Emission and Transport of Light In Photonic Crystals

Koenderink, A.F.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 4

Broadband Fivefold Reduction of Vacuum Fluctuations Probed by Dyes

We have observed for the first time a strong angle-independent modification of spontaneous emission spectra from laser dyes in photonic crystals, made of inverse opals in titania. We show that both the fluorescence quantum efficiency and weak disorder play a key role in interpreting the experimental data. We compare the angle-independent emission spectra of dye in photonic crystals with spectra from such crystals with much smaller lattice spacings, for which emission is in the long wavelength limit. The data reveal inhibition of emission up to a factor $\sim 5$ over a large bandwidth of 13% of the first order Bragg resonance frequency. The center frequency and bandwidth of the inhibition agree with the calculated total density of states, but the measured inhibition of the vacuum fluctuations is much larger. Due to the specific location of the dye molecules, we likely probe the strongly modulated local photonic density of states.

4.1 Introduction

Within the framework of quantum electrodynamics (QED), it has long been recognized that the properties of the electromagnetic mode density may be used to tailor fundamental atom-radiation interactions [1]. Numerous cavity QED experiments have demonstrated the effects of manipulating vacuum fluctuations. Prime examples are reductions and enhancements of spontaneous emission rates and energy transfer processes, cavity induced energy level shifts, and Van der Waals and Casimir forces [1–5]. Cavity QED experiments are generally limited to narrow spectral bandwidths, and small spatial volumes, i.e., near the center of the cavity. It is highly desirable to be able to manipulate vacuum fluctuations over large bandwidths and extended spatial volumes in solid state systems, as proposed for photonic band gap materials [6–8].

Complete suppression of vacuum fluctuations is expected in the case of a photonic band gap, a frequency range for which no electromagnetic modes exist. As explained in Chapter 2, a photonic band gap arises from strongly coupled Bragg diffrac-
Inhibited emission of dye in strongly photonic crystals

Inhibitions in periodic dielectric structures with periodicity comparable to the wavelength of interest. Such a complete suppression of the density of states is hard to realize. In pioneering experiments on 3D photonic crystals, the inhibition was limited to a few percent by the small dielectric contrast [9–12]. Significant inhibition of spontaneous emission by strongly photonic crystals has not yet been reported, although several authors have (mis)interpreted stop gaps in emission as such [13–16]. A change of the spontaneous emission rate of a dipole is clearly an angle-integrated property, that can not be addressed by measuring the emission spectrum in one particular direction without further justification. Furthermore, a main complication is to find a proper reference system to which emission properties inside a photonic crystal can be compared, and to properly account for the role of luminescence quantum efficiency in the experiment. In this chapter, we examine the angle-independent spontaneous emission power from dyes in photonic crystals, compared to reference spectra obtained from chemically identical crystals with a much smaller lattice constant, for which the dye emission is in the long wavelength limit. We report broadband inhibition of spontaneous emission in strongly photonic titania air sphere crystals. This work opens up new research opportunities for studies of quantum optical phenomena in condensed matter environments.

4.22 Fermi’s Golden Rule and quantum efficiency

The aim of the experiment presented in this chapter, is to verify the degree to which spontaneous emission is influenced by the photonic total or local radiative density of states (DOS, resp. LDOS) for frequencies in the pseudogap of titania inverse opals. The pseudo gap is the range of frequencies starting at and just above the L-gap, the stop gap associated with the lowest order Bragg diffraction (see Fig. 2.4). The local radiative density of states $N_{\text{rad}}(r, \hat{d}, \omega)$ affects the radiative decay rate $\Gamma_{\text{rad}}(r)$ of a dipole transition with transition frequency $\omega_0$ at dipole position $r$ through Fermi’s Golden Rule according to

$$\Gamma_{\text{rad}}(r) = \frac{\pi \omega_0 \mu^2}{3 \hbar \varepsilon_0} N_{\text{rad}}(r, \hat{d}, \omega_0),$$

