Observation of Inhibited Spontaneous Emission in a Periodic Dielectric Structure

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Inhibition of the radiative decay of dye molecules embedded in an ordered aqueous suspension of polystyrene spheres has been measured using picosecond pump-probe techniques. The inhibition is interpreted in terms of excluded vacuum modes and compared with results based on the Wigner-Weisskopf formalism and a 3D scattering model for the fcc colloidal structures.

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In 1946 Purcell[1] pointed out that the spontaneous emission rate of a two-level atom can be significantly increased if it is placed in a resonant cavity. When the atom is placed in a cavity with a quality factor Q, the Einstein coefficient A assumes the value $A = A_0 Q$, where A_0 is the free-space transition rate. This effect can be interpreted as a resonant enhancement of the vacuum-mode intensity inside the structure due to constructive interference. This increase must in turn be mirrored by a decrease in vacuum-mode amplitude in surrounding space, in order to conserve the photon-mode probability amplitude. Conversely, as Kleppner pointed out, the spontaneous emission can be inhibited if the transition frequency lies below the fundamental frequency of the cavity, thus excluding the mode from the interior of the cavity.[2]

Pioneering experimental work showed that such effects can be observed in transitions between cyclotron levels of a free electron in a Penning trap[3] and Rydberg levels of alkali-metal atoms.[4] In the latter case the experimental challenge of finding a system whose emission wavelength was long enough to allow for the construction of a cavity with reasonable dimensions was solved using the 700-μm emission in Cs.

Along with the first observation of inhibited spontaneous emission in a cavity, a great deal of interest in cavity QED effects was generated.[5] Recent work has examined the energy exchange in coupled atom-field systems and the spontaneous emission properties of atoms interacting with a frequency-dependent vacuum reservoir.[6] In addition to cavity effects, there have been several other interesting effects observed when atoms or molecules are close to a reflecting metallic or dielectric surface.[7,8]

Most recently, Yablonovitch suggested that periodic dielectric structures with strong scattering properties could result in photonic band gaps and inhibited spontaneous emission.[9] Yablonovitch and Gmitter demonstrated photon bands in periodic structures composed of low-loss dielectric materials fabricated with conventional machine tools.[10] This photonic band gap is achieved when the ratio of the scattering-sphere dielectric constant to that of the surrounding medium exceeds a critical value ($\varepsilon_r > 10$). The bands were observed in the microwave region of the spectrum owing to the large dimensions of the scattering medium.

Although their relative scattering ($\varepsilon_r = 1.45$) is weaker than the criterion cited, colloidal crystals composed of charged polystyrene spheres have been known to exhibit strong optical Bragg scattering of visible light since 1963.[11] These systems, prepared as single crystals in a variety of solvents, exhibit an intense Bragg reflection from their fcc (111) plane system which has been used to produce distributed feedback lasers in the visible region of the spectrum.[12]

In a finite system with $|\varepsilon_r| < 10$, it is expected that Bragg reflection by the structure will exclude a finite amount of vacuum-mode amplitude from the structure. This result may be viewed as a local perturbation of the spatial part of the quantized electromagnetic modes in free space which causes evanescent solutions within the structure. Excited atoms or molecules placed within a periodic structure whose Bragg resonances are longer than the transition wavelength of these atoms or molecules interact with a locally diminished vacuum field amplitude and are expected to spontaneously decay at a reduced rate. This result contrasts with the condition for inhibition obtained in a Fabry-Pérot cavity, where radiation due to vacuum fluctuations is suppressed for any frequency smaller than half the fundamental frequency of the cavity.[4] All wavelengths within the bandwidth of the radiative system will be Bragg reflected at a given angle if the Bragg condition at normal incidence for an array of crystalline planes is satisfied at a wavelength longer than the maximum emission wavelength. Reflection from the crystalline array of planes is achieved for any wave whose wavelength satisfies the condition $2d\cos\theta = \lambda/n$, where d is the separation of two consecutive planes, n is the index of refraction of the medium, and θ is the angle between the normal to the set of planes and the incident wave.

