# Enhanced two-photon fluorescence of molecules adsorbed on silver particle films

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The two-photon fluorescence intensity from Rhodamine *B* molecules adsorbed onto silver particle films is enhanced 150-fold compared with molecules in solution. This is accounted for in terms of local-field amplification of the incident intensity when the absorbing state of the molecules lies within the plasma resonance bandwidth of the silver particles. For diphenylanthracene and Nile Blue, when the absorbing state lies above the particle resonance, no enhancement is observed, even though the luminescence falls within the resonance bandwidth.

Since the discovery of surface-enhanced Raman scattering[1] much effort has been devoted to understanding the nature of the interaction of molecules with rough metal surfaces. Several experiments have shown that the enhanced Raman cross section on rough surfaces is due to the amplification of the incident and radiated optical fields by plasma resonances of the metal as described theoretically by a simple electromagnetic model.[2]

It is evident from this model that other linear and nonlinear optical processes close to or within small metal particles should also be enhanced. It has already been demonstrated[3] that the luminescence of dye molecules adsorbed onto silver and gold particle films is enhanced when the dye molecule absorption falls within the plasma resonance bandwidth of the films. Enhanced second-harmonic generation without absorbed molecules has also been demonstrated.[4]

The purpose of this Communication is to demonstrate that the two-photon absorption cross section of molecules on silver particle films is enhanced by the amplified local field on resonance. Conditions for which enhancement occur are investigated by varying the optical properties of the particle film and the adsorbed molecules whereby either the absorbing or emitting state falls within the resonance bandwidth.

## I. LOCAL-FIELD ENHANCEMENT OF LINEAR AND TWO-PHOTON FLUORESCENCE

The local field $E_{\rm loc}$ close to, but outside the surface of a metal particle, which is small compared to the wavelength of the incident light, is[4,5]

$$E_{\rm loc}=\left(\frac{\epsilon(\omega_i)}{1+A[\epsilon(\omega_i)-1]}\right)E_{\rm inc}=f(\omega_i)E_{\rm inc}\ , \quad (1)$$

where $\epsilon(\omega_i)=\epsilon_1(\omega_i)+i\epsilon_2(\omega_i)$ is the dielectric function of the metal at the incident optical frequency $\omega_i$, $A$ is a modified depolarization factor which depends on the particle shape and particle density, and $E_{\rm inc}$ is the incident optical field. The local-field factor $f(\omega_i)$ can become large on resonance where $\epsilon(\omega_i)\sim 1-1/A$.

The excitation rate $R$ of molecules adsorbed onto the particles can now be written

$$R=N\sigma I_{\rm loc}(\omega_i)$$
$$=N\sigma_0 f^2(\omega_i)I(\omega_i)+N\sigma_1 f^4(\omega_i)I^2(\omega_i)\ ,$$

where only the linear absorption cross section $\sigma_0$ and two-photon cross section $\sigma_1$ are included. $N$ is the density of adsorbed molecules and $I_{\rm loc}(\omega_i)$, $I(\omega_i)$ are the local and incident intensities. On resonance the linear excitation rate is enhanced by the factor $f^2(\omega_i)$, while the two-photon excitation rate is enhanced by the factor $f^4(\omega_i)$ provided the molecule absorption falls within the resonance bandwidth of the metal particles.

Following excitation the molecule may decay radiatively at frequency $\omega_R$ or nonradiatively by relaxation within the molecules, or by excitation transfer to the silver particle.

The intensity of luminescence $I(\omega_L)$ is $qR|f'(\omega_L)|^2$, where $q$ is the radiative quantum efficiency of the molecule which depends on the molecule-particle coupling and $f'(\omega_L)$ is the local-field factor appropriate for luminescence.

## II. EXPERIMENTAL PROCEDURE

Three frequency parameters can be controlled experimentally: $\omega_i$, $\omega_L$, and $f(\omega)$. The absorption and luminescence spectra of the molecules define $\omega_i$ and $\omega_L$ while the microstructure of the silver film defines $f(\omega)$. We have shown previously[3] how a silver wedge film having a mass thickness $d_m$ varying continuously from zero to 200 Å provides a structure of

continuously varying optical properties as a function of position on a glass or sapphire substrate. The plasma resonance shifts to longer wavelengths with increasing mass thickness of film. Dilute solutions ($\sim 10^{-3}$ to $10^{-4}M$) of molecules in ethanol or cyclohexane are spun at 2000 rpm onto the substrate before or after evaporation of the silver island wedge. The thickness of the adsorbed layer varies according to the concentration of the solution and can be adjusted to give approximately a monolayer coverage, as determined by optical absorption of the coated substrate.

