# Spontaneous Emission in a Disordered Dielectric Medium

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(Received 7 September 1990)

We observed the change in fluorescence lifetime from a molecular dye embedded in a colloidal suspension of polystyrene spheres when the mean separation between spheres remains less than the wavelength of emission. At high densities of colloidal particles the spontaneous emission is inhibited, while as the density of colloidal particles is lowered the spontaneous emission is enhanced. This phenomenon is interpreted in terms of coherent interference from the electric field radiated by the molecular dipole and the reradiated field from the dielectric spheres.

PACS numbers: 42.50.Wm, 12.20.Fv, 42.50.Kb, 78.90+t

The radiative properties of an atomic or molecular system may be significantly altered by a neighboring dielectric interface. Extensive theoretical and experimental work has focused on the modified fluorescence-decay lifetime[1-3] and frequency shift[3,4] of a molecular transition in front of an infinite plane mirror. At short distances the direct and reflected beam will interfere destructively leading to inhibited spontaneous emission. A more complete description of the experimental results is obtained when a second dielectric interface (radiative-system/air) is considered.[5] Inhibited spontaneous emission has also been observed from radiative systems placed inside a cavity where a decrease in the vacuum-mode amplitude may be achieved when the transmission frequency lies below the fundamental frequency of the cavity.[6,7] Periodic dielectric structures comprised of spheres or ellipsoids with a high relative dielectric constant may present photonic band gaps and also inhibit the spontaneous emission.[8,9] The presence of a photonic band gap in such periodic dielectric structures has also been predicted to cause light shifts and inhibit resonant molecular transfer.[10,11] Partial inhibition of the spontaneous emission of a radiative system embedded in a crystal composed of negatively charged colloidal spheres, showing strong Bragg scattering of visible light, has been recently reported.[12]

Along with the study of the radiative properties of matter in the neighborhood of an ordered dielectric configuration, there has been an increasing interest in the scattering of light by a disordered medium. Of particular importance in this regard have been questions concerning the possibility of the weak and strong localization of light and the renormalization of dissipative response.[13-16] The problem is the photon analog of Anderson localization with the additional effects imposed by the vector nature of light. Most of the experimental work in this area has been on coherent-backscattering signatures and optical-pulse-broadening effects.[17-19] It is also important to mention that although most of the emphasis has been focused on dielectric composite media with "liquidlike" structure factors, recent theoretical work has shown that crystalline structures with weak disorder may provide a more effective medium for observing these effects.[20]

In this Letter we present time-resolved measurements of the radiative decay of a dye molecular solution embedded in a medium constituted of dielectric spheres randomly distributed in space. In this suspension the mean separation between spheres is smaller than the wavelength of the radiated field. Our experimental results indicate that at high densities of colloidal particles the spontaneous emission is inhibited. As the concentration of particles is lowered the fluorescence decay is enhanced. When the volume fraction is less than 1% the free-space radiative decay rate of the molecular dye is recovered. The observed behavior is not what would be expected from a photon-trapping picture since higher scattering-particle densities would imply higher local photon densities and a stimulated-emission component to the decay. This would result in a shorter lifetime at the closest sphere separations, the opposite of what is observed. The phenomenon we observe is instead attributed to the coherent interference between the radiated field of a dye molecule and the field radiated from an effective Hertzian dipole induced on the closest spheres.

Our experiments time resolved the fluorescent decay of an aqueous solution of Kiton Red using picosecond pump-probe techniques. The Kiton Red dye singlet has an $S_0 \rightarrow S_1$ monomer absorption maximum at 570 nm and a fluorescence which peaks at 590 nm with a 35-nm full width at half maximum. Its decay time into free space was determined to be 1.2 ns. The dye solution was pumped to the singlet excited level using 10-ps long pulses from a mode-locked rhodamine-6G laser tuned to 570 nm. Picosecond pulses from a mode-locked DCM dye laser[21] tuned to 625 nm were used as probes to mea-

