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journal homepage: [www.elsevier.com/locate/optlastec](http://www.elsevier.com/locate/optlastec) $\chi^{(3)}$  measurement and optical limiting studies of urea picrateK. Naseema<sup>a</sup>, M. Shyma<sup>b</sup>, K.B. Manjunatha<sup>c</sup>, A. Muralidharan<sup>b</sup>, G. Umesh<sup>c</sup>, Vijayalakshmi Rao<sup>a,\*</sup><sup>a</sup> Department of Materials Science, Mangalore University, Mangalagangothri-574199, India<sup>b</sup> Department of Chemistry, NAS College, Kanhangad-671315, India<sup>c</sup> Department of Physics, NITK, Surathkal, Mangalore-575025, India

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## ABSTRACT

The molecular charge complex urea picrate (UP) was synthesized and its third order nonlinear optical properties have been investigated using a single beam Z-scan technique with nanosecond laser pulses at 532 nm. Open aperture data of the compound indicates two photon absorption at this wavelength. The nonlinear refractive index  $n_2$ , nonlinear absorption coefficient  $\beta$ , magnitude of effective third order susceptibility  $\chi^{(3)}$ , the second order hyperpolarizability  $\gamma_h$  and the coupling factor  $\rho$  have been estimated. The experimentally determined values of  $\beta$ ,  $n_2$ ,  $\text{Re } \chi^{(3)}$  and  $\text{Im } \chi^{(3)}$ ,  $\gamma_h$  and  $\rho$  of the compound UP are 2.146 cm/GW,  $-1.258 \times 10^{-11}$  esu,  $-1.347 \times 10^{-13}$  esu,  $0.377 \times 10^{-13}$  esu,  $0.69 \times 10^{-32}$  esu and 0.28, respectively. The compound exhibits good optical limiting at 532 nm with the limiting threshold of 80  $\mu\text{J}/\text{pulse}$ . Our studies suggest that compound UP is a potential candidate for optical device applications such as optical limiters.

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## 1. Introduction

Materials possessing nonlinear optical response [1] can be exploited for the manipulation of optical signals in a variety of optical devices. NLO materials possessing the required properties for specific applications continue to be a topic of research in spite of extensive investigations carried out in the past on a large variety of materials such as semiconductors [2], conjugated organic polymers [3], porphyrins [3], liquid crystals [4], dyes [5,6], fullerenes [7], nanocomposites [8], charge transfer complexes [9] and organometallics [10], etc.

Recently the phenomenon of optical power limiting, a nonlinear optical effect, has attracted much attention due to its application to protection of eyes and sensitive optical devices from high power laser pulses. Since the discovery of optical limiting phenomenon, much work has been done in synthesizing new materials with adequate optical limiting property. The optical limiting property is facilitated by the presence of strong nonlinear absorption.

An optical limiter strongly attenuates the laser pulses of high intensity where as it is completely transparent at lower light intensities. Ideally, the laser pulse energy transmitted through the limiter rises linearly with input energy and saturates to a constant value at high energies. The limiting threshold is defined as the input energy at which the transmittance is fifty percent. Above the threshold, the output energy is clamped to the saturated value which depends on the material [11].

Generally, optical limiting property exhibited by organic molecules is related to high delocalization of the pi-electrons. The optical limiting behavior resulting from nonlinear absorption can occur due to reverse saturable absorption, two photon absorption, nonlinear refraction and nonlinear scattering. Nonlinear optical property observed in some materials such as semiconductor can be explained on the basis of two photon absorption wherein the material absorbs two photons simultaneously at the higher light intensity [12].

Investigation of the NLO properties of supramolecules and adduct formed due to self-assembly of two or more molecular components has been a topic of considerable recent interest. Hydrogen bonding, electrostatic interactions, pi-pi bonding and Vander-waals forces have been employed to explain the behavior of such molecules.

Glycine picrate [13] and L-Alaninium oxalate [14], nonlinear optical materials from the amino acid family have been reported to show third order nonlinear optical properties.

