

Article

# Electroabsorption in Metallic Nanoparticles within Transparent Dielectric Media

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**Abstract:** Electroabsorption in metallic nanoparticles within transparent dielectric media has been measured. In particular, gold nanoparticles in glass and subnanometer-size metallic domains in iodine doped nonconjugated conductive polymer have been studied. Measurements have been made for applied ac fields at 4 kHz, at a wavelength close to the onset of the surface plasmon resonance. The measured electroabsorption (imaginary part of  $\chi^{(3)}$  or Kerr coefficient) has a quadratic dependence on electric field. Its magnitudes were compared for different sizes of the metallic nanoparticles down to the subnanometer-size particles in iodine-doped nonconjugated conductive polymer. As in the case of quadratic electro-optic effect reported earlier, electroabsorption has approximately a  $1/d^3$  dependence,  $d$  being the diameter of nanoparticle. This is consistent with existing theories on confined metallic systems.

**Keywords:** electroabsorption; metallic nano- and subnanometer particles; nonlinear optics; Kerr coefficient; nonconjugated conductive polymers

## 1. Introduction

Nonlinear optics in metal nanoparticles within transparent dielectric media has been studied extensively [1–13]. In particular, third order optics using ultrashort (femtosecond) laser pulses in such metal nanoparticle systems have been widely studied and reported. The metallic nanoparticles of smaller diameters ( $< \sim 10$  nm) are also called quantum dots since many of their properties can be understood considering the quantum confinement of the electrons within nanometer dimensions. The third-order susceptibilities ( $\chi^{(3)}$ ) and response times of various metallic nanoparticles in dielectric media have been measured for different diameters of nanoparticles. Saturation of absorption and two-photon absorption in specific nanometallic systems have also been studied [1–12]. Very recently, we have reported quadratic electro-optic effect in metallic nanoparticles within dielectric media [6]. As our literature review has revealed no measurement of electroabsorption in metal nanoparticles has been published or known in the prior art. Using high intensity short pulses second order optical effect has also been shown for specific nanoparticles utilizing the asymmetry involved in shapes/interfaces [14]. Second order optics is not relevant to electroabsorption presented here. In our recent article, we have compared quadratic electro-optic effect in metal (gold) nanoparticles in glass with that of subnanometer-size metallic domains within doped nonconjugated conductive polymers [5]. Quadratic electro-optic effect and electroabsorption have applications in ultrafast electro-optic modulation/switching and other applications in lasers and optoelectronics.

The focus of the present report is on measurement of electroabsorption in gold nanoparticles of various sizes to further elucidate the mechanisms of nonlinear optics in these important systems. The materials also include iodine doped nonconjugated conductive polymers, such as polyisoprene, which have the smallest known metallic particles in the subnanometer domain. While electroabsorption in iodine-doped nonconjugated conductive polymers was mentioned in previous reports [15–21], here

we discuss more details and compare with gold nanoparticles in a dielectric medium. The quadratic electro-optic effect is given by:  $\Delta n = K\lambda E^2$ , where  $\Delta n$  is the change in refractive index (induced birefringence),  $K$  is defined as the real part of Kerr coefficient,  $\lambda$  is the wavelength, and  $E$  stands for the applied electric field. Since the magnitude of Kerr coefficient is typically small in metal nanoparticles within glass, a long—up to about 3 cm sample-length is used to obtain detectable modulation. For nonconjugated conductive polymers the electro-optic effect is the largest known, therefore only microns-thick samples are used for measurements. Quadratic electro-optic measurements were successfully carried out and a clear correlation between the real part of Kerr coefficient ( $K$ ) and diameter of metal nanoparticles was established down to the subnanometer domain [6]. The magnitude of the real part of Kerr coefficient ( $K$ ) was shown to have a  $\sim 1/d^3$  dependence, where  $d$  represents diameter of the metallic nanoparticle.