This sample preparation technique provides a continuous variation of $f(\omega)$ across the substrate while keeping $\omega_i$, $\omega_L$, and other experimental variables, such as optical alignment, constant. The local-field factor can be calculated from the measured optical absorption $A(\omega_i,d_m)$ and transmission $T(\omega_i,d_m)$ as a function of position[5]

$$|f(\omega_i,d_m)|^2=\frac{\lambda_i}{2\pi d_m}\frac{A(\omega_i,d_m)}{T(\omega_i,d_m)}\frac{|\epsilon(\omega_i)|^2}{\epsilon_2(\omega_i)} .$$

This makes the approximation that $\epsilon(\omega)$ of the outside surface of the particles is unity, which is only expected to be good for dye layers of submonolayer thickness.[6]

The experimental data reported here correspond to three distinct cases: (a) Rhodamine $B$, for which $\omega_i \sim \omega_L \sim \omega_p$ for linear excitation and $2\omega_i \sim \omega_L \sim \omega_p$ for two-photon excitation. $\omega_p$ is a frequency within the broad plasma resonance of the silver film observed in absorption.[3] (b) Diphenylanthracene (DPA), which for linear excitation $\omega_i \gg \omega_p$ and $\omega_L \sim \omega_p$ and for two-photon excitation $\omega_i$, $\omega_L \sim \omega_p$. (c) Nile Blue, which has two linear absorption bands such that either $\omega_i$, $\omega_L \sim \omega_p$ or $\omega_i > \omega_p$ and $\omega_L \sim \omega_p$. This last experiment was designed to distinguish the enhancement factor for absorption, $f(\omega_i)$, from that due to luminescence $f'(\omega_L)$. For two-photon excitation the samples were excited by a continuous train of pulses of average power $\sim$300 mW, from a mode-locked Nd:YAG laser at 1.06 $\mu$m (140-ps pulses) or with a model-locked $Ar^+$ laser at 514.5 nm (100-ps pulses). This allowed us to excite the molecules with high peak intensity without burning the silver films. Sapphire substrates were used to heat sink the particles. Quadratic dependence of the luminescence intensity on the input power was verified and the usual precautions for filtering luminescence were taken. For the linear excitation experiments the sources were either a flashlamp-pumped dye laser using Coumarin 522 for 530- and 260-nm excitation (frequency doubled), oxazine 170 frequency doubled for 360-nm excitation, and a c.w. HeNe laser for 632.8-nm excitation. The peak dye laser intensity was kept below 1 kW/cm$^2$ to avoid nonlinear effects.

## III. RESULTS

### A. Rhodamine B

The luminescence intensity at 0.59 $\mu$m from Rhodamine $B$ using linear excitation at 0.53 $\mu$m and two-photon excitation at 1.06 $\mu$m is shown in Fig. 1(a) as a function of mass thickness on the same silver film. The left- and right-hand sides of the figure correspond to luminescence from molecules on sapphire (zero Ag thickness) and thick silver films (>500 Å) which have no particulate structure. An intensity reference of $6\times10^{14}$ molecules/cm$^2$ was obtained with a 1-mm-thick cell of $10^{-5}M$ solution of Rhodamine $B$ in ethanol, inserted in place of the sample. The density of dye molecules on the sapphire was estimated from the linear optical absorption assuming the same absorption cross section as the molecules in solution. From these data the linear and two-photon luminescence efficiency per molecule on the silver film could be compared with the same molecule in solution. These ratios are plotted on the vertical axes of Fig. 1(a).

The linear luminescence intensity peaks at a silver mass thickness of about 60 Å, the peak intensity being five to six times that from the dye-coated sap-

