

Third-order optical nonlinearities in methoxy-substituted 1,3 diphenyl propenones by Z-scan and Optical Limiting studies

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Employing the single beam Z-scan technique with nanosecond laser pulses at 532nm, the refractive and absorptive nonlinearities of methoxy-substituted (2E)-1-(3,4-dimethoxyphenyl)-3-phenylprop-2-en-1-one have been studied. The methoxy substitution makes 3,4-dimethoxy chalcone derivatives a donor-acceptor-donor (D-A-D) type intramolecular charge transfer molecule. The sign of the nonlinear index of refraction (n_2) is found to be negative and the magnitude n_2 is of the order of 10^{-11} esu. The variation of NLA coefficient (β_{eff}) with input intensity (I_0) is studied and the nonlinear absorption mechanism is found to be sequential two-photon absorption (TPA) leading to thermal effects in the solutions. The enhancement of nonlinearity due to the methoxy substitution is in accordance with the dipole-like formation in the said molecules. The compounds exhibit good optical limiting as well.

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1. Introduction

Conjugated organic nonlinear optical (NLO) materials are drawing steady attention due to their wide range of applications such as optical limiting, optical communication, optical switching, and optical information processing [1]. Organic materials exhibit a tremendous range of structural, conformational and orientational degrees of freedom with the aid of novel synthetic chemistry [2]. High values of the nonlinear refractive index n_2 are essential for electro-optical and all optical switching, whereas in optical limiters, it is usually the phenomenon of nonlinear absorption, for instance, two-photon absorption (2PA) and three-photon absorption (3PA), that is extremely important [3]. The enhancement of third-order nonlinearity of these conjugated organic compounds can be achieved by different methods and in this work we employ the method of synthesizing a donor-acceptor-donor (D-A-D) motif by substituting (2E)-1-(3,4-dimethoxyphenyl)-3-phenylprop-2-en-1-one with methoxy groups.

Our sample of study belongs to a class of organic compounds called chalcones. Chalcones are 1,3-Diphenylpropenone (benzylidenacetophenone) and its derivatives formed by substitution. They are low molecular weight charge transfer compounds (CT) that show large third-order nonlinear optical (NLO) properties [4-6]. The third-order nonlinear optical property of the chalcones named, p-methoxy dibenzylideneacetone and

methoxy-substituted 1-3-diaryl-propenones containing 4-methylthiophenyl moieties has been reported [5, 6]. A study on 4'-methoxy substituted chalcone was also reported with a maximum n_2 value of 2.44×10^{-11} esu [7]. However, so far no study has been carried out on the chalcone named, (2E)-1-(3,4-dimethoxyphenyl)-3-phenylprop-2-en-1-one with methoxy substitution at different positions of the phenyl ring. In this paper, we report on our effort to study the effects of methoxy substitution on (2E)-1-(3,4-dimethoxyphenyl)-3-phenylprop-2-en-1-one by using the strategy discussed in literature [8]. We observed the enhancement of nonlinearity in this chalcone upon the substitution of methoxy groups at different positions of phenyl ring of this molecule. The single beam Z-scan technique was used to study the nonlinear properties [9]. This method allows the simultaneous measurement of both nonlinear refraction and absorption. An attempt is made to understand the mechanism responsible for the observed nonlinear refractive index and nonlinear absorption coefficient. The good optical limiting behaviour caused by strong nonlinear absorption in these compounds is also demonstrated.

2. Experiment

The compounds were synthesized using a standard procedure reported in the literature [10]. The chemical structures of the synthesized compounds (2E)-1-(3,4-dimethoxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one

(DM2), (2*E*)-1,3-bis(3,4-dimethoxyphenyl)prop-2-en-1-one (DM3), (2*E*)-1-(3,4-dimethoxyphenyl)-3-(3,4,5-trimethoxyphenyl) prop-2-en-1-one (DM4) are shown in Fig.1(a), (b) and (c) respectively.