where $\hat{d}$ is the transition dipole orientation, and $\mu$ the transition dipole moment [17]. The most obvious experiment consists of taking a two level system, keeping the ‘atom’ part ($\omega_0$ and $\mu$) fixed, and comparing the decay rate $\Gamma$ of a source at a well defined position in the crystal with the decay rate of the source in a reference system with a known local radiative density of states. For total DOS characterization, one would need to average the result over all source sites and orientations in the crystal unit cell. Such a measurement is based on having (i) a source with quantum efficiency near unity, (ii) a chemically identical reference system with controlled LDOS, and (iii) knowledge of or control over the location of the luminescent sources. In Sections 4.2 and 4.3, we explain the intricacies associated with the source quantum efficiency and discuss the optimal choice of reference satisfying these criteria.
4.2. Fermi’s Golden Rule and quantum efficiency

In a time-resolved fluorescence measurement the recorded signal is proportional to the excited state population at time $t$, which decays with a decay rate $\Gamma_{tot}$. This total decay rate is determined by the sum of both the radiative and all nonradiative decay channels, and reads $\Gamma_{tot} = \Gamma_{rad} + \Gamma_{NR}$. Here the nonradiative decay rate $\Gamma_{NR}$ results from all competing nonradiative decay channels. Evidently, changes in $\Gamma_{rad}$ can only be determined from a dynamic measurement if the quantum efficiency $\eta = \Gamma_{rad}/\Gamma_{tot}$ is of order unity. At the risk of obscuring the discussion, we note that the quantum efficiency depends on the source position in the case of a spatially inhomogeneous local radiative DOS, unless nonradiative decay can be ruled out completely.

Naively, one might expect that the total emission power in a continuous wave (cw) experiment may also reflect the local radiative density of states, since a gap in the LDOS would obviously result in a total absence of emitted photons. However, closer examination shows that the total emission power is not indicative of the LDOS for sources with near unit quantum efficiency. We consider an effective two-level system that is pumped at a constant rate $P$. The excited state population is governed by

$$\frac{dN_2}{dt} = P - \Gamma_{tot} N_2$$  \hspace{1cm} (4.2)$$

and amounts to $N_2 = P/\Gamma_{tot}$ in the stationary case. The number of photons $I$ emitted per unit time is the fraction $\eta$ of decay instances $\Gamma_{tot} N_2$ in which a photon is actually emitted, i.e., $I = \eta \Gamma_{tot} N_2 = \eta P = P \Gamma_{rad}/\Gamma_{tot}$. For unit quantum efficiency this relation simply states that every incident pump photon is converted into an emitted photon and implies that the emitted power at fixed pump rate is not related to the DOS. Still, this result apparently conflicts with the notion that the emitted power vanishes if the source frequency matches a gap in the DOS. This controversy is easily resolved by noting that a constant nonzero pump rate can not be achieved for identically zero decay rate, i.e., in the case of a transition in the photonic band gap and unit quantum efficiency. Then, the pump rate drops to zero as soon as all light sources are excited. Generally, this saturation argument comes into play for pump energy densities $W_D$ such that the absorption rate per emitter $\frac{W_D}{h_c} \sigma_a$ (where $\sigma_a$ is the absorption cross-section) is comparable to or larger than the decay rate $\Gamma_{tot}$. This regime is not met in the experiments reported in this thesis, but is automatically met if $\Gamma_{tot} = 0$. An alternative perspective originates from classical electromagnetic theory for a radiating dipole antenna [18]. In this picture, a constant pump rate corresponds to a dipole antenna in which a constant power is fed and which therefore radiates at a constant output power. As the local radiative density of states decreases, a larger dipole current is needed to input the same power. For a frequency in the gap an infinite current would be needed to drive the dipole at the specified power. The converse notion is at the heart of FDTD calculations [19], where the emitted power at given dipole current is used to determine the LDOS.

