

# Sensitized nonlinear emission of gold nanoparticles

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**Abstract:** We have studied Stokes and anti-Stokes emission of Au nanoparticles suspended in pure methanol and methanol solution of rhodamine 6G dye. In the presence of dye, excitation of anti-Stokes emission of gold involves two-photon absorption in rhodamine 6G molecules followed by the energy transfer to Au nanoparticles with simultaneous absorption of one pumping photon by Au. The sensitization by dye molecules caused six-fold enhancement of the anti-Stokes emission of gold nanoparticles.

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**OCIS codes:** (190.0190) Nonlinear Optics; (260.3800) Luminescence; (260.2160) Energy transfer; (350.4990) Particles

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## 1. Introduction

Luminescence of noble metals was first observed by Mooradian in 1969 [1]. The emission of gold was broadband, with the maximum at 520 nm and the efficiency of the order of 10-10 [1]. Photoluminescence from Au surfaces and nanoparticles with the maximum ranging between 500 and 590 nm has been reported in a number of more recent publications [2-6]. Several researchers observed emission of gold nanoparticles with the maximum at 410-430 nm [2,3,7].

Luminescence in metals is a three-step process involving photoexcitation of electro-hole pairs, relaxation of excited electrons and holes, and emission from the electron-hole recombination [1, 2]. In gold, the range of emission wavelength 500-590 nm corresponds to electronic transitions between the *sp* band just below the Fermi level and the first *d* band ( $d_1$ ) in the vicinity of the point L in the Brillouin zone, process A in Fig. 1. The second emission band, 410-430 nm, is due to recombination of electrons with holes in the lower energy band  $d_2$ , process B in Fig. 1.

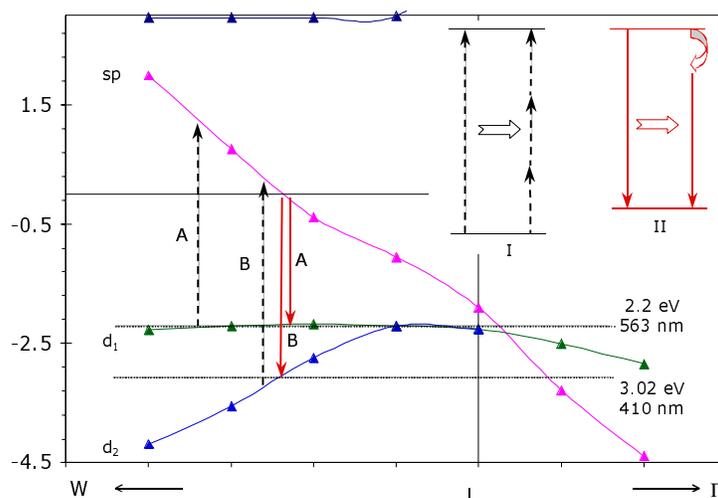


Fig. 1. Fragment of the calculated energy level diagram of Au in the vicinity of the high-symmetry point L. Dashed lines – absorption transitions stimulated by 354.7 nm photons creating holes in the d-bands. Solid lines – spontaneous emission caused by recombination of electrons relaxed to the Fermi level and holes in the two d-bands. Inset schematically illustrates modification of the excitation scheme at 1064 nm pumping: one-photon pumping is replaced by three-photon pumping.

Emission of Au nanostructures is strongly enhanced (up to four-to-six orders of magnitude) by surface plasmon resonances occurring in nanostructures [2-6]. The two alternative mechanisms by which surface plasmons (SPs) can increase the emission intensity are: (1) enhancement of radiative electron-hole recombination by local fields [2, 6] and (2) nonradiative electron-hole recombination emitting surface plasmons which, in turn, radiate giving rise to luminescence [3]. SPs play a particularly important role in multi-photon induced emission of gold, which can be observed on roughened surfaces but not on smooth surfaces [2]. The decay time of Au luminescence is short,  $\leq 3.2$  ps according to Ref. [3] and  $\leq 50$  fs according to Ref. [5].