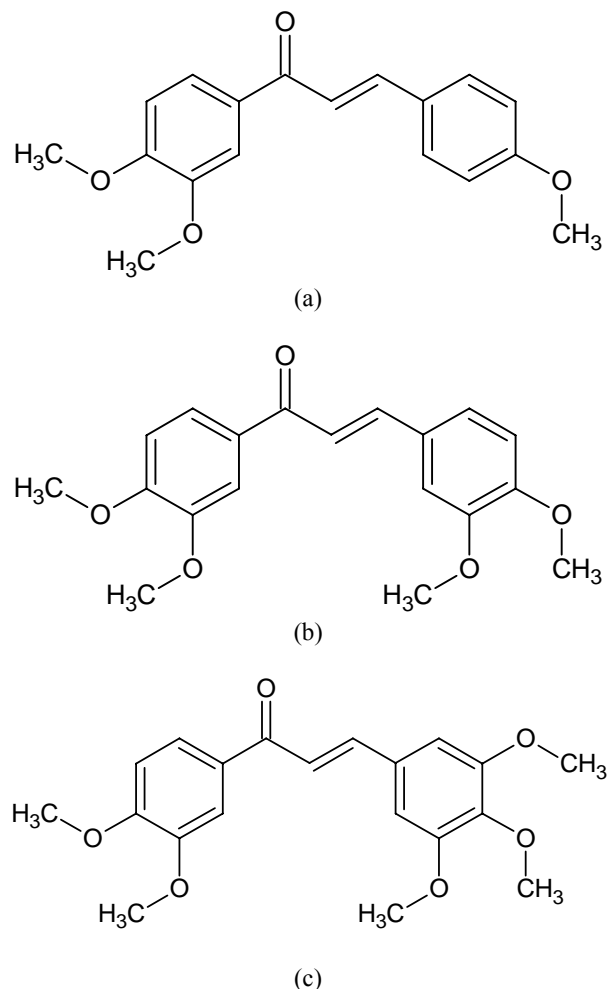


Fig. 1. Chemical structures of the samples (a) DM2, (b) DM3 and (c) DM4.

The linear absorption spectra of the samples in dimethyl formamide (DMF) solutions with a concentration of 3×10^{-5} M, are recorded at room temperature using a SHIMADZU UV-2450PC Series spectrophotometer, shown in Fig.2. They reveal that, at the wavelength of 532 nm, the samples are transparent and hence the measurement is purely non-resonant. Moreover, the linear absorption spectrum conveys that, at the wavelength of 266nm, there is linear absorption peak, indicating that it could cause the two photon absorption in these materials for a 532nm laser. The linear absorption coefficients obtained are listed in the Table.1.

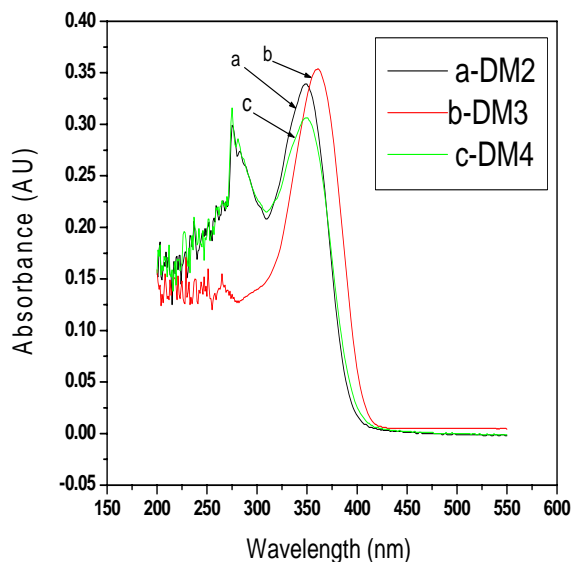


Fig. 2. Linear absorption spectra of samples DM2, DM3 and DM4 in dimethyl formamide with a concentration of 3×10^{-5} M.

