

# Spatial Coherency of Light and Nonlinear Optical Properties of Colloidal Gold Studied by CW Z-Scan Technique

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## Abstract

Nonlinear refraction and absorption of a suspension of Au nanoparticles was studied by CW Z-scan at near-resonant excitation. Spatial coherency and self-interference of the laser beam results in the emerging of ring-like interference pattern observed at the plane of the detector. The number of the interference fringes and their diameter depends on volume fraction of the nanoparticles and laser fluence at focal point. Periodical light intensity distribution across the laser beam causes modulation in the output signal that should be considered for the correct interpretation of Z-scan data.

## Keywords

Nanoparticles (NPs), Localized surface plasmon resonances, Z-scan technique, Photodetector

## Introduction

Nanophotonics based on metal nanoparticles (NPs) and their systems is a rapidly growing field of a modern technology. The main attention to metal NPs is driven by specific electronic excitations within the nanoparticles induced by impinging electromagnetic waves. Those oscillations of free electrons are known as localized surface plasmon resonances or LSPR. Especially perspective are noble metal (Au, Ag, Cu) NPs since the resonant frequency of the localized surface plasmons is observed in the visible spectral range. Any practical application of the NPs implies they are always embedded in a host medium that mainly serves as a supporting structure firmly preserving the particles' arrangement. Optical usage of the NPs requires transparency of the host matrix in corresponding spectral range. In other words, the entire system is considered as a nanocomposite that combines properties of the host and metal NPs inclusions. Specific interactions of LSPR in metal NPs with surrounding medium give rise to the nonlinear-optical phenomena that appear at high intensities of the electromagnetic field. Therefore, studies of nanocomposite materials comprising noble metal NPs embedded in solids or suspended in liquids, are of great importance [1].

Nonlinear-optical response of a nanocomposite exhibit dual origin. First, it is associated with the nanoparticles themselves, their large surface-to-volume ratio that contributes to the second harmonic generation [2]. Photoinduced changes of the absorption coefficient also affect scattering pattern by the NPs and thus, the nonlinear refraction of the nanoparticles assembly (via Kramers-

Kronig relations) [3]. Second, nonlinear optical (NLO) properties of a nanocomposite are due to modifications in the host matrix properties, namely thermal density fluctuations known as thermal lensing effect [4], and Stark effect [5]. Obviously, NLO response of a nanocomposite depends on the volume fraction of NPs, their surface properties and dielectric environment as well.

It is well established that NLO effects in noble metal NPs are greatly increased due to the enhancement of the local electric field around each nanoparticle when the frequency of incident light is close to that of LSPR [6, 7]. Since the spectral band associated with LSPR in gold NPs 20/50 nm in diameter is located at the wavelength of 520/540 nm, the resonant interaction of light with Au nanoparticles can be easily realized using second harmonic radiation of Nd:YAG laser at  $\lambda = 532$  nm. Applying resonant irradiation one can achieve nonlinear-optical response of Au NPs suspension at relatively low light intensities.

In present paper we report on studies of the third-order refraction of Au NP aqueous suspension employing Z-scan technique. Some effects of the spatial coherency of the laser beam which occur after passing the sample are also discussed. Those effects should be taken into account for proper interpretation of experimental Z-scan data. Despite its experimental simplicity the method allows precise determining of the value of both real and imaginary parts of third-order susceptibility and their sign.

## Experimental

### Synthesis and characterization of Au nanoparticles

Gold nanoparticles were synthesized by homogeneous nucleation technique via reduction of  $\text{HAuCl}_4$  solution in water with  $\text{Au}^{3+}$  concentration of 1.3 g/l by hydrazine hydrate  $\text{N}_2\text{H}_4 \cdot 0.5\text{H}_2\text{O}$  at the presence of oligoperoxide as surfactant. The latter was prepared by radical copolymerization of N-vinyl pyrrolidone, peroxide monomer 5-(tert-Butylperoxy)-5-methylhex-1-en-3-yne, and glycidyl methacrylate as described in Inoye et al. [8]. To provide strong adhesion of oligoperoxide molecules on the nanoparticles surface the molecules were modified with thiol groups ( $[\text{S}] = 9.6\%$ ). Synthesis was performed at the temperature of  $T = 300$  K in alkali environment with  $\text{pH} = 10.6$  for the molar ratio of  $[\text{HAuCl}_4]:[\text{N}_2\text{H}_4] = 1:20$ . The reaction produces Au nanoparticles coated with thin (~1-2 nm) polymer layer that prevents particles from aggregation.