When foreign ions are removed from the water by adding an ion-exchange resin to the solution,[13] a monodisperse (coefficient of variation: 5%) colloidal suspension of negatively charged polystyrene spheres crystal-

lizes in an fcc (Ref. 14) structure with planes separated by optical dimensions. This remarkable effect occurs because of a screened Coulomb interaction between the spheres which causes crystallization when the Debye screening length becomes comparable to the interparticle spacing. Our experimental measurements on the transmission at normal incidence of the (111) planes of a 200-μm-thick fcc crystal made of polystyrene spheres of 0.121 μm in diameter with a volume fraction of 0.101 (density: 1.04×10^{14} spheres/cm^3) showed that when the Bragg condition is satisfied at 630 nm the extinction length is 2 μm. The extinction length reflects the magnitude of the coupling between the incident wave and the Bragg reflected wave and is defined as the inverse of the coupling constant.[15]

The experiment we performed utilized a $10^{-4}M$ aqueous solution of Kiton Red as an active medium; this dye has an $S_0 \rightarrow S_1$ monomer absorption maximum at 570 nm and a fluorescence peaked at 590 nm with a 35 nm full width at half maximum. The spontaneous emission rate of the dye embedded within the colloidal crystal was measured using picosecond pump-probe techniques. A dye solution embedded in a colloidal crystal with a Bragg notch (region of a Bragg spectrum where the transmission is minimum, cf. Fig. 2) at approximately 630 nm was pumped to the singlet excited level using 10-ps-long pulses from a mode-locked rhodamine 6G laser tuned to 570 nm. This solution was embedded in an fcc crystalline structure to inhibit the spontaneous emission. Picosecond pulses from a mode-locked DCM (Ref. 16) laser tuned to 625 nm were used as a probe to measure 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 on the average power of the train of pulses of the probe beam. 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 these changes. The sample was contained in a cell 200 μm 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 over periods of the order of 30 min. The experimental error in determining the fluorescence lifetime was 12%.

Experimental data for the fluorescence decay time of the dye solution in three different configurations are given in Fig. 1. Curve A shows a fluorescence decay of the dye solution embedded in a crystal composed of spheres 0.121 μm in diameter, contained in a cell 200 μm thick, with a maximum Bragg rejection at 630 nm at normal incidence. To demonstrate that spontaneous emission was inhibited a time-resolved measurement of the fluorescence decay of the same dye solution embedded in a crystal with the same extinction length but satisfying the Bragg condition at 480 nm was taken and plotted in Fig. 1 (curve B). This crystal was composed of spheres of 0.1 μm in diameter (density: 1.55×10^{14}/cm^3) in order to maintain the same ratio of dielectric surface area and charge to molecular density. Comparison between these two curves shows that the fluorescence lifetime in the case of a Bragg scattering at a longer wavelength than the dye emission is 1.75 times longer than that of the crystal with Bragg scattering at shorter wavelengths.

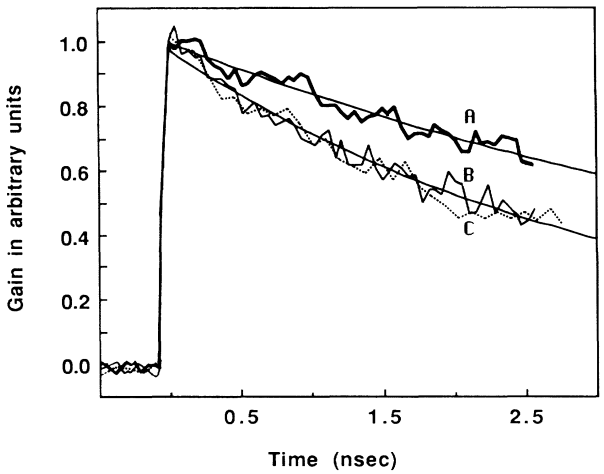

FIG. 1. Gain signal of a Kiton Red solution in water in an ordered colloidal suspension of 0.121-μm-diam spheres vs relative pump and probe delay time in nanoseconds (curve A), and in a suspension of 0.1-μm-diam spheres (curve B). The Bragg condition is verified at normal incidence at 630 nm in the first case and 480 nm in the second case. Curve C (dotted line) shows the gain signal of the same dye solution embedded in a disordered sample of spheres 0.121 μm in diameter.