The linear refractive indices of the samples dissolved in DMF were measured using an Abbe refractometer and the measured values are listed in Table.1. A Q-switched Nd:YAG (Quanta Ray) laser delivering pulses of width 7 ns at a repetition rate of 10 Hz was used as the light source. A lens of focal length 23 cm was used to focus the laser pulses into a 1 mm-quartz-cuvette containing sample in DMF solution with a concentration of 0.02M. The beam waist at the focus was $17.94 \mu\text{m}$ and the Rayleigh length (z_0) was estimated to be 1.90 mm. As the sample length was less than the diffraction length of the focused beam, the thin sample approximation was used to analyze the data. The sample was mounted on a computer-controlled translation stage that moved the sample along the z-axis with respect to the focus of the lens. The Z-scan was carried out at different pulse energies, including $50 \mu\text{J}$ which corresponds to a peak intensity of $1.33 \text{ GW}/\text{cm}^2$ and the closed aperture (CA) measurements were carried out with 50% linear aperture transmittance. The sample solution concentration used for the Z-scan study is 0.02mol/L. In order to avoid cumulative thermal effects, data were collected in single shot mode.

3. Results and discussion

3.1 Nonlinear absorption studies

Multiphoton absorption process takes place when by focusing an intense laser light, two or more photons are simultaneously absorbed by the material. So, in the case of absorptive nonlinearity, the light field induces an intensity-dependent absorption that can be expressed by [11],

$$\alpha = \alpha_0 + \alpha_2 I + \alpha_3 I^2 + \alpha_4 I^3 + \alpha_5 I^4 + \dots \quad (1)$$

where $\alpha_0, \alpha_2, \alpha_3, \alpha_4$ and α_5 are the linear, two, three, four and five-photon absorption coefficients, respectively. Assuming a spatial and temporal Gaussian profile for laser pulses and utilizing the open aperture Z-scan theory for multi-photon absorption (MPA) [12,13], we can have the general equation for the open aperture (OA) normalized energy transmittance given by,

$$T_{OA(nPA)} = \frac{1}{\left[1 + (n-1)\alpha_n L \left(I_0 / \left(1 + (z/z_0)^2 \right) \right)^{n-1} \right]^{1/n-1}} \quad (2)$$

where α_n is the effective MPA coefficient ($n = 2$ for 2PA, $n = 3$ for 3PA, and so on), I_0 is the input irradiance, 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 ($z = 0$), L is the sample length, and λ is the laser wavelength. For fitting the data with eq. (2), we consider L_{eff} & L'_{eff} as the effective path lengths in the case of 2PA and 3PA, respectively, and are defined by $L_{eff} = 1 - e^{-\alpha_0 L} / \alpha_0$ and $L'_{eff} = 1 - e^{-2\alpha_0 L} / 2\alpha_0$, where α_0 is the linear absorption coefficient. By fitting the open aperture Z-scan curves to eq. (2), we can obtain the nonlinear absorption coefficient α_n . Further, absorption is usually quantified by absorption cross-section σ , which has the unit of area. In the nonlinear absorption case, the n-photon absorption cross-section is given by [14]

$$\sigma_{nPA} = \frac{\alpha_n (h\nu)^{n-1}}{N_0} \quad (3)$$

where $h\nu$ is the photon energy, N_0 being the concentration of the absorbing species/cm³

