# Harmonic Generation in Metallic Nanoscale Systems

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In general, the optical response of a material brings information on the reaction of electronic structure to optical excitation and its subsequent interaction with the medium [1]. Whenever a nonlinear (NL) relation between *e.g.* the incoming electric field and the system response (polarization, polarizability) is effective, an enhancement of the response of the medium is observed. In particular, the occurrence of resonances in the material determines favorable conditions for an amplified response of the system.

In the case of metallic nanostructured materials such as nanoparticles embedded in transparent dielectric media, several electronic resonances have been investigated by means of linear optical diagnostic techniques [2]. These extensive studies have been made possible in part by the ease in obtaining reproducible samples of fairly uniform nanoparticle size. By varying the latter parameter, quantum confinement effects have been detected at small scales, followed by surface plasmon resonances which dominate the optical response in the tens of nanometer scale. A tremendous amplification of these effects occur when the nonlinear response is considered [3]. This is especially true when one considers for a comparison the relative amount of active material. Indeed, very small amounts of metal are needed for obtaining strong nonlinear effects. These have been observed in second harmonic (SH) [4], third harmonic generation [5], parametric and four-wave-mixing effects [6]. In addition, one may also take into account the effect of density of individual nanostructures. In the dilute case the response may be thought of as the nonlinear equivalent of the Rayleigh scattering, with independent NL response of individual nanoparticles. On the contrary, in a condensed material a macroscopic polarization picture well represents the experimental situation. Correlation in the optical response in this case gives rise to coherent and collimated optical beams.

In an effort towards a more complete understanding of the NL optical response occurring in nanostructures, we have studied the SH generation in metal nanoparticle monolayers and multilayers obtained by evaporation – condensation in the Vollmer-Weber mode on transparent substrates. The second-order nonlinear interaction of femtosecond laser pulses gives rise to a SH signal in the transmitted direction as well as in reflection. By changing the nanoparticle size or, alternatively, by varying the laser wavelength one obtains a resonant behavior for the nonlinear transmittance/reflectance. Similar evidence of an increase in the optical nonlinear response is obtained when these metal nanoparticles are subject to temperature cycling across the solid (at ≈ 150 K) to liquid (at room temperature) phase transition [7]. Here the effects of hysteresis in the response is amplified by significant factors with respect to the linear optical response. All these observations concur to the notion of an enhanced optical response in the nonlinear domain for materials structured on a nanometric scale.

References:
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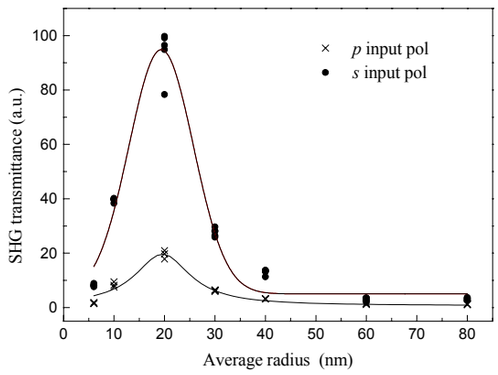


Figure 1. Nonlinear transmittance at near normal incidence of Ga nanoparticle monolayers embedded in $TiO_2$ matrix as a function of mean particle radius. The excitation source is a 130 fs Ti:sapphire laser operating at 810 nm in both input *p* and *s* polarizations. The input fluence is 4 $10^{-5}$ J/cm$^2$.

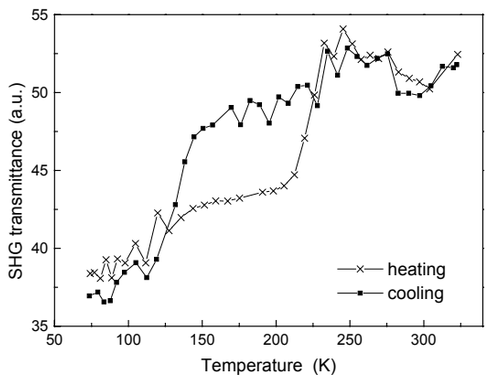


Figure 2. Nonlinear transmittance at near normal incidence of a 20 nm average radius Ga nanoparticle monolayer (pump wavelength at 810 nm) as a function of sample temperature. Squares refer to the cooling cycle from room temperature, crosses to heating from $LN_2$ back to room temperature.