In this report, we discuss electroabsorption which is given by:  $\Delta\alpha = 4\pi K'E^2$ , where  $K'$  is defined as the imaginary part of the Kerr coefficient and  $\Delta\alpha$  is the change in absorption coefficient. The magnitude of  $K'$  is related to saturation of absorption and two-photon absorption coefficient ( $\alpha_2$ ), where two-photon absorption is given by  $\Delta\alpha = \alpha_2 I$ , and  $I$  stands for optical intensity. The magnitude of  $\alpha_2$  is proportional to the imaginary part of the third order susceptibility ( $\chi^{(3)}$ ). As stated earlier, while saturation of absorption and two-photon absorption in gold nanoparticles were previously reported, no measurements of electroabsorption have been reported as of yet. In this report, we discuss results of electroabsorption measurements in gold nanoparticles as well as in specific doped nonconjugated conductive polymers which have subnanometer-size metallic domains (quantum dots).

## 2. Experimental

Samples of gold nanoparticles in glass (dimensions  $\sim 4\text{ cm} \times 4\text{ cm} \times 3\text{ mm}$ ), with specific diameters of nanoparticles were purchased from a commercial vendor. These samples were characterized using optical absorption spectroscopy and the wavelengths of the surface-plasmon-resonances (abbreviated as spr) were determined. Particle sizes were determined using the surface-plasmon resonances and the relative peak intensities, utilizing established procedures [5,8,13]. These samples were used for measurement of electroabsorption at a specific wavelength.

Metal electrodes were applied on the samples of gold nanoparticles in glass samples so that the optical interaction length for modulation was about 3 cm. An ac field at 4 kHz was applied to these electrodes. The electroabsorption measurements were made using the set-up shown in Figure 1 [15–21]. Briefly, the measurements were made as discussed in the following. A He:Ne laser (wavelength 633 nm) was used since this wavelength was near the onset of the absorption due to surface-plasmon-resonance (Figure 2). Therefore, at this wavelength enhanced magnitudes of the Kerr coefficient could be expected. The laser beam passed through a polarizer, then the sample, and then through an analyzer before being detected by a photo-detector (photodiode). The polarizer and analyzer were set parallel to provide the orientation of polarization along the applied electric field. A lock-in amplifier (with 2f synchronization) and an oscilloscope were used to record the modulations. The modulation signal due to electroabsorption was recorded for various applied ac electric fields and was found to depend quadratically on the applied electric field. The imaginary part of the Kerr coefficient ( $K'$ ) was determined from the observed electroabsorption modulation, applied electric field, and interaction path-length within the samples, at a given wavelength.

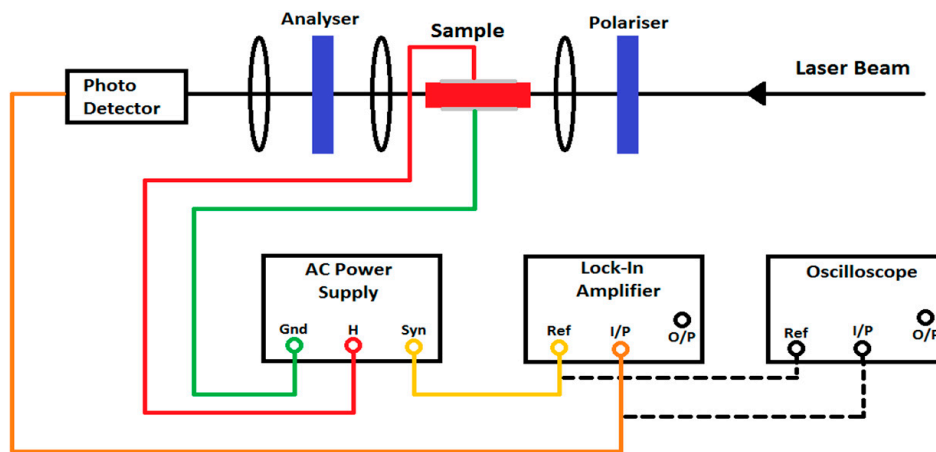


Figure 1. Experimental set-up for measurement of electroabsorption.

