Nonlinear optical properties of Au-nanoparticles conjugated with lipoic acid in water

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Gold nanoparticles were chemically conjugated with lipoic acid to control their optical properties. Z-scan and other optical techniques were used to characterize the non-linear behavior of the resulting nanostructured materials. The results show that the nonlinearity is of thermal origin, which can be controlled by the use of lipoic acid as well as other organic molecules conjugated onto metal nanoparticles. In particular, the presence of lipoic acid increases n_2, θ and dn/dt.
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1 INTRODUCTION

Nowadays nanoparticles have reached great interest into various researching areas, due to unique electronic, magnetic and optical properties [1, 2]. Some potential applications go from biological to electronic applications, some of them are: sensor technology [3]–[5], biological labeling, drug delivery system and treatment for some cancers [6, 7], surface-enhanced Raman scattering, paintings [8], optical diodes, high speed optical logic devices [9]; on the other hand, properties of nanoparticles as the thermal conductivity and nonlinear optical properties, are interesting, because by using nanoparticles it is possible to elevate the thermal conductivity of fluids being these metallic [10]–[12], or nonmetallic [13, 14] with different shapes and sizes, and suspended in different fluids, which modified the nonlinear optical properties of fluids. Nonlinear optical gives origin to nonlinear optical phenomena as modulation instability [15, 16], self-diffraction [17, 18], nonlinear shock waves [19, 20], stabilization of complex soliton structures [21, 22], and these phenomena can be applied to design optical limiters, multiplexors, modulators, ultrafast optical communication [23]–[25]. In particular, the behavior of Au-nanoparticles in different media has been reported by using the z-scan technique [25]–[27]. However, optical properties of Au nanoparticles can be modified when they are conjugated with other molecules. This is interesting because it plays a crucial role in determining their linear and nonlinear optical properties [29]–[33]. In this work we study how the nonlinear optical properties of fluids with Au-nanoparticles present change. They were performed using the Z-scan technique (at millisecond range), and applying two models: Bahae formalism and thermal lens to obtain n_2, dn/dt. [23]–[33]

2 THEORY

Consider an incident Gaussian beam in a medium. The medium absorbs the light and then gives a local heating immediately, the temperature modified in the surroundings of a laser beam producing the refractive index changes too, the nonlocal effect and the influence in the nonlinear refractive index present, have to be considered. The refractive index is assumed to depend linearly on temperature and the nonlinearity is due to this nonlocal dependence of the refractive index on the local light intensity. The magnitude of this nonlocality can be estimated by degree of nonlocality. This parameter depends on the optical and thermal properties of the material and can be given by Ghofraniha et al [34]

$$\sigma = \sqrt{\frac{\kappa |n_2|}{\alpha_0 \left| \frac{\partial n}{\partial T} \right| \omega_0^2}} \tag{1}$$

Where $\omega_0$is the minimum beam waist, n_2, k, dn/dT, α_0 are the nonlinear refractive index, the heat conductivity, the thermo-optical and the linear absorption coefficients of the medium. The larger the value of σ, the more nonlocal is the medium.

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On the other hand if $\sigma = 0$ the medium can only present a local nonlinearity

The elements that can be measured are α_0, n_2, and dn/dT, these last are nonlinear optical properties of the medium. One of the easiest techniques to study the nonlinear optical properties is the Z-scan technique. It was developed by Bahae [35] and it is the most known for determining the nonlinearity of materials. To interpret the results obtained by z-scan technique we used diverse models; the Sheik-Bahae formalism and the thermal lens model, [36] because both help to describe nonlocal systems in time; Bahae formalism does it once the system has reached a steady status (we used a chopper at milliseconds to achieve this), and the thermal model, which describes the nonlinearity with thermal origin.

2.1 Sheik-Bahae Formalism

Consider a medium illuminated by a Gaussian laser beam; it is an electric field ($\boldsymbol{E}$), and respectively frequency, the nonlinear refraction index $n_2$can be defined by:

$$n = n_0 + \frac{1}{2} n_2 E^2 \tag{2}$$

Where n is the refractive index. For a sample where nonlinear absorption is negligible, the on-axis normalized transmittance can be obtained approximately by:

$$T(z) = 1 + \Delta\Phi_0 \frac{4x}{(1+x^2)(9+x^2)} \tag{3}$$

Where $\Delta\Phi_0$ is the on axis nonlinear phase shift at focus, x is the dimensionless sample position, $x = \frac{z}{z_0}$, $z_0 = \frac{\pi\omega^2}{\lambda}$ is the Rayleigh parameter of the Gaussian beam with waist ω_0. The peak-valley difference ΔT is:

$$\Delta T = 0.406\,|\Delta\Phi_0| \tag{4}$$

The nonlinear phase shift is given by

$$\Delta\Phi_0 = \frac{2\pi d(1 - e^{-\alpha L})}{\lambda\alpha} n_2 I_0 \tag{5}$$

