Characterization of the optical non-linear response of the *(E)*-4-(4-dimetylaminophenyl) but-3-en-2-one and *(E)*-4-(4-nitrophenyl) but-3-en-2-one by Z-Scan

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Abstract. We presents the study carried out by the technique Z-Scan, to analyse the nonlinear optical properties of (E)-4-(4-dimetylaminophenyl) but-3-en-2-one and (E)-4-(4-nitrophenyl) but-3-en-2-one, diluted in Ethyl Acetate with concentration levels of [0.02M, 0.08M, 0.23M] and [0.0047M, 0.013M, 0.041M] respectively. The measurements were performed using a Nd:YAG laser emitting at 532nm, for samples with L_{eff} =1mm thickness, and a automated scanning of 10cm symmetric to the lens focus, the iris diameter was 1mm, the samples were also characterized by an UV-Vis Spectroscopy. We calculated the nonlinear refractive index ($\eta 2$), the nonlinear absorption coefficient (β) and the the third-order nonlinear optical susceptibility ($\chi 3$) of the two researched compounds. The results show a combination of thermal response and nonlinear self-defocusing and self-focusing, which make their application interesting as new optoelectronic materials.

1. Introduction

The aromatic ketones α,β-unsaturated are known because they have in their structure a benzene ring, separated by three carbon atoms, two are connected by a double bond and the third is part of a carbonyl group. The presence of the carbonyl group and the olefin unit together confer the butenone high reactivity, placing them as an interesting class of molecules to study both in projects in basic science, applications in areas such as medicine [1-3,] agriculture and industry. Likewise, some small aromatic ketones have been used in the development of frequency amplification devices due to its SHG high activity (Second Harmonic Generation) [4].

The Z-Scan technique [5-6] is used to monitor the transmittance of the sample according to its Z position, in relationship with the position of the focal plane of the main lens [7-8]. The scan range depends on the parameters of the beam and the thickness of the sample. A critical parameter is the length of the diffraction of the focused beam, which is defined as $\pi\omega 02/\lambda$ for a Gaussian beam where the waist of the beam $\omega 0$ is the waist of the beam in the focal plane (1/e2). The nonlinear optical effects arise due to the nonlinear properties of the sample such as changes in the index of refraction and the absorption coefficient that takes place during the strong light intensity.

2. Experimental

Molecules are synthesized by Claisen-Schmidt [9-10] condensation procedure. We added acetone in excess (2 mL), benzaldehyde (1mmol), and the reaction is carried at 0°C temperature, then added drop-by-drop sodium hydroxide 10% p/v (5mL) and ethanol (3mL). After 12 hours of agitation a precipitate was obtained, filtered with cold ethanol and water. The butenone crystal obtained was

recrystallized with ethanol at 50°C temperature. The molecular structure of (E)-4-(4-dimetilaminofenil) but-3-en-2-ona and (E)-4-(4-nitrophenyl) but-3-en-2-ona is shown in Figure 1.

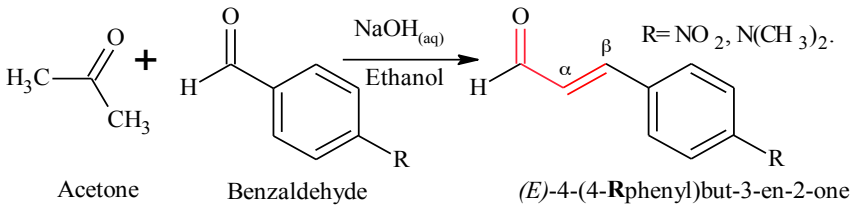

Figure 1. Molecular structure of *(E)*-4-(4-dimetylaminophenyl) but-3-en-2-one and *(E)*-4-(4-nitrophenyl) but-3-en-2-one.

The UV-Vis spectres of the sample were taken in the wavelength range of 200-400nm using an UV-vis EVOLUTION 220 Thermo Scientific spectrophotometer, in Figure 2 high absorbance between 250nm to 425nm is observed for both compounds. In the region of 500nm to 700nm absorbance is practically zero, making possible to use a 532nm laser for the study, this wavelength with high transmittance which allows ensures observe nonlinear effects. From the crystals obtained during the process, compound dilutions were prepared at 10mg/L, taking 1mL aliquots en quartz cells.