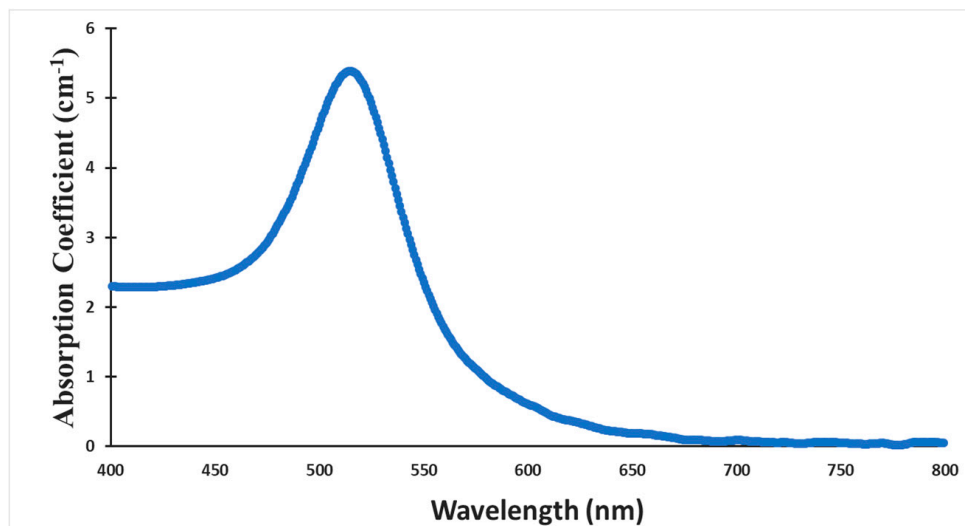


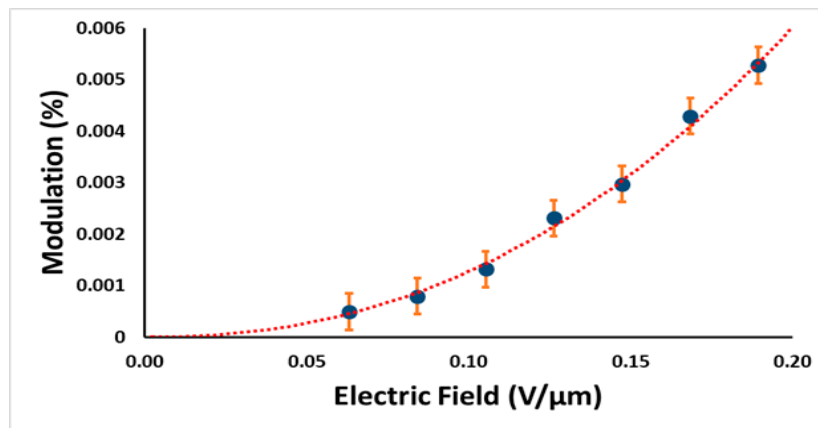
Figure 2. Surface plasmon resonance spectrum of gold nanoparticles in glass (Sample 3, peak at ~520 nm). The particle diameter ~15 nm.

### 3. Results and Discussion

Three samples gold nanoparticles in glass with three different average particle-diameters were studied as discussed in the following. Optical absorption spectrum was recorded for light travelling through the thickness of the sample-plate. The absorption peak appears at shorter wavelengths and the relative intensity of the peak decreases for smaller nanoparticles [5,8,13]. These were all discussed in our recently published article [5]. For sample 1, the peak was at ~534 nm wavelength which corresponds to a particle diameter of about 50 nm. For sample 2, the peak was at ~527 nm wavelength which corresponds to a particle diameter of about 25 nm. For sample 3 (Figure 2), the peak was at ~520 nm wavelength which corresponds to a particle diameter of about 15 nm. The absorption coefficient as given is small ( $\sim 5.3 \text{ cm}^{-1}$  at 520 nm) consistent with a low concentration ( $\sim 10^{-9} \text{ M}$ ) of gold nanoparticles in glass [5,8].

