Nonlinear refractive index of gold nanoparticles dispersed in vegetable biodiesel

Genaro López Gamboa, José Luis Jiménez-Pérez, Zormy Nacary Correa-Pacheco

***Abstract*— Colloids of vegetable biodiesel with gold nanoparticles were prepared. Gold nanoparticles were prepared by microemulsion method. The non-linear refractive index of vegetable biodiesel in presence of gold nanoparticles with different concentration (1/5, 3/5, 5/5, 7/5, 8/5 and 10/5 mg/mL) using the Z-scan technique was measured. The size of the nanoparticles was found to be about 9 nm as analyzed using transmission electron microscopy (TEM). The results show that, this colloidal system presents a thermal non-linear refractive index n_2, in the order magnitude of 2.4, 6.11, 6.2, 5.6, 2.8, 2.3 × 10^{-8} cm^2/W with a negative sign for each concentration, respectively. The non-lineal refractive index was obtained by using Z-scan experimental setup using a CW diode laser (λ= 532 nm), with 14 Hz of modulation frequency as source of excitation. Therefore self-defocusing phenomena is taking placed for the colloids. Non-linear refractive index of Z-scan was obtained by fitting the theoretical expression to the experimental data.**

***Index Terms*— Colloidal, Non-linear refractive index, Nanoparticles, Z-scan, biodiesel**

I. INTRODUCTION

Biodiesel, a biofuel comprised in general of long-chain fatty acid methyl esters (FAMEs) derived from vegetable oils or animal fats, is an alternative to fossil fuels and it can also be used as a fuel additive. The advantages of biodiesel fuels over diesels fuel are well known: less smoke and particulates production, higher cetane number, domestic origin, lower carbon monoxide and hydrocarbon emissions. They also are biodegradable and non-toxic, and provide engine lubricity to low sulfur diesel [1]. The scarcity of traditional fossil fuels, growing emissions of combustion-generated pollutants and their increasing costs (including extraction costs) have made biofuels more attractive. Biodiesel fuels are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines [2]. Biodiesel can offer benefits including reduction of greenhouse gas emissions, regional development, energy security, energy independence and social structure [3].

The Z-scan technique has been widely used in several applications such as the measurement of non-linear properties of semiconductors and crystals, organic molecules or carbon basis molecules, nanoparticles and liquid crystals with non-linearity [3]-[6]. Z-scan provides the advantage of indicate the sign and type of non-linearity (refractive or absorptive). The aim of this work is the synthesis of Au nanoparticles and the study of the non-linear optical properties of these nanoparticles with biodiesel under power continuous wave diode laser irradiation. Non-linear refractive index, n_2 was measured by Z-scan method. The Z-scan technique has been extensively used to measure nonlinear optical of material because of its simplicity and high accuracy [7], [8]. The obtained nanoparticles were also characterized by means photoacoustic spectroscopy (PAS), and transmission electron microscopy (TEM).

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II. MATERIALS AND METHOD

Au nanoparticles were prepared by the reduction of Gold (III) chloride trihydrate using hydrazine as a reducing agent in a microemulsion (reverse micelle) system containing isooctane, deionized water, dioctylsulfosuccinate sodium salt as surfactant and dodecanethiol as co-surfactant. Next, the Au nanoparticles were mixed into biodiesel, purchased from Biofuels of Mexico (biodiesel C4), to obtain six sample materials with different concentrations of Au nanoparticles (1/5, 3/5, 5/5, 7/5, 8/5, and 10/5 mg/mL).

The absorption spectra data were collected of PAS using a photoacoustic cell, using light of a Xe lamp. The spectra were recorded by a PC. TEM image was obtained using a JEOL model JEM-100CX microscope at an acceleration voltage of 80 kV. The specimen was prepared by dropping the nanoparticles dispersion onto an amorphous carbon coated mesh copper grid and allowing the solvent to evaporate. The investigation of the nonlinear optical characteristics of gold nanoparticles suspensions (1/5. 3/5, 5/5, 7/5, 8/5, 10/5 (mg/mL)) was carried out using the quartz cell of 1 mm of thickness.