The size of the nanoparticles was determined by transmission electron microscope (TEM) operated at acceleration voltage of 100 kV. The TEM image of Au NPs is demonstrated in Figure 1 along with the histogram nanoparticles size distribution. The TEM image was processed by freely available program ImageJ. Image analysis yields mean diameter of the nanoparticles  $\langle d \rangle = 19.3$  nm with a standard deviation  $\sigma_d = 8.03$  nm. X-ray studies of Au NPs confirm crystal stability of nanoparticles that contain no dopants (Figure 2). The size of the NPs was also determined from FWHM of the diffraction peaks using well known Scherrer expression. The range of coherent scattering correlates with

the size of NPs determined from TEM image.

### Optical spectra of Au nanoparticles

The absorption spectra of Au NPs suspension was measured with diffraction monochromator with the focal length of 600 mm equipped with a stabilized halogen lamp as a light source. Quartz cell poured with the suspension was placed into the photometric sphere. The thickness of the cell is 1 mm. The signal was registered by a photomultiplier tube exploiting in the photon counting mode.

Experimentally measured absorption spectrum exhibits good agreement with one calculated by Mie theory. The calculations were performed for each fraction that represents specific size of the NPs according to the histogram in Figure 1. Total absorption spectrum of Au NPs suspension under investigation was found as a sum of partial spectra. As can be seen in Figure 3 the LSPR bandwidth for experimental spectrum exceeds that for calculated one. The discrepancy is due to inhomogeneous broadening of spectral band caused by the dispersion of the nanoparticles size and deviation of the shape of NPs from ideal sphere as well.

Absorption spectrum was used to determine the concentration of nanoparticles in the suspension. To obtain samples with lower nanoparticles concentration the initial suspension was diluted with distilled water.

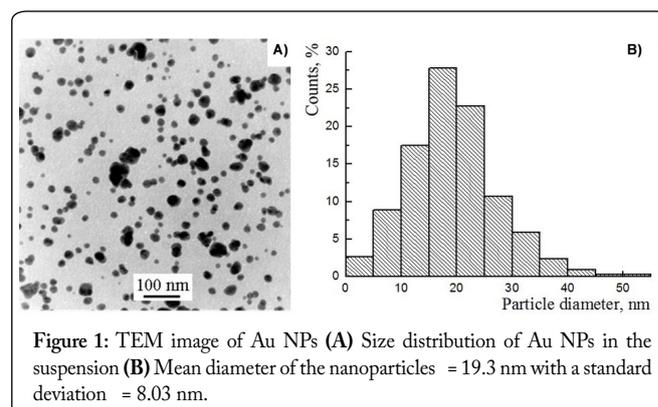


Figure 1: TEM image of Au NPs (A) Size distribution of Au NPs in the suspension (B) Mean diameter of the nanoparticles = 19.3 nm with a standard deviation = 8.03 nm.

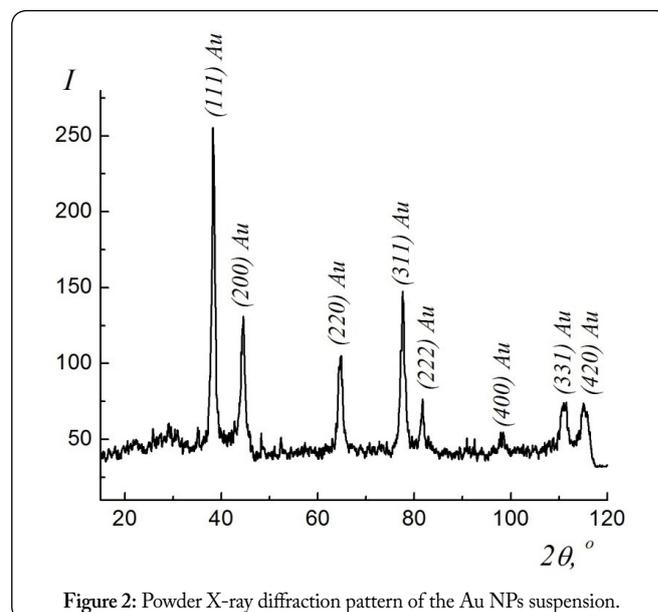


Figure 2: Powder X-ray diffraction pattern of the Au NPs suspension.