Where α is the linear absorption coefficient, L is the thickness of the sample, I_0 is the peak intensity at the focus and λ is the wavelength of the laser beam. An advantage of this method is that we can obtain the magnitude and sign of nonlinear refractive index by using a close aperture and the nonlinear absorption coefficient by employing an open aperture in the detector.

The nonlinear absorption coefficient (β) is related to the transmittance by [38]

$$\Delta T(z) \approx -\frac{q_0}{2\sqrt{2}} \frac{1}{[1 + Z^2/Z_0^1}} \tag{6}$$

where $q_0 = I_0 L_{eff} \beta$.

2.2 Thermal Lens Model

When a Gaussian beam is propagated across the absorbent medium, a local heating immediately occurs. This change of temperature around the beam laser gives origin to a change in the refractive index of the medium, papers describing this phenomena are found [35, 39]. Analysis of Gordon et al, has predicted a parabolic approximation to the temperature field and an approximation to the optical effects due the temperature as the behavior of a simple lens. The time dependent expression [40] for the far- field on-axis transmittance is

$$T_N = \frac{I(z,t)}{I(z,0)} = \frac{1}{1 + \left(\frac{\theta}{1+t_c/2t}\right)\left(\frac{2x}{1+x^2}\right) + \left(\frac{\theta}{1+t_c/2t}\right)^2 \left(\frac{1}{1+x^2}\right)} \tag{7}$$

Where $x = \frac{z}{z_0}$, $z_0 = \frac{\pi\omega^2}{\lambda}$, $t_c = \frac{\omega^2}{4k/C_p}$ $t_c$is thermal diffusion time, k is the thermal conductivity and C_p is the specific heat per volume at constant pressure, The on-axis phase shift is given by

$$\theta = \frac{\alpha P L}{\lambda\kappa} \frac{\partial n}{\partial T} \tag{8}$$

Where P is the power of the Gaussian beam and$T$ is the temperature. To lower power the nonlinear phase shifts $\theta \ll 1$, then the second term of Eq. (7) in the denominator is neglected. When the steady state has been reached can be considering $t >> t_c$then Eq. (7) is given by

$$T_N = \frac{1}{1 + (\theta)\left(\frac{2x}{1+x^2}\right)} \tag{9}$$

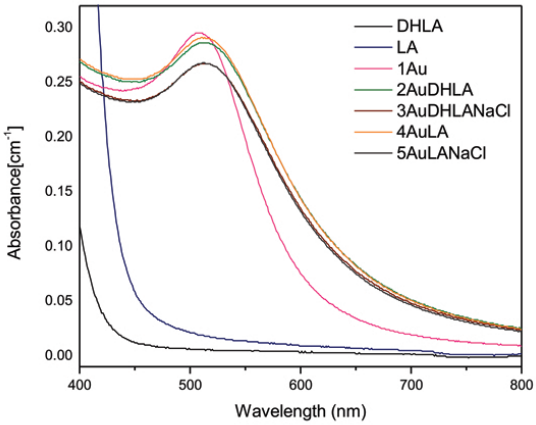
The z-scan curve then corresponds to Eq. (9).

3 EXPERIMENTAL SETUP

Gold nanoparticles stabilized with lipoic acid were prepared taking into account Brust's method [41] to prepare small gold nanoparticles, and the sulfhydryl groups' affinity with gold for forming covalent bonds. Briefly, sodium borohydride was added to a solution of tetrachloroauric acid in water. The molar ratio between sodium borohydride and tetrachloroauric acid is directly related with the final gold particle size. The samples were prepared using a molar ratio of 5:1 between $NaBH_4$ and $HAuCl_4$, respectively. Once the gold nanoparticles were synthesized, lipoic acid (LA) or reduced lipoic acid (DHLA) were used to stabilize the gold nanoparticle colloids. To determine the quantity of LA and DHLA to be used, the size and concentration of the colloids were estimated according to W. Haiss et al. method [42]. Based on these results, and the estimated area occupied by one molecule, LA and DHLA

Name	Solution
1Au	Au nanoparticules in water
2AuDHLA	Au nanoparticules with reduced lipoic acid in water
3AuDHLANaCl	Au nanoparticules with reduced lipoic acid and sodium chloride in water
4AuLA	Au nanoparticules with lipoic acid in water
5AuLANaCl	Au nanoparticules with lipoic acid and sodium chloride in water

TABLE 1 Characteristics of gold colloid samples.