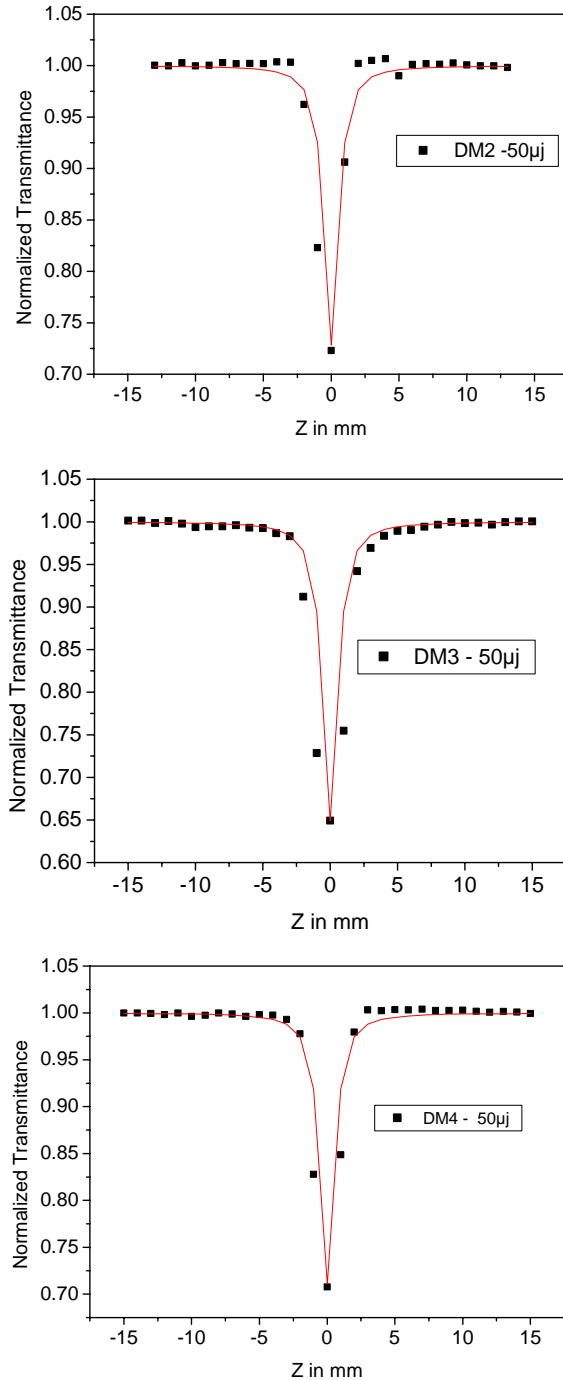


Fig. 3. Open aperture curves for DM2, DM3 and DM4. The solid lines are the theoretical fits of data to eq. (2) assuming 2PA.

Fig. 3 gives the open aperture (OA) data of the samples DM2, DM3 and DM4. The data points are indicated with circles while the theoretical fit assuming 2PA is represented by the solid lines in the graph. From the fitting curves, it is very clear that the OA data is fitting well with the 2PA process and hence this result can be accounted for the 2PA [12, 15 and 16].

The study of NLA coefficient (β_{eff}) with input intensity (I_0) would help us understand the NLA mechanisms in these molecules. If the mechanism is a simple two-photon absorption, β_{eff} should be a constant that is independent of the on axis intensity I_0 . If it is a direct three-photon absorption process, β_{eff} should be a linearly increasing function of I_0 and the intercepts on the vertical axis should be zero. When the mechanism is due to the excited state RSA, β_{eff} should also be a linearly increasing function of I_0 but the intercepts on the vertical axis should be nonzero [17]. On the other hand, if β_{eff} decreases with the increase of I_0 , the NLA mechanism for several organic materials in different time scales are attributed to different processes, such as sequential TPA, saturation of instantaneous two-photon absorption, fifth-order effects, nonlinear scattering, a strong ESA induced by weak TPA, thermal blooming, and triplet-triplet annihilation [7, 18-21].

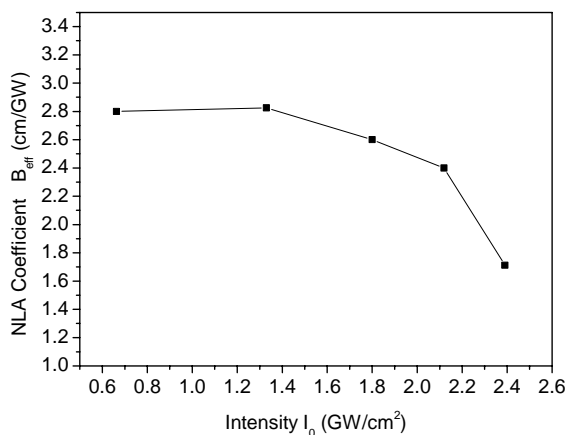


Fig. 4. Variation of nonlinear absorption coefficient β_{eff} with intensity I_0 of the input laser pulse in DM2.