Considering the nonlinear optical properties of urea and picric acid, in the present work, an attempt has been made to synthesize urea-picrate (UP), a new organic NLO material and its third order nonlinear optical properties have been investigated. This compound was first reported in 1886 [15] and its second isomorphous form was described in 1947 [16].

## 2. Synthesis and characterization

## 2.1. Synthesis

Solution of equimolar amounts of urea and picric acid in Methanol were prepared separately. After mixing the two solutions,

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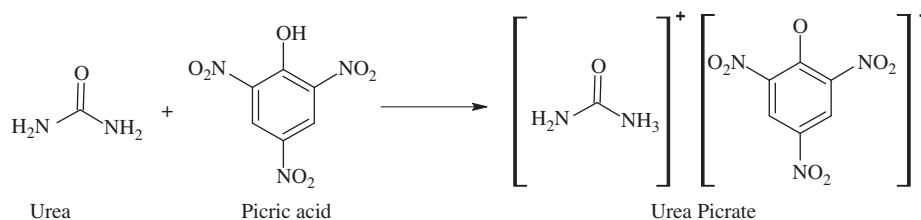


Fig. 1. Scheme of formation of UP.

Table 1  
Elemental analysis data.

	% of carbon	% of hydrogen	% of nitrogen
Experimental value	30.18	2.3	23.41
Theoretical value	29.07	2.4	24.2

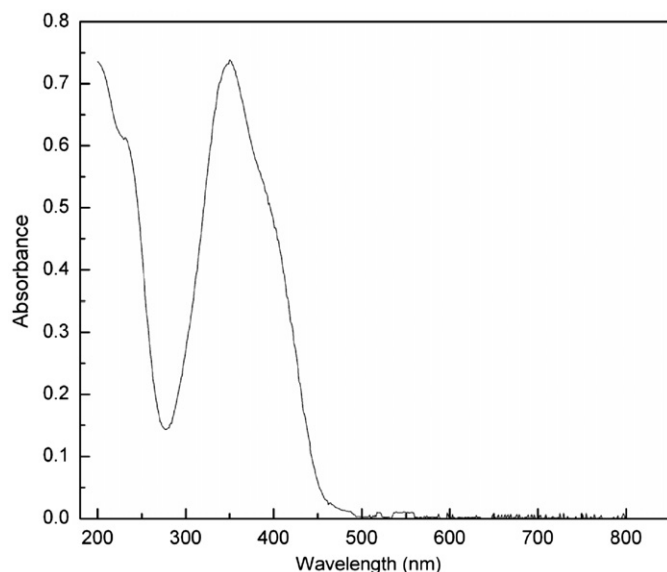


Fig. 2. UV-visible spectrum of UP.

the resultant solution is stirred well. Within two days, bright yellow crystals of UP were formed and repeatedly recrystallized from methanol to enhance the degree of purity. The change in colour of the crystal may be due to the formation of charge transfer complex between urea and picric acid. The scheme of reaction for the formation of the compound is given in Fig. 1.

## 2.2. CHN analysis

The elemental analysis data (Table 1) shows good agreement between the experimentally determined values and the theoretically calculated values within the limits of permissible error. The result indicates that UP is free from impurities and devoid of water molecules. Further it confirms the stoichiometry and hence the molecular formula of the material.

## 2.3. UV-visible spectral studies

UV-visible spectroscopy helps in determining the transparency, purity and cutoff wavelength for visible light for the material. UV-visible spectrum (Fig. 2) of the grown crystal was recorded and it has good transparency in the visible range with a cutoff wavelength at 450 nm. There is no absorption of light at 532 nm.