A most surprising result is obtained if one considers a system of low quantum efficiency. Then, the total decay rate $\Gamma_{tot} = \Gamma_{NR}(1 + \eta + O(\eta^2))$ is completely determined by the nonradiative decay channels. The emitted power $I = P \Gamma_{rad}/\Gamma_{tot} \approx P \Gamma_{rad}/\Gamma_{NR}$
is therefore an excellent signature of the radiative decay rate if it is referenced to a system with the same nonradiative decay channels. In conclusion, cw and time-resolved measurements can be used in complementary cases to probe the photonic density of states. For efficient sources the emission power only reflects the pump rate and the decay time reveals the LDOS. For inefficient sources on the other hand, the emission power reflects the LDOS, but the total decay time is not affected by the photonic environment.

### 4.3 Nonphotonic reference host

The choice of reference host in which to embed the chosen luminescent species is of prime importance for a comparison with the photonic system. It is essential that the reference system provides the same chemical environment as the photonic system to ensure an unchanged transition dipole moment, the same nonradiative decay rate and the same inhomogeneous broadening. Lifetime changes observed in several time-resolved experiments in which the refractive index mismatch in a photonic system was tuned by infilling with different solvents were rather due to changes in the transition dipole moment or chemical interactions [20], than to photonic effects [9, 10]. Indeed it is well known that, e.g., the polarity of a solvent influences the emission properties of organic dyes. Furthermore it is clear from the discussion above, that especially in the case of a cw measurement, the reference material should provide the same nonradiative decay rate $\Gamma_{\text{NR}}$ in order to make a comparison of emitted powers possible.

It is beneficial to choose a luminescence species with a large inhomogeneous linewidth if the emission power of inefficient sources is to be probed. Sources with a narrow homogeneous linewidth should be chosen to ensure that each emitter probes the local radiative DOS in a frequency window narrow compared to the spectral features of the LDOS. If an ensemble of sources is chosen with a large inhomogeneous linewidth, many frequencies can be probed independently but simultaneously. In addition, a large inhomogeneous linewidth facilitates comparison of the emitted power from photonic and reference systems, independent from differences in pump efficiency. Comparison of the emitted power for the photonic and reference system only reveals the variation of the LDOS unambiguously, if differences in the pump rate are accounted for. A priori, this necessitates quantifying the detection- and pump efficiency for both the photonic and reference experiment. For an inhomogeneously broadened lineshape, the ratio of the photonic to the reference spectrum of inefficient sources

$$\frac{I_{\text{photonic}}}{I_{\text{reference}}} = \frac{P_{\text{photonic}} \Gamma_{\text{rad,photonic}}}{P_{\text{reference}} \Gamma_{\text{rad,reference}}} = A \frac{\langle N_{\text{rad,photonic}} \rangle(\omega)}{\langle N_{\text{rad,reference}} \rangle(\omega)} \quad (4.3)$$

reveals the frequency dependence of the ratio of the photonic and reference local radiative DOS (averaged over source positions $\mathbf{r}$ and orientations $\hat{\mathbf{d}}$, as $\langle \rangle$ indicates) over a large frequency range. The constant of proportionality $A$ contains the differences in
pump- and detection efficiency, and can be eliminated if the ratio of $\langle N_{\text{rad,photonic}}(\omega) \rangle$ to $\langle N_{\text{rad,reference}}(\omega) \rangle$ is explicitly known at some specific frequency, particularly if the inhomogeneous spectrum of the photonic sample extends to frequencies below the window of photonic behavior.

