Effect of metallic surface on electric dipole and magnetic dipole emission transitions in Eu$^{3+}$ doped polymeric film

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Abstract: Spontaneous emission of Eu$^{3+}$ ions is studied in thin organic films deposited onto several different substrates. It has been demonstrated that the presence of a metallic surface in close vicinity to emitting Eu$^{3+}$ ions causes modifications of their spontaneous emission spectra, in particular, the change in the relative strengths of magnetic-dipole and electric-dipole transitions. The character and the magnitude of the effect depend on the polarization and the observation angle. The experimental data are discussed in terms of modification of transition probabilities and account for the interference between directly emitted and reflected light waves.

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References and links


Introduction

Metamaterials have recently become a hot research topic because of their interesting physics and exciting applications, including negative index of refraction [1,2], imaging with subwavelength resolution [1,3] and optical cloaking [2,4]. Unique properties of metamaterials critically depend on their responses to electric and magnetic fields. Although field
distributions in metamaterials are routinely calculated theoretically, they have never been measured experimentally. Direct nanoscopic studies of local electric and magnetic fields in metamaterials can lead to the development of a new fundamental knowledge and unparalleled applications.

It has been proposed [5] that strengths of electric and magnetic fields in the vicinity to metallic films or nanostructures can be studied directly by monitoring luminescence intensity of Eu$^{3+}$ ions. Although in naturally existing materials, magnetic responses at optical frequencies are so weak that they cannot significantly affect the index of refraction [6], they can be sufficiently strong to monitor magnetic fields.

Spontaneous emission of Eu$^{3+}$ ions at $\lambda \approx 590 \text{ nm}$ ($^5D_0 \rightarrow ^7F_1$) and $\lambda \approx 614 \text{ nm}$ ($^5D_0 \rightarrow ^7F_2$) has contributions from both magnetic-dipole and electric-dipole transitions [7], with the magnetic-dipole transition predominating at $\lambda \approx 590 \text{ nm}$ and the electric-dipole transition being stronger at $\lambda \approx 614 \text{ nm}$ [5,8]. By analyzing relative intensities of these two spectrally close transitions, one can probe relative strengths of magnetic and electric fields and portray the spatial distribution of optical modes in the system.

Organic systems doped with Eu$^{3+}$, in particular single crystals and solid solutions of europium nitrate with bipyridine, Eu(NO$_3$)$_3$·Bpy$_2$, are good candidates for such applications. Eu(NO$_3$)$_3$·Bpy$_2$ is a highly efficient luminescent material. A pyridine ligand can be excited by ultraviolet light, after which an electronic excitation is transferred to Eu$^{3+}$ ions with high rate and efficiency [9]. The synthesis of such system, Eu(NO$_3$)$_3$·Bpy$_2$ dispersed in a host polymer (gelatin), and first experiments with thin films are described in Ref [5]. It has been shown that the emission spectrum and the emission kinetics are sensitive to the distribution of magnetic and electric components of the optical field, which is modified in the vicinity of a metallic mirror. In order to better understand the applicability and specifics of this spectroscopic method, we performed detailed experiments with a variety of Eu$^{3+}$ systems, in which we studied the dependence of the emission spectra on the observation angle, polarization, and the distance to the metallic surface.

**Experimental samples and setup**

Experimental samples were thin films of solid solution of Eu(NO$_3$)$_3$·Bpy$_2$ in polyvinylpyrrolidone (PVP) (10 wt.%) deposited onto a variety of substrates, including glass slide (sample G$_0$), gold film on glass (sample Au$_0$), silver film on glass (sample S$_0$), and multi-layered structures (samples S$_1$, S$_2$) consisting of silver films (on glass) topped with a thin layer of mercaptoundecanoic acid (MUA) molecules serving as a spacer between Ag and Eu(NO$_3$)$_3$·Bpy$_2$, Fig. 1(a).