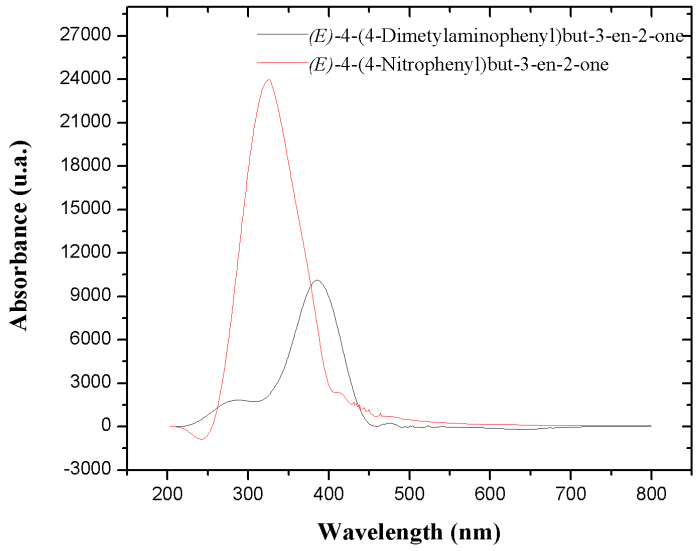

Figure 2. Absorption curves in the UV-Vis of *(E)*-4-(4-dimetylaminophenyl) but-3-en-2-one and *(E)*-4-(4-nitrophenyl) but-3-en-2-one diluted in ethanol at 10mg/L.

Z-Scan measurements were performed using a Nd:YAG laser doubled in frequency emitting at 532 nm, focused by a 10cm focal length lens and with a waist radius of 27 microns; the cell used to contain diluted samples is 1mm thick. The beam transmission obtained in closed and open cell geometry, was determined with a detector (see Figure 3). The Z-Scan curves of the butenones are shown in Figures 4 and 5.

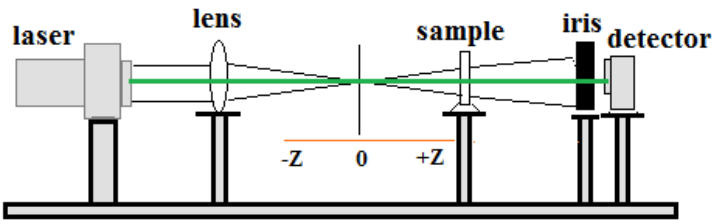

Figura 3. Z-Scan experimental setup.

3. Results and experimental analysis

As seen in the UV-Vis spectrum, the absorption generated by the HOMO-LUMO transition of unsaturated α,β system established for (E)-4-(4-dimetylaminophenyl)but-3-en-2-one and for (E)-4-(4-Nitrophenyl)but-3-en-2-one to contain this system in its structure, exhibit a maximum of absorption of visible light around 375nm and 323nm, respectively. This band of absorption is characteristic of the aromatic ketone, showing that a molecular fragment attracts electrons and other gives electrons (push-pull system) generating a process of electronic intramolecular transfer.

The substitution on the functional group $N(CH_3)_2$ with NO_2 alters conjugation of π system , therefore affects the absorption maximum observed that moves to a shorter wavelength. The spectrum shown in Figure 2 clearly exhibits this behaviour characteristic of the (E)-4-(4-phenyl)but-3-en-2-ones with a yellow coloration due to this displacement bathochromic derived from the change of an electron donor group instead of electron attractors, to realize studies for Z-Scan is recommended to utilize a wavelength of 532nm due to transmittance is high. The compounds demonstrate fluorescence, a phenomenon that is being studied, because of that they can be good candidates to photonic materials.

The Figures 4 and 5 show smooth curves of the experiment result of Z-scan in closed configuration. These materials have a self-defocusing thermal response that can be identified because the curve starts with a peak followed by a valley. The variation in the behaviour of the curves is due to the effect of substituent groups; in the case of the amino group, the nitrogen atom has a free electron pair, conferring an effect delocalized electron donor by interaction with the π system of the aromatic ring. In the case of nitro groups, there is an additional electron density, by the presence of double bonds in the nitrogen, this cause different behaviour and widening nonlinear absorption curve. The Figure 4 presents curves for Z-Scan (E)-4-(4-dimetylaminophenyl)but-3-en-2-one, at a concentration of 0.02M nonlinear effect begins to appear at Z=38.99mm, at a concentration of 0.08 M nonlinear effect appears at Z=21.39mm and at a concentration of 0.23M the effect appears at Z=4.89mm. In Figure 5 the Z-Scan by transmission in closed configuration is observed for (E)-4-(4-nitrophenyl)but-3-en-2-one at a concentration of 0.0047M nonlinear effect occurs in Z=32.43mm, at a concentration of 0.013 M nonlinear effect appears at Z=27.00mm and at a concentration of 0.041M the effect appears at Z=17.17mm. As the concentration increases, $\mathbf{\Delta Z_{p\text{-}v}}$ increases and a broadening in the peak-valley distance, lowest concentration is best because self- defocusing thermal effect is better.