The excited state absorption cross-section, σ_{ex} and the ground state absorption cross-section, σ_g , for all the three compounds were determined by the procedure described in literature [22]. The σ_{ex} value of all the three

compounds were found to be in the order of 10^{-18} cm^2 , ie, $0.67 \times 10^{-18} \text{ cm}^2$, $1.08 \times 10^{-18} \text{ cm}^2$ and $0.73 \times 10^{-18} \text{ cm}^2$ for DM2, DM3 and DM4 respectively. The ground state absorption cross-section, σ_g , for all the three samples were found to be in the order of 10^{-22} cm^2 , ie, $1.66 \times 10^{-22} \text{ cm}^2$. So it is very clear that the value of σ_{ex} is larger than the value of σ_g , ie ($\sigma_{ex} > \sigma_g$), which is the condition for observing reverse saturation of absorption (RSA).

The Fig. 4 shows a decrease of β_{eff} with increase of I_0 in DM2 sample. The DM3 and DM4 samples also exhibited the same variation. The fall-off of β_{eff} with increase of I_0 can be observed for the instantaneous saturation of absorption (SA) if $\sigma_{ex} < \sigma_g$. But here in our samples, the $\sigma_{ex} > \sigma_g$, hence we can rule out the possibility of saturation of instantaneous two-photon absorption. In a recently reported work by Anthony John Kiran et al [22], the fall-off of β_{eff} with intensity I_0 was attributed to be sequential TPA leading to thermal effects in solutions. Here in our samples also, the condition for sequential TPA to occur, ie, $\sigma_{ex} < \sigma_g$ is satisfied. In the Z-scan experiment with nano second pulses, the thermal lens which can grow up during the pulse time and the multiphoton absorption can contribute to the thermal effects. Hence we remark that femto-second time-resolved thermal lens experiments would give valuable informations for the complete understanding of the nonlinear properties of these molecules.

3.2 Nonlinear refraction studies

The single beam closed aperture Z-scan technique is used for measuring nonlinear refraction effect. The CA data is sensitive to both the nonlinear refraction and absorption, while the open aperture data is sensitive only to the latter. The method of division of the CA data by the OA data has been employed to extract the pure nonlinear refraction curve [23]. The nonlinear transmittance in the case of pure nonlinear refraction is given by

$$T = 1 + \frac{4\Delta\phi_0 x}{(x^2 + 1)(x^2 + 9)}, \quad (4)$$

where, $\Delta\phi_0$ is the on-axis nonlinear phase shift and $x = z/z_0$. Then one can easily obtain the index of nonlinear refraction n_2 through the relation $\Delta\phi_0 = kn_2 I_0 L_{eff}$, where $k = 2\pi/\lambda$ is the wave vector.

