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Study on Effect of Gamma Radiation on Some Linear and Nonlinear Properties of Pyronine Y

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Abstract. This study was conducted to analyse the effects of gamma radiation on Pyronine Y (C17H10ClN2O) solution by investigating its structural properties, third-order nonlinearities, and the chemical's optical limiting characteristics. Typical absorbance characteristics were recorded by irradiating pristine samples with radiation in the 300-700 nm wavelength range. The parameters defining the non-linear optical characteristics displayed changes in response to different irradiation times. The experiment used a 532 nm continuous-wave (CW) laser (SDL-532-100T) to study the optical limiting properties of the sample. Optical limiting was observed to increase with a corresponding increase in irradiation dose. The study also highlights the potential use of gamma irradiation to enhance the nonlinear properties in optical applications.

Keywords: gamma irradiation, pyronine y, laser, optical limiting, optical device

INTRODUCTION

Given the number of practical applications of micro-scale optoelectronics, the nonlinear properties of substances are being studied with great interest and detail. Organic materials have witnessed significant growth in demand for nonlinear optical (NLO) applications. These materials may be used in devices like electro-optic modulators, second-harmonic generator, frequency converters, among other applications [1],[2]. Organic materials present other significant advantages such as thermal and chemical stability, spectral broadband response, low cost, simple structure and preparation, both in solution form and polymer film form [3],[4]. These advantages have led researchers to thoroughly investigate these organic materials for novel optical use cases such as optical power limiting, optical data storage, optical switching, and signal processing [5,8] that require a larger nonlinearity and quicker response time. Organic materials also include organic dyes that are fascinating materials for the examination of the non-linear optical characteristics. The dyes have large nonlinearities, better response time, and stronger light absorption in the visible part of the spectrum [9]. Additionally, the dyes have distinct flexibility and superior thermal and chemical stability in the form of dye-doped solid polymer films. Due to these characteristics, the dyes are often the substance of choice for nonlinear optical experiments. Optical limiting has massive and important applications and has received much attention. Researchers have experimented with many materials using nonlinear optical mechanisms to study optical limiting behaviour [10-16].

During the past three decades, the behaviour of optical limiting of organic, inorganic and semiconductors materials [17] have been studied. Among these materials, organic materials [18] have been given a good properties due to the properties they possess, such as high optical nonlinearity, fast response time[19], damage threshold and easy molecular design [20].Many of these materials have proven to be effective as optical limiter [20],[21]. This attention given to organic materials is not only due to their applications as optical limiter, but due to its utilized in optical phase conjugation [22], high density optical data storage [23], optical bistability [24] and all-optical switching [19].

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In this research, Pyronine Y was irradiated with different sets of Gamma rays and the z-scanning technique was used to evaluate the third-order nonlinear optical characteristics. The optical limiting behavior was studied for a pristine sample of Pyronine Y being subjected to different doses of Gamma radiation.

EXPERIMENTAL DETAILS

MATERIAL PREPARATION

Pyronine Y dye, Cationic dye that intercalates RNA and is visible as a red band during electrophoresis. Shown to accumulate in the mitochondria of viable cells. At low concentrations the cytostatic effect is cell arrest in the G1 phase, whereas at high concentrations the cytotoxic effect is cell arrest in the G2 and S phase. Used in combination with Alcian Blue to assess and study pulmonary diseases, and in combination with Methyl Green to stain nucleic acids in paraffin sections. Additionally, has been used to measure RNA in CHO cells by flow cytometry, has the chemical formula $C17H10ClN2O$. A 0.04 mM sample of Pyronine Y dye was subjected to different Gamma-ray doses. Caesuim-137 was used as the source of the Gamma radiation with energy equal to 0.662 MeV, and the sample was exposed at a rate of 0.56 Gy/min. Every dose was administered with the samples placed simultaneously at the centre of the chamber and were surrounded for radiation equilibrium. The sample preparation method is specified next: 3 gm (0.01253 mol) of the dye was subjected to radiation at different doses – 21, 42, 62, and 82 KGy. After a month, 0.0121gm of Pyronine Y, having absorbed 21 KGy, was dissolved in 50 ml of concentrated methanol to prepare a 0.08mM bulk solution. After stirring for 50 minutes, 1.25 ml of the bulk solution was added to 3.75 ml methanol to reduce the concentration to 0.04 mM. Other samples were prepared similarly. Sample codes are used to denote the differently irradiated samples. For 0.04 mM pristine, the code is pristine. For the other samples the numbers indicate the radiation doses received by those samples. The designations are 21 KGy, 42 KGy, 62 KGy, and 82 KGy. A UV-visible spectrometer (Cecil Reflectascan CE 3055) was used to measure the absorption spectra of the pristine and irradiated samples in the 300-700 nm wavelength range. Pyronine Y dye has a complex molecular structure. There are typical UV-visible overlapping and continuous absorption band patterns due to the superposition of vibrations and electronic interactions. Two absorption bands were seen in the visible region. The excitation of the outer electrons is responsible for these bands and they provide useful information about the electronic transitions of the molecular of the test sample. They can be attributed to π-π^* bonding orbital-antibonding orbital transitions and the ions present in Pyronine Y [25],[26]. UV absorption is primarily due to the transition of electrons or anions from the top of the valence band to the bottom of the conduction band [27]. The absorbance of the pristine and Gamma irradiated samples (21, 42, and 62 KGy) exhibits an exponential increase with the dose for the 491 nm band. On the other hand, the absorbance shows an exponential decrease with dose in the 530 nm band for all samples. The increase in dose causes Chlorine ions to break from the carbon in Pyronine Y. H and OH free radicals are produced from the hydrolysis of the solvent during Gamma irradiation. The effects of radiation on unirradiated Pyronine Y and its irradiated samples were studied using a UV-visible spectrometer. The 82 KGy irradiated sample has lesser absorbance than pristine Pyronine Y. Figure 1 shows the absorption spectra.