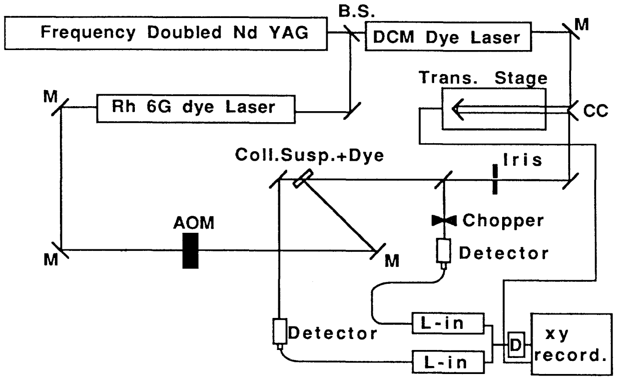

FIG. 1. Experimental setup, where B.S. indicates a 50% beam splitter, M are 99% reflectors, CC is a corner cube, AOM is an acousto-optic modulator, L-in indicates lock-in amplifier, and D is a voltage divider. The dye solution embedded in a colloidal suspension is contained in a cell mounted at the place where the two beams intersect.

sure relative excited-state population densities at different delay times with respect to the pump pulse.

Measurements of the induced gain on the DCM pulses were obtained by modulating the train of pulses of the pump beam and subsequently lock-in detecting the relative change of the average power of the train of pulses of the probe beam. The gain signals were recorded on an $x$-$y$ plotter, where the $x$ axis corresponded to the delay between the pump pulse and the probe pulse and the $y$ axis corresponded to gain induced in the probe pulse. Analog data were digitized at intervals of 0.05 ns or smaller, and the lifetime was determined from the slope of the logarithmic function of the gain versus delay time. Modulation was implemented using an acousto-optic modulator operating at 72.6 kHz in order to reduce the noise associated with heating of the sample. Beam walk and beam diffraction were corrected by dividing the measured signal by a reference signal subject to the same changes. The sample was contained in a cell 200 $\mu$m thick with an area of 3 cm$^2$. In addition, the sample was rotated at a rate of 1 Hz to avoid continuous heating and thermal dye degradation which take place over a period of the order of 30 min. The experimental setup is shown in Fig. 1.

The fluorescence lifetime of the dye solution embedded in a suspension composed of spheres of 0.1 $\mu$m in diameter is shown in Fig. 2, as a function of $d$, where $2d = (3/4\pi\rho)^{1/3}$ is the mean separation between spheres and $\rho$ is the density of colloidal particles. The lifetime is given relative to the free-space lifetime. In our experiments we utilized a monodispersive (coefficient of variation 5.3%) suspension of negatively charged spheres. These suspensions are commercially available at a maximum volume fraction of 8.4% or a sphere density of $1.55\times10^{14}$ spheres/cm$^3$. In order to avoid chemical surface effects that could strongly modify the fluorescence decay rate we chose an anionic dye that was repelled by the sphere surface. Similar measurements were performed using a colloidal suspension composed of spheres of 0.046 $\mu$m in diameter. The fluorescence lifetime of the dye as a function of the density of colloidal particles showed the same behavior.

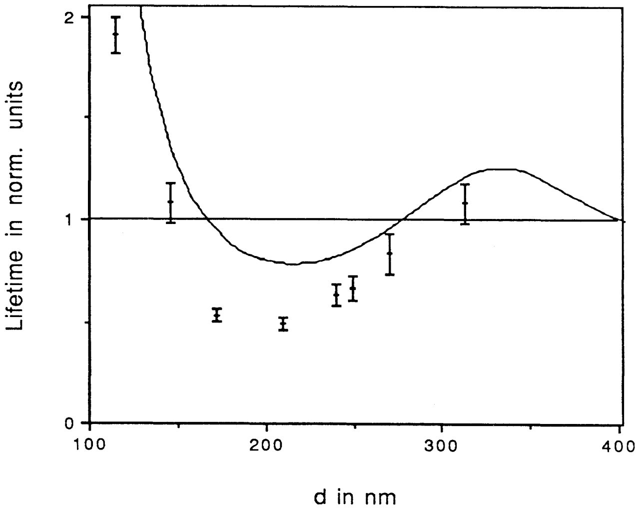

FIG. 2. Lifetime of a Kiton Red solution in water embedded in a disordered colloidal suspension of 0.1-$\mu$m-diam spheres vs mean separation between centers of spheres. The crosses with error bars represent the experimentally measured lifetime relative to the lifetime in free space. The solid line represents the lifetime of an oscillating electric dipole in a disordered medium constituted of dielectric spheres.