In this work, we studied Stokes and anti-Stokes emission of Au nanoparticles suspended in methanol and methanol solution of rhodamine 6G laser dye. We have explained strong anti-Stokes emission of gold in the presence of dye in terms of two-photon absorption in rhodamine 6G molecules followed by the energy transfer to Au nanoparticles with simultaneous absorption of one pumping photon by Au.

## 2. Absorption spectra of bulk gold and gold nanoparticles

The electronic energy structure of bulk gold and the projected density of states (PDOS) have been calculated using the density functional theory (DFT) [8-10] in a generalized gradient approximation (GGA) [10], employing ultra-soft *ab initio* pseudopotentials (PP) [11] and accounting for relativistic effects. The quasi-particle (QP) corrections to electron eigenvalues have been calculated according to Ref. [12]. The fragment of the calculated energy diagram is shown in Fig. 1. The calculated QP-corrected electron energy values are in good agreement with the recent results of the time-dependent current-density functional theory analysis of Ref. [13].

Optical absorption spectra, Fig. 2, have been calculated using the computed eigenfunctions and eigenenergies of bulk Au as inputs. Interband electronic contributions to the optical absorption spectra have been calculated within the random phase approximation (RPA) [14]. Free electron contribution is incorporated through the addition of the Drude term to the optical response function. The calculated absorption spectrum of bulk gold features, among others, the bands in the vicinity of 350 nm and 416 nm, Fig. 2. The absorption spectrum of Au derived from the data published in Ref. [15] is in a reasonably good agreement with the calculated one.

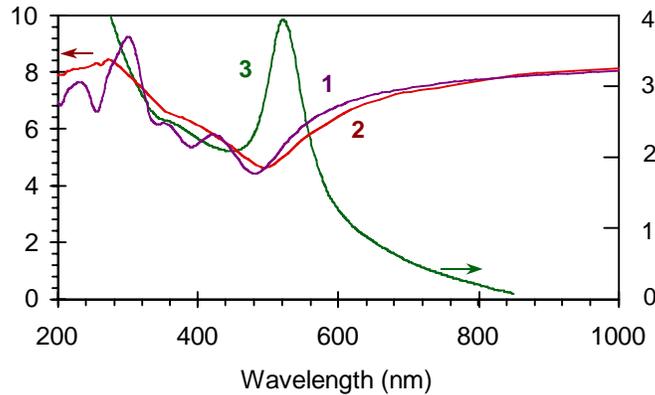


Fig. 2. Trace 1 - Calculated absorption spectrum of bulk gold; trace 2 – absorption spectrum of bulk gold derived from the data published in Ref. [15]; trace 3 – experimental absorption spectrum of the suspension of Au nanoparticles in methanol, exposed to laser radiation.

The majority of Au particles in the experimental samples were shaped as slightly deformed spheres with the average diameter of the order of  $d \approx 200-250$  nm. In addition, Au powder contained clusters of  $\leq 50$  nm nanoparticles, which sizes were close to the resolution limit of our scanning electron microscope (SEM). The original unexposed suspension of Au particles in methanol was almost colorless, with a light golden tint.

When the suspension of Au particles was exposed to a laser radiation for several minutes ( $\lambda = 1064$  nm,  $t_{\text{pulse}} \approx 10$  ns, 10 Hz repetition rate, 18 mJ per pulse, pumped spot diameter 0.3 to 2 mm), it became opaque with intense dark bluish coloration. SEM images of the sample after the laser exposure showed clusters of almost perfectly shaped 200-400 nm nanospheres as

well as many small  $\leq 50$  nm nanoparticles. The resolution of our SEM did not allow us to see the difference between small nanoparticles before and after the laser exposure.