### Nonlinear-optical measurements

Nonlinear refraction in Au NPs suspension was determined employing standard Z-scan technique with closed aperture [9]. The experimental arrangement is shown in Figure 4. All measurements were performed at ambient temperature using second harmonic radiation from CW Nd:YAG laser at  $\lambda = 532$  nm. The output power of laser beam was 45 mW. The parameters of the focused laser beam satisfied the main requirements of Z-scan method. The Rayleigh length was 1.197 mm with laser power density at focal point  $I_0 = 1.15 \times 10^4$  W/cm<sup>2</sup>. The third order refractive index and nonlinear absorption were determined from normalized Z-scan transmission curves according to the procedure given by Sheik-Bahae et al. [9]. Corresponding values for the Au NP suspension being studied are  $n_2 = -2.18 \times 10^{-7}$  cm<sup>2</sup>/W and  $\beta = 10.75 \times 10^{-3}$  cm/W.

To determine nonlinear absorption all the light passed through the sample should be registered by photodetector. So, open aperture configuration with a collecting lens was employed. Si photodetector was used for recording of the optical transmission.

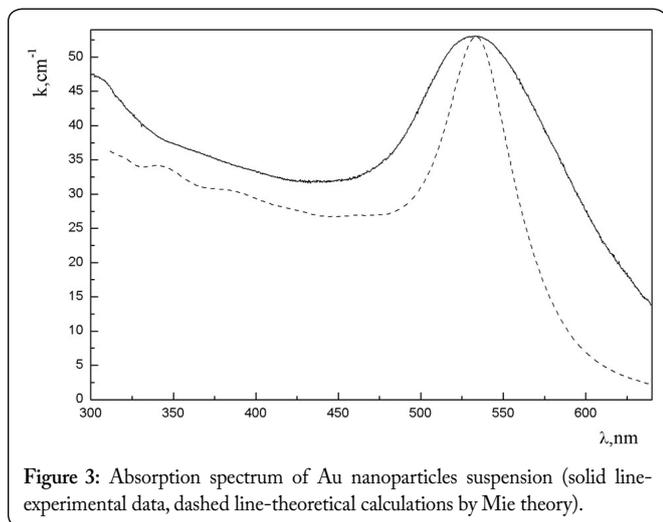


Figure 3: Absorption spectrum of Au nanoparticles suspension (solid line-experimental data, dashed line-theoretical calculations by Mie theory).

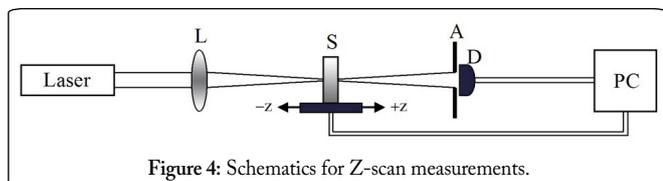


Figure 4: Schematics for Z-scan measurements.

### Results and Discussion

An interference pattern is observed in the far field after an intense light beam travels through a medium possessing optical nonlinearities [10]. The pattern appears as a number of concentric rings that can be visualized by an opaque screen placed instead of the aperture. The ring pattern is a result of spatial phase-modulation across the Gaussian laser beam that is due to intensity dependent refractive index of the nonlinear medium. We observe the interference pattern for Au NPs suspension with a volume fraction  $f = 1.3 \times 10^{-5}$  at laser power density  $I_0 = 1.15 \times 10^4$  W/cm<sup>2</sup> (Figure 5).