Sample	Peak (*nm*)	α (cm^{-1})
DHLA	514	0.005
LA	514	0.018
1Au	508 (514)	0.295 (0.293)
2AuDHLA	514	0.286
3AuDHLANaCl	514	0.267
4AuLA	514	0.290
5AuLANaCl	514	0.267

FIG. 1 Uv-vis spectra of the different solutions.

plus thirty times more were calculated in order to ensure that all the surface of the gold nanoparticles were covered. Finally, NaCl was added to the samples to study the stability of gold colloids and the effect on the optical properties. Table 1 shows the different samples prepared. The concentration of nanoparticles in each solution was 300 nM/l (nanomols/litre).

The UV-vis spectra of the solutions are shown in Figure 1. Water as it is known, does not absorb in visible, note the lipoic acid and reduced lipoic acid do not absorb in visible too. The peak absorption band of Au nanoparticles suspended in water is at 508 nm, with a valley at 450 nm, which is characteristic of spherical gold nanoparticles. The solutions with lipoic acid and reduced acid lipoic do not affect the linear absorption but sodium chloride slightly decreases it. Since the Au nanoparticles have a diameter smaller than the wavelength of the incident light, surface plasmon resonance (SPR) takes place during our experiment. UV-vis shows a peak at 514 nm, which corresponds precisely to a surface plasmon resonance absorption peak. This wavelength shift to the plasmon peak of Au, appears when adding HLA, LA and NaCL. It is known that Au nanoparticles dispersed in solutions have great linear absorption and they absorb energy due to SPR of the electron. The absorbed energy will first be transfered to the phonon modes of the metal nanoparticles and then the surrounding liquid, so the local temperature will increase in the solution. Then, most of the nonlinear effects that we observe will have a thermal origin.

The z-scan experimental setup for the CW laser is shown schematically in Figure 2. CW Ar laser at 514 nm with variable power (using at *10, 16* and 25 mW), propagating in z direction, was focused using a lens (18 cm focus) and a waist beam of 29.16 μm was obtained. A mechanical chopper was used to modulate the intensity, to measure at the millisecond range, providing nearly square pulses width of 20 and 10 ms. The sample was moving using a control PC-system [43] to constant velocity. The liquid sample was collocated in a 2 mm thick cell, and moved along the z-direction; the transmitted intensity was measured through the finite aperture in the far field (80 cm) as a function of the sample position z; measured with respect to the focal plane. As the sample moves through the beam focus (at $z = 0$), self-focusing or defocusing modifies

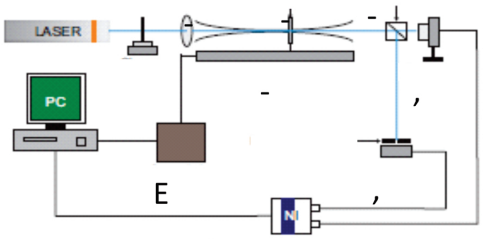


FIG. 2 Z-scan experimental setup.

the wave front phase, thereby modifying detected beam intensity. The nonlinear coefficient of refraction and absorption can be measured with a close and open aperture, respectively.

4 RESULTS AND DISCUSSION

A beam of laser at different power incised the solutions. The laser power was increased from 10 mW to 250 mW, and rings were obtained by self-diffraction phenomena, except at 10 mW that they were not observed. At 25 mW it was possible to observe one ring, the self-diffraction phenomena, note that the number of the rings was minimum. It implies that we had a low phase shift. In Figure 3, it is shown the results for open aperture Z-scan measurement of the samples at different powers. It was not possible to determine the values of nonlinear absorption for all samples by simply using Eq. (**??**), because the adjustment of R-square was less than 0.7 in most of the samples, despite the tendency shown by the experimental data. Figure 3 shows a typical curve of two-photon absorption (TPA). The best adjustment was for the 5AuLANaCl sample, $\beta = 10.7258x10^{-6}$ m/W, and the 3AuDHLANaCl sample, $\beta = 10.9258x10^{-6}$ m/W was obtained at 25 mW with $R^2 = 0.60939$ and $R^2 = 0.63395$, respectively. Nadjari et al. [44] report a $\beta = 23x10^{-6}$ m/W for gold nanocolloids at 532 nm and 5.2x10^{-6} fractional volume. Interestinlgy, despite that we had smaller Au nanoparticles concentration, the value order of β was similar, because we were exciting at peak of plasmon wavelength.