The absorption spectrum of the suspension of Au nanoparticles *after* the laser exposure is dominated by the intense band centered at 522 nm (Fig. 2), which is attributed to surface plasmon (SP) resonance in metallic nanospheres. (The Mie theory predicts the maximum of the SP resonance in small ( $d \leq 50$  nm) gold particles suspended in methanol to be at  $\lambda \approx 522$  nm [15,16].) A less pronounced absorption shoulder is seen at  $\approx 365$  nm. It closely matches the absorption bands predicted theoretically (Fig. 2, trace 1) and reported in Ref. [15]. We hypothesize that small Au nanoparticles, which determine the color of the suspension after irradiation, appear in result of breaking clusters of  $\leq 50$  nm nanoparticles or fracturing larger Au particles by intense laser light. According to the Mie theory, a strong red shift of the SP extinction band is expected at  $d > 50$  nm [15,16]. The fact that no significant red-shifted absorption or scattering has been observed experimentally suggests that the concentration of large gold particles was low or they quickly precipitated to the bottom of the cuvette.

### 3. Stokes and anti-Stokes emission of gold nanoparticles suspended in methanol

At excitation of the suspension of Au nanoparticles in methanol with the third harmonic of Q-switched Nd:YAG laser ( $\lambda = 355$  nm,  $t_{\text{pulse}} \approx 10$  ns), we have recorded the emission spectrum consisting of two bands centered at  $\sim 555$  nm and  $\sim 425$  nm, Fig. 3. The emission was collected from the front of the cuvette, which was exposed to the laser light. The emission spectra were normalized to the spectral response of the apparatus. The two observed emission bands were red shifted in respect to the two absorption bands (at 522 nm and 365 nm) depicted in Fig. 2. The careful analysis of the absorption and emission spectra, Figs. 2 and 3, suggests that the valley between the two emission bands is not due to spectral filtering caused by the SP absorption.

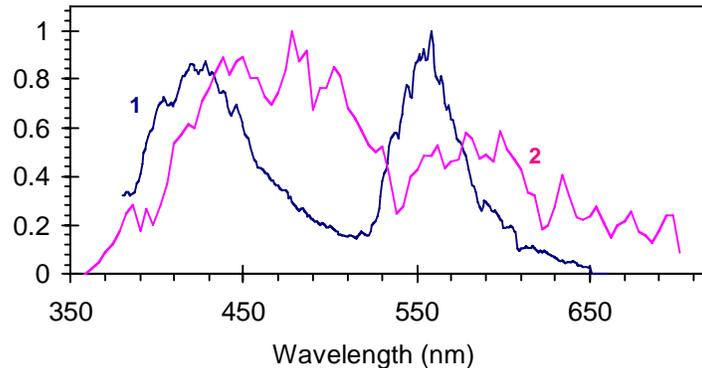


Fig. 3. Trace 1 - emission spectrum of the suspension of Au particles in methanol excited by the 3rd harmonic of the Q-switched Nd:YAG laser ( $\lambda = 354.7$  nm); trace 2 emission spectrum of the same suspension pumped by the fundamental wavelength ( $\lambda = 1064$  nm).

Following Boyd *et al.* [2], we assumed the scheme of excitation and emission depicted in Fig. 1. At the first step, electrons are excited from the  $d$ -bands below the Fermi level to the  $sp$  band above the Fermi level. After that electrons relax to the Fermi level *via* a variety of radiationless processes as well as holes scatter within the  $d$ -bands to match the positions of electrons in the momentum space. Finally, vertical recombination transitions terminating at the two bands  $d_1$  and  $d_2$  generate luminescence in the yellow-green and violet ranges of the spectrum. The predicted emission maxima correspond to  $\sim 563$  nm (experiment 555 nm) and  $\sim 410$  nm (experiment 425 nm). This is a remarkably good agreement between the experiment and the theory. A small difference between the calculated and experimentally measured

maxima of the emission bands can be explained by the tendency of the emission bands to shift toward the maximum of the SP band (522 nm), where the field enhancement facilitates the radiative recombination.

An emission spectrum resembling that recorded at the 354.6 nm excitation has been observed at the 1064 nm pumping ( $t_{\text{pulse}} \approx 15$  ns), Fig. 3. The emission bands at the infrared excitation were weak, noisy, and red-shifted in comparison to those observed at the ultraviolet pumping. At small pumping energy, the emission intensities in both spectral bands were proportional to cubic power of the pumping energy, which confirms three-photon character of absorption.