A theoretical basis for these experimental observations may be provided by a classical electromagnetic treatment of the effective radiating dipole when the source (dye molecules) is surrounded by localized dielectrics (spheres). In this picture, the field radiated from a molecular dipole induces an oscillating dipole on each one of the spheres, which produces a secondary field that interferes coherently with the primary field. This is the classical limit of the virtual emission and phase-dependent absorption or stimulated emission of a real photon by the molecule. In our approach we will describe the dye molecule as a dipole oscillating at a frequency $\omega = 2\pi c/\lambda$ ($\lambda$ is the wavelength of the field in the medium) given by

$$p = p_0 e^{i\omega t} . \qquad (1)$$

The classical limit of the radiated field in the regime where the size of the dipole is small compared to the radiated wavelength $\lambda$ and to the distance at the observation point, $d$, may be written as[22]

$$\mathbf{E} = \frac{p e^{-ikd}}{4\pi\varepsilon_0} [\rho_\parallel(kd) \sin\theta e^{i\phi_\parallel(kd)} \hat{\boldsymbol{\theta}} + \rho_\perp(kd) \cos\theta e^{i\phi_\perp(kd)} \hat{\mathbf{r}}] \qquad (2)$$

with

$$\rho_{\parallel}(kd) = (1/d^3)[(1-k^2d^2)^2 + k^2d^2]^{1/2}, \tag{3}$$

$$\phi_{\parallel}(kd) = \tan^{-1}\left[\frac{kd}{1-k^2d^2}\right] + \begin{cases} 0 & (d > \lambda/2\pi) \\ \pi & (d < \lambda/2\pi) \end{cases}, \tag{4}$$

$$\rho_{\perp}(kd) = (1/d^3)[1 + k^2d^2]^{1/2}, \tag{5}$$

$$\phi_{\perp}(kd) = \tan^{-1}(kd) + \pi, \tag{6}$$

where $k = 2\pi/\lambda$, $\theta$ is the angle between the dipole axis and the direction of propagation of the field, and $\hat{\mathbf{r}}$ and $\hat{\boldsymbol{\theta}}$ are the unit vectors in spherical coordinates. Assuming that the electric field is constant over all the volume of the sphere, the induced dipole at the center of the sphere will take the following form:

$$\mathbf{p}_{s\parallel,\perp} = \mp \frac{ps^3(\varepsilon_r - 1)}{3} \rho_{\parallel,\perp}(kd) e^{-i(kd - \phi_{\parallel,\perp})} \hat{\mathbf{z}}, \tag{7}$$

where the molecular dipole is taken to be parallel to the $z$ axis, $s$ is the radius of the dielectric sphere, and $\varepsilon_r = \varepsilon_s/\varepsilon_w$ is the relative dielectric constant between the sphere ($\varepsilon_s = 2.56$) and the medium containing the dye solution (the dielectric constant of water $\varepsilon_w = 1.77$).