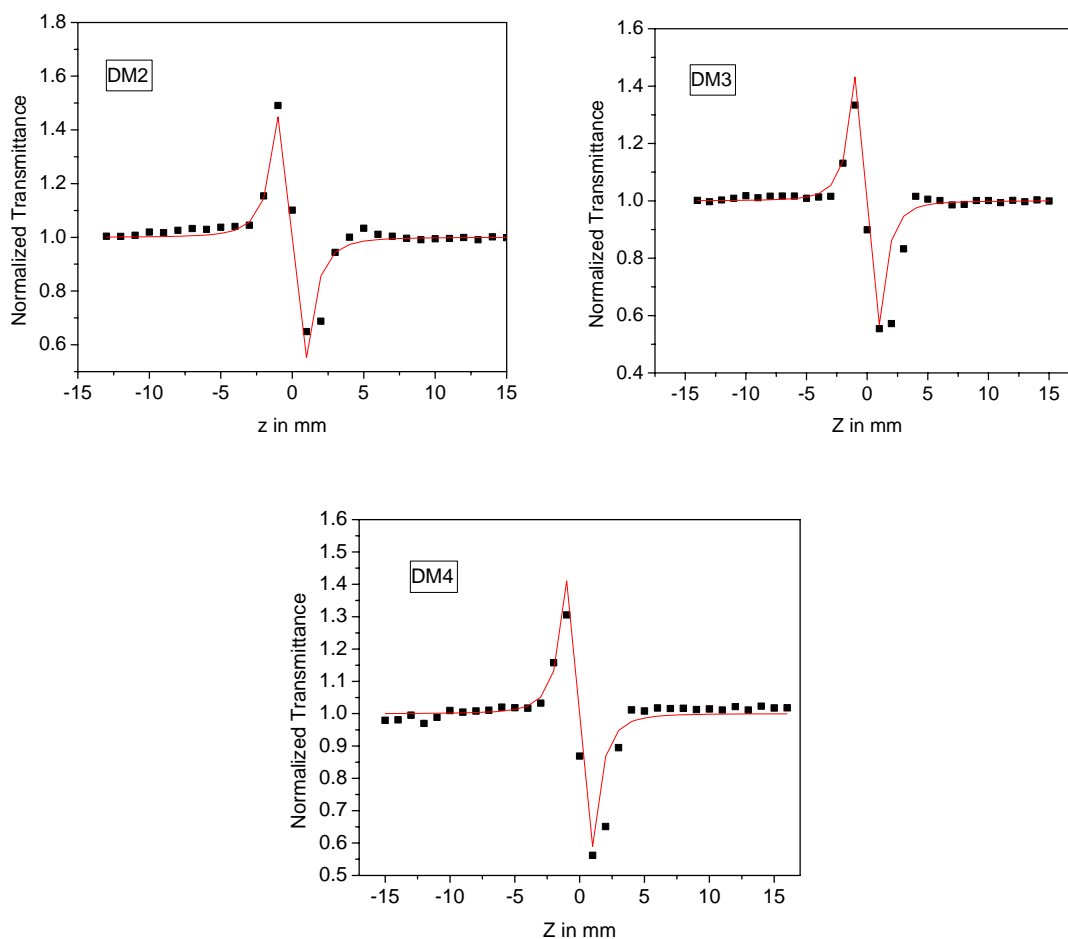


Fig. 5. The pure nonlinear refraction curve obtained through dividing the CA data by the OA data. The dotted points are the experimental data points and solid lines are the theoretical fits for DM2, DM3 and DM4

The experimental data obtained for pure refractive nonlinearity for all the samples at pulse energy of $50 \mu\text{J}$ is depicted in Fig.4. The peak-to-valley configuration of the pure refractive Z-scan curves for all the three samples reveal a self-defocusing effect, and sign of the refractive index is negative. Theoretically the on-axis Z-scan transmittance for a cubic nonlinearity and a small phase change, the peak-valley separation is determined to be $\Delta Z_{p-v} = 1.7z_0$ [23]. The measured peak-valley separation for our samples are also found to be $1.7z_0$ and it confirms that the origin of nonlinearity in our samples at nanosecond domain is purely third order.

In addition to the all measurements, to determine the contribution of the solvent to n_2 , we carried out Z-scan experiment on the pure DMF, and found that neither nonlinear refraction nor nonlinear absorption was observed at the input energy used. Hence, the contribution from the solvent to the nonlinearity of the samples is not coming in

to the picture. The nonlinear optical parameters estimated in this study are listed in Table 1.