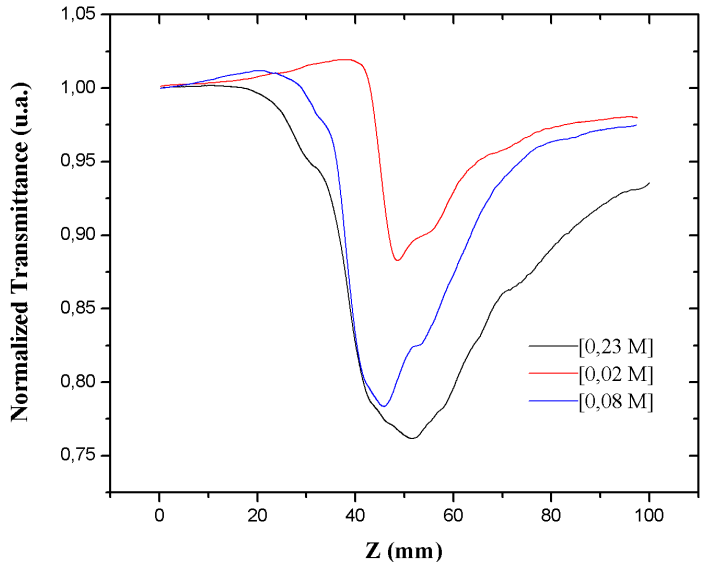

Figure 4. Z-Scan by transmission in closed configuration for (E)-4-(4-dimethylaminophenyl) but-3-en-2-one, Analysing the behaviour at different concentrations, with laser power of 195Mw in ethyl acetate.

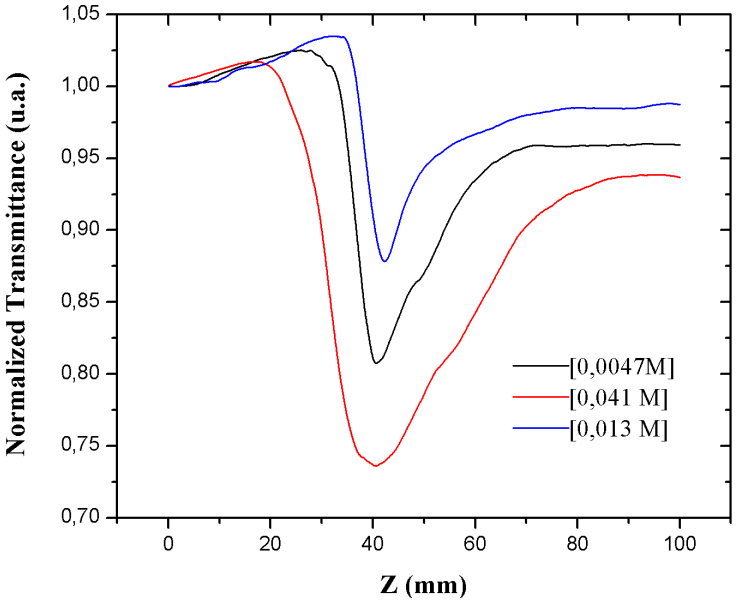

Figure 5. Z-Scan by transmission in closed configuration for (E)-4-(4-nitrophenyl)but-3-en-2-one, Analysing the behaviour at different concentrations with laser power of 195mW in ethyl acetate.