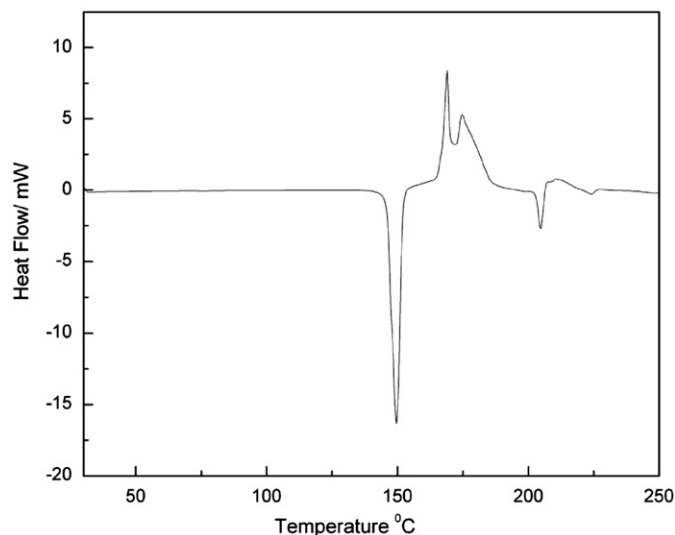


Fig. 3. DSC thermogram of UP.

The molecular complexes in which extensive charge transfer interaction occurs between the donor and the acceptor molecules are also expected to have high NLO properties. When the donor and the acceptor molecules, likely to form loose molecular complex are mixed together, very often a new featureless absorption band appears at a longer wavelength in the UV-visible spectrum. This band arises due to the transition of an electron from the highest filled molecular orbital of the donor to the lowest empty molecular orbital of the acceptor. Promotion of an electron to the higher unoccupied orbitals of the acceptor gives additional charge-transfer bands.

The absorption spectrum of the charge transfer complex UP in Fig. 2 revealed a strong absorption band at 350 nm attributed to the charge transfer interaction. This band, which is assigned to  $\pi \rightarrow \pi^*$  transition, is not present in the spectra of the free reactants. The reactants urea and picric acid absorb at 200 and 210 nm, respectively. The absorption of the formed complex at a longer wavelength with respect to the reactants reveals the formation of charge transfer complex. This longer wavelength absorption band owes to the promotion of an electron from the highest occupied molecular orbital (HOMO) of urea (donor) to the lowest unoccupied molecular orbital of picric acid (acceptor) and confirms the formation of charge transfer complex. The value of band gap energy was found to be 2.5 eV.

## 2.4. Thermal analysis

The thermal stability of UP was studied by differential scanning calorimetry (DSC). The DSC analysis was carried out using Mettler Toledo DSC 822e machine, between 30 and 300 °C at a heating rate of 10 K/min in the nitrogen atmosphere. In the DSC curve (Fig. 3), there is an endothermic peak at 149 °C indicating the melting point of the material. In the literature, urea picrate is

reported to have a melting point of 142 °C [16]. This value is in good agreement with the experimentally determined value using melting point apparatus (148 °C) and is greater than the melting points of urea (132 °C) and picric acid (122 °C).

### 3. Transmission measurements

The third order optical nonlinearity was investigated by the Z-scan technique which has become a popular method for the measurement of optical nonlinearities of materials. It not only has the advantages of simplicity and high sensitivity, but also enables simultaneous measurement of magnitude and sign of the nonlinear refractive index and the nonlinear absorption coefficient of the samples [17]. Basically, the method consists of translating a sample through the focus of a Gaussian beam and monitoring the changes in the far field intensity pattern. When the intensity of the incident laser beam is sufficient to induce nonlinearity in the sample, it either converges (self-focusing) or diverges (self-defocusing) the beam, depending on the nature of that nonlinearity. By moving the sample through the focus, the intensity dependent absorption is measured as a change of transmittance through the sample (open aperture). The nonlinear refraction is determined by the intensity variation at the plane of a finite aperture placed in front of the detector (closed aperture), because the sample itself acts as a thin lens with varying focal length as it moves through the focal plane.