The non-linear optical properties of Au nanoparticles with biodiesel were investigated, using a continuous wave diode laser at a wavelength of 514 nm. The effective non-linear coefficient, n_2 of Au nanoparticles was determined by closed aperture Z-scan technique. An aperture was fixed at the distance of 120 cm from the focal plane. The Z-scan experimental set-up for the non-linear laser spectroscopy is shown in Fig. 1. The samples were moved along the z-axis through the focal plane of 10 cm focal length lens, the closed and open aperture signals are proportional to the real and imaginary parts of n_2, respectively. Dc and Do are the closed and the open apertures, respectively.

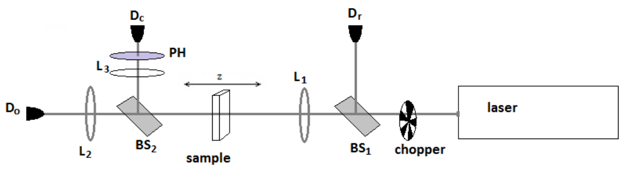

Fig. 1: Experimental setup for the non-linear laser spectroscopy

III. Math

It is well known that the relationship of the effective nonlinear refractive index, n_2, and the total index of refraction, n, is $n = n_0 + n_2 I_0$, where n_0 is the linear index of refraction, $I_0 = 1.8 \times 10^3$ W/cm^2 is the incident illumination intensity at focal point, P is the laser power, and ω_0 is the radius of the waist of the illumination beam inside the sample. With λ= 530 nm, ω_0 = 40 μm, the condition $z_0 = \pi\, \omega_0^2 / \lambda$ (= 9.78 mm) > L can be satisfied. Here the samples thickness, L is 1mm, thus the samples can be considered a thin film medium. The phase shift $\Delta\Phi_0$ on the optical axis can be obtained from (1):

$$\Delta T_{pv} = 0.406\,(1-S)^{0.25}\,|\Delta\Phi_0| \qquad (1)$$

where ΔT_{pv} is the difference between the normalized peak transmittance and valley transmittance, S is the aperture linear transmittance. Here, $\Delta\Phi_0$ relates to n_2 through the following expression:

$$|\Delta\Phi_0| = -\left(\frac{2\pi}{\lambda}\right)\Delta n L_{eff} = -\left(\frac{2\pi}{\lambda}\right) n_2\, I_0 L_{eff} \qquad (2)$$

where the effective thickness L_{eff} of the sample is defined as $L_{eff} = \left(\frac{1-e^{\alpha L}}{\alpha}\right)$, where α is the linear absorption coefficient of the samples (L denotes the sample thick-ness) [9]. ΔΦo is induced phase shift, proportional at the transmittance variation between peak and valley positions describe for :

$$T(z,\Delta\Phi) = 1 + 4\Delta\Phi_0\left(\frac{z}{z_0}\right)/\left(\left(\frac{z}{z_0}\right)^2+1\right)\left(\left(\frac{z}{z_0}\right)+9\right) \qquad (3)$$

Where z is the position, z_0 is the Rayleigh length, finally the induced phase shift is determinates by (4):

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}\,|\Delta\Phi_0| \qquad (4)$$

Here S is the linear transmittance of the aperture and the sample was scanned along a Z-axis by our system.

The sample itself acts as a thin lens with varying focal length as it moves through the focal plane [10]. The non-linear behavior of the sample is equivalent to the formation of an induced positive or negative lens for self-focusing (positive) or self-defocusing (negative) [11], [12].

IV. Results and Discussion

PA optical absorption spectra of biodiesel (pure) and with different concentrations of nanoparticles Au (1/5, 7/5, 8/5, 10/5 mg/mL) are shown in the Fig. 2. In these spectra are in the 300-650 nm regions. It is observe that biodiesel with nanoparticles have a strong optical absorption band, with a maximum at 350 nm. As the number of nanoparticles increases, the intensity of the resonance increases and its position remain at the same wavelength. Fig. 3 shows the TEM image of Au nanoparticles with average size of 9 nm.