The theory developed by Sheik-Bahae[11] shows that $|\Delta\Phi o| \propto \Delta Tpv$ analogously $|\Delta\Phi o| \propto \eta 2$, Where $\Delta\Phi o$ is the maximum nonlinear phase change induced, it is related to the nonlinear refractive index $\eta 2$, as follows:

$$\Delta T_{pv}=0.406(1-S)^{0.25}k\ \eta_2 I L_{eff} \quad (1)$$

If clear η_2 de (1),

$$\eta_2=\Delta T_{pv}/(0.406(1-S)^{0.25}kIL_{eff}) \quad (2)$$

By replacing **k** (number of green laser wave) and **I** (Beam intensity green laser in focus) for $P/\pi\omega_0^2$ an equation that depends on the power and wavelength of laser is obtained.

$$\eta_2=\Delta T_{pv}\omega_0^2\lambda/[1.624(1-S)^{0.25}PL_{eff}] \quad (3)$$

If used the definition of Rayleigh parameter, we obtained.

$$\eta_2=\Delta T_{pv}\Delta Z_{pv}\lambda^2/[2.7608\pi(1-S)^{0.25}PL_{eff}] \quad (4)$$

If S<<1, (4) takes the following form:

$$\eta_2=\Delta T_{pv}\Delta Z_{pv}\lambda^2/[2.7608\pi PL_{eff}] \quad (5)$$

Equation (5) is used to obtain the value of nonlinear refractive index η_2. $L_{eff} \approx L=0.1$cm for transparent samples.

The Table 1 contains the values of the nonlinear refractive index calculated according to the concentration of samples, a fixed laser power excitation was set at 195mW, an increase is observed at higher concentrations. Figure 6 It is shown as (E)-4-(4-dimetylaminophenyl) but-3-en-2-one y (E)-4-(4-nitrophenyl)but-3-en-2-one values of η_2 in function of concentration have a linear behaviour to the concentrations tested.

Table 1. Values of refractive index nonlinear obtained from transmittance curve in closed configuration for (E)-4-(4-dimetylaminophenyl) but-3-en-2-one y (E)-4-(4-nitrophenyl) but-3-en-2-one; **P**=0.195 W, L_{eff}=0.1cm.

Molecule	*(E)*-4-(4-dimetylaminophenyl) but-3-en-2-one			(E)-4-(4-nitrophenyl) but-3-en-2-one		
concentration	0.02M	0.08M	0.23M	0.0047M	0.013M	0.041M
ΔT_{p-v}	0.0381	0.2288	0.2186	0.155	0.2171	0.2816
ΔZ_{p-v}(cm)	0.0933	0.2431	0.3625	0.0980	0.1367	0.2328
η_2 (cm^2/W)	$5.948x10^{-11}$	$3.424x10^{-10}$	$1.3261x10^{-9}$	$2.55x10^{-10}$	$4.690x10^{-10}$	$1.0970x10^{-9}$

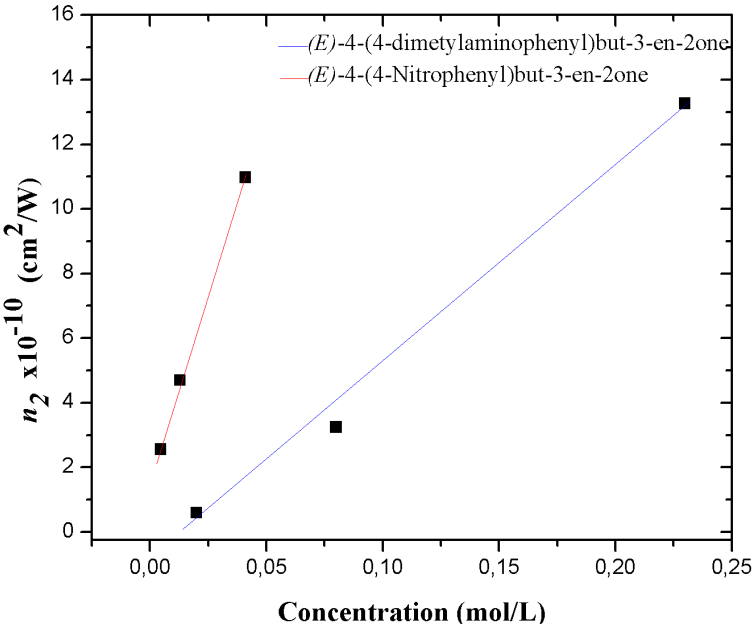

Figure 6. Variation nonlinear refractive index depending on the concentration.