A Q-switched Nd:YAG nanosecond laser with a pulse width of 8 ns at 532 nm and a pulse repetition rate of 10 Hz was used as a source of light in our experiment. The output of the laser beam had a nearly Gaussian intensity profile. Solutions of the compounds in dimethyl formamide (DMF) were prepared and the concentration of the solution was  $1 \times 10^{-2}$  mol/l. The Gaussian laser beam was focused using a lens of focal length 25 cm, into the sample solution contained in a 1 mm quartz cuvette. The resulting beam waist radius at the focus was calculated using the formula,  $\omega_0 = 1.22f\lambda/d$ , where 'f' is the focal length of the lens and 'd' the diameter of the aperture. It was found to be 18.9  $\mu\text{m}$ . The corresponding Rayleigh length, calculated using the formula  $Z_R = \pi\omega_0^2/\lambda$ , was found to be 2.11 mm. The sample thickness of 1 mm was less than the Rayleigh length and hence it could be treated as a 'thin medium'. The Z-scan was performed at laser pulse energy of 200  $\mu\text{J}$ , which resulted in an on-axis peak irradiance of 4.78  $\text{GW}/\text{cm}^2$ . The measurements were done at room temperature. The optical limiting measurements were carried out keeping the sample at the focal point and varying the input energy and recording the output energy without placing an aperture in front of the detector. Two pyroelectric detectors along with the Laser Probe Rj-7620 energy meter were used to record the incident and the transmitted energies simultaneously. In order to avoid cumulative thermal effect, the data were collected in a single shot mode [18].

The nonlinear transmission of compounds with and without an aperture placed in front of the detector were measured in the far field as the sample was moved through the focal point. This allows us to separate the nonlinear refraction from the nonlinear absorption. In the open aperture curve which shows the normalized transmission without an aperture at 532 nm, the curves are nearly symmetric with respect to the focus ( $Z=0$ ), where it has a minimum transmission, showing an intensity dependent absorption effect. This may include nonlinear optical processes like two photon absorption (TPA), excited state absorption (ESA), free carrier absorption and reverse saturable absorption. Nonlinear absorption under nanosecond excitation can be explained using the five level energy diagram [19–21] as shown in Fig. 4. Ground state  $S_0$ , the first singlet state  $S_1$ , the next higher excited singlet

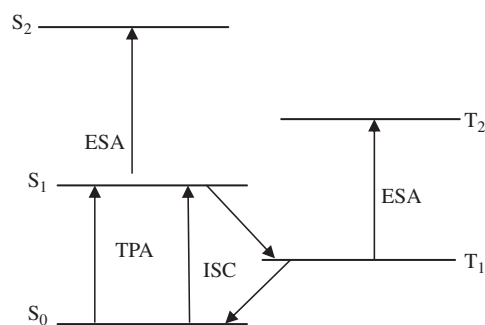


Fig. 4. Energy level diagram showing both two-photon absorption and excited state absorption (five level models).

state  $S_2$ , lower triplet state  $T_1$  and next higher triplet state  $T_2$  form the different levels. When two photons of the same or different energy are simultaneously absorbed from the ground state to a higher excited state ( $S_1 \leftarrow S_0$ ), it is denoted as two-photon absorption. When excited state absorption occurs, molecules are excited from an already excited state to a higher excited state ( $S_2 \leftarrow S_1$  or  $T_2 \leftarrow T_1$ ). The population of the excited state ( $S_1$  or  $T_1$ ) needs to be high so that the probability of photon absorption from that state is high. In nanosecond timescale, singlet transition does not deplete the population of  $S_1$  level appreciably, since atoms excited to  $S_2$  decay to  $S_1$  itself within in picoseconds. From  $S_1$ , electrons are transferred to  $T_1$  via intersystem crossing (ISC), from where transitions to  $T_2$  occur. If more absorption occurs from the excited state than from the ground state, it is usually called reverse saturable absorption. The triplet excited state absorption may result in RSA if the absorption cross section of triplet excited state is greater than that of singlet excited state. With excitation of laser pulses on the nanosecond scale, which is true in our case, triplet-triplet transitions are expected to make significant contribution to nonlinear absorption.