The nonlinear refraction coefficient the n_2 (cm^2/W) together with the values of linear absorption of all suspensions can be obtained in the present work are listed on Table 1. The normalized curves of close aperture Z-scan have a pair of sharp peak and valley which can be identified as self-defocusing materials (Figs. 4-10). Since the peak of the transmittance precedes the valley, the sign of the refractive nonlinearity of Au nanoparticles suspension is negative (i.e., the negative lens effects). In Fig. 11 the variation of the nonlinear refraction index coefficient as a function of concentration for different ratios is observed. However the increase of nonlinear of refractive with the Au concentrations did not show a linear relationship as can be seen in Fig. 5.

R. F. Souza et al. [13] studied the nonlinearity properties of castor oils using Z-scan technique. Results showed that castor oil, with laser wavelength in the CW regime, has a large negative nonlinear refractive index $n_2 = -3.2\ 10^{-8}$ cm^2 / W for the laser wavelength at 514 nm [13], the authors obtained values for nonlinear coefficient refractive index of the same order found in this work.

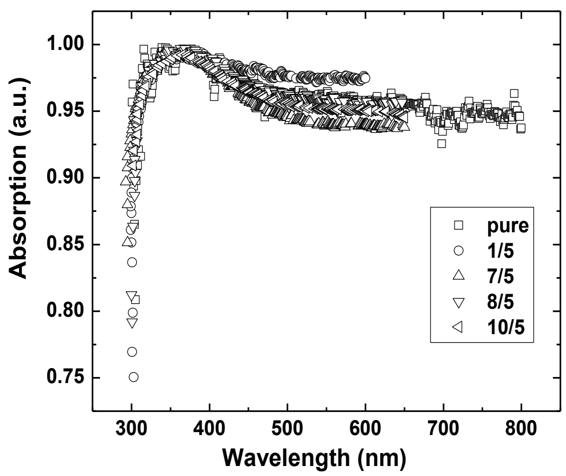

Fig. 2: PA Absorption spectra of biodiesel oil (pure) and with nanoparticles de Au with four different concentrations (1/5, 7/5, 8/5 and 10/5 mg/mL)

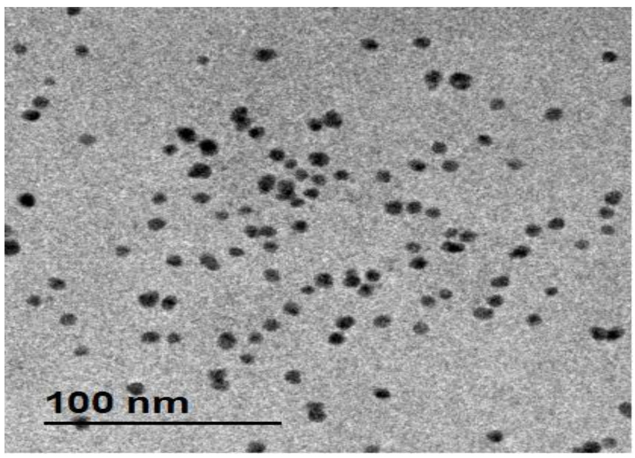

Fig.3: TEM image of the gold nanoparticles.

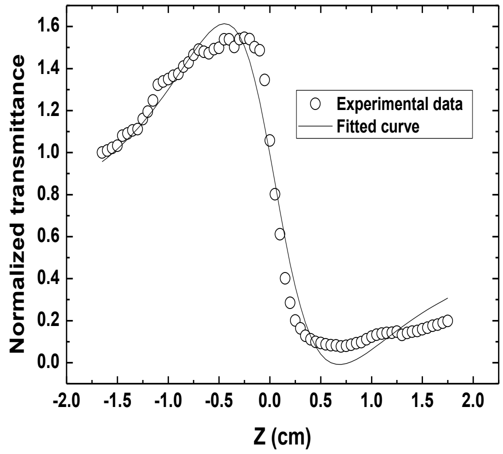

Fig. 4: Closed aperture Z-scan curve for pure biodiesel.