Within the constraint of identical chemical composition, one may consider, e.g., disordered titania composites, such as powders or pulverized samples as suitable references for experiments on titania inverse opals. However, such a material would be highly multiply scattering [21], possibly giving rise to a strongly modulated and position dependent local radiative DOS [22]. A titania inverse opal with a very small lattice constant on the other hand, is optimally suited as a reference environment. As outlined in Chapter 2, the band structure depends only on the normalized frequency $\omega a/2n$. A crystal with small lattice parameter $a$ will therefore only be photonic for large frequencies. For sufficiently small lattice constant, the spectrum of the emitter will probe the long wavelength regime of such chemically identical crystals. In this regime the crystals behave as weakly scattering effectively homogeneous media, and provide a DOS with a quadratic frequency dependence typical for a medium with the effective refractive index of the titania inverse opals.

### 4.4 Experiment

Analogous to the experiment documented in Chapter 3, we studied titania inverse opals with cubic lattice parameters $a = 430$ and 480 nm doped with the organic laser dye Rhodamine 6G (R6G), and with lattice parameter $a = 510$ nm doped with the organic laser dye Nile Blue [23]. These dyes feature emission spectra with a large inhomogeneous width of order 5000 cm$^{-1}$. The homogeneous linewidth is of order $\approx 170$ cm$^{-1}$, as borne out by photon echo experiments [24], and cavity enhanced emission of dye in microspheres [4, 25]. In addition to the aforementioned 'photonic' samples, titania inverse opals with lattice spacing $a = 350$ nm were prepared as reference hosts. The reference crystals, manufactured along the same preparation route as the 'photonic' samples, but starting from smaller template spheres, were doped with dye according to the same procedure used for the photonic samples. Explicitly, the R6G-doped samples were prepared by 30 min. immersion in a dilute $\sim 1 \mu$mol solution of R6G in ethanol, followed by rinsing and drying. Nile Blue samples were similarly immersed for 24 h., rinsed and dried, using a 70 $\mu$mol solution of Nile Blue in ethanol. To select emission from the bulk of the photonic crystals, the dye adsorbed near the external sample surface was irreversibly bleached by illuminating the crystals with an intense laser beam at the Bragg angle [26]. Bleaching was monitored by the saturation of the stop gap depth in the $\alpha = 0^\circ$ emission spectrum, where $\alpha$ is the emission angle relative to the surface normal, which coincides with the 111 reciprocal lattice vector. For the reference samples, surface bleaching was attempted using the 457 nm line of an Argon laser at normal incidence. Bleaching of the reference samples caused an overall reduction of emission intensity at constant pump power, without introducing drastic changes of the angle-independent emission lineshapes. As the dye
molecules are adsorbed onto the titania, our probe of the local radiative DOS is limited by the volume fraction of solid material, which comprises less than 12% of the unit cell volume.

The dye in the crystals was excited with a $p$-polarized laser beam emitted by cw Argon ion lasers\(^1\) tuned to a wavelength of $\lambda = 488$ nm in the case of R6G-doped samples (see Fig. 4.1). For spectral measurements of emission from Nile-Blue doped samples, as well as for time-resolved fluorescence decay measurements, $p$-polarized emission from a mode-locked frequency-doubled Nd\(^{3+}:\)YAG laser was employed. The actively mode-locked Nd\(^{3+}:\)YAG laser (Spectra Physics 3800) generated 12 W average output power in TEM\(_{00}\) mode in 100-150 ps pulses (full width at half maximum) at a 80 MHz repetition rate. These pulses were shortened to 5–10 ps in a Spectra Physics 3595 fiber/grading pulse compressor to achieve a high power for second harmonic generation. The system was actively stabilized at a constant average power of $\sim 400$ mW at 532 nm. In all experiments, the cw excitation power at the sample was below 10 $\mu$W focused to a spot 30 $\mu$m in diameter. Samples were mounted on a goniometer allowing to vary the detection angle $\alpha$ relative to the surface normal. Stop gaps in the emission spectra (see previous chapter) were used as a quality check.

