openaperture and (c) Close aperture division open aperture, Solid line shows theoretical fit to the experimental data.

The measurement results are listed in the Table 2. The result exhibits that PVP: NR dye solution possesses a relation large third order NLO.

Table 2 : Measurement detail and the results of the Z-scan technique.

Laser beam wavelength (λ)	657.2 nm
Optical intensity at the focus	*5.09 kWatt/cm²*
Nonlinear absorption coefficient (β)	1.13×10^{-5}cm /W
Nonlinear refractive index (n_2)	-1.91×10^{-9}cm²/W

When we compare the value of n_2 calculated for the neutral red : Polyvinylpyrrolidone (PVP) solution with the one reported by Kozich et al.for the CS_2 Kerr nonlinearity [$n_2 = (2.5 \pm 0.4)x10^{-14} cm^2 / w$] [21] , we can see that the neutral red: Polyvinylpyrrolidone (PVP) solution $n_2 x10^5$ times bigger than that of CS_2 .
Elsewhere, knowing that this neutral red: Polyvinylpyrrolidone (PVP) solution has also nonlinear absorption, we calculate its figure of merit as Mizrahi et al. proposed in 1989 [22]. They have shown that for a nonlinear optical material to be interesting for all-optical purposes it should satisfy the condition

$$\frac{2\beta\lambda}{n_2} \leq 1$$

For the neutral red: Polyvinylpyrrolidone (PVP) solution we have determined that $\frac{2\beta\lambda}{n_2} = 0.7762$ .That is a very interesting result for this sample.

The high nonlinear refraction index and its attractive figure of merit, the sample has additional advantages: it is easy to prepare stable in front laser radiation and exhibits no toxic and no pollutant properties as CS_2.

Conclusion

NR doped PVP film has a lower cutoff wavelength (220nm) and a wide transparency (entire visible region) which makes it suitable for the realization of short wavelength laser light (by frequency doubling phenomenon) in the UV-VIS region .The high transmission, low absorbance, low reflectance and low refractive index of NR doped PVP film in the UV-VIS region make the material a prominent one for antireflection coating in solar thermal devices. The low extinction value (10^{-2}) and electrical conductivity (10^5 Ωcm^{-1}) show the semicoducting nature of the material. The third-order nonlinear refraction index $\boldsymbol{n_2}$ and nonlinear absorption coefficient $\boldsymbol{\beta}$, of NR : PVP solution was studied using a single beam Z-scan technique under CW laser with excitation at 657.2 nm. The Z-scan measurement indicates that the sample exhibited large nonlinear optical properties. $\boldsymbol{n_2}$, $\boldsymbol{\beta}$ and $\boldsymbol{\Delta n}$ values was found to be -1.91×10^{-9}cm²/W, 1.13×10^{-5}cm /W and -9.76×10^{-6} , respectively. The nonlinear absorption is regarded as a two photon absorption process. Thus the sample with many attracting linear and nonlinear optical properties is suitable candidate for optoelectronic applications.

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