Silver and gold films with the thickness in the range 60–120 nm (measured with DekTec-6 profilometer) were deposited onto glass substrates using the vapor deposition technique. To fabricate samples with an intermediate MUA layer, silver films were immersed into ethanol solution of MUA (with concentrations 1.8, 3.6, and 24 mM) for 45 min, rinsed by distilled water to remove excess of non-adsorbed organic molecules, dried in air, and finally coated with Eu$^{3+}$-containing polymer. The Eu$^{3+}$-containing compound was fabricated using Eu(NO$_3$)$_3$·Bpy$_2$ crystals, grown following the procedure described in Refs [5,9]. The crystals along with PVP were dissolved in a water/ethanol mix, after which thin films of Eu-doped PVP were deposited onto the substrates described above with a spin coating technique.
Optical studies were done in the Fluoromax-3 spectrofluorometer setup consisting of an excitation lamp, excitation monochromator, sample holder, polarizer, emission monochromator, and photodetector. The excitation wavelength $\lambda = 300$ nm corresponded to the strong absorption band of Eu(NO$_3$)$_3$.Bpy$_2$. The emission spectra were recorded in the 550 nm - 650 nm spectral range in s and p polarizations at multiple positions of the goniometer and corresponding to them different observation angles $\theta$ (measured between the normal to the film surface and the direction to the detector). The spectra were normalized to unity in the maximum of the predominantly electric-dipole emission peak at $\lambda = 614$ nm (Fig. 1(c)), and the relative intensities of the predominantly magnetic-dipole emission transitions at $\lambda = 590$ nm (or the ratios of the emission intensities at 590 nm and 614 nm, $I^{590}/I^{614}$) have been analyzed.

**Experimental results**

The emission spectra of Eu(NO$_3$)$_3$.Bpy$_2$ in sample $S_1$ recorded at $\theta = 70^\circ$ in s and p polarizations are shown in Fig. 1(c). In this particular measurement, the intensity ratio $I^{590}/I^{614}$ in p polarization (0.15) was different from that in s polarization (0.24). In Fig. 2, the ratios of the emission intensities at 590 nm and 614 nm, $I^{590}/I^{614}$, are plotted versus angle for five samples studied.

![Fig. 1](image1.png)

*Fig. 1. a) Schematic of the sample; b) arrangement of the experiment in the Fluoromax-3 spectrofluorometer; c) Typical emission spectra at s and p polarizations normalized to the transition at 614 nm.*

![Fig. 2](image2.png)

*Fig. 2. Intensity ratios $I^{590}/I^{614}$ plotted versus angle $\theta$ for s polarization (squares) and p polarization (diamonds) for: (a) sample $G_0$ – Eu-PVP film on glass, (b) sample $Au_0$ – Eu-PVP film on gold, (c) sample $S_0$ – Eu-PVP film on silver, (d) sample $S_1$ – Eu-PVP film on silver/MUA (combined thickness of MUA/Eu-PVP ~42 nm), and (e) sample $S_2$ – Eu-PVP film on silver MUA (combined thickness of MUA/Eu-PVP ~73 nm). Solid lines – guides for eye; the error bars approximately correspond to the character sizes.*
In the film on a glass substrate, sample G0, there is practically no angular dependence of $I^{590}/I^{614}$ or the difference between $s$ and $p$ polarizations, Fig. 2(a). To the contrary, in the Eu–PVP films deposited on gold and silver/MUA substrates (samples Au0, S1, and S2), the ratios $I^{590}/I^{614}$ depend on both observation angle and polarization (being larger for $s$ polarization than for $p$ polarization), Figs. 2(b), 2(d), 2(e). In sample Au0, the ratio $I^{590}/I^{614}$ monotonically grows with an increase of $\theta$ through the whole range of angles, while in samples S1 and S2 the initial growth saturates and rolls over at $\theta = 40-70^\circ$.

At the same time, sample S0, in which Eu-PVP film is deposited directly onto silver without intermediate MUA layer, behaves similarly to the film on glass (compare Figs. 2(c) and 2(a)), showing practically no dependence on the polarization or angle. We explain this by chemical damage of silver (etching) caused by Eu(NO3)3·Bpy2, which resulted in visible deterioration of the reflecting silver surface. Eu(NO3)3·Bpy2 did not etch gold, and MUA layer protected silver from deterioration. That is why, the emission curves in samples Au0, S1 and S2 (samples with undamaged metallic mirror surfaces) behave nearly similarly to each other.

With the increase of the combined thickness of the MUA and Eu-PVP layers, which corresponded to the increase of the average distance between Eu$^{3+}$ ions and silver film, the ratio $I^{590}/I^{614}$ decreased in both $s$ and $p$ polarizations and its angular dependence slightly reshaped, Figs. 2(d) and 2(e).

Summarizing the experimental results, the presence of a metallic surface in close vicinity causes modification of the spontaneous emission spectrum of Eu$^{3+}$, in particular, change in the relative strengths of the predominantly magnetic-dipole and the predominantly electric-dipole emission transitions. In the samples with high quality (not damaged) metallic films, like Au and Ag on the top of MUA, the ratio $I^{590}/I^{614}$ is higher in $s$ polarization than in $p$ polarization. The difference between two polarizations is negligible at $0^\circ$ (since at normal direction there is no difference between $p$ and $s$ polarizations) and grows with the increase of the observation angle. The ratio $I^{590}/I^{614}$ becomes smaller with an increase of the thickness of the combined MUA/Eu-PVP layer, and the effect vanishes at deterioration of the metallic surface.