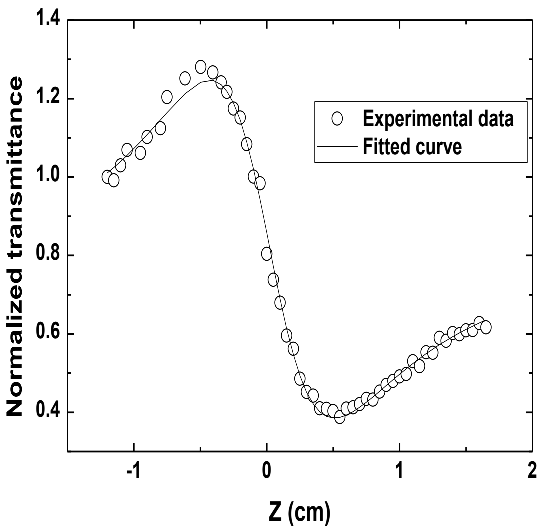

Fig. 5: Closed aperture Z-scan curve for biodiesel with nanoparticles of Au at a concentration (1/5) mg/mL.

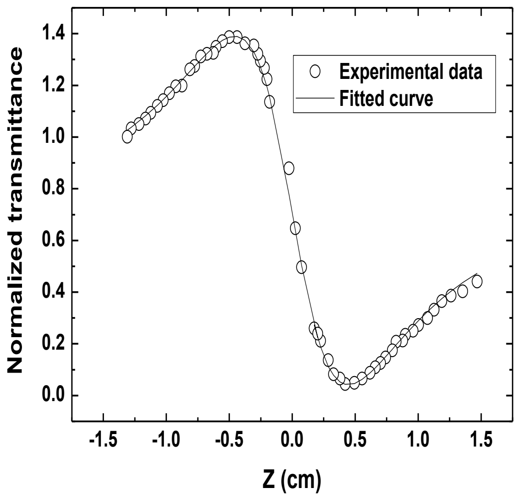

Fig. 6: Closed aperture Z-scan curve for biodiesel with nanoparticles of Au at a concentration (3/5) mg/mL.

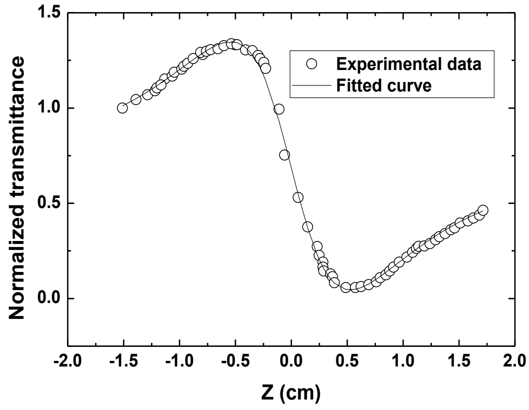

Fig. 7: Closed aperture Z-scan curve for biodiesel with nanoparticles of Au at a concentration (5/5) mg/mL.

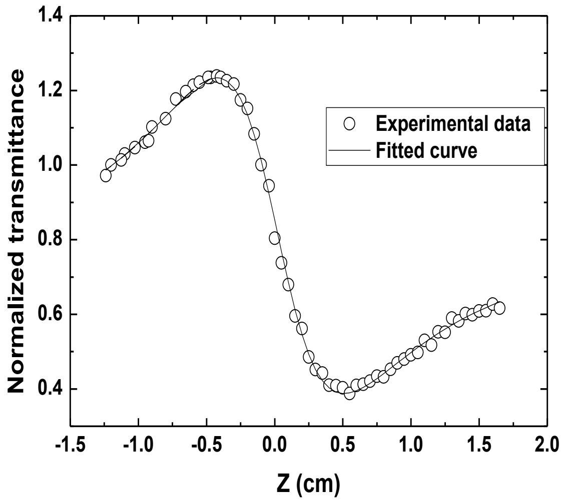

Fig. 8: Closed aperture Z-scan curve for biodiesel with nanoparticles of Au at a concentration (7/5) mg/mL.

