Fluorescence lifetimes and linewidths of dye in photonic crystals

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We have measured spectrally resolved fluorescence lifetimes of dye incorporated in high-quality photonic crystals, made of colloidal spheres. The emission spectrum shows a pronounced Bragg notch. In contrast, the fluorescence lifetime does not depend on the interaction between light and the photonic crystal. The results are explained with a simple model of an atom in a cavity. The effects of homogeneous and inhomogeneous broadening of the emission spectrum of dye inside photonic crystals are discussed. [S1050-2947(99)03906-2]

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I. INTRODUCTION

Photonic crystals are three-dimensional periodic dielectric composites in which the refractive index varies on length scales of the order of optical wavelengths. The propagation of light in such photonic materials is analogous to the well-known wavelike propagation of electrons in a crystalline structure [1]. The periodic structure gives rise to Bragg diffraction, which is associated with stop gaps for propagation in certain directions. In the direction of a stop gap light is excluded from the material. The situation is reminiscent of atoms or molecules in one-dimensional Fabry-Pérot cavities [2–4]. A Fabry-Pérot cavity can modify the spontaneous emission rate of atoms or molecules inside [2,4]. The main difference between Fabry-Pérot cavities and photonic crystals is that photonic crystals act as three-dimensional cavities. Ultimately, if light is very strongly coupled to a photonic crystal, a photonic band gap is expected, i.e., a frequency range for which no light can propagate in any direction. Such a photonic band gap will lead to fundamental changes. One of the most important consequences is that spontaneous emission of excited atoms or molecules with a transition frequency in the gap is inhibited [5], which may serve as the basis for lasers without threshold [6].

Surprisingly, experimental studies of excited atoms or molecules in photonic crystals are scarce [7,8], and important aspects of spontaneous emission have not been addressed, i.e., the spectral width of stop gaps or band gaps as compared to the emission linewidth and the mechanism that is responsible for this linewidth. The relevance of line broadening becomes clear if one considers the emission linewidth of atoms or molecules in a photonic band gap crystal in relation to the width of the gap. The linewidths of important systems such as efficiently radiating dyes or photoluminescing semiconductors are generally very large, i.e., comparable to the width of the gap, which justifies the question of whether a photonic gap will ever cause any observable effect on the radiative lifetime at all [9]. We will argue below, however, that under specific conditions a wide luminescence spectrum is actually an advantage rather than an obstacle for observing radiative lifetime changes.

In this paper, we experimentally investigate the fluorescence lifetime of dye in photonic crystals consisting of colloidal spheres. We have studied the wavelength dependence of the lifetimes, for dye in spheres in crystals and in a colloidal liquid. The emission spectra for crystals with different densities are very different, whereas the fluorescence lifetimes are equal within experimental accuracy. This observation indicates that the influence of the photonic band structure on lifetimes in these crystals is small. The apparent lifetimes in the colloidal liquid are slightly longer than in the crystals due to extra optical path length.

II. EXPERIMENT

To experimentally realize spontaneously emitting sources inside photonic crystals, we dope colloidal particles with fluorescent dye. The structure of the crystals is drawn schematically in Fig. 1. We have synthesized spheres of 121 nm radius and a size variation of only 1.5% [10]. The dye is homogeneously distributed in a layer inside the spheres. The density of rhodamine isothiocyanate dye molecules in the layer was intentionally kept below 0.5 mmol/l to avoid reabsorption and nonradiative transfer [11]. The low density of dye has a negligible effect on the refractive index. The dye molecules are covalently attached to the silica in the spheres and covered by a 50 nm thick layer of silica, to avoid washing out by the suspending liquid. This arrangement prevents unwanted chemical interactions of the dye with the liquid or

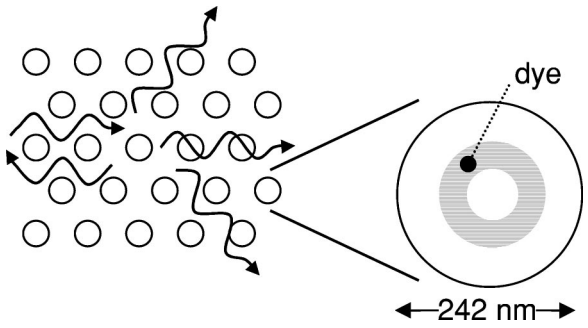

FIG. 1. Schematic drawing of the structure of the colloidal crystals and of one individual colloidal sphere. The arrows symbolize fluorescent light, with wavelengths of the order of the distance between lattice planes. Note that all the spheres are dyed.