**Comparison of the experimental result with the model predictions**

Radiation characteristics of emitting dipoles in the vicinity of reflecting surfaces have been studied in publications [8,10–16] and references therein. It has been shown that the emission rate, the spatial distribution of the emission and the quantum yield of the emission can be strongly altered due to the presence of an interface.

Theoretical studies [10–16] have been primarily focused on emission characteristics of electric dipoles. The properties of magnetic dipoles are in some sense complementary to those of electric dipoles [15]. Thus in the vicinity of a mirror, the emission rate of a magnetic dipole doubles and that of an electric dipole vanishes if a dipole is oriented parallel to the reflecting surface. To the contrary, if the dipole is oriented perpendicular to the mirror, then the emission rate of an electric dipole doubles and that of a magnetic dipole vanishes [8,10,15,16]. These effects can significantly affect the emission dynamics [5] and alter relative intensities of magnetic-dipole and electric-dipole transitions.

The probability $\Gamma_{EM}$ of the electric-dipole/magnetic-dipole transition is proportional to the photonic mode density, $\rho_{E,M}$, and square of the corresponding off-diagonal matrix element [15]. As it has been discussed in [13], the interface-related effects are primarily associated with the modification of photonic modes. If both magnetic-dipole and electric-dipole transitions originate from the same state (as in the case of our experiment), the ratio of the probabilities of these transitions is equal to

$$\frac{\Gamma_M}{\Gamma_E} = \frac{\Gamma_{M0} \rho_M}{\Gamma_{E0} \rho_E},$$  \hspace{1cm} (1)

where $\Gamma_{E0,M0}$ is the probability of electric-dipole or magnetic-dipole transition in free space.

Equation (1) describes redistribution between two transitions of irradiated power integrated over all possible angles. To estimate the ratio of emission powers radiated in small
solid angle $d\Omega$ in the direction $\Omega$, one should take into account the fraction of photonic modes $\Phi(\Omega) d\Omega$ supporting photons which propagate in this direction. This yields for the ratio of magnetic-dipole and electric-dipole transition intensities, $I_M/I_E$:

$$
I_M = \frac{\Phi_M(\Omega) d\Omega}{\rho_M h\nu_M} = \frac{\Gamma_M}{\rho_E} \frac{\Phi_E(\Omega) d\Omega}{\rho_E h\nu_E} \frac{\Phi_M(\Omega)}{\Phi_E(\Omega)} \frac{\nu_M}{\nu_E} \frac{1}{\rho_E},
$$

where $h$ is the Plank constant and $\nu_{E,M}$ is the corresponding transition frequency. In the case of our experiment, the frequency of electrical dipole and magnetic dipole transitions are very close, $\nu_E \approx \nu_M$. In the Fraunhofer approximation (a far-field pattern), fields of the corresponding modes can be found as the superposition of the direct dipole radiation and its reflection off the mirror surface [8,15]. In the geometry of our experiment, the corresponding emission intensities, normalized to the emission intensities of free single dipoles, are given by the following formulae.

Electric dipole in plane of the mirror:

s polarization, $I_s^e = 1 + |\rho_s|^2 + 2 |\rho_s| \cos(\phi + \delta_s)$, \hspace{1cm} (3a)

p polarization, $I_p^e = \left(1 + |\rho_p|^2 + 2 |\rho_p| \cos(\phi + \delta_p + \pi)\right) \cos^2 \theta_0$. \hspace{1cm} (3b)

Electric dipole normal to the mirror:

s polarization, $I_s^\perp = 0$, \hspace{1cm} (3c)

p polarization, $I_p^\perp = \left(1 + |\rho_p|^2 - 2 |\rho_p| \cos(\phi + \delta_p + \pi)\right) \sin^2 \theta_0$. \hspace{1cm} (3d)