The number of the rings observed depends on the

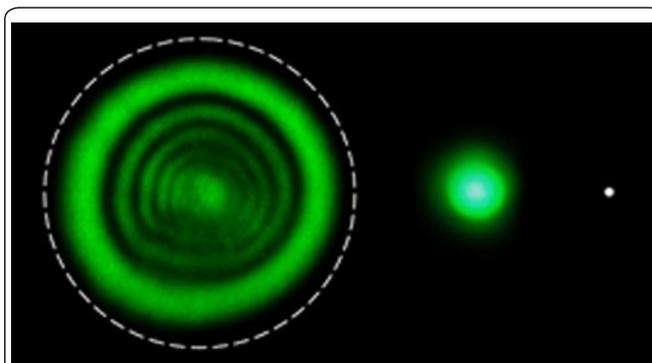


Figure 5: The interference pattern as observed in the plane of the aperture. The dash line represents an open aperture (collecting lens) used for nonlinear absorption measurements. The white disk on the right represents the size of the aperture for NLR measurements (closed aperture configuration).

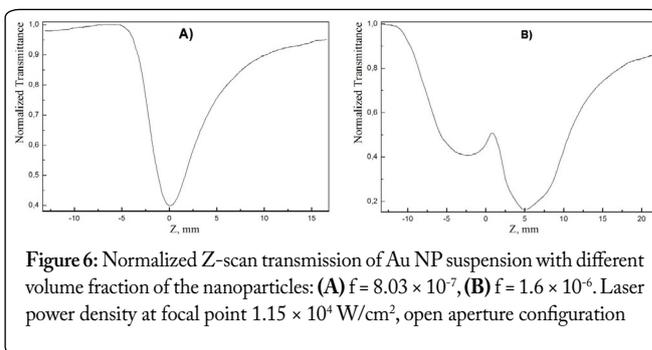


Figure 6: Normalized Z-scan transmission of Au NP suspension with different volume fraction of the nanoparticles: (A)  $f = 8.03 \times 10^{-7}$ , (B)  $f = 1.6 \times 10^{-6}$ . Laser power density at focal point  $1.15 \times 10^4$  W/cm<sup>2</sup>, open aperture configuration

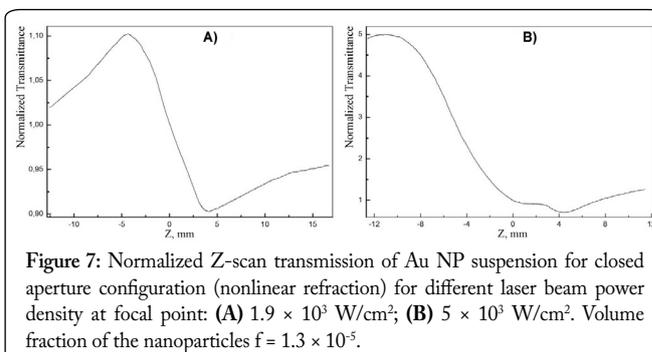


Figure 7: Normalized Z-scan transmission of Au NP suspension for closed aperture configuration (nonlinear refraction) for different laser beam power density at focal point: (A)  $1.9 \times 10^3$  W/cm<sup>2</sup>; (B)  $5 \times 10^3$  W/cm<sup>2</sup>. Volume fraction of the nanoparticles  $f = 1.3 \times 10^{-5}$ .

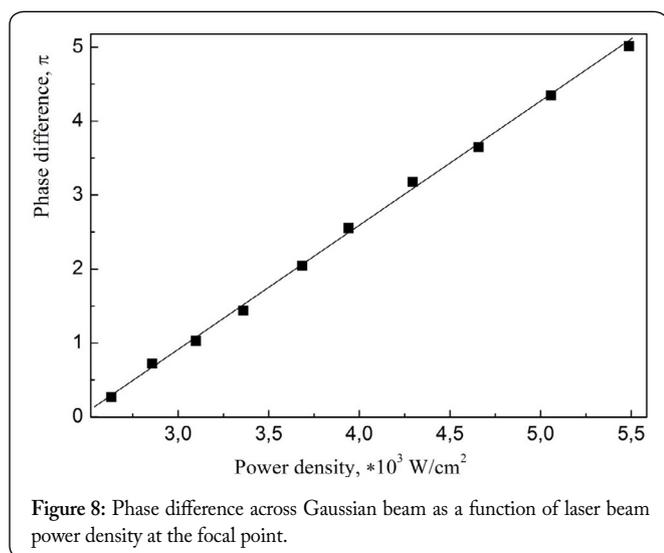
magnitude of nonlinear refractive index  $n_2$ , i.e. it is determined by the intensity of laser beam at focal point and concentration of NPs. Decreasing of the beam intensity results in disappearing of the rings. The same effect is observed when the concentration of the nanoparticles in the suspension decreases. It should be noted here that emerging of the pattern is accompanied by changes in the shape of a typical Z-scan curve. This situation is illustrated in Figure 6 and 7. The normalized Z-scan transmission curves at a constant beam intensity of  $1.15 \times 10^4$  W/cm<sup>2</sup> for Au NP suspension with different particles concentration is presented in Figure 6, while Figure 7 depicts the curves recorded at different intensities of laser beam for the same concentration of the nanoparticles ( $f = 1.3 \times 10^{-5}$ ).