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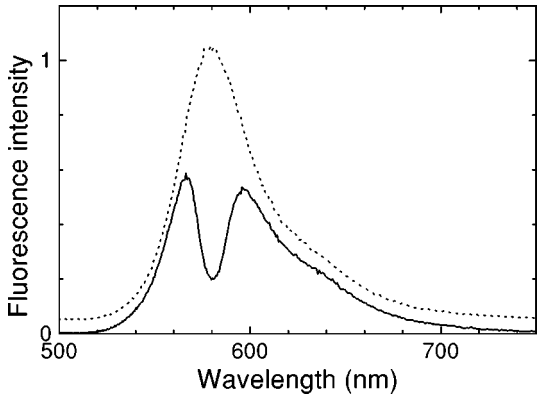

FIG. 2. Fluorescence spectrum of dye in a colloidal crystal (solid curve) and in a colloidal liquid (dotted curve, offset).

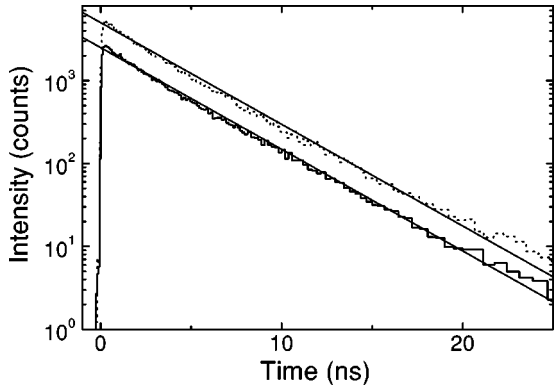

FIG. 3. Time-resolved fluorescence of dye inside a photonic colloidal crystal of 65 vol % (solid curve) and in a colloidal liquid (dotted curve, offset by a factor of 2), at 577 nm wavelength. The mean lifetimes of 3.54 ± 0.02 ns are indicated by straight lines.

with particle surfaces [12]. The silica spheres (refractive index $n = 1.45$) are suspended in water ($n = 1.33$). From the resulting colloidal suspension we grow large, highly ordered fcc crystals with the (111) planes parallel to the walls, as revealed by our synchrotron small-angle x-ray diffraction studies [13]. The spacing of the crystal planes varies with height in the sample due to gravity. The spacing ranges from 206 to 221 nm, which corresponds to a density range of 53–65 vol %. Higher up in the sample, the less dense colloidal liquid phase coexists. The samples are contained in long flat glass capillaries of 3 mm width and 0.3 mm internal path length. The capillaries were mounted on a rotation stage to orient the crystals with the surface normal pointing to the detector. Fluorescence spectra were obtained by exciting the dye in the sample with less than 1 mW of power from a cw argon ion laser operating at a wavelength of 488 nm; the spectra were collected with a prism spectrometer, equipped with a photomultiplier. The spectrometer has a resolving power of 1 nm. We verified that the laser did not damage the dye in the sample by measuring the fluorescence intensity as a function of time. Fluorescence lifetimes were obtained using a time-correlated single photon counting technique [14]. For the lifetime measurements, the dye is excited at a wavelength of around 320 nm by a cavity-dumped Kiton Red dye laser, synchronously pumped by a frequency-doubled pulse-compressed mode-locked Spectra Physics Nd^{3+}:YAG laser (YAG denotes yttrium aluminum garnet). With this setup we achieve a time resolution of 55 ps.