To obtain the nonlinear absorption coefficient β, open cell geometry was used and data of the normalized transmittance for each sample were used as well, from [11] is known that small losses for nonlinear third-order has $\Delta\alpha L=\beta I L_{eff}<1$.

Where L_{eff} =1mm is the sample thickness, $\mathbf{I_0}$=8519W/cm^2 is the intensity of the laser beam, in Figure 7 shows β Vs Concentration obtained by Z-Scan in open configuration for the studied samples, data can be calculated from.

$$\beta=2(2\Delta T_{vp})^{1/2}/I_0L_{eff} \quad (6)$$

Where ΔT_{vp} is the value of the valley-peak difference in the Z-Scan curve open cell geometry.

To analyse the effect that causes the laser power to influence the sample (E)-4-(4-dimethylaminophenyl)but-3-en-2-one [0.02M], transmittance measurements were performed at different laser powers in the open configuration, in Figure 8, variations were observed for the non-linear effect as the laser power increases to less than 45mW, the nonlinear effect begins to be notice; but for the power between 90-200 range mW increases the effect and it is noted that near the 190mW curves suffer a widening, indicating a local thermal effect, heating product produced by the laser at the point where focuses on the sample begins to be significant. This effect is observed at the beginning and at the end in the Z-Scan curve.

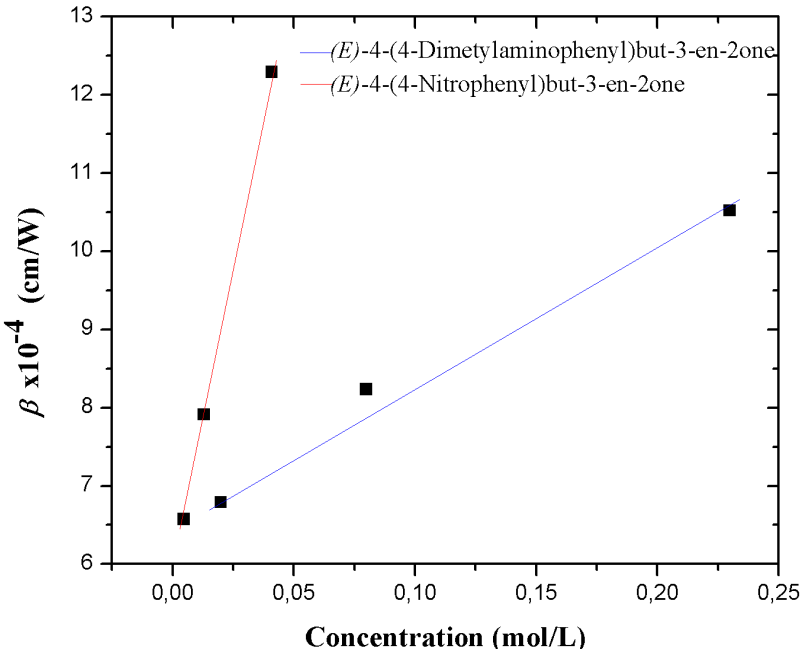

Figure 7. Variation of nonlinear coefficient absorption for samples with different concentrations according to Table 2.