The model described in [17] was used to determine the magnitude of nonlinear absorption coefficient ( $\beta$ ) and the third order susceptibility  $\chi^{(3)}$  of the samples. The nonlinear absorption coefficient was determined using Eq. (1), since the laser beam has nearly a Gaussian transverse intensity distribution. The normalized transmittance for the open aperture Z-scan is given by [17]

$$T(z) = \ln[1 + q_0(z)]/q_0(z) \quad \text{for } |q_0(z)| < 1$$

$$q_0(z) = I_0 \beta_{\text{eff}} L_{\text{eff}} / (1 + z^2/z_0^2) \quad (1)$$

where  $I_0$  is the on-axis peak irradiance at the focus,  $L_{\text{eff}}$  is the effective thickness of the sample,  $\beta_{\text{eff}}$  is an effective value of the two-photon absorption coefficient and  $z_0$  is the Rayleigh length. When there is no linear absorption,  $L_{\text{eff}}=L$ , the thickness of the nonlinear medium.

In order to extract the information on nonlinear refraction, the sample is moved through the focal point and the nonlinear transmission was measured as a function of sample position with an aperture placed in front of the detector. In almost all materials, the nonlinear refraction (NLR) is accompanied by the nonlinear absorption (NLA). Thus, in the case of materials having negative refractive nonlinearity, the transmittance curve for the closed aperture Z-scan should have a smaller peak and a larger valley. To obtain a pure nonlinear refraction curve, we have used the division method described in [17]. The peak and valley configuration of the curve thus obtained by dividing closed aperture curve by open aperture curve clearly indicates that the material has a negative nonlinear refractive index. The response is electronic in origin and the thermal effect is not the dominant effect for the third order nonlinear response of the solution. The difference between the peak and valley ( $\Delta T_p - v$ ) in the pure nonlinear

refraction (NLR) curve is used to calculate the nonlinear refractive index ( $\gamma$ ) of the compounds using the relation

$$\gamma = \Delta\phi_0 \lambda / 2\pi L_{\text{eff}} I_0 \quad (\text{m}^2/\text{W}) \quad (2)$$

where  $\lambda$  is the wavelength of the laser light and  $\Delta\phi_0$  is the nonlinear phase shift given by the relation

$$|\Delta\phi_0| = \Delta T p - v / 0.406(1-S)^{0.25} \quad \text{for } |\Delta\phi_0| \leq \pi \quad (3)$$

where  $S$  (50%) is the aperture linear transmittance.

The real and imaginary parts of the third order nonlinear susceptibility can be calculated using the relations

$$\chi_R^{(3)} = 2n_0^2 \epsilon_0 c \gamma \quad (4)$$

$$\chi_I^{(3)} = n_0^2 \epsilon_0 c^2 \beta / \omega \quad (5)$$

where  $n_0$  is the linear refractive index,  $\epsilon_0$  is the permittivity of free space and  $c$  is the velocity of light in vacuum. The nonlinear refractive index  $n_2$  (in esu) can be obtained by the conversion formula

$$n_2 = (cn_0/40\pi)\gamma \quad (\text{esu}) \quad (6)$$

The second order hyperpolarizability  $\gamma_h$  of a molecule in an isotropic medium is related to the macroscopic third order susceptibility as follows [22]:

$$\gamma_h = \chi^{(3)} / N_c L^4 \quad (7)$$

where  $N_c$  is the density of molecules (in the unit of number of molecules per  $\text{cm}^3$ ) and  $L$  is the local field factor given by  $L = (n^2 + 2)/3$ ; here  $n$  is the linear refractive index of the medium.

The coupling factor  $\rho$  is the ratio of imaginary part to real part of third order nonlinear susceptibility i.e.