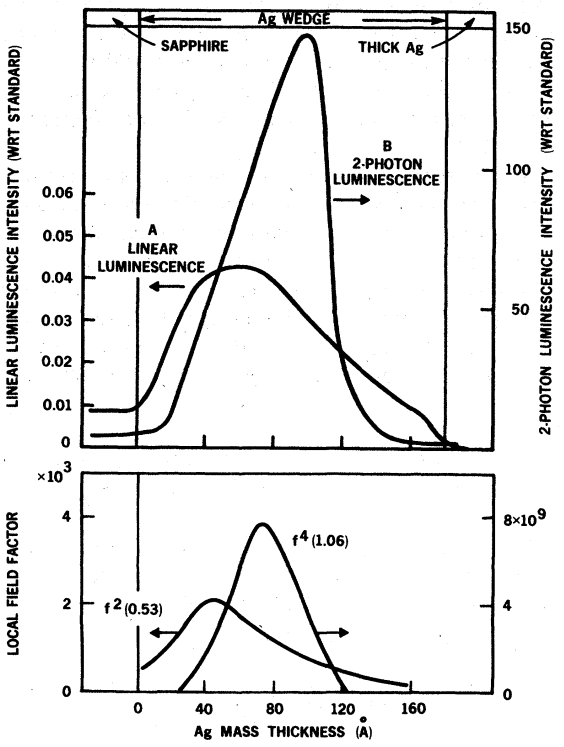


FIG. 1. (a) Linear and two-photon luminescence of rhodamine $B$ at 0.59 $\mu$m as a function of silver film thickness for incident wavelengths of 0.53 and 1.06 $\mu$m, respectively. (b) Calculated local-field factors $f^2(0.53)$ and $f^4(1.06)$ for linear and two-photon absorption.

phire. The quantum efficiency is considerably less than unity at all positions on the substrate. The luminescence following two-photon excitation is seen in Fig. 1(a) to peak at greater mass thickness of silver than the linear luminescence and the peak intensity is some 150 times greater than the reference sample.

To verify that the luminescence was indeed due to two-photon absorption and not due to linear absorption of 0.53-$\mu$m light generated by surface second-harmonic generation (SHG) in the silver particles, the SHG intensity was measured directly on the same film. The SHG signal was considerably smaller than the two-photon luminescence.

The local-field factor $f^2(0.53)$ and $f^4(1.06)$ for linear and two-photon excitation, calculated from the optical-absorption and transmission data, are plotted in Fig. 1(b). The luminescence enhancement factor $f'(\omega_L)$ cannot be obtained directly from the absorption data. However, if we take $f'(0.59)=1$, which is justified later by the experiments with Nile Blue, then qualitative agreement between Figs. 1(a) and 1(b) is seen to be good. The observed shift of the luminescence maximum toward greater mass thickness of silver for two-photon excitation is predicted by the model, and the general shapes of the two sets of curves are similar. Quantitative comparison of the two figures cannot be made because of the unknown value of the luminescence quantum efficiency $q$ of molecules on the silver films, and because of the unknown effect of $f'(\omega_L)$. Quenching of the luminescence by excitation transfer from the molecules to the metal particles decreases the observed enhancement and this appears to be important in these experiments. The predicted enhancement of the absorption process alone is about $8\times10^9$ for two-photon excitation compared with only 150 observed experimentally. The major part of the predicted enhancement ($\sim10^7$) is due to the large negative value of $\epsilon_1$ at 1.06 $\mu$m. In any case, there are obvious limitations to the simple model of dye-coated ellipsoids. Those molecules which fall between particles on the sapphire substrate experience smaller local fields and lower quenching rate than molecules directly on the silver surface, and not all molecules on the particles experience the same local field.

### B. Diphenylathracene

In the preceding experiment with Rhodamine $B$ all the optical frequencies lay within the plasma resonance bandwidth of the silver particles. DPA on the other hand has an excited state at 260 nm, well above the silver resonance, which has a large two-photon cross section for 514.5-nm excitation. The luminescence lies at 430 nm within the silver resonance bandwidth. Measurements of the luminescence intensity, with respect to a reference solution

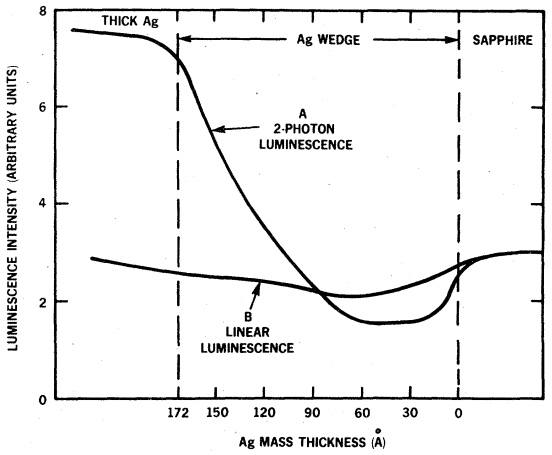


FIG. 2. Linear and two-photon luminescence of diphenylanthracene at 0.43 $\mu$m as a function of silver film thickness for incident wavelengths of 0.268 and 0.5145 $\mu$m, respectively.

as before, are shown in Fig. 2. Neither two-photon excitation at 514.5 nm nor linear excitation at 260 nm results in any enhanced luminescence on any part of the film. Indeed, a slight quenching is observed in the region of silver particles. The luminescence increases somewhat with increasing silver thickness because of reflected light at the silver surface.