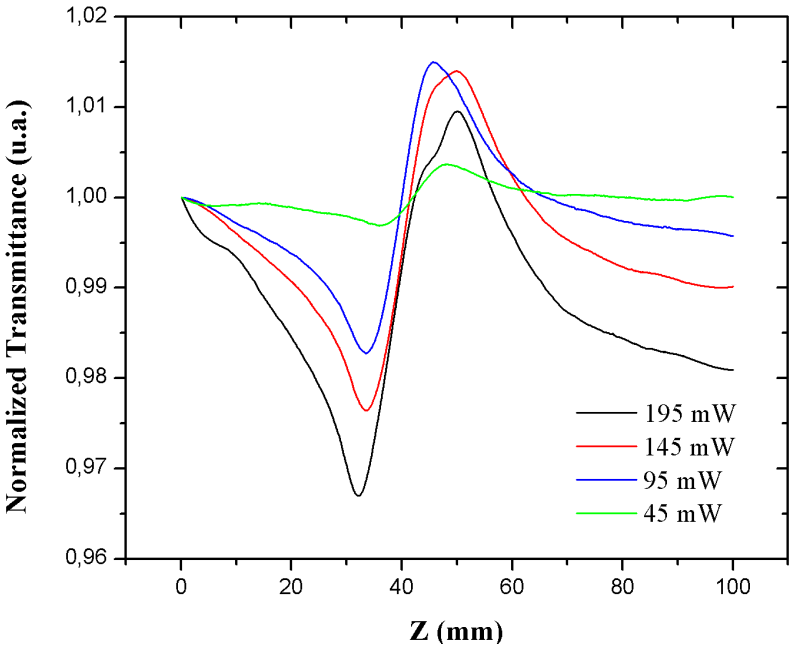

Figure 8. Normalized transmittance curve in open configuration of (E)-4-(4-dimethylaminophenyl)but-3-en-2-one [0.02 M] in ethyl acetate, for each samples a scan of 100 mm was performed at symmetrical lens focus with L_{eff}=1mm.

Determining the refractive index of the samples η_0 became necessary in the parameter to determining third order nonlinear optical susceptibility Re $\chi 3$, which it was obtained by applying Snell's law. The obtained values of nonlinear refractive index and absorption coefficient (E)-4-(4-dimetylaminophenyl) but-3-en-2-one and (E)-4-(4-nitrophenyl)but-3-en-2-one are used to determine the actual value of the nonlinear optical susceptibility of the third order according to the following relationship: [12]

$$\mathrm{Re}\chi 3\ (\mathrm{esu}) = (10^{-4}\xi_0 c^2\ \eta_0^2/\pi)\ \eta_2 \qquad (7)$$

Where ξ_0 is the vacuum electric permittivity (8.8542×10^{-16} C/Nm^2) and **c** (3×10^{10}cm/s) is the speed of light.

The results obtained are summarized in Table 2 that shows molecule (E)-4-(4-dimetylaminophenyl)but-3-en-2-one, $\chi 3$ presents values in a range 1.6633×10^{-13} to 3.8511×10^{-13} esu at the concentrations studied, demonstrating an upward linear behaviour, likewise occurs (E)-4-(4-nitrophenyl)but-3-en-2-one with values in a range χ 3 $7.1311x10^{-13}$ to $3.1857x10^{-13}$ esu.

Table 2. Values of nonlinear absorption coefficient and nonlinear optical susceptibility of the third order obtained for (E)-4-(4-dimetylaminophenyl)but-3-en-2-one and (E)-4-(4-nitrophenyl)but-3-en-2-one; $\mathbf{I_0}$=8519W/cm^2.

Molecule	(E)-4-(4-dimetylaminophenyl) but-3-en-2-one			(E)-4-(4-nitrophenyl) but-3-en-2-one		
Concentration	0.02M	0.08M	0.23M	0.0047M	0.013M	0.041M
ΔT_{p-v}(cm)	0.0418	0.0761	0.1004	0.0392	0.1391	0.151
β (cm/W)	$6.788x10^{-4}$	$8.233x10^{-4}$	$1.0520x10^{-3}$	$6.5726x10^{-4}$	$7.912x10^{-4}$	$1.2901x10^{-3}$
η_0 (u.a)	1.05	1.06	1.07	1.05	1.06	1.07
Re χ3(esu)	$1.6633x10^{-13}$	$9.7587x10^{-13}$	$38.511x10^{-13}$	$7.1311x10^{-13}$	$13.367x10^{-13}$	$31.857x10^{-13}$

4. Conclusion

Measurements made with the technique Z-Scan on (E)-4-(4-dimetylaminophenyl)but-3-en-2-one and (E)-4-(4-nitrophenyl)but-3-en-2-one, using a Nd:YAG laser showed high transmittance at 532 nm, they allowed us to obtain experimental values reported for the first time η_0, η_2, β y Reχ3, The nonlinear refractive index and nonlinear absorption coefficient are linear function of concentration, it shows that they are affected by the ligand group bonded to the molecular structure. The presence of the nitro group in (E)-4-(4-nitrophenyl)but-3-en-2-one shows better linearity than in (E)-4-(4-dimetylaminophenyl)but-3-en-2-one as shown in Figures 6 and 7, for this result the effect of the laser power is highlighted on the samples, when concentration increases there are more particles resulting stirred thermally enhanced nonlinear effect. The values obtained for Reχ3 in the order of 10^{-13} show that the effect of the interaction of light with molecules samples studied and it make it interesting for application as new optoelectronic materials. Varying the nonlinear refractive index is directly proportional to the third order electric susceptibility and the applied field strength.

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