International Journal of Applied Physics – IJAP
Volume 1 : Issue 1
Publication Date : 30 September, 2014

Third-order Optical Nonlinearity of Permethylazine

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*Abstract***— Third-order nonlinear optical materials are needed for numerous optoelectronic device applications including self-focusing, optical limiting, optical switching and data storage. Organic materials are potential candidate as nonlinear optical materials due to their synthetic flexibility, high damage resistance and large optical nonlinearity. In this paper, we investigate third-order nonlinear optical properties of permethylazine by using single beam z-scan technique with Q-switched, frequency doubled Nd:YAG laser (*λ*=532 nm) at 5 ns pulse. The values of nonlinear absorption coefficient(*β*), nonlinear refractive index (n_2) and third-order nonlinear optical susceptibility ($\chi^{(3)}$) of permethylazine were found to be** $9.17\times10^{-9}cm/W$, $7.1\times10^{-14}cm^2/W$ **and** $4.43\times10^{-12}esu$ **, respectively. We found, the signature of nonlinear refractive index in permethylazine is positive, and hence, it could be used as good self-focusing material.**

*Keywords***— Nonlinear optics; nonlinear refractive index; nonlinear absorption; nonlinear materials; z-scan.**

I. Introduction

Third-order nonlinear optical (NLO) materials exhibiting a large optical nonlinearity are in great demand because of their functional applications in optical power limiting, optical switching, optical data storage and micro fabrication [1-4]. Among various third-order NLO materials, organic materials are promising candidate materials due to their synthetic flexibility, high damage resistance and a large optical nonlinearity [5]. In organic materials, conjugate systems have received much attention as they show large density of polarizable π-electrons along the backbone and electron donating/accepting character [6-7]. Permethylazine is one of the important molecules of π-electron conjugate system which consists of an alternate pair of nitrogen and carbon atoms and electron donating amino group at both end of the chain. The presence of pair of nitrogen atoms in permethylazine provides increased stability towards oxidation and hydrolysis, which makes permethylazine as an environmentally stable material [8]. Beside, nitrogen atoms also serve to modulate the electron density along the chain and leading to charge transfer within the permethylazine molecules [9]. These typical features of permethylazine, stimulated our interest to synthesize and investigate its third-order nonlinear optical properties for possible functional applications.

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Cubic optical nonlinearity have been characterized by various techniques [5,10]. These techniques, have their own merits and demerits and therefore they occupy a special place in nonlinear optics. Among them, z-scan technique [11] has a great advantage because of its simplicity and high sensitivity, from which one can characterize simultaneously nonlinear absorption and refraction of optical materials via open and closed aperture measurements, respectively. In addition, signature of optical nonlinearity can also be identified by this technique. Very recently, third-order nonlinear optical properties of conjugated polymer [12] and thiophene based conjugated polymer [13] have been investigated by two-photon-induced fluorescence method and z-scan technique, respectively. Wang et al. [12] shown that the two-photon absorption cross section of conjugate polymers varies inversely proportional to the concentration of the solvents but independent of polarity of the solvents, while Poornesh et al. [13] pointed out that the origin of a large third-order optical nonlinearity lies in strong delocalization of π-electrons along the polymer chain. Here, we report the third-order nonlinear optical properties of as-prepared permethylazine compound by using z-scan technique with Q-switched frequency doubled Nd: YAG laser (532 nm) at 5 nsec pulse.

II. Theory

Z-scan technique is based on the measurement of the nonlinear transmission of the optical materials in open and close aperture configuration. The transmittance is measured in the linear diffraction regime.

A. Open aperture:

In open aperture measurements, the normalized transmittance is given by [11]

$$T(z,S=1)=\sum_{m=0}^{\infty}\frac{[-q_0(z)]^m}{(m+1)^{3/2}} \qquad \text{for } q_0(z)<1 \qquad (1)$$

Where $q_0(z)=\dfrac{\beta I_0(1-\exp(-\alpha L))}{(1+z^2/z_0^{\,2})\alpha}$, β is nonlinear absorption coefficient, α is the linear absorption coefficient I_0 is the on-axis excitation intensity at the focus, L is the length of sample, z is the sample position, $z_0=\pi\omega_0^{\,2}/\lambda$, is the Rayleigh range with ω_0 being the beam waist radius at the focal point ($z=0$), and λ is the laser wavelength. By knowledge of nonlinear absorption coefficient (β), one may also compute corresponding imaginary part of third-order susceptibility ($\operatorname{Im}\chi^{(3)}$) by following relations:

$$\operatorname{Im}\chi^{(3)}(SI)=\frac{2\varepsilon_0 c^2 n_0^{\,2}\beta(SI)}{3\omega} \qquad 2(a)$$

$$\mathrm{Im}\,\chi^{(3)}(esu)=\frac{9\times10^{8}\,\mathrm{Im}\,\chi^{(3)}(SI)}{4\pi} \qquad 2(b)$$

where ε_0 is the permittivity of free space, n_0 is linear refractive index and c is speed of light in vacuum.