Measurements of the fluorescence lifetime taken at different incident angles of the probe beam with respect to the normal of the (111) planes showed the same increase in the fluorescence lifetime, indicating the absence of nonlinear index effects.

A time-resolved fluorescence decay of a Kiton Red solution embedded in a disordered suspension of spheres 0.121 μm in diameter is plotted in Fig. 1 (curve C). A disordered sample corresponds to a vanishing coupling constant and consequently the radiative decay rate remains unchanged. A comparison between curve B and curve C in Fig. 1 shows no difference in the fluorescence lifetime, indicating that the effects in curve A are due to a *periodic* dielectric medium.

The Bragg notch of a colloidal crystal can be displaced to the long-wavelength region of the spectrum by dilution of the sphere concentration. In addition, dilution of the colloidal particle concentration results in a decrease of the strength of the scattering of any array of planes of the crystal lattice. A comparison of the Bragg transmission of the (111) planes of two fcc crystals with an extinction length differing by a factor of ~7 is given in

Fig. 2. Measurements of fluorescence decay rate of a dye solution embedded in a crystalline structure made of 0.1-μm spheres (density: 7.75×10^{13} spheres/cm^3), resonant at 600 nm, but with an angular rejection 0.35 times smaller than the crystal composed of 0.121-μm spheres, showed no increase in the fluorescence decay time. These results are in accordance with the decrease in the strength of the cooperative scattering by the crystal planes.

The different fluorescence decays of the same dye showed in Fig. 1 are not due to chemical effects associated with the dye-sphere interaction since (1) the dye is repelled by the sphere's surface, (2) the total charge in 1 cm^3 is 4.3×10^{-2} C for the colloidal suspension of spheres 0.121 μm in diameter as well as for the colloidal suspension of spheres of 0.1 μm in diameter, and (3) the total polystyrene surface in 1 cm^3 is 4.78×10^4 cm^2 for the colloidal suspension of spheres of 0.121 μm in diameter and 4.87×10^4 cm^2 for the colloidal suspension of 0.1 μm in diameter.

A quantitative evaluation of the decrease of the fluorescent decay due to amplitude-mode rejection provided by a periodic structure was obtained using the Wigner-Weisskopf theory of the natural linewidth.[17] The amplitude of electromagnetic modes in the Wigner-Weisskopf theory will be modified according to the solutions of the Maxwell-wave equation when the dielectric constant is a function of space. A solution of the new eigenmodes of the wave equation was derived using the method of variation of constants.[18]

The theoretical model assumed a one-dimensional Bragg structure of length D along the z axis, composed of (111) planes (separated a distance d) of an fcc crystal

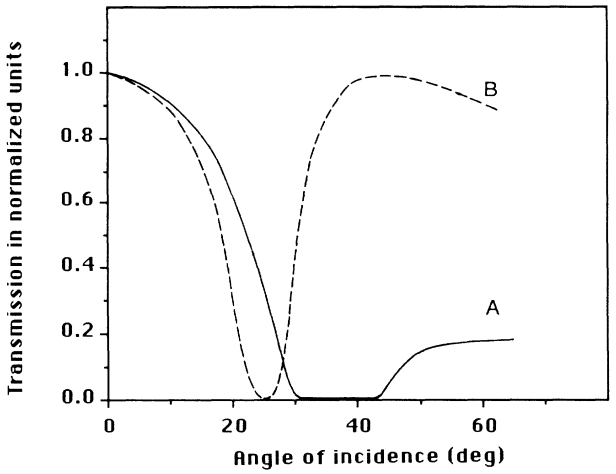

FIG. 2. Transmission as a function of the angle of incidence of an aqueous solution of Kiton Red embedded in a colloidal crystal of 0.121-μm-diam spheres and a sphere density of 1.04×10^{14} spheres/cm^3 (curve A). Curve B: same as curve A for particles of 0.1-μm diameter and a density of 7.8×10^{13} spheres/cm^3.