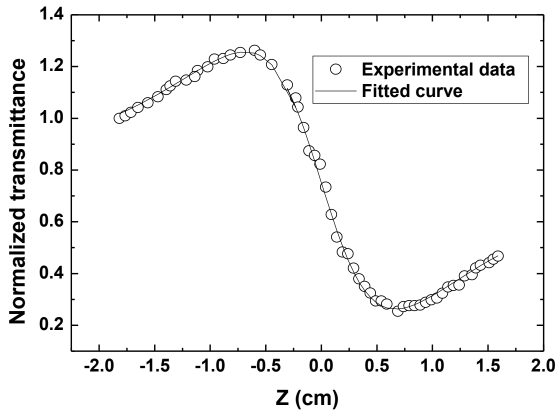

Fig. 9: Closed aperture Z-scan curve for biodiesel with nanoparticles of Au at a concentration (8/5) mg/mL.

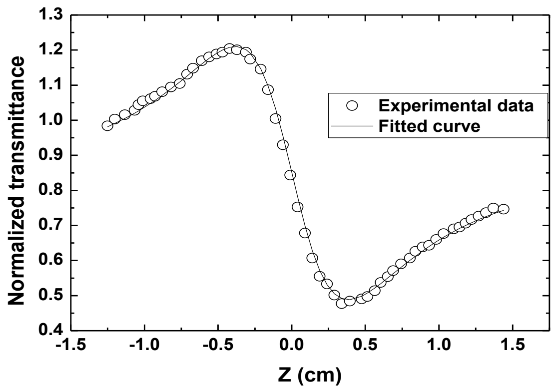

Fig. 10: Closed aperture Z-scan curve for biodiesel with nanoparticles of Au at a concentration (10/5) mg/mL.

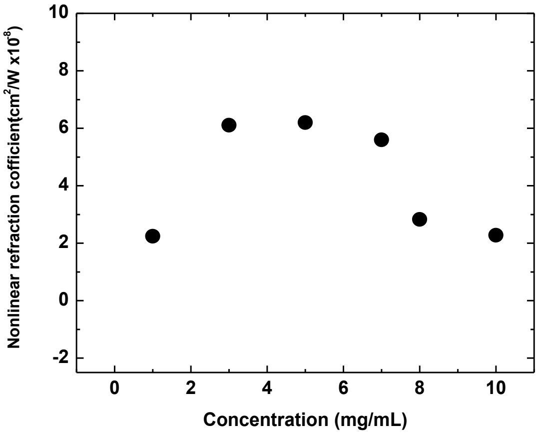

Fig. 11: Results presented of the nonlinear refractive index coefficient as a function of concentration ratio.

Table 1: Nonlinear optical properties of biodiesel and nanoparticles for the different concentrations.

Concentration mg/mL	ΔT_{pv}	$\Delta\varphi_0$	α (cm^{-1})	n_2 (cm^2/W)
pure	3.19	8.58	0.99	- 3.98 ×10^{-7}
1/5	1.2	3.51	0.98	- 2.24 ×10^{-8}
3/5	3.29	9.63	0.97	- 6.11 ×10^{-8}
5/5	3.34	9.78	0.97	- 6.20 ×10^{-8}
7/5	2.99	8.75	0.99	- 5.60 ×10^{-8}
8/5	1.51	4.42	0.99	- 2.83 ×10^{-8}
10/5	1.22	3.57	0.99	- 2.28 ×10^{-8}

V. Conclusion

Au nanoparticles were prepared by the reduction of Gold in a microemulsion (reverse micelle) system. The nanoparticles were characterized by their PAS absorption spectra and by transmission electron microscopy. The average particle size obtained from TEM analysis was 9 nm. The non-linear optical properties of the Au nanoparticles with biodiesel were also studied using the Z-scan technique. The obtained value of the non-linear refraction index, n_2, was in the order of 10^{-8} cm^2/W. The negative sign of non-linear refraction indicate self-defocusing phenomena for Au nanoparticles with biodiesel and the values of the refractive nonlinearities of gold nanoparticles are of interest from the point of view of final applications.

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