\(^{1}\)In order of appearance: Spectra Physics 2016, Coherent Innova 90, Lexel 85
of the crystals. The position of the pump spot on the sample, and the alignment of the sample and beam relative to the goniometer axis were monitored and controlled to within 20 μm using a small long working-distance microscope. Fluorescence was imaged onto the entrance slit of a Carl Leiss monochromator equipped with a flint prism. The slit width was set to accommodate the low count rates due to the limited dye concentrations, providing a resolution of ~ 100 cm⁻¹. A Hamamatsu R3809U Micro Channel plate (MCP) detector was used to record the fluorescence. For time-resolved measurements, both the MCP signal and pulses from a trigger photodiode monitoring the pump beam were passed through constant fraction discriminators. The time lag between the MCP signal and trigger was fed to a multi-channel analyzer as a voltage generated by a time to amplitude converter (TAC). The MCP-pulses (average rate of ≤ 10⁴ s⁻¹) were used as TAC start pulses, while the trigger-diode output was connected to the TAC stop input. This time-correlated single-photon counting technique provides a resolution of 55 ps [27].

In order to verify the quantum efficiency of dye on titania, we measured the luminescence decay of dye on a powder of anatase titania particles (Aldrich). For R6G on titania (see Fig. 4.2) we find a very fast decay, characterized by a ~ 500 ps decay time. After rapid decay over ~ 1 decade, a slower time tail sets in. The luminescence decay of R6G dissolved in ethanol, on the other hand, is observed to be single-exponential with a decay time of 3.6 ns, as expected from literature [28]. Evidently, the quantum efficiency of R6G on titania is strongly reduced compared to the ~ 95 % quantum efficiency in ethanol. We use the first moment of the data as a measure of the decay time. Comparison to the expected radiative decay rate (3.6 ns)⁻¹ yields an estimate of the quantum efficiency less than 10% [28, 29]. The relevant nonradiative decay mechanism for organic dyes on semiconductors is a well-documented electron-transfer process [30]. In this process the excited state of the dye has an energy above the con-
Inhibited emission of dye in strongly photonic crystals

Inhibition band of the TiO$_2$ to which it is adsorbed. After excitation the excited electron is transferred to the semiconductor, leaving the dye molecule oxidized. This efficient electron transfer process is the basis of the so-called ‘organic solar cell’ developed by O’Regan and Grätzel [31]. The oxazine dye Nile Blue has a low quantum efficiency $\leq 15\%$ both in solution [23] and on titania. Several schemes were considered to prevent the electron transfer in order to retain a high quantum efficiency. Any scheme in which the dye is incorporated in the crystal (for instance incorporated in small SiO$_2$ spheres) before the titania is formed is incompatible with the heating stage necessary to form and crystallize the titania, as dyes generally do not withstand temperatures in excess of 350$^\circ$C. Coating of the TiO$_2$ surface with a $\sim$ 5 nm layer of SiO$_2$ prior to adsorbing the dye was demonstrated to prevent the electron transfer in the case of titania powders [32]. New methods are currently being developed to coat the inner surface of the titania air sphere crystals with such an insulating layer [33]. Given the low quantum efficiency of dyes on titania, we have designed a cw experiment to probe the photonic DOS.

As alternative luminescent species, quantum dots or lanthanide ions may be considered. Unfortunately, most colloidal quantum dots are not stable when exposed to air and water, do not usually have a quantum efficiency near unity, and may not be immune to electron transfer processes [34]. Still, quantum dots with inorganic coating (such as CdSe-ZnS/ZnSe/ZnS/CdS core-shell nanocrystals) to passivate the surface electronically and chemically appear to be among the most promising and flexible light sources for future experiments [35–38]. Rare earth ions on the other hand have the disadvantage of not providing an inhomogeneously broadened spectrum. Their narrow spectrum compared to the large bandwidth of the L-gap and pseudo gap, would necessitate a much larger set of lattice spacings $a$ to map the LDOS over the normalized frequency ($\omega a/2\pi c$) range of interest. Furthermore, the efficiency of luminescence for rare earth ions strongly depends on the chemical environment, and is not well studied for titania hosts. Typically, efficient emission is obtained only after shielding the ions, using organic ligands for instance [39, 40].