Let us discuss those effects in details. Typical shape of normalized Z-scan absorption curve measured in open aperture configuration is observed for the suspensions with low NPs concentration, e.g.  $f = 8.03 \times 10^{-7}$  (Figure 6A). The ring pattern does not appear on the screen in that case. After the concentration reaches certain value of  $f = 1.6 \times 10^{-6}$  the

additional maximum emerges on Z-scan curve (Figure 6B). We assign this maximum to the changes in spatial distribution of the laser beam intensity due to self-interference of the Gaussian beam. In other words, the intensity of the output electric signal produced by a photodetector is a function of a number of interference fringes and their distribution across the sensor.

Figure 7 depicts normalized Z-scan curves corresponding to nonlinear refraction. Unlike the previous case the measurements were performed for concentrated suspension with  $f = 1.3 \times 10^{-5}$  at different levels of irradiation. Increasing of the laser beam power density results in the increase of peak-to-valley ratio in the curve and to the emerging of an additional weak maximum (Figure 7B). These effects make the correct determination of nonlinear refraction difficult.

The emerging of interference fringes is due to significant distortion of the wavefront that occur when light beam travels through the medium with optical nonlinearities. Single beam Z-scan technique is known to be a highly sensitive technique that allows one to register phase difference on the order of  $\lambda/300$  [11]. The nonlinear optical effects in a nanocomposite containing metal NPs are enhanced in the LSPR region, so the phase difference reaches high magnitudes. We easily register phase difference up to  $6\pi$  while studying Au NPs suspension within the concentration range and excitation intensities noted above. Phase difference were determined by counting the number of interference fringes projected on the opaque screen. This number increases with the increase of laser fluence. It was found experimentally that phase difference linearly depends on the laser power density at focal point. In order to measure mentioned dependence we performed Z-scan measurements simply using attenuation of the laser beam by neutral filters. The corresponding plot is shown in Figure 8. One can see that notable phase difference is observed even at low nanoparticles concentration and/or laser fluence at resonant excitation.



Obviously, the size of the interference pattern and the number of the fringes depend on laser fluence (see also Figure 5). At some point, for large laser power density, the size of the pattern exceeds that of the aperture placed in a front

of a photodetector, i.e. the outer fringes do not impinge the surface of the latter. Even though the nonlinear optical effects are strong in this case, the photodetector produces weaker output signal. This weakening manifests itself as an additional maximum in Z-scan absorption curve as discussed above. Such a dependence resembles that for saturable absorption observed at high intensities of the laser beam [12] and might be wrongly attributed to the latter. Therefore, in order to determine the nonlinear-optical parameters of Au NPs suspensions correctly low particle concentration is needed.

## Conclusions

We studied both nonlinear refraction and absorption in the aqueous suspension of gold nanoparticles at near-resonant excitation. The magnitude of nonlinear refraction confirms high optical nonlinearity of the suspension. Self-interference of the spatially coherent Gaussian beam as it travels through the medium with optical nonlinearities results in appearing of interference pattern that can be observed at the plane of the detector. The number of interference fringes and their size depends on volume fraction of the nanoparticles and laser fluence at focal point. Expanding of the interference pattern caused by the increase of the laser power density leads to the decrease in the amount of light that reaches photodetector, i.e. part of the beam goes out of the sensing area. Thus, the output signal produced by the detector become weaker for higher levels of laser fluence and the additional maximum emerges in Z-scan absorption curve. Such dependence is similar to the absorption saturation observed at high intensities of the laser excitation. The described phenomenon should be taken into account when considering nonlinear-optical properties of metal nanoparticle composite in order to interpret experimental Z-scan data correctly.

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