We obtained the data using the PC-system for each solution;

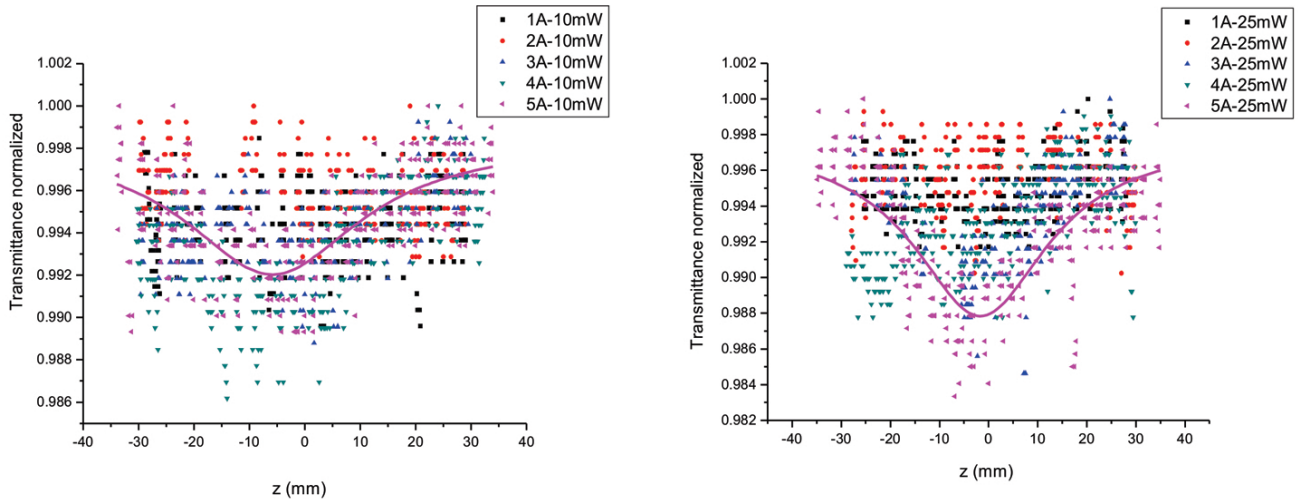


FIG. 3 Open aperture z-scan measurement to 5 solutions, $\beta = 17x10^{-6}$ m/W ($R^2 = 0.47$) and 10.72 $x10^{-6}$ mW ($R^2 = 0.60$) to 10 mW and 25 mW respectively were obtained using Eq. (6).

closed aperture z-scan measurement to 1Au solution at different powers and frequencies were shown at Figure 4, the curves were fit using Eq. (3). Depending on the experimental conditions and on the sample absorption properties, thermal nonlinearities must be taken into account, especially on a time scale of milliseconds, the response given by Eq. (3) also describes systems nonlocal time, once they have reached a steady state [35]. Our experimental conditions allowed to apply laser wavelength to the colloid SPR peak to enhance the linear absorption, and this induced a larger thermal nonlinear refraction in the medium. It must be noticed that the SPR peak position was related to the gold nanoparticle size; therefore, this effect can play important roles on its thermo-optical properties. It is common that, in liquids, the local refractive index decreases with the increase of temperature, therefore, a temperature gradient result in a change of the local refractive index of the solution. In our case, we have an intense heat accumulated because the irradiation is at 514 nm with a CW laser, which corresponds to the resonance absorption peak of Au nanoparticles. This effect leads to the creation of larger thermal-induced negative nonlinear refractive index inside the solutions. Additionally, in this kind of thermal process, the nonlinear refraction index (n_2) is not a constant value and depends on the incident intensity.