B. Closed aperture:

The nonlinear refractive index (n_2) can be obtained by the normalized transmittance of close aperture described by following relation;

$$T=1+\frac{4\Delta\phi_0 x}{[x^2+1][x^2+9]} \qquad (3)$$

where $x=z/z_0$ and $\Delta\phi_0$ is the phase change given by $\Delta\phi_0=kn_2I_0L_{eff}$, where $k(=\frac{2\pi}{\lambda})$ is wave number and L_{eff} is the effective length in the sample. The dependence of normalized transmittance on aperture and phase shift is given by [22]

$$\Delta T_{p-v}=0.406(1-S)^{0.25}\left|\Delta\phi_0\right|, \qquad (4)$$

where ΔT_{P-V} (denoting T_P-T_V) is the difference between normalized peak and valley transmittance and $S(=1-e^{(-2r_a^{\,2}/r_b^{\,2})})$ represent the aperture linear transmittance, where r_a denoting the aperture radius and r_b denoting the beam radius at the aperture.

Also, by knowledge of index of nonlinear refraction one may obtain corresponding real part of third-order optical susceptibility using following relations:

$$\mathrm{Re}\,\chi^{(3)}(SI)=\frac{4\varepsilon_0 c n_0^{\,2} n_2(SI)}{3} \qquad 5(a)$$

$$\mathrm{Re}\,\chi^{(3)}(esu)=\frac{9\times10^{8}\,\mathrm{Re}\,\chi^{(3)}(SI)}{4\pi} \qquad 5(b)$$

Finally using equation (2) and (5), magnitude of $\chi^{(3)}$ can be obtained as:

$$\chi^{(3)}=\left|(\mathrm{Re}(\chi^{(3)}))^2+(\mathrm{Im}(\chi^{(3)}))^2\right|^{1/2}. \qquad (6)$$

III. Experimental

Permethylazine was synthesized and characterized as reported by Haur et al. [14]. A schematic sketch of the single beam z-scan experimental set-up [11,15] is shown in Fig. 1. The sample was irradiated by a Q-switched frequency doubled (λ=532 nm) Nd:YAG laser (Quanta system, HYL-101) having a 5 nsec pulse duration with pulse repition rate of 10 Hz. The fundamental Gaussian laser beam was tightly focused to a; w_o=15 µm spot, where w_o is the spot size of the beam. Firstly, z-scan experimental set-up was calibrated with CS_2 and subsequently measurements of third-order nonlinear absorption and refraction coefficients of permethylazine were performed.

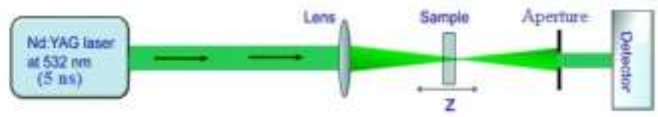

Fig. 1 Z-scan experimental arrangement.

In order to investigate nonlinear optical properties of permethylazine, as-prepared sample was dissolved in dimethyl sulphoxide (≈8 *mM* concentration) and kept in a quartz cell of *1.0 mm* path length (*l*). Thin sample approximation i.e. $l<z_0$ ($z_0=\pi w_0^{\,2}/\lambda$ is the Rayleigh range,) was ensured. The sample holder was mounted on a xyz translation stage and the transmitted pulse energy was collected by a detector (Thorlab DET 110). The output energy recorded by 200 MHz digital storage oscilloscope. Open and closed aperture configurations were used for measuring nonlinear absorption and refraction of the sample, respectively. For closed aperture measurement, an aperture was placed in front of transmission detector and the transmittance was recorded as a function of sample position along the z-axis. We noticed that scattering and thermal effects were very weak around these excitation levels and hence these effects neglected without losing the generality of the problem [16]. Moreover, low repition rate of the laser allows one to neglect the contribution of pulse-to-pulse build up effect in nonlinear optical response of permethylazine [17].

IV. Results and Discussion

An open aperture transmission of the sample was measured in the far-field region. A decrease in value of transmittance around the focal point, is indicative of nonlinear absorption in permethylazine (See Fig. 2).