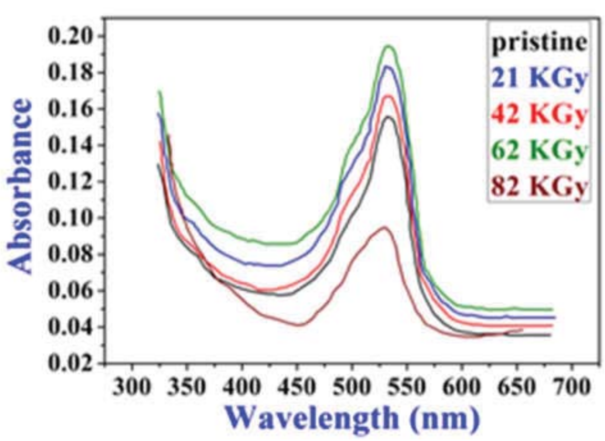

FIGURE 1. Absorbance spectra of Pyronine Y for pristine and different gamma irradiated

Z-SCAN MEASUREMENTS

The experiment was conducted using the Z-scan setup that is used to determine the non-linear optical characteristics as per Hussain A. Badran [28]. The test used a 532 nm diode-pumped CW laser (SDL-532-100T). The laser beam was set at a 5 cm focal length to ensure proper focus. The peak and valley transmission values were used and the difference in terms of phase shift at the focal axis is specified as [28,30]: Where [31] is the aperture linear transmittance and has a value of 0.32. ra denotes the radius of the aperture and denotes the radius of the beam at the aperture. The nonlinear third-order refractive index is specified as [32],[33]:

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}\Delta\varphi_{\circ} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where $S = 1 - exp(-r_a^2/\omega_a^2)$ [31] is the aperture linear transmittance and has a value of 0.32. r_a denotes the radius of the aperture and ω_a denotes the radius of the beam at the aperture. The nonlinear third-order refractive index is specified as [32,33]:

$$n_2 = \Delta\varphi_{\circ}/(I_{\circ}\, kL_{eff}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where $\Delta\varphi_{\circ}$ denotes the on-axis phase shift. $(L_{eff} = (1 - exp(-\alpha L))/\alpha)$.[34] represents the effective thickness of the sample. L denotes the sample thickness, and 'α'represents the optical linear absorption coefficient. The beam was focused using a lens with a focal length of +50mm. The solutions used in the experiment were placed in a 1mm thick quartz cell that was attached to a stepper motor and moved along the beam direction. A photo detector was used to feed the data to a digital Field Max II-To+OP-2 Vis Sensor power meter to measure the beam transmission.

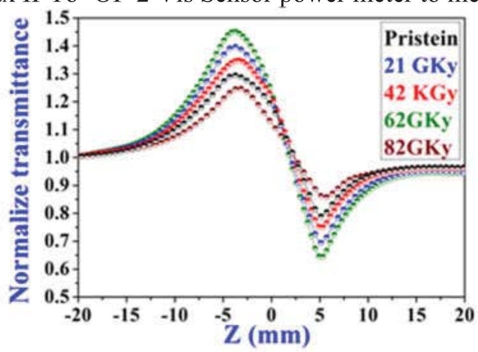

FIGURE 2. Pure data and theoretical fitting curves of Pyronine Y solution for different gamma irradiation.