of spheres of finite size. A molecular radiative system with a finite bandwidth was placed in the middle of the periodic structure. Propagation of electromagnetic fields in a three-dimensional periodic structure can be treated in terms of independent one-dimensional periodic structures in the limit that the dielectric perturbation amplitude is far from the photonic band-gap condition, i.e., $\varepsilon_r \ll 10$.[10] In addition, the shortest dimension across the crystal is 100 times larger than the extinction length; the approximation placing the radiative system in the center of the periodic structure in a theoretical model of the experiment is a reasonable one. We will also assume that the emitted radiation is completely depolarized since rotation of dye molecules is several orders of magnitude faster than their radiative decay time. Under the conditions given, the expression derived for the spontaneous emission rate in a periodic structure relative to the spontaneous emission rate in free space takes the following form:[18]

$$\Gamma^{ps}(\lambda)=\frac{\Gamma^{fs}(\lambda)}{2}\left[4\int_{-1}^{1}d(\cos\theta)|A_\lambda(0)+B_\lambda(0)|^2-6\right], \tag{1}$$

where the factor of 4 accounts for the four sets of (111) planes in an fcc structure. The coefficient $A_\lambda(z)+B_\lambda(z)$ is the new amplitude coefficient for a normal mode with wavelength λ. In the limit of a vanishing dielectric perturbation $A_\lambda(0)\rightarrow 1$ and $B_\lambda(0)\rightarrow 0$. As the strength of the Bragg scattering is increased by varying the crystal thickness or the dielectric scattering volume fraction, the amplitude coefficients $A_\lambda(0)$ and $B_\lambda(0)$ will approach zero, resulting in total inhibition. The expression for $A_\lambda(z)$ and $B_\lambda(z)$ at the origin is

$$A_\lambda(0)=\frac{s\cosh[s(D/2)]+(\Delta k'/2)\sinh[s(D/2)]}{s\cosh(sD)+i(\Delta k'/2)\sinh(sD)}, \tag{2}$$

$$B_\lambda(0)=\frac{-i\kappa e^{i(\Delta k'D/2)}\sinh[s(D/2)]}{s\cosh(sD)+i(\Delta k'/2)\sinh(sD)}, \tag{3}$$

where D is the length of the periodic structure and s and $\Delta k'$ are equal to

$$s=[|\kappa|^2-(\Delta k'/2)^2]^{1/2}, \tag{4}$$

$$\Delta k'=2\pi/d-(4\pi/\lambda)\cos\theta, \tag{5}$$

where κ^{-1} is the extinction length and is a function of the relative dielectric constant as well as the volume fraction of scattering dielectric material. λ is the wavelength in the medium and θ is the angle between the reciprocal vector and the wave vector of the electromagnetic modes. The prime indicates that only the z component of the wave vector is backscattered by the periodic structure.

The extinction length for the crystal structure can be experimentally obtained from curve A in Fig. 2, knowing that for any set of planes of a crystal structure, the half-

width of the corresponding notch is given by $\Delta k' = 2|\kappa|$.[15] The direction of wave propagation inside the crystal needs to be corrected with respect to the angle of incidence given in Fig. 2, due to Fresnel diffraction at the air-colloidal suspension interface. Evaluation of the decay time using this approach with an extinction length of 2 μm and an average crystal size of 200 μm results in a degree of inhibition factor of 1.5. This value is in reasonable agreement with the experimentally measured degree of inhibition of 1.75. In the theoretical model we did not include the refraction of electromagnetic modes at the colloidal suspension-air interface which leads to a larger inhibition factor.

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