The mechanism of excitation of anti-Stokes emission can be similar to that shown in Fig. 1, with the only difference that three-photon absorption occurs in place of single-photon absorption. According to Fig. 1, the energy of two 1064 nm photons would be sufficient for the excitation of electrons from *d*-bands to *sp*-bands above the Fermi level. The second order process with two-photon excitation and one outgoing photon (second harmonic generation) is not allowed in centro-symmetric crystals of gold. Two-photon excitation is allowed only as a part of a third order process (two-photon absorption or other processes involving virtual electron states) and should result in a slope efficiency equal to three. That is why no emission signal with the slope equal to 2 should be expected from the bulk of Au nanoparticles. According to our model, the emission of Au nanoparticles is a volume effect characteristic of bulk gold. The effect of the SP resonance on the positions of the emission bands is small (if any). Correspondingly, particles of all sizes could contribute to the observed luminescence.

The red shift of the emission spectrum at the three-photon pumping can possibly be explained by the two reasons. (1) Contributions to the emission are coming not only from the transition in the vicinity of the high symmetry point L (Fig. 1), but also from other low symmetry *k*-points within the Brillouin zone, which correspond to optical transitions with slightly different energies. If at single-photon pumping and at three-photon pumping these transitions are excited with different *relative* probabilities, this may explain the difference between the corresponding emission spectra. (2) Strong 1064 nm pumping could cause the temperature increase of Au nanoparticles. One can speculate that at high temperature, phonon-assisted radiative transitions become significant and determine the red shift of emission. The study of the phonon-related effects in Au nanoparticles is beyond the scope of this paper.

#### 4. Sensitized emission of gold nanoparticles in the presence of rhodamine 6G dye

Rhodamine 590 Chloride (rhodamine 6G or R6G) was dissolved in methanol in concentrations ranging from 0.01 g/l ( $2.1 \times 10^{-5}$  M) to 2.5 g/l ( $5.3 \times 10^{-3}$  M). The absorption spectrum of R6G features strong 528 nm band and much weaker 346 nm band, which are assigned to the transitions between the electronic and vibronic levels of the ground singlet state  $S_0$  and excited singlet states  $S_1$  and  $S_2$ , respectively [17]. At the 354.6 nm excitation, the Stokes-shifted emission bands corresponding to the same two transitions are found at ~566 nm and ~398 nm, respectively, Fig. 4.

A relatively strong emission of R6G dye with the maximum at ~572 nm was observed at the 1064 nm pumping. At the same time, no detectable emission signal in the vicinity of 400 nm was found at the infrared excitation in pure R6G dye solution.

The emission spectrum of the mixture of R6G dye with Au nanoparticles is shown in Fig. 5. The band of yellow-green emission with the maximum at 574 nm resembles that in pure R6G dye. Based on the spectral shape of this band, we conclude that it is predominantly due to the emission of dye. At the same time, the shape of the violet emission band with the maximum at 438 nm is closer to that of gold than that of R6G, Fig. 5. Correspondingly, we assign this band to Au nanoparticles. The second emission band of gold (around 555 nm) is covered by a much stronger 574 nm emission band of R6G.