From Eqs. (2) and (7) we can derive an expression for the absolute effective decay rate of a system with an effective dipole matrix element composed of a molecular dipole and the dipole induced in the dielectric sphere of relative dielectric constant $\varepsilon_r$,

$$\gamma^{\parallel} = \gamma_0 \left[ 1 + \frac{s^3(\varepsilon_r - 1)}{2} \frac{\rho_{\parallel}(kd)}{(kd)^3} \{[1-(kd)^2][\sin(kd - \phi_{\parallel} + 1) - \sin(kd - \phi_{\parallel} - 1)] \right.$$
$$\left. + kd[\cos(kd - \phi_{\perp} + 1) + \cos(kd - \phi_{\perp} - 1)]\} \right], \tag{8}$$

where we assumed the symmetry axis of the molecular dipole to be parallel with the closest surface region of the sphere. In addition, we have assumed that the primary field from the molecular dipole in the radiation zone remains unperturbed by the presence of the sphere due to the small cross section of this sphere. When this symmetry axis is perpendicular to the closest surface region of the sphere, the decay rate is given by

$$\gamma^{\perp} = \gamma_0 \left[ 1 + s^3(\varepsilon_r - 1) \frac{\rho_{\parallel}(kd)}{(kd)^2} \{-kd[\cos(kd - \phi_{\parallel} + 1) + \cos(kd - \phi_{\parallel} - 1)] + \sin(kd - \phi_{\perp} + 1) - \sin(kd - \phi_{\perp} - 1)\} \right], \tag{9}$$

where $\gamma_0$ is the free-space value of the radiative decay. From Eqs. (8) and (9) we may conclude that the molecular radiative decay rate for an isotropic distribution of molecular dipole configurations is[23]

$$\gamma = \tfrac{2}{3}\gamma^{\parallel} + \tfrac{1}{3}\gamma^{\perp}. \tag{10}$$

As an approximation to the instantaneous distribution of spheres we assume that the dielectric spheres are distributed in an hexagonal-like configuration and that each sphere occupies a volume $v = 1/\rho$, where $\rho$ is the density of colloidal particles. In this configuration the center of the four closest spheres are at a distance $d = (3/4\pi\rho)^{1/3}$ from a given molecular dipole (since the chromophore of the dye molecule was chosen to be anionic, and is expected to adiabatically adjust to the electrostatic minimum of any given sphere cavity configuration). In the limit of a low relative dielectric constant, the secondary radiated field from each sphere may be treated independently from each other, which leads to an expression for the radiative decay of an isotropic distribution of molecular dipoles equal to the expression given in Eq. (10), where $\varepsilon_r - 1$ is replaced by $4(\varepsilon_r - 1)$.

In the above discussion we have omitted the fluctuations about the mean value of the volume $v$ occupied by each sphere. If the colloidal suspension is treated as a physical system composed of noninteracting particles, the mean square fluctuations will scale as the square of the mean volume $v$. Because of these fluctuations, at any given time half of the particles located on a spherical shell of radius $2d$ will be at a distance $d' < 2d$ from the molecular dipole. Assuming a second layer containing $4\pi(2d)^2/\pi d^2 = 16$ spheres, we may conclude that a more accurate expression for the radiative decay can be obtained when $\varepsilon_r - 1$ in Eq. (10) is replaced by $12(\varepsilon_r - 1)$. We will neglect the alteration of the radiative decay rate caused by the presence of any dielectric sphere located at a distance $D > 2d$ from the molecular dipole, since the changes on the total radiated intensity due to a large number of spheres will average to zero due to the fluctuation about the mean position of each sphere relative to the position of the molecular dipole. The absolute radiative lifetime as a function of the distance $d$ using the model we described is shown in Fig. 2. The parameter multiplying $\varepsilon_r - 1$ is to a certain degree arbitrary and in a rigorous discussion should be substituted by a pair-correlation function of a physical system composed of spherical particles interacting via a screened Coulomb potential.

A comparison between the measured spontaneous emission for the dye molecule at different densities of the colloidal suspension and the predicted behavior indicates that our classical treatment of the radiative sources provides a reasonable explanation for the most salient features of the dependence of the lifetime of the Kiton Red on the mean separation between dielectric spheres. It is important to notice that in this approach the effective oscillating dipole of a nearby sphere is induced by the radiative terms of the electric field as well as the nonradiative terms. A more accurate approach that will consider the finite size of the sphere diameter relative to the wavelength of the emitted radiation, as well as the nonuniformity of the field across the volume of the sphere, is in progress.

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