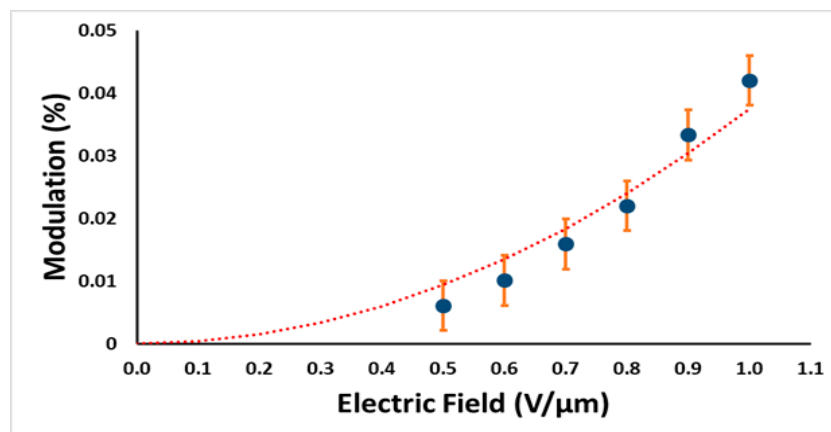
Electroabsorption measurements were made in these plates at different applied ac fields as discussed above. The beam at 633 nm from a He:Ne laser was passed through the long dimension of the plate with interaction length of 3 cm. For samples 1 and 2 having particle diameters of 50 nm and 25 nm respectively, the modulation due to electroabsorption was too weak to measure. The results of the measurements for sample 3, having a particle diameter of 15 nm, are shown in Figure 3. The imaginary

part of Kerr coefficient ( $K'$ ) as determined from the observed modulation signals is  $\sim 4 \times 10^{-15} \text{ m/V}^2$  at 633 nm.



**Figure 3.** Electroabsorption modulation in gold nanoparticles within glass for different applied electric fields. Particle diameter  $\sim 15$  nm. Interaction length  $\sim 3$  cm.

Results of measurements following identical experimental procedure but using about  $1 \mu\text{m}$  thick films of an iodine-doped nonconjugated conductive polymer (polyisoprene) are shown in Figure 4. Considering previous reports, subnanometer-size metallic domains are formed in nonconjugated conductive polymers upon doping with iodine [15–21]. A charge-transfer from an isolated carbon–carbon double bond to the dopant creates such highly confined metallic domains/quantum dots (surface plasmon resonance  $\sim 400$  nm and radical cation at  $\sim 300$  nm). The electrical conductivity, optical absorption, spectral line-width, EPR, magnetic susceptibility, vibration spectroscopic, and thermal characteristics of doped nonconjugated conductive polymer are all consistent with metallic particles of subnanometer sizes [15–21]. The optical absorption peak of nonconjugated conductive polymer is at  $\sim 400$  nm which is much smaller than that of the smallest metal nanoparticles reported so far ( $\sim 2$  nm). The absorption line-width is much wider compared to that of the smallest metal nanoparticles reported. These are as would be expected considering the particle size [8]. In addition, due to the subnanometer-sizes these metallic particles have shown the largest known Kerr coefficient and two-photon absorption coefficient for any material [13–17]. In this study, we have measured electroabsorption which is the imaginary part of Kerr coefficient ( $K$ ). The imaginary part of Kerr coefficient ( $K$ ) as measured is  $\sim 3.2 \times 10^{-11} \text{ m/V}^2$  at 633 nm for iodine-doped polyisoprene. All the magnitudes of the Kerr coefficient stated here are for about the same optical density at 633 nm.



**Figure 4.** Electroabsorption modulation in a nonconjugated conductive polymer (iodine-doped polyisoprene) for different applied electric fields. Film thickness  $\sim 1 \mu\text{m}$ .

As these results show, electroabsorption/the imaginary part of Kerr coefficient (K) increases rapidly as particle size is decreased. For particles of diameters 25 nm and 50 nm, the magnitudes of K' were too small to measure. Comparing with doped nonconjugated conductive polymer, the increase roughly goes as  $d^{-3}$ , where  $d$  is the nanoparticle-diameter. This is identical to the dependence of the real part of Kerr coefficient (K) on  $d$  as reported earlier [6]. For quadratic electro-optic measurements, the magnitudes of modulations were large enough to measure for all three sizes of gold nanoparticles in glass [6].