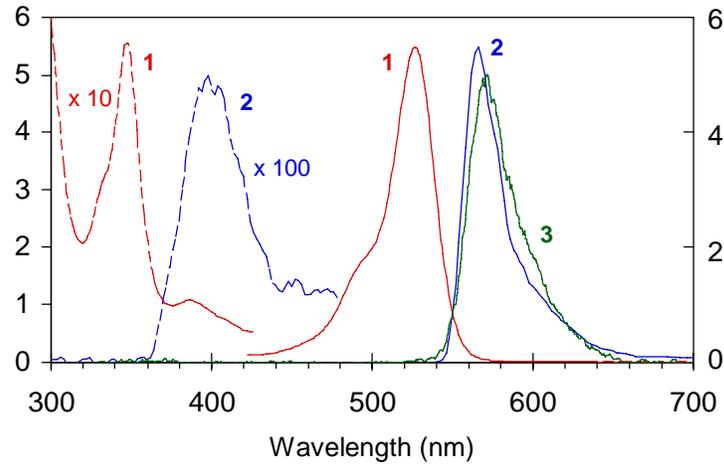


Fig. 4. Absorption spectrum (1) and emission spectra (2,3) of the methanol solution of rhodamine 6G, 10 mg/l ( $2.1 \times 10^{-5}$  M). The emission is excited by 354.6 nm light (trace 2) and 1064 nm light (trace 3). Short-wavelength absorption and emission bands are magnified tenfold and hundred-fold, respectively.

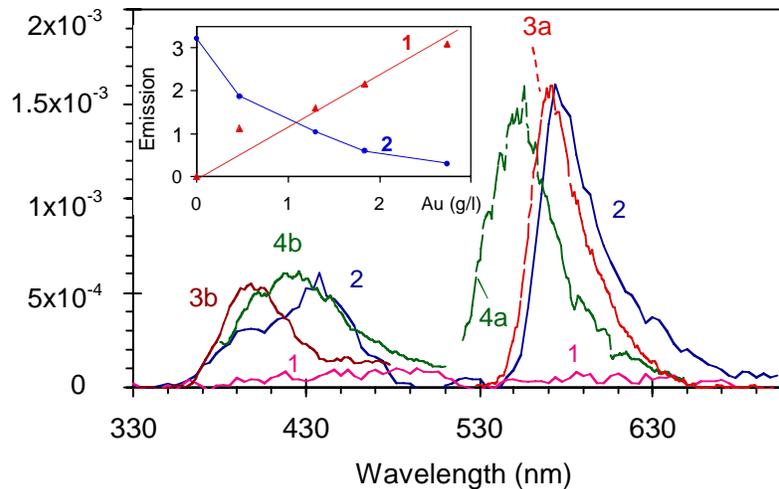


Fig. 5. Emission spectrum of the suspension of Au nanoparticles in methanol (trace 1) and in methanol solution of R6G (trace 2) at excitation with Q-switched laser pulses at  $\lambda=1064$  nm. Concentration of Au nanoparticles is 3.4 g/l, and concentration of R6G (in the case of trace 2) is 0.5 g/l ( $1.04 \times 10^{-3}$  M). Spectra 3 and 4 are added for comparison. Trace 3a – R6G solution pumped at 1064 nm. Trace 3b – R6G solution pumped at 354.7 nm. Traces 4a and 4b – suspension of Au nanoparticles in methanol pumped at 354.7 nm; traces 4a and 4b have different multiplication factors. Inset: Dependence of the intensity of the violet emission band (1) and yellow-green emission band (2) on Au concentration in the Au-R6G mixture pumped at 1064 nm. Starting concentration of R6G in the solution is 0.1 g/l ( $2.1 \times 10^{-4}$  M).

The intensity of the violet anti-Stokes emission of gold increased dramatically as Au nanoparticles and R6G dye were mixed together. When R6G dye (in concentration 0.5 g/l ( $1.04 \times 10^{-3}$  M)) was added to the suspension of Au nanoparticles (in concentration 3.4 g/l), the intensity of the violet anti-Stokes emission increased six-fold, Fig. 5.

When Au nanoparticles were added to a pure R6G solution, the violet emission increased nearly linearly starting from zero, inset of Fig. 5. At the same time, the intensity of the yellow-green R6G emission in the mixture decreased with the increase of Au concentration. This behavior suggests an existence of the energy transfer from R6G to Au that significantly enhances the efficiency of the violet anti-Stokes emission of gold. The proposed mechanism of the sensitization of anti-Stokes emission of Au nanoparticles by R6G dye is shown schematically in Fig. 6. In the presence of dye, the excitation of anti-Stokes emission of gold involves two-photon absorption in rhodamine 6G molecules followed by the energy transfer to Au nanoparticles with simultaneous absorption of one pumping photon by Au. We assume that the R6G→Au energy transfer is of the Förster type. Correspondingly, its efficiency should be proportional to the overlap integral of the emission spectrum of dye and the absorption spectrum of gold and independent of the pumping intensity.