Here $\phi = 4\pi nd \cos(\theta_0)/\lambda$ is the phase shift due to the extra path length propagated by the reflected light through the dielectric medium, $d$ is the distance between the dipole and the mirror, $n$ is the index of refraction of an isotropic dielectric medium, $\lambda$ is the vacuum wavelength, and $\theta_0$ is the internal angle between the direction of light propagation and the normal to the surface inside the PVP layer. This angle sweeps from 0° to the angle of total internal reflection at the PVP-air interface, which ranges from 0° to 90°, via the Snell’s law. The complex amplitude reflection coefficients are equal to [17]

$$
\rho_s = \frac{e_1 \cos \theta - \sqrt{e_2 - e_1 \sin^2 \theta}}{\sqrt{e_1 \cos \theta + \sqrt{e_2 - e_1 \sin^2 \theta}}}, \quad \rho_p = \frac{e_1 \cos \theta_0 - \sqrt{e_2 - e_1 \sin^2 \theta}}{e_1 \cos \theta_0 + \sqrt{e_2 - e_1 \sin^2 \theta}},
$$

where $e_1$ and $e_2$ are the complex dielectric functions of the dielectric medium and the metal, correspondingly.

Magnetic dipole in plane of the mirror:

s polarization, $I_s^m = \left(1 + |\rho_s|^2 - 2 |\rho_s| \cos(\phi + \delta_s)\right) \cos^2 \theta_0$. \hspace{1cm} (4a)

p polarization, $I_p^m = 1 + |\rho_p|^2 - 2 |\rho_p| \cos(\phi + \delta_p + \pi)$. \hspace{1cm} (4b)

Magnetic dipole normal to the mirror:
s polarization, \[ I_s = \left(1 + |\rho_s|^2 + 2|\rho_s^i| \cos(\phi + \delta_s)\right)\sin^2 \theta_0, \quad (4c) \]
p polarization, \[ I_p = 0. \quad (4d) \]

Since both 590 nm and 614 nm emission lines of Eu\(^{3+}\) originate from a mixture of electric dipole and magnetic-dipole transitions [7] we modeled the corresponding emission intensities as \[ I_s = \alpha_s I_5 + \alpha_m I_6 \] and \[ I_p = \alpha_s I_5 + \alpha_m I_6 \] at s and p polarizations correspondingly, where \( \alpha_s \) and \( \alpha_m \) are the weight factors and \( \lambda \) is the wavelength.

The angular dependences \( I_{590}/I_{614}^{590} \) calculated in p and s polarizations for the case of random dipole orientations, at \( \varepsilon_1 = 2.27 \), \( \varepsilon_2 = -13.38 + i0.886 \) (silver at 590.4 nm [18]), plausible weight factors \( \alpha_s \) and \( \alpha_m \), and realistic distances \( d \) between Eu\(^{3+}\) ions and the metallic surface are plotted in Figs. 3(a) and 3(b). One can see that the calculated results are in a good qualitative and reasonable quantitative agreement with the experimentally measured ratios \( I_{590}/I_{614}^{590} \) depicted in Figs. 2(b), 2(d), 2(e). The calculations correctly predict the shapes of the experimental curves, the relative magnitudes of the \( I_{590}/I_{614}^{590} \) ratios in s and p polarizations, and the dependence of \( I_{590}/I_{614}^{590} \) on distance \( d \).

![Fig. 3. Emission intensity ratios \( I_{590}/I_{614}^{590} \) calculated for s and p polarizations and two different distances between Eu\(^{3+}\) ions and metallic surface, \( d = 25 \) nm (a) and \( d = 100 \) nm (b). The weight factors are \( a_{s590} = 0.3 \), \( a_{m590} = 0.7 \), \( a_{s614} = 0.9 \), \( a_{m614} = 0.1 \).](image)

**Summary**

We have experimentally studied emission from thin films of Eu(NO\(_3\))\(_3\)-Bpy\(_2\)-polyvinylpyrrolidone (Eu-PVP) deposited on the top of silver and gold films. At 300 nm excitation, the emission was strong and easy to detect even in thin, \~40 nm, Eu-doped layers. We have shown that the emission from the predominantly electric-dipole transition (614 nm, \( 5D_0 \rightarrow 7F_2 \)) can be differentiated from the emission from the predominantly magnetic-dipole transition (590 nm, \( 5D_0 \rightarrow 7F_1 \)) based on its angular and polarization dependences. The effect vanishes when Eu(NO\(_3\))\(_3\)-Bpy\(_2\) etches silver film. A protective layer of mercaptoundecanoic acid (MUA) molecules can prevent silver film from deterioration. No chemical damage is produced by Eu(NO\(_3\))\(_3\)-Bpy\(_2\) molecules to gold. The experimental results can be adequately described taking into account linear superposition of directly emitted and reflected waves. The developed material can potentially be used a sensor for mapping local electric field and magnetic field distributions in photonic metamaterials. Such experiments are in progress; the results will be published elsewhere.

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