$$\rho = \text{Im} \chi^{(3)} / \text{Re} \chi^{(3)} \quad (8)$$

It is known that the nonlinear absorption coefficient  $\beta$  depends on the number of absorptive centers in a unit volume. Assuming this number is  $N_0$  in units of  $\text{cm}^{-3}$ , then for a solution system, we have [23,24]

$$\beta = \sigma_2 N_0 = \sigma_2 N_A d \times 10^{-3} \quad (9)$$

here  $N_0$  is the molecular density of the sample,  $\sigma_2$  is the molecular two photon absorption (TPA) coefficient of the same compound (in units of  $\text{cm}^4/\text{GW}$ ),  $d$  is the concentration of TPA compound in the solution (in units of mol/l) and  $N_A$  is the Avogadro number. For a known  $d$ , the value of  $\sigma_2$  can be easily calculated. Further, the molecular TPA cross section can also be expressed as

$$\sigma_2^1 = \sigma_2 h\nu \quad (10)$$

where  $\sigma_2^1$  is in units of  $\text{cm}^4 \text{ s}$  and  $h\nu$  is the energy (in Joules) of an incident photon.

The values of effective excited state absorption cross-section of the compounds are found from the relation  $\sigma_{\text{ex}} = q_0 F_0 L_{\text{eff}} / h\nu$  where  $F_0$  is the on-axis fluence at the focus, which is related to the incident energy as  $F_0 = E_{\text{total}} / \pi \omega_0^2$ . The ground state absorption was calculated using the relation  $\sigma_g = \alpha / N_A C$  where  $N_A$  is the Avogadro number and  $C$  the concentration in mol/L.

#### 4. Results and discussion

The third order nonlinear optical properties of the compound is studied by conducting the Z-scan experiment. The model described in [17] was used to determine the magnitude of nonlinear absorption coefficient ( $\beta$ ) and the third order susceptibility  $\chi^{(3)}$  of the samples.

The open aperture Z-scan traces of the compound obtained by performing the open aperture Z-scan experiment are given in Fig. 5. The open aperture curve of the compound demonstrates

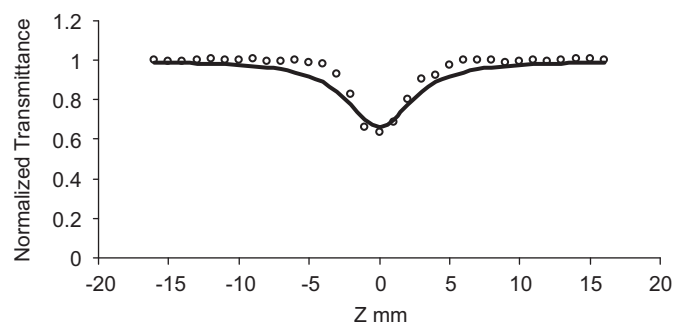


Fig. 5. Open aperture Z-scan curve.

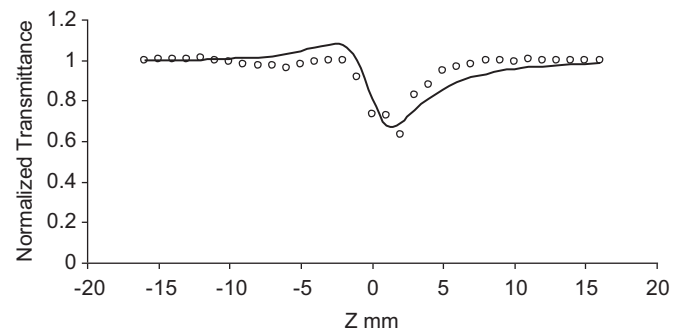


Fig. 6. Closed aperture Z-scan curve.

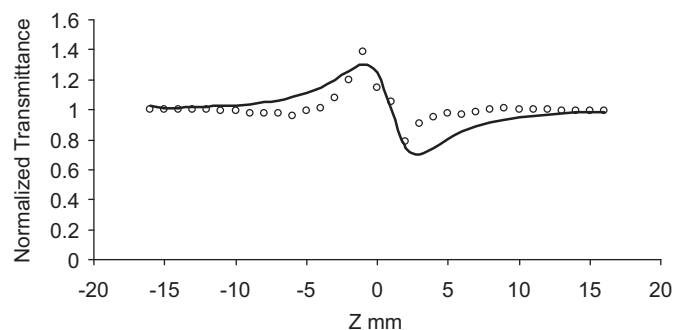


Fig. 7. Nonlinear refraction curve.

the occurrence of two photon absorption at 532 nm. The magnitude of nonlinear absorption coefficient  $\beta$  is calculated from the open aperture Z-scan traces.