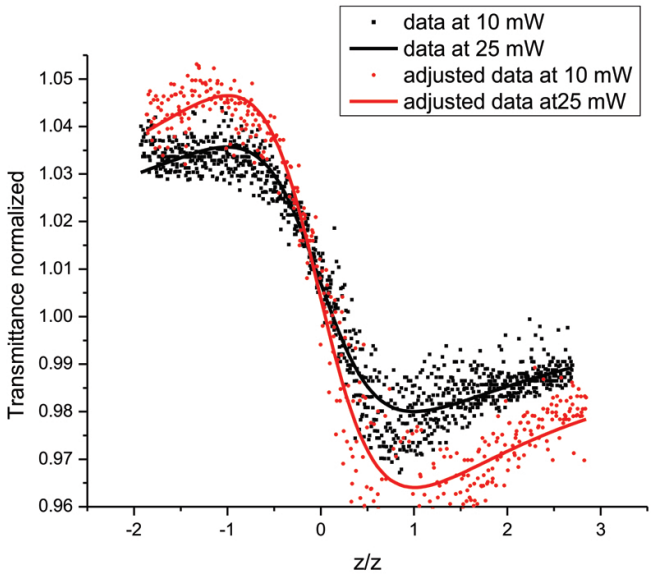


FIG. 4 Close aperture z-scan measurement to 1Au solution at 100 hz and 10 mW and 25 m using Eq. (3).

Figure 5 shows the behavior of parameters ($n_2, \theta, dn/dt$) of samples according to the laser power. θ (thermal induced phase shift) and dn/dt (thermal-optic coefficient) are not constant values, these depend on the incident laser intensity and the intrinsic properties of the material as κ, and D (thermal conductivity and thermal diffusion respectively), because a radial direction was taking place in the diffusion of the heat (perpendicular to the z direction), then temperature field with spatial distribution had risen and had a different distribution to the laser beam temperature. As a consequence, the physical properties of the Au nanoparticles changed, affecting the propagation of the light beam itself. Note θ, increases their value with the increase of the laser power due that the temperature was increased in consequence, self-diffraction occurred, while dn/dt, and n_2, which are negative, decreased. However, we note the thermal effect decreases with the frequency increase.

Table 2 shows values, standard error and adjusted R-square to each of n_2, θ, dn/dt and σ were obtained for each solution at 10 mW and 100 Hz respectively. These values were obtained using Eq. (3), Eq. (9), Eq. (8) and Eq. (1), respectively. Commonly, the tendency of thermal conductivity enhancement with increase of nanoparticles concentration was observed. However, Shalkevich et al [?] makes reference to that the in tests done in fluids, only small changes in the thermal conductivity are within the uncertainty of the measurements. Accordingly we consider that due to the nanoparticles concentration being of 0.0004% per volume is low, and the size of the nanoparticles on average is of 4.5 nm and that the use of k value will be close to the reported in [?], thus, using Eq. (8), this shall imply that the dn/dt value shall be the minimum ex-