III. RESULTS

We have obtained fluorescence spectra of dye in many different photonic crystals. A typical example is shown in Fig. 2 and compared to the spectrum of dye in a colloidal liquid. The photonic crystal changes the fluorescence spectrum of the dye considerably: the spectrum acquires a pronounced stop gap. The stop gap is caused by the (111) crystal planes. The crystal planes act as Bragg mirrors for the fluorescence of the internal sources, preventing part of the light from leaving the crystal. At fixed wavelength, the associated angular variations in intensity consist of cones directed about the normal of the lattice planes. Such cones are familiar from x-ray fluorescence, where they are referred to as Kossel lines [15]. However, there is an important difference between stop gaps for sources inside, such as Kossel lines or Bragg mirrors, and stop gaps for external sources: the attenuation in the stop gap for internal sources is strikingly reduced compared to transmission of light from outside [16]. It turns out that the attenuation in the stop gap is a simple, unambiguous criterion for the attainment of a photonic band gap [16]. The appearance of a stop gap in the dye spectrum suggests that the photonic band structure might also affect the radiative lifetime of the dye.

Figure 3 shows two typical time-resolved fluorescence traces, one of dye in a colloidal crystal and one of dye in a colloidal liquid, measured at a wavelength of 577 nm, corresponding to the crystal's stop gap. The measured fluorescence intensities extend over three full decades. The fluorescence decay is very close to single exponential, which indicates that unwanted nonradiative effects are effectively reduced by the low dye concentration and the protective cover layer [11]. From the fluorescence decay curves we have obtained lifetimes by calculating the average time at which a photon is detected. The lifetimes for the curves in Fig. 3 are both 3.5 ns, i.e., there is no large difference in lifetime for a crystal and a colloidal liquid. Figure 4 shows fluorescence lifetimes as a function of wavelength in the dye

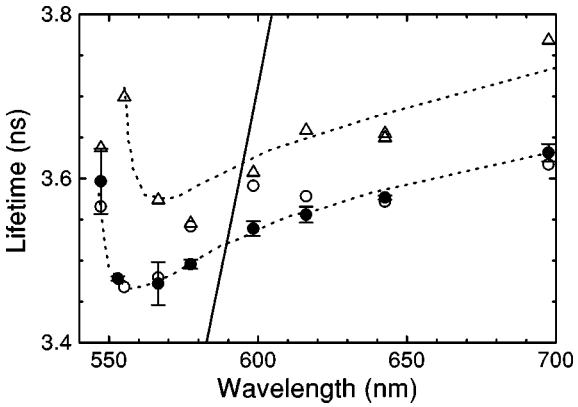

FIG. 4. Excited state lifetime of dye inside photonic crystals (open and solid circles, densities of 65 and 53 vol %, respectively) and in a colloidal liquid (triangles), at various wavelengths in the dye spectrum. The solid circles are an average of two measurements, indicated by error bars. The dotted curves are a guide to the eye.

spectrum, for two photonic crystals with different densities, and for a colloidal liquid. We will discuss fluorescence lifetimes in the crystals first, later on we will come back to the colloidal liquid. The densities of the crystals that we have used were 65 and 53 vol %. Due to the density difference the center wavelength of the stop gaps of the crystals differ: for the low-density crystal the stop gap is at 617 ± 9 nm, whereas for the high-density crystal it is at 582 ± 2 nm. Since the stop gap wavelengths of the two crystals differ, the densities of optical modes of the two crystals should also display different wavelength dependencies. This difference should become visible in the measured lifetimes. However, the measured lifetimes in these crystals do not show a significant wavelength dependence. The variations in lifetime are on the order of only 0.05 ns, or 2%. This observation shows that the influence of the photonic band structure on lifetime in these crystals is surprisingly small, considering the large changes in the spectra. Below we will resolve this seeming paradox.

IV. DISCUSSION

We can interpret the variation in lifetimes by comparing this variation to the width of the stop gaps of the crystals. A simple model connects the lifetimes to the width of the stop gaps, and it explains why the photonic crystals under study have only a small influence on lifetimes. In the direction of a stop gap, light cannot be emitted since the zero point fluctuations are expelled from the photonic crystal by repeated reflection from the lattice planes. Since our crystals do not have a photonic band gap, light at a specific wavelength is reflected only for certain directions, in the other directions the emission persists. We expect that the relative change in radiative lifetime of the fluorescent molecules is of the order of the solid angle Ω subtended by the Bragg reflections, compared to the full 4π solid angle which is available in the absence of a crystal. For atoms in a Fabry-Pérot interferometer the results of this approach are in excellent agreement with the experiments of Heinzen *et al.* [2]. The lifetime change for a stop gap at a specific frequency is

$$\frac{\Delta\tau}{\tau} = \frac{\Omega}{4\pi} = 4 \times 2 \times \frac{2\pi(\cos\theta_- - \cos\theta_+)}{4\pi}. \qquad (1)$$