Closed aperture Z-scan was performed to determine the sign and magnitude of nonlinear refraction. The peak-valley configuration of the curve (Fig. 6) clearly demonstrates that the index change is negative, exhibiting defocusing effect.

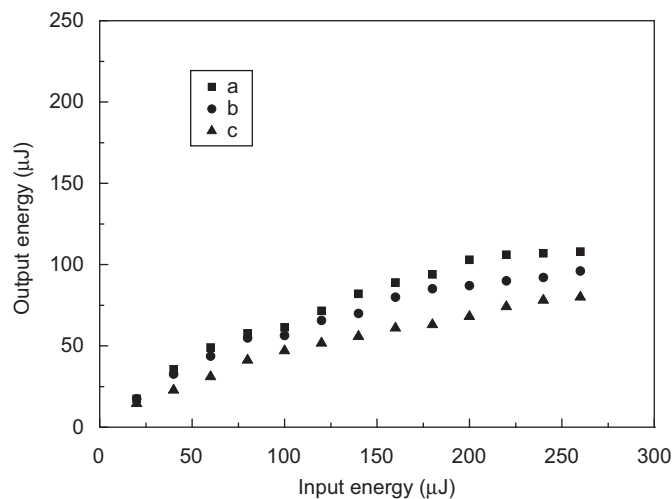
The open aperture and closed aperture Z-scan traces together yield the pure nonlinear refraction curve (Fig. 7), with peak-valley configuration showing negative nonlinear refractive index. The difference between the peak and valley in the pure nonlinear refraction curve is used to calculate the nonlinear refractive index of the compounds.

The experimentally determined values of nonlinear optical parameters of UP are given in Table 2. The value of coupling factor  $\rho$  indicates the electronic origin of nonlinearity. The  $\gamma_h$  values obtained in the present investigation are comparable with the values reported for 4-methoxy chalcone derivatives, reported by Ravindra et al. [25], with that of thiophene (hexamer) [26], with copolymers by John Kiran et al. [27] and with chalcone derivatives in polymer host, reported by Shettigar et al. [28]. These values are

**Table 2**

The experimental values of nonlinear optical parameters of UP.

Parameter	Experimental value	Parameter	Experimental value
$\beta$	2.146 cm/GW	$\gamma_{\text{h}}$	$0.69 \times 10^{-32}$ esu
$\text{Re } \chi^{(3)}$	$-1.347 \times 10^{-13}$ esu	$\sigma_{\text{g}}$	$0.435 \times 10^{-21}$ cm <sup>2</sup>
$\text{Im } \chi^{(3)}$	$0.377 \times 10^{-13}$ esu	$\sigma_{\text{ex}}$	$22.164 \times 10^{-19}$ cm <sup>2</sup>
$\rho$	0.28	$\sigma_2$	$0.356 \times 10^{-27}$ cm <sup>4</sup> /GW
$n_2$	$-1.258 \times 10^{-11}$ esu	$\sigma_1^2$	$1.34 \times 10^{-46}$ cm <sup>4</sup> s/photon

**Fig. 8.** Optical limiting of compound UP for different concentrations. (a)  $1 \times 10^{-2}$  mole/l, (b)  $2 \times 10^{-2}$  mole/l and (c)  $4 \times 10^{-2}$  mole/l.

found to be greater than that of thiophene (dimer, trimer, tetra and pentamers) [26].

The nonlinear absorption coefficient  $\beta$  is found to be 2.146 cm/GW, which is greater than the reported values of acet hydrazides [29]. From the nonlinear absorption coefficient  $\beta$ , the molecular TPA cross section  $\sigma_1^2$  has been found to be of the order of  $10^{-46}$  cm<sup>4</sup> s/photon, which is comparable with that for the studied hydrazones. It is found that the effective TPA cross-section of the compounds are of the order of  $10^{-46}$  cm<sup>4</sup> s/photon, which are comparable with that for bis-chalcone derivatives in polymer host, reported by Shettigar et al. [30].