Using an incident intensity I0 =1.045 kW/cm2, Z-scan data was obtained and is depicted in fig 2. In the previous study, it was observed that when the cw laser was used on the solution during the z-scan technique, the cause of the defocusing effect is the thermal nonlinearity caused by the absorption of radiation. Figure 3 highlights the measured z-scan data in the case of an open aperture setup of Pyronine Y with both unirradiated (pristine) and samples irradiated with different doses.

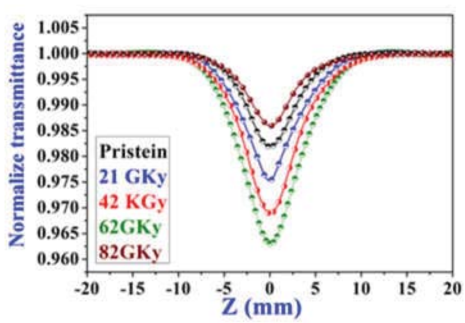

FIGURE 3. Open-aperture data and theoretical fitting curves for different gamma irradiation

The open aperture Z-scan data is used to determine the nonlinear absorption coefficient [35-37];

$$\beta = 2\sqrt{2}\Delta T / I_{\circ} L_{eff} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where ΔT represents one valley transmittances for the open aperture Z-scan curve, $I_o = 2P / \pi\omega_o^2$ is the intensity of laser beam at focus, and ω_o depicts the beam radius at the focus. The nonlinear absorption coefficient β (cm/W) and nonlinear refractive index n_2 (cm^2/W) for the Pyronine Y solution sample for the unirradiated (pristine) solution and solutions irradiated with different doses are determined from the open and closed aperture normalised transmittance whose values are mentioned in table 1.

TABLE 1. Linear and Nonlinear optical parameters of sample with different gamma irradiation.

Sample	β x10^{-4} (cm/W)	Δn x10^{-4}	n_2 x10^{-7} (cm^2/W)	$\alpha(cm^{-1})$
Pristine	6.1	1.9	1.9	3.58
21 KGy	8.1	2.3	2.24	3.84
42 KGy	10.6	2.8	2.7	4.2
62 KGy	12.7	3.2	3.1	4.47
82 KGy	4.5	1.4	1.34	2.18

n_2 is observed to be larger for samples of Pyronine Y irradiated with different doses of gamma radiation when compared to the pristine samples. Irradiation of Pyronine Y, ($C_{17}H_{10}ClN_2O$) causes the molecule to lose Chlorine and also causes detachment of ions and unsaturated carbon bonds (−C = C−). The values of n_2 and β correspond to the unirradiated and irradiated samples of Pyronine Y dye. An increase in gamma irradiation causes an increase in the nonlinear refractive index as depicted in fig 5. This observation could be attributed to the structural changes in Pyronine Y upon irradiation. Cross-linking, formation of free radicals, irreversible bond cleaving, among others, are the chemical changes that cause fragmentation among the molecules and allow the creation of saturated and unsaturated groups. All processes introduce "defects" at the molecular level and those are responsible for the observed nonlinear optical, mechanical, electrical, and chemical properties of the material [38].

In order to determine which has the better nonlinear optical properties comparing between the Pyronine Y dye in terms of the nonlinear reflective index. For this purpose, concentration 0.04 mM was selected for dye solution. The nonlinear reflective index value of the Pyronine Y dye solution used in present work is compared with materials known to have proven to be an n_2 by having a good value such as [2‑(2,3‑dimethyl phenylamino)‑*N*‑Phenyl benzamide (n_2 =1.105x10^{-7} cm^2 /W) [13], Sudan III solution (n_2 =2.34 x 10^{-11} m^2 /W)[39], Azo dye solution (n_2 =2.73 x $10^{-7}cm^2$ /W) [40], Metanil yellow dye (n_2 = 2.33 x $10^{-7}cm^2$ /W)[41], Acid blue 7 (n_2 =0.32 x $10^{-7}cm^2$ /W) [42], Fluorescein dye (n_2 = 0.29 x 10^{-7} cm^2 /W) [43]. All the n_2 values for the materials above are measured under CW laser. It is noticed that the Pyronine Y dye has a nonlinear reflective index value (n_2 = 3.1 x 10^{-7} cm^2 /W) larger than these materials, which means that it have a better nonlinear optical properties compared to these materials. Therefore, the Pyronine Y dye is a good candidate to be used as an optical device.