### 4.5 Inhibition of emission and the DOS

Emission spectra at several detection angles for a R6G doped crystal with $a = 480$ nm are presented in Fig. 4.3. As described in Chapter 3, internal Bragg diffraction of the diffusely propagating luminescence causes clearly observable stop bands suppressing the spectra in angle-dependent frequency ranges, as apparent in Fig. 4.3(a). Before discussing the connection between angle-dependent, angle-integrated, and reference emission spectra, it is instructive to discuss the experimental signatures indicative of good or bad sample quality. Lineshapes reported on in this chapter (apart from Fig. 4.3(b)) are from samples with $a = 430$, 480 and 510 nm which showed clear stop gaps and well reproducing line shapes over extended sample areas. Of the many crystals with these lattice parameters examined in the experiment, a fraction $\approx 30\%$ was found for which emission spectra did not show any signature of photonic behavior.
Several samples showed both areas resulting in clear stop gaps, and apparently disordered areas. In the latter cases, no stop gaps or gaps with depths less than 10% were found to affect the spectra, as apparent in Fig. 4.3(b) ($a = 480$ nm, R6G doped sample). Visual inspection of such samples or sample areas showed only faint or no opalescence, and SEM and optical microscopy indicated that large unstructured lumps of titania covered the sample surfaces. Such lumps may have been formed where the polystyrene template did not stick to the capillary walls during infiltration with the TiO$_2$ precursor. Emission lineshapes from these crystals, for which the fabrication was apparently not satisfactory, significantly differ from the emission lineshapes observed at any angle for the obviously photonic samples. Although lack of stop gaps, absence of opalescence, and the observation of solid titania chunks only provide information on surface quality, we regard these crystals as apparently disordered. Emission spectra from the apparently disordered samples resemble spectra from dye in the reference hosts, apart from a broadening. We note that crystals with bad surface quality can not be surface-selectively bleached by using a pump beam at the Bragg angle. Sets of spectra without stop gaps may therefore be mixtures of emission from dye near the surface, from dye in disordered, and from dye in ordered air sphere arrays. The 'photonic' spectra presented in this chapter were reproduced over sample areas at least ($\sim 0.5$ mm)$^2$ in size, as probed by measuring lineshapes at many angles for a detection focus that was systematically scanned over grids with spacings 50 to 100 $\mu$m over the sample surfaces.

Figure 4.3(a) shows that the frequency range in which spectra are suppressed due to Bragg diffraction shifts to higher frequencies with increasing angle. Modification of the spectra ceased for angles $\alpha$ exceeding 60°. The line shapes were independent

**Figure 4.3:** (a) Internal Bragg diffraction causes strongly angle-dependent emission spectra (see Chapter 3) from well ordered photonic crystals (R6G, $a = 480$ nm). Horizontal bars indicate the stop bands that attenuate the spectra and shift to higher frequency with increasing angle (see Chapter 3). (b) Emission spectra of R6G on a apparently disordered sample made from a template with the same sphere size. No visible opalescence was discernible from the area coincident with the pump and detection focus.
Inhibited emission of dye in strongly photonic crystals

Figure 4.4: (a) Emission spectra of R6G in TiO2 inverse opals with a = 430, 480 nm (grey, resp. black) detected at α = 60° strongly differ from the angle-independent emission spectrum of R6G in a TiO2 inverse opals with a = 350 nm (not photonic in the frequency range shown). (b) same for Nile Blue on a sample with a = 510 nm (black curve) and in the reference (a = 350 nm, dashed curve). Horizontal bars in both panels indicate the L-gaps of the relevant crystals (same color coding as the curves).