Here, θ_- and θ_+ are the inner and outer half apex angles of the Kossel cone. The factor of 4 is included because there are four pairs of {111} planes, the factor of 2 accounts for the two sides of the planes. The change in lifetime depends on the emission frequencies of the fluorescent molecules via the angles θ_+ and θ_-. To estimate θ_+ and θ_- we have calculated the stop gap width using an extended version of conventional dynamical diffraction theory [15]. We have extended the theory to incorporate reflection at angles close to backscattering, and we have refrained from the customary approximation that the Kossel line occurs close to the conventional Bragg reflection. We consider here only polarization perpendicular to the scattering plane; this polarization gives the largest stop gaps. We will express the results in terms of the photonic strength parameter Ψ [17]. It appears that the solid angle contained in a stop gap is largest when the full Kossel cone has just come into view close to normal incidence on a set of planes, i.e., when $\theta_- = 0$. This situation occurs when the frequency of the light is at the top of the stop gap for normal incidence. The Kossel cone then extends to θ_+, which is determined by

$$\tan\theta_+ = \sqrt{2\Psi\frac{1+\Psi}{1-\Psi}} \approx \sqrt{2\Psi}. \qquad (2)$$

The resulting change in lifetime is

$$\frac{\Delta\tau}{\tau} = 4\left(1 - \frac{1}{\sqrt{1+2\Psi(1+\Psi)/(1-\Psi)}}\right) \approx 4\Psi, \qquad (3)$$

where the factor of 4 is due to the four pairs of {111} planes. The relative change in lifetime is directly related to the relative width of the stop gap in the spectrum. The relative spectral width $\Delta\omega/\omega$ of the stop gap for transmission normal to the crystal planes is

$$\frac{\Delta\omega}{\omega} = \sqrt{1+\Psi} - \sqrt{1-\Psi} \approx \Psi. \qquad (4)$$

We can obtain this width from, e.g., the fluorescence spectrum in Fig. 2. However, one should realize that the width of the stop gap in the fluorescence spectrum is not exclusively caused by the photonic band structure. The stop gap may be broadened by structural defects [15,18]. Indeed the stop gap in fluorescence spectra is usually wider than the peak in reflection spectra. The widths of observed reflection peaks agree well with theoretical calculations [18]. For our estimate of the lifetime change [Eq. (1)] we have used a stop gap width of 2%, which corresponds to a change in radiative lifetime of only 0.3 ns. The estimated radiative lifetime change provides an upper bound for changes in fluorescence lifetimes. This upper bound is consistent with the measured variations in τ of the crystals in Fig. 4. Apparently a large change in fluorescence spectrum can coincide with an only minor change in fluorescence lifetime, which resolves the paradox mentioned above.

The observed small change in lifetime contrasts with earlier results. Martorell and Lawandy [7] found a change in lifetime by a factor 1.8 for their crystals of polystyrene spheres in water with rhodamine dye dissolved in the liquid. It has been suggested that their large change in lifetime is not caused by photonic band structure but by other factors such as chemical interactions and adsorption of the dye on the sphere surfaces [12]. To avoid such effects, we have carefully synthesized spheres in which the dye is incorporated and shielded inside, see Fig. 1. Petrov *et al.* [8] have measured fluorescence of dye in a polymer-filled opal. The decay curves were fitted with a distribution of lifetimes, in which the short lifetimes were about half as long as the long lifetimes. The nonexponential decay was attributed to a modified density of optical modes while chemical or nonradiative effects were not considered. The fluorescence lifetimes were not spectrally resolved to demonstrate the variation in density of optical modes with wavelength. In both of the previous studies, the widths of the stop gaps of the samples are the same as the width of the stop gaps of our crystals, hence the change of the radiative lifetimes should in all cases be similar to the data in Figs. 3 and 4.