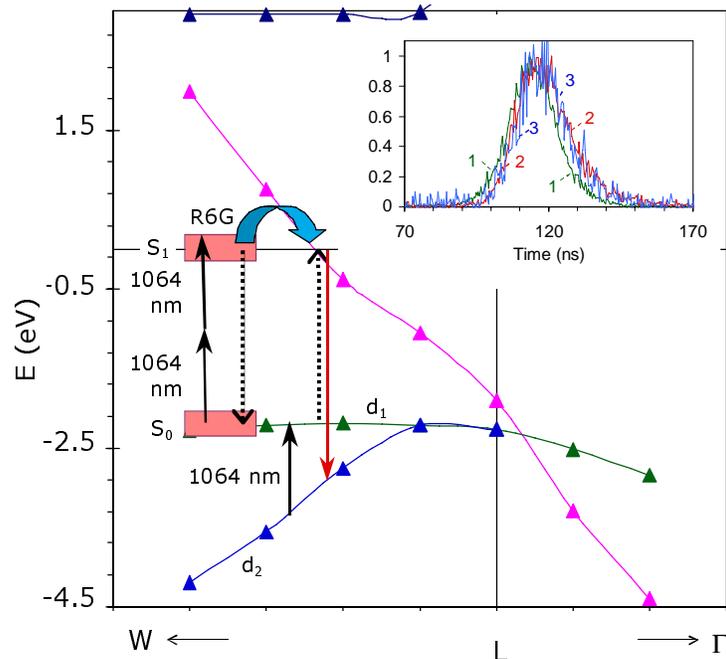


Fig. 6. Sensitization of anti-Stokes emission of Au nanoparticles by R6G dye. The process involves a two-photon absorption in R6G (1064 nm photons); R6G → Au energy transfer, promoting electron from the upper d band to the sp band (dotted lines); absorption of the 1064 nm photon at the transition  $d_2 \rightarrow d_1$ , and emission of the violet photon. Inset: 1 – pumping pulse at  $\lambda=1064$  nm, 2 – two-photon pumped emission kinetics of R6G dye at  $\lambda=570$  nm; and 3 – emission kinetics of Au at  $\lambda=400$  nm. Concentrations of R6G and Au in the mixture are 2.5g/l ( $5.3 \times 10^{-3}$  M) and 4 g/l, respectively.

Note that none of the anti-Stokes emission signals discussed in this paper could be observed in pure methanol or empty glass cuvette.

Although the duration of the pumping pulse, ~15 ns, was rather long in comparison with the characteristic luminescence decay times in the samples studied, we were able to make two useful observations. (I) The 570 nm emission of dye in pure R6G and Au-R6G mixtures was delayed by several nanoseconds in comparison to the pumping pulse and its decay kinetics

was noticeably elongated. (II) Anti-Stokes emission kinetics of gold ( $\lambda=400$  nm) in the Au-R6G dye mixture closely resembled the emission kinetics of dye, inset of Fig. 6.

The rate equation analysis, which will be published elsewhere, shows that the delay and the elongation of the emission kinetics of dye are due to a relatively long life-time  $\tau$  of the singlet state  $S_1$  (few nanoseconds) and reabsorption in highly concentrated R6G solution. Based on the resemblance of the emission kinetics of dye and the anti-Stokes kinetics of Au, we conclude that R6G $\rightarrow$ Au energy transfer is an integral part of the excitation mechanism of luminescence in gold (in agreement with the conclusion based on the emission intensity measurements, Fig. 5).

## 5. Summary

To summarize, we have observed a new mechanism of excitation of anti-Stokes emission of gold. Sensitization *via* energy transfer from excited dye molecules strongly enhances emission of Au nanoparticles in rhodamine 6G solution.

## Acknowledgment

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