The observed nonlinearity in samples was in the order of $DM3 > DM4 > DM2$. Here, in the case of, the value of DM3, n_2 obtained is higher compared to DM2 and DM4 samples and this can be attributed to the symmetric structure of the molecule, which brings the charge transfer and the dipole effect in the sample to the maximum. The symmetric structure of DM3 is produced by equally distributed dimethoxy groups at both ends of the 1,3-diphenyl propenone molecule and hence the charge density at the both ends will be the same and the strong electron acceptor group, carbonyl at the center provides a dipole like effect in the molecule. In the case of DM4, the dipole effect is reduced due to the excess methoxy group at one end of the molecule and in DM2, there is only one methoxy group at one end of the molecule which makes the charge density and the dipole effect in the sample relatively less, correspondingly the nonlinearity as well.

Table.1. Experimentally determined values of Linear and nonlinear optical parameters

n_0 (cm^{-1})	α_0 ($10^{-11} esu$)	n_2 (cm/GW)	β_{eff} ($10^{-13} esu$)	$Re \chi^{(3)}$ ($10^{-13} esu$)	$Im \chi^{(3)}$ ($10^{-13} esu$)	$\chi^{(3)}$	
DM2	1.4145	0.002	7.16	4.1	7.65	0.62	7.67
DM3	1.4182	0.003	7.42	2.82	7.88	0.43	7.89
DM4	1.4145	0.025	6.80	3.07	7.23	0.46	7.24

3.3 Optical limiting studies

Materials with strong nonlinear effect, the absorption of light increases with intensity such that beyond a certain input intensity the output intensity approaches a constant value. Such materials can be used to limit the amount of optical power entering in a system and find applications in protecting delicate sensors, protective goggles etc. Here we carried out the optical limiting experiment in all the three samples with 7n laser pulses at 532nm and the output and input pulse energies are measured using pyroelectric detectors.

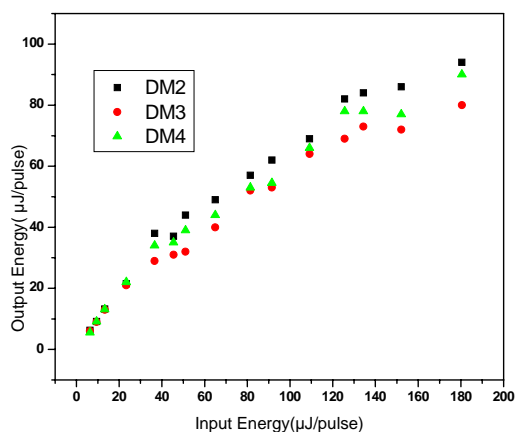


Fig. 6. Optical limiting in DM2, DM3 and DM4

The optical limiting behaviour of all the three compounds is shown in figure 5. For incident energies less than 40 μJ /pulse the output linearly increasing with the input. But the optical limiting of the pulses was observed for energies more than 40 μJ /pulse. The compound DM3 exhibited better optical limiting compared to the compounds DM4 and DM2. The optical limiting behaviour was found to be in the order of compounds $DM3 > DM2 > DM4$. The optical limiting was found to vary according to the methoxy substitution in the 1,3-diphenyl propenone molecule. The major factor responsible for good optical limiting is the 2PA at this nanosecond excitation regime [15].

4. Conclusions

We have measured the nonlinear refraction index (n_2), the nonlinear absorption coefficient (β_{eff}) for methoxy substituted (2E)-1-(3,4-dimethoxyphenyl)-3-phenylprop-2-en-1-one using the Z-scan technique at 532nm. The Z-scan measurement indicated that the samples exhibit large nonlinear optical properties and the measured n_2 values for DM2, DM3 and DM4, were found to be 7.42×10^{-11} esu, 7.16×10^{-11} esu, and 6.80×10^{-11} esu, respectively. All the three samples exhibit 2PA and the measured values of 2PA cross sections are quite promising for possible application in nonlinear optical devices. All the three compounds exhibit good optical limiting property at 532nm. The compound DM3 showed the best optical limiting behavior compared to the compounds DM2 and DM4. These compounds could be used for optical limiting applications.

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