OPTICAL LIMITING

Optical limiting is a nonlinear optical process in which the transmittance of a material decreases with increased incident light intensity [10]. It has been demonstrated that optical limiting can be used for pulse shaping, smoothing and pulse compression [44]. The potential applications of optical limiting devices are optical sensor and eye protection [45]. Nonlinear refraction (self-defocusing) was the basis for optical limiting measurements. The Pyronine Y solution was placed where the valley falls in the closed aperture. The measurements were taken after varying the laser beam input power. Using power meters, the values of the input and the output power of the lasers were recorded. The optical limiting behaviour of the Pyronine Y dye solution is depicted in fig 5. The laser input power was varied from 0-45 mW and the output is plotted as a function of the input power.

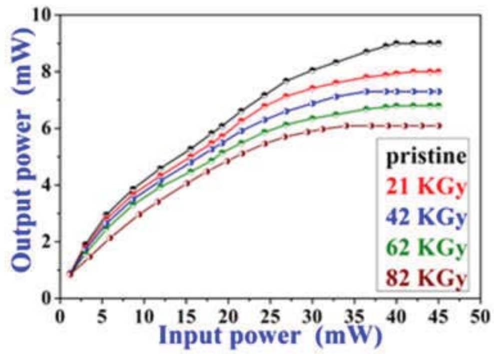

FIGURE 4. Optical limiting with different gamma irradiation of Pyronine Y dye solution

At low input power, the linear variation in output is clear. However, at high optical limiting input power, the output starts to deviate from its linear response. Further increase in the input causes the output power to reach a plateau where the output power remains relatively constant for a further increase in the input power. This value of input where the output power beings to saturate is called the power limiting threshold. At this input power, the sample transmittance drops to one half of its initial linear transmittance [46]. For the unirradiated and radiated forms of the Pyronine Y dye solution, the threshold power is plotted as shown in Figure 6 (values are reflected on the drawing). It is clear that optical power limiting depends on the dose of the Gamma radiation that the solution is subject to. Optical power limiting increases with Gamma irradiation time, whereas the power limiting threshold drops with an increase in irradiation. When Pyronine Y dye was subjected to high irradiation, the output power plateaued at low input power. At this point, the sample has strong optical limiting characteristics.

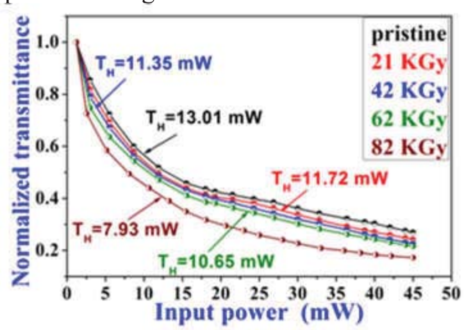

FIGURE 5. Power limiting threshold for pristine and different gamma irradiation dose.

Saturated output values are depicted in fig 6 that cause optical limiting for pristine and samples irradiated with different gamma-ray doses (time).

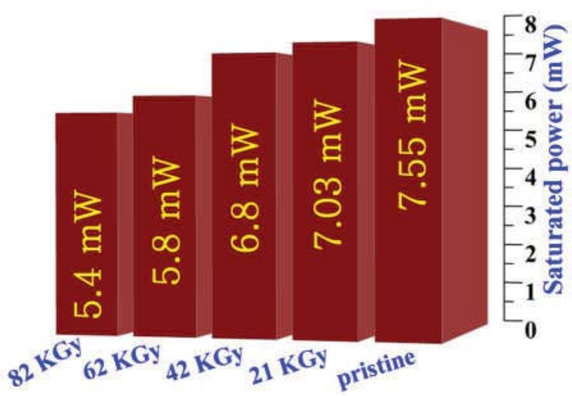

FIGURE 6. Histogram curve of saturated output value of samples.

CONCLUSIONS

During the experiment, the third-order nonlinear optical properties in the Pyronine Y sample were measured for un-irradiated and differently irradiated dose samples at a wavelength of 532 nm using the Z-scan technique. Optical nonlinearity observed in the CW regime is caused by thermal variations in the local refractive index in the medium. It is also indicated that the samples exhibit self-defocusing nonlinearities. The irradiated samples were observed to have a higher nonlinear refractive index and nonlinear absorption coefficients than the pristine unirradiated samples. Four samples – one unirradiated, and three having different levels of Gamma radiation doses – were used and the output power was measured as a function of the input. The threshold input and output clamping power were analysed for all the samples. The results of the experiment show that Pyronine Y is a suitable candidate for varied applications in optical devices.

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