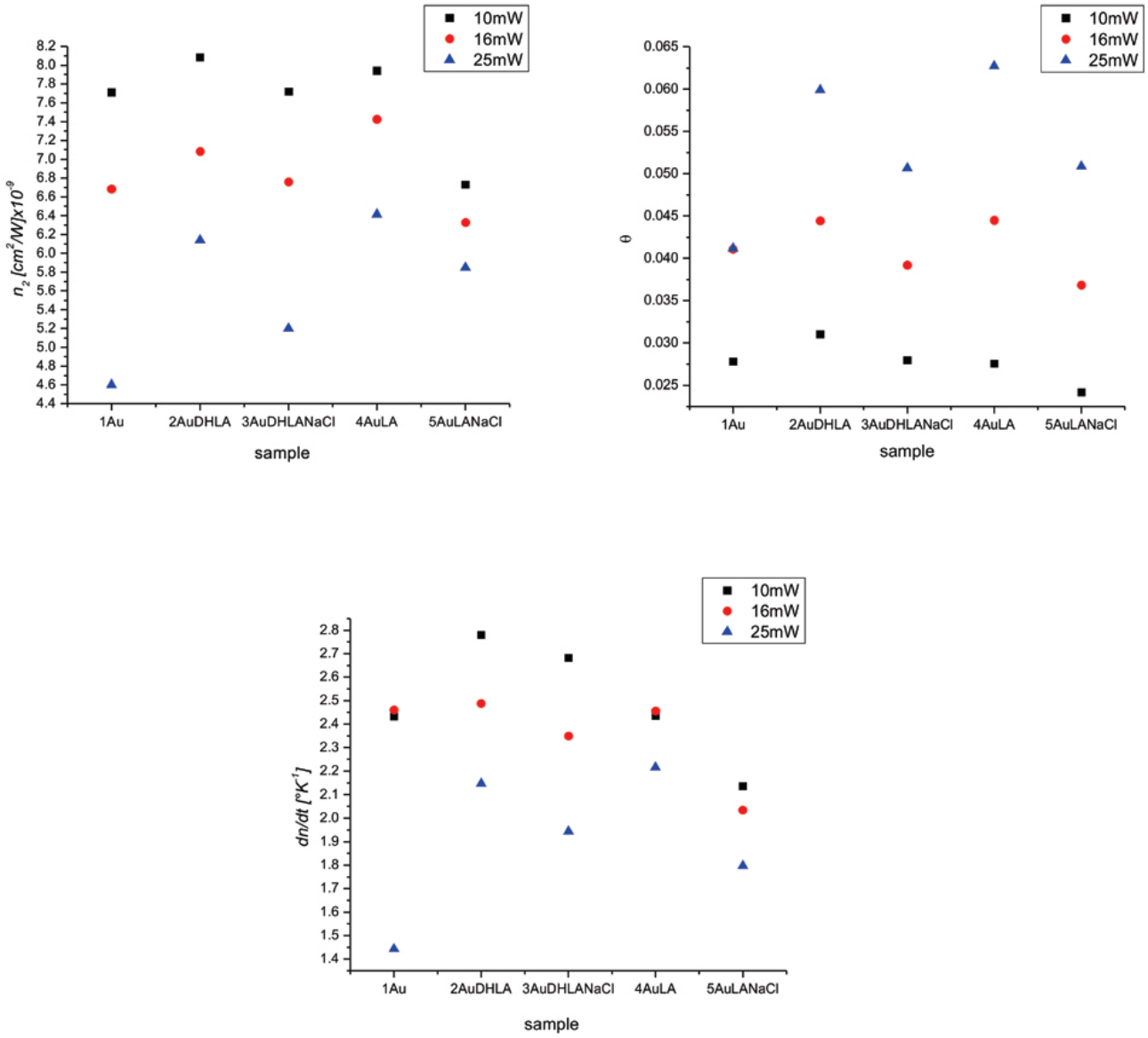


FIG. 5 n_2, θ, dn/dt, to different powers at 100 Hz to five samples.

pected. The sigma value is in agreement with the heating that firstly occurs close to the entering face, due to the strong absorption enriched by the SPR phenomena. Some simulations confirm this kind of process [35] which report having this behavior within their samples.

Analyzing the changes of five samples at 100 Hz and different powers, we noted that n_2, θ, and dn/dt, how the presence of lipodic acid (reduced or not) increased the value of these parameters but when the NaCl was added it decreased the values, this was due to the fact that the NaCl solution has a lower C_p (specific heat), which decreased the thermal diffusion time, besides it is an ionic liquid, the ionic liquid has nonlinear phenomenon nonlocal too [45], producing a reduction in the self-diffraction phenomenon (see Figure 5).

5 CONCLUSIONS

All Au solutions prepared presented nonlinear optical properties. The origin of these properties is thermal. Thermal nonlinear response is an important area for photonic applications

sample	n_2 x 10^{-9} [cm^2/W]	Standard error [x 10^{-11}]	Adj. R-square	θ	Standard error [x 10^{-4}]	Adj. R-square	dn/dt x10^{-4} [°K^{-1}]	Standard error [x 10^{-6}]	Adj. R-square	σ
1Au	-7.70999	4.872668	0.96299	0.02781	1.70616	0.96432	1.55139	0.915943	0.96443	0.356183372
2AuDHLA	-8.08399	5.16374	0.96124	0.03103	2.01313	0.96281	1.77325	1.09507	0.96292	0.345291527
3AuDHLANaCl	-7.71928	4.65434	0.96809	0.02795	1.65631	0.96846	1.71094	1.00868	0.96850	0.35551376
4AuLA	-7.9402	5.46494	0.95142	0.02756	2.15928	0.94913	1.5532	1.12223	0.94928	0.363114899
5AuLANaCl	-6.7296	4.65399	0.95723	0.02417	1.72777	0.95322	1.47409	1.0005	0.95336	0.357616899

TABLE 2 Values of $n_2, \theta, dn/dt$, and σ, standard error and R-square, obtained by fit to experimental data.

that require CW or higher power lasers, where thermo optical effects can be exploited to be able to use nonlocal nolinear phenomena, such as spatial solitons and shock waves. Au nanoparticles properties depend on wavelength and intensity laser. Presence of lipodic acid increase the n_2, θ and dn/dt values. Presence of NaCl decreases these values, this implies we can controlled the nonlocal linearity and add or substract NaCl solution or ionic liquids at samples.

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