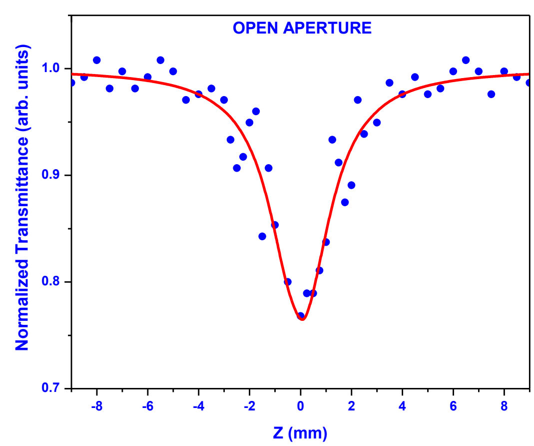

Fig. 2 Open aperture measurements (at 532 nm) of permethylazine. *"Symbols"* represent experimental data and *"solid lines"* represent theoretical fit.

In this figure, *"symbols"* represent experimental transmission data, while *"solid lines"* are obtained by fitting the experimental data to the nonlinear transmittance given by equation (1). For theoretically fitting, we assumed $q_0(0) < 1$ and β as a fitting parameter. Open aperture experimental data of permethylazine are found fit well for typical values of β and found to be $9.17 \times 10^{-9} cm/W$, where imaginary part of third-order susceptibilities ($\mathrm{Im}\,\chi^{(3)}$), corresponding to β , is evaluated using equation (2) and found to be $2.12 \times 10^{-12} esu$.

By closed aperture measurements, nonlinear refractive properties e.g. self-focusing/defocusing of the sample can be studied. The closed aperture scan of permethylazine is shown in Fig. 3. In this figure, *"symbols"* represent experimental transmission data, while *"solid lines"* are obtained by fitting the experimental data to the nonlinear transmittance given by equation (3). Here, nonlinear refractive index (n_2) is taken to be a fitting parameter. Close aperture experimental data of permethylazine is found fit well for typical values of $n_2 (= 7.1 \times 10^{-14} cm^2/W)$.

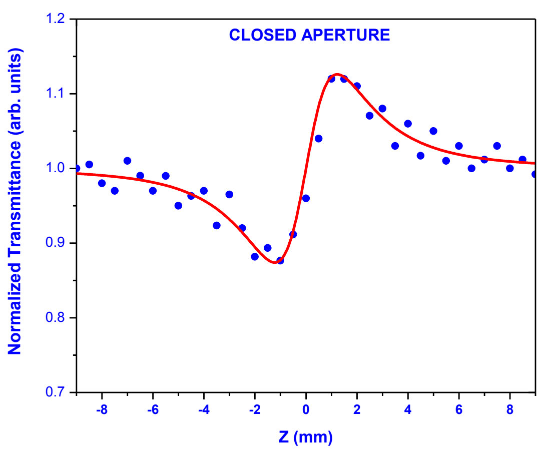

Fig. 3: Closed aperture measurements (at 532 nm) of permethylazine. *"Symbols"* represent experimental data and *"solid lines"* represent theoretical fit.

Real part of third-order susceptibilities ($\mathrm{Re}\,\chi^{(3)}$), corresponding to n_2, is computed using equation (5) and found to be $3.82 \times 10^{-12} esu$. Also, $\chi^{(3)}$ was calculated by using equation (6) and found to be $4.43 \times 10^{-12} esu$. It is clearly evident from Fig. 3, that the sample exhibits prefocal valley and post focal peak characteristics, which is direct indication of positive n_2 (positive lens) and it suggests permethylazine can also be used as self-focusing materials around 532 nm. In addition, the reliability of measurements of nonlinear refraction in permethylazine is confirmed by peak-valley character of permethylazine, which satisfies the condition of $\Delta Z_{P-V} \sim 1.7 z_0$ (where, ΔZ_{P-V} is the separation between the maxima and minima of the closed aperture curves) [11]. Interestingly, our reported values of nonlinear optical coefficients β, n_2 and $\chi^{(3)}$ are larger than the values measured in permethylazine using third harmonic generation technique [18] and quoted for other conjugated organic materials [19,20] under similar experimental conditions. Here it is worth mentioning that, in all cases, empty quartz cell, pure dimethyl sulphoxide (DMSO) and tetrahydrofuran (THF) were separately measured under the same experimental conditions and their magnitude of $\chi^{(3)}$ were found to be $\approx 10^{-15}$ esu, which is nearly 10^3 smaller than the values reported in this study.

V. Conclusions

Third-order nonlinear optical properties of permethylazine were investigated by z-scan technique with frequency doubled, Q-switched 5 nsec Nd: YAG laser at wavelength 532 nm with repition rate of 10 Hz. The values of β , n_2 and $\chi^{(3)}$ of permethylazine are found to be $9.17 \times 10^{-9} cm/W$, $7.1 \times 10^{-14} cm^2/W$ and $4.43 \times 10^{-12} esu$, respectively and it is noticed that these values are nearly ten times larger than the values reported elsewhere. Results also suggest that permethylazine can be one of the promising candidate materials for third-order nonlinearity based optical devices.

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