As in the case of quadratic electro-optic effect, this correlation between electroabsorption and  $d$  can be explained using an earlier theoretical treatment as well as more recent theory on dimensionally confined electronic systems [3,4,22–25]. According to these theories  $\chi^{(3)}$  should increase as  $d^{-3}$ . The Kerr coefficient is proportional to  $\chi^{(3)}(\omega; \omega, 0, 0)$ . In particular, K is proportional to the real part of  $\chi^{(3)}$  and K' is proportional to the imaginary part. The measurements reported here were made at 633 nm which is near the onset of the surface plasmon resonance. Therefore,  $\chi^{(3)}$  at this wavelength is complex with real and imaginary parts. The theoretical treatment mentioned above predicts that the maximum value of  $\chi^{(3)}$  is proportional to  $T_1 T_2 (1-d/d_0)/d^3$ , where  $T_1$  is the excited state life-time,  $T_2$  is the dephasing time,  $d_0$  is a characteristic threshold diameter of the system, and  $d$  is the diameter of the nanoparticle. Therefore, for  $d < d_0$ ,  $\chi^{(3)}$  increases as  $d^{-3}$ . The particle concentration would alter absorption coefficient the same way as it would alter Kerr coefficient. Since the optical density is about the same for all samples (at 633 nm) we can compare the magnitudes of Kerr coefficients at the fundamental level. As the results show, the Kerr coefficient follows the theory and increases as  $\sim d^{-3}$ .

An alternative interpretation of the  $d^{-3}$  dependence is that for any given excitation the fraction of electrons excited in a nanoparticle is higher in a smaller particle since the total number of electrons in a smaller nanoparticle is less. Therefore, a larger optical nonlinearity is expected. This is essentially a result predicted by the phase-space filling model [22–25] which states that  $\delta f/f = -(N/N_s)$ , where  $\delta f$  represents change in oscillator strength ( $f$ ),  $N$  represents the number of electrons excited, and  $N_s$  represents the total number of electrons participating in the excitation process. The value of  $N_s$  is proportional to the particle volume ( $\sim \pi d^3/6$ ) that confines the electrons. Therefore, the change in absorption coefficient  $\Delta\alpha$  which is proportional to the change in oscillator strength  $\delta f$ , should have a  $d^{-3}$  dependence. As a result, K' also has a  $d^{-3}$  dependence.

Metallic nanoparticles within transparent dielectric media are expected to have various applications in ultrafast electro-optic switching/modulation, Kerr cells and others. As the absorption coefficient is small ( $\sim 0.2 \text{ cm}^{-1}$  at 633 nm), the figure of merit for applications is high for these materials. Although this report involves metal nanoparticles in glass, the results presented can be extended to metal nanoparticles in other transparent dielectric media.

#### 4. Conclusions

Electroabsorption has been measured for the first time for metallic nanoparticles in transparent dielectric media. In particular, gold nanoparticles in glass and subnanometer-size metallic domains in iodine-doped nonconjugated conductive polymer have been studied. The measurements have been made using ac field at 4 kHz. Electroabsorption has a quadratic dependence on electric field. The imaginary part of Kerr coefficient (K) has been determined for different sizes of metallic nanoparticles. The magnitude of K' has been found to increase rapidly (as  $\sim d^{-3}$ ) for smaller diameters ( $d$ ) of nanoparticles. The magnitudes of K' are:  $\sim 4 \times 10^{-15} \text{ m/V}^2$  for 15 nm gold particles and  $\sim 3.2 \times 10^{-11} \text{ m/V}^2$  for subnanometer metallic domains in nonconjugated conductive polymer respectively at 633 nm. This is similar to the results obtained in the quadratic electro-optic measurements (real part of Kerr coefficient) of these systems reported recently [6]. Nonconjugated conductive polymers have metallic domains of subnanometer dimensions (quantum dots) leading to the largest known Kerr coefficients (real and imaginary parts). The results reported here imply various applications of these systems in ultrafast switching/modulation, and other applications in laser-optics and optoelectronics.

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