This result was unexpected since a local-field enhancement factor $f^4(0.5145)\sim7\times10^6$ was calculated from the optical spectra. The different behavior of DPA and rhodamine $B$ may be attributable to the fact that $f^4(0.5145)$ is 1000-fold smaller than $f^4(1.06)$ (due to the smaller magnitude of $\epsilon_1$ at shorter wavelengths) with the result that quenching of the luminescence by excitation transfer to the silver is dominant. The excited state of DPA lies well above the plasma resonance of the silver particles for all positions on the film, and falls within the spectrum of interband transitions of silver. This does not explain why some luminescence is observed, even on the solid silver, unless a fraction of the molecules are not close to the silver surface due to clustering of molecules.

It is also worth noting that no enhancement of the surface second harmonic signal was observed from these particle films with 0.5145-$\mu$m excitation. The polarization at the second harmonic must be damped by carrier excitation in the silver particles.

### C. Nile Blue

The previous experiments demonstrate that luminescence enhancement occurs only when the excited state of the molecule lies within the plasma resonance bandwidth of the silver particles. To investigate this further, Nile Blue was chosen because it has

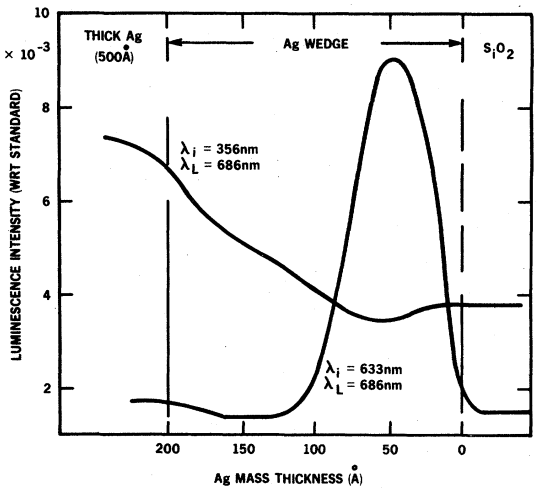


FIG. 3. Linear luminescence of Nile Blue at 0.686 $\mu$m when excited at 0.356 and 0.633 $\mu$m as a function of silver film thickness.

one absorption band at 0.63 $\mu$m within the plasma resonance bandwidth and a second weaker absorption band lying above the resonance at 360 nm, in the region where the silver film is most transparent. In solution, excitation in either of these bands gives rise to luminescence at 0.69 $\mu$m within the particle resonance bandwidth. Thus it may be possible to separate the enhancement factor of the emitted wave from that of the incident waves. The results are shown in Fig. 3. As before,[3] a pronounced maximum of the luminescence is observed for a silver mass thickness near 60 Å when excited with 632.8-nm radiation. However, when the same film is excited with 360-nm radiation no luminescence enhancement is observed.

Since only the wavelength of the exciting light was charged, this experiment suggests that the observed enhancement is due to local-field amplification of the incident intensity $f(\omega)$ and not due to amplification of the luminescence $[f'(\omega) \sim 1]$.

## IV. DISCUSSION

The factor $f(\omega)$, calculated from Eq. (1) from the measured optical absorption of the film, corresponds to the case of a coherent set of interacting point dipoles excited by the incident light. The interaction leads to the shift of the observed resonance to larger wavelengths from that of the isolated particle. However, $f'(\omega)$ cannot be obtained directly from the absorption data since the coupling of the incoherent molecular emission with higher-order multipoles of the silver particles may be important.[7] The small value of $f'(\omega)$ suggested by the Nile Blue experiments implies rather weak coupling of the emitting molecule with the dipole mode of the particle.

This explanation also accounts for the absence of enhanced luminescence with linear excitation of DPA. However, two photon excitation of DPA with 514.5-nm radiation should lead to enhanced absorption and hence enhanced luminescence which was not observed experimentally. We can only account for this in terms of quenching of the excited state by alternative nonradiative relaxation paths in the silver particle.

Finally, the results for linear and two-photon excitation of Rhodamine *B* are in good agreement with the electromagnetic model. The observed two-photon cross section is enhanced over two orders of magnitude compared with molecules in solution. The shift of the luminescence maximum to thicker silver films with two-photon excitation compared with linear excitation is in agreement with prediction of the electromagnetic model. These results afford further demonstration of enhanced optical processes due to local-field enhancement near plasma particles.

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