We will now discuss the lifetimes that we measured in a colloidal liquid. We find that in the colloidal liquid, the fluorescence lifetimes are generally slightly longer than in the photonic crystals. This increase in lifetime is probably a result of random multiple scattering rather than the photonic band structure. Random multiple scattering can considerably increase the path length from dye to detector. If the light propagates diffusively through the sample, then the length of the traversed path s is proportional to the square of the displacement d, $s/l=(d/l)^2$, where l is the mean free path. The mean free path l in the sample can be estimated from the Mie scattering cross section σ of the spheres and the density n, $l=(n\sigma)^{-1}=10\pm 2$ μm. For displacements d of the order of the sample thickness, 0.3 mm, the resulting path length s is 8.8 mm. Such a path length corresponds to a delay of 0.04 ns, of the order of the observed difference in lifetimes between the crystals and the colloidal liquid.

Apart from the small systematic difference in lifetimes between the photonic crystals and the colloidal liquid, it appears that all the measured lifetimes show a common trend in their wavelength dependence. The excited state lifetime τ that we have measured corresponds to a transition rate $1/\tau$ which is a sum of both radiative and nonradiative transition rates, $1/\tau=1/\tau_{\mathrm{rad}}+n_{\mathrm{nonrad}}$. The radiative decay rate can be calculated with Fermi's golden rule using the density of optical modes. It is through this density of modes that a strongly photonic crystal may influence the excited state lifetime. Even without photonic crystal the density of modes has a pronounced frequency dependence. In vacuum, the density of modes per unit volume $\rho_{\mathrm{vac}}=\omega^2/(\pi^2c^3)$ [19]. The transition dipole matrix element in Fermi's golden rule contributes yet another factor ω to the transition rate [19], hence we have plotted a cubic function in Fig. 4 for comparison. The frequency dependence of the radiative transition rate explains why the lifetime is shorter at short wavelengths, but the line is clearly much too steep compared to the data. The leveling of the slope may be due to nonradiative decay. Nonradiative decay is expected to become faster towards lower frequencies [20], hence the slope of the lifetimes τ in Fig. 4 is not as steep as the cubic curve. The curve is still sloping upward because the variation in density of states ρ_{vac} dominates the nonradiative decay, since quantum efficiencies of dyes are high [21].

Finally we want to point out that the phenomenon of line broadening is pertinent to the determination of the density of modes via fluorescence lifetime measurements. There are two kinds of line broadening, each with a different effect on lifetimes. The two contributions to the total width of the spectrum are called homogeneous linewidth and inhomogeneous linewidth [19,22]. The homogeneous linewidth is the width of the spectrum of individual atoms or molecules. This width can be measured by techniques like spectral hole burning or photon echo [22]. The homogeneous linewidth can be much larger than the natural linewidth due to interactions with the environment, i.e., dephasing. The inhomogeneous linewidth corresponds to the variation in center frequencies of the atoms or molecules. Due to this variation, the total spectral width of an ensemble of molecules is larger than the linewidth of an individual molecule. Measured fluorescence lifetimes are inherently an average over a wavelength region corresponding to the spectrum of individual molecules, i.e., over the homogeneous linewidths [22]. Thus, to avoid averaging out any changes in lifetime due to photonic band structure, it is desirable to have a homogeneous linewidth smaller than the width of peaks and valleys in the density of modes. However, one would also like to have a wide fluorescence spectrum so the photonic band structure can be probed at various frequencies. These two requirements may seem contradictory at first, but both conditions are satisfied at once if one uses a system with an inhomogeneously broadened emission spectrum, i.e., if one uses an ensemble of molecules with different center frequencies. Each molecule will probe the density of optical modes within its own narrow homogeneous linewidth; the ensemble of molecules will reveal the density of optical modes over the whole wide inhomogeneously broadened emission spectrum. Organic fluorescent dyes are especially suited as probes of the optical density because of their large inhomogeneous broadening. The homogeneous linewidth of the dye can be reduced by lowering the temperature [22]. Reducing the linewidth is profitable since it increases the wavelength resolution when measuring the density of optical modes. Lowering the temperature also reduces the nonradiative decay rate advantageously [20].

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