The larger values of excited state cross section  $\sigma_{\text{ex}}$ , as compared to ground state absorption cross section  $\sigma_{\text{g}}$ , indicates that the major nonlinear process causing the limiting behavior is reverse saturable absorption [31–33]. The obtained values of excited state and ground state absorption cross sections of the compounds are less than the values obtained for organometallic phthalocyanine [34] and thiophene based conjugated polymer [35] and comparable with the values of benzohydrazone derivatives reported by Vijayakumar et al. [36]. Umadevi et al. [13] have reported that glycine picrate possess third order nonlinearity and has a positive nonlinear refractive index of  $4.6 \times 10^{-8}$  cm<sup>2</sup>/W for a laser wavelength of 532 nm.

The title compound shows good optical limiting at 532 nm (Fig. 8). The nonlinear absorption increases with the increase in concentration. For a concentration of  $1 \times 10^{-2}$  mole/l, the output energy increases linearly with the increase in input energy, till 200  $\mu\text{J}/\text{pulse}$ . With further increase in the input energy, the output energy gets stabilized to nearly a constant value of 108  $\mu\text{J}/\text{pulse}$ . It is seen that the power limiting threshold decreases with increasing concentration. In the case of higher concentration,  $2 \times 10^{-2}$  mole/l, the output energy is almost constant assuming

the value of 96  $\mu\text{J}/\text{pulse}$ . Further increasing the concentration to  $4 \times 10^{-2}$  mole/l, the output energy is almost clamped around 80  $\mu\text{J}/\text{pulse}$ .

The basic requirements for optical limiting application, positive nonlinear absorption is observed in the title compound. It is confirmed by the presence of optical limiting. A smaller linear absorption at 532 nm and the measured  $\sigma_{\text{ex}}$  values indicate that there is a contribution from excited absorption to the observed nonlinear absorption. In order to observe reverse saturable absorption, the excited state absorption cross section should be higher than that of the ground state absorption cross section and is consistent with the present result. Therefore, in this compound, the two photon assisted excited state absorption leading to reverse saturable absorption may be responsible for the optical limiting action. These results suggest that the compound UP may be used for the optical device applications such as optical limiters.

## 5. Conclusion

Urea and picric acid are associated through the charge transfer mechanism to form the title compound urea picrate (UP); a new class of organic NLO crystals. Urea functions as the  $\pi$  electron donor and picric acid as the acceptor species in the intermolecular charge transfer complex, UP. The open aperture curve of the compound demonstrates the occurrence of two photon absorption at 532 nm. The open aperture and closed aperture Z-scan traces together yield the pure nonlinear refraction curve, with peak–valley configuration showing negative nonlinear refractive index. The nonlinear refractive index  $n_2$ , nonlinear absorption coefficient  $\beta$ , magnitude of effective third order susceptibility  $\chi^{(3)}$ , the second order hyperpolarizability  $\gamma_{\text{h}}$  and the coupling factor  $\rho$  have been estimated. The experimentally determined values of  $\beta$ ,  $n_2$ ,  $\text{Re } \chi^{(3)}$  and  $\text{Im } \chi^{(3)}$ ,  $\gamma_{\text{h}}$  and  $\rho$  of the compound UP are 2.146 cm/GW,  $-1.258 \times 10^{-11}$  esu,  $-1.347 \times 10^{-13}$  esu,  $0.377 \times 10^{-13}$  esu,  $0.69 \times 10^{-32}$  esu and 0.28, respectively. The observed value of the coupling factor  $\rho$  for the molecules indicates the electronic origin of nonlinearity. The compound exhibits good optical limiting at 532 nm with the limiting threshold of 80  $\mu\text{J}/\text{pulse}$ . The third order studies reveal that in this compound, the two photon assisted excited state absorption leading to reverse saturable absorption may be responsible for the optical limiting action. These results suggest that the compound UP may be used for the optical device applications such as optical limiters.

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