of pump intensity, and the emission intensity was found to increase in proportion to the pump power. The α ≥ 60° spectra are representative of the angle-averaged total emission power, as discussed below. The α = 60° spectra for R6G doped samples with a = 430, 480 nm differ significantly from spectra of R6G in reference samples with a = 350 nm, as shown in Fig. 4.4(a). A sizable reduction of emission power in the frequency window from ~ 15500 to 20000 cm⁻¹ is apparent when the spectra are scaled to match on the low frequency side below any Bragg condition. The reduction, which occurs in a frequency window blue shifted relative to the L-gap, results in clear red shifts of the maximum emission frequencies. A similar spectral shift was observed when comparing α = 60° spectra of the Nile Blue sample (a = 510 nm) with its reference, see Fig. 4.4(b). The reference line shapes reproduced well on a multitude of reference samples, and were independent of angle, due to the fact that the lowest order Bragg diffraction occurs at 22000 cm⁻¹, far above the dye emission frequencies. The reduction is not due to differences in chemical interactions of the dye with its environment, since the reference samples are chemically identical to the photonic samples. Red shifts due to reabsorption are excluded, since the dye concentrations were sufficiently low by at least two orders of magnitude.

We extract the photonic LDOS effect on the total emission by dividing the α = 60° spectra by the emission spectrum of the same dye in the reference samples, as shown in Fig. 4.5 both for the R6G data sets with a = 480, 430 nm, and for the Nile Blue sample with a = 510 nm. Due to the low efficiency of these dyes on titania, the intensity ratios, which are scaled to unity on the low frequency shoulder, represent the LDOS probed by the dye, divided by the reference LDOS. The lowest order stop gap of the
4.5. Inhibition of emission and the DOS

Figure 4.5: Intensity ratios of spectra in Fig. 4.4 to the reference spectrum for R6G, with $a = 480$ nm (dashed) and $a = 430$ nm (dotted) and Nile Blue, for $a = 510$ nm to the Nile Blue reference spectrum. The inhibition shifts to the red with increasing lattice constant $a$. Horizontal bars indicate the L-gaps.

reference samples at 22000 cm$^{-1}$ is far above the dye spectrum. Hence, the reference LDOS has a well defined quadratic frequency dependence [41, 42]. The width of the inhibition range $\sim 2000$ cm$^{-1}$, i.e., 13% of the L-gap center frequency, attests to the strongly photonic character of the inverse opals. The inhibition range is blue shifted relative to the L-gap. Indeed, from a simple angle-dependent stop-gap consideration one expects that the blue edge of the L-gap corresponds to the frequency for which the largest fraction of solid angle is simultaneously contained in a stop gap [43]. The shift of the inhibition to higher frequency with smaller lattice parameter, confirms that the spectral changes are due to the photonic crystal properties.

A crucial observation is that the $\alpha = 60^\circ$ spectra are representative of the spectral distribution of angle-averaged luminescence in the bulk. Due to the bleaching it is clear that all the luminescence is generated in the bulk of the photonic crystal, and the surface LDOS does not play a role. Still, the surface crystal layers affect the angle-dependent emission spectra through internal reflection. Here, we explain how the angle-averaged luminescence can be extracted from the angle-resolved spectra. Scattering by disorder plays a key role in the interpretation. Since the transport mean-free path $\sim 15 \mu$m [44] is much smaller than the sample thickness $\sim 200 \mu$m, the luminescence propagates diffusively through the bulk of the crystals. The spectral distribution $W(\omega)$ of the diffuse luminescence in the bulk is the $4\pi$ sr average of spectra of all dye molecules in the pump volume, and is thus determined only by the LDOS and the inhomogeneous line broadening of the dye. The diffuse luminescence acquires an angular dependence only when it exits the sample, as explained in Chapter 3. This angle and frequency-dependent modification of the diffuse luminescence spectrum is due to internal Bragg diffraction [45] and may be calculated from diffusion theory with internal reflection [46–48]. In Chapter 7 the applicability of this model will be discussed, based on theory and on experiments us-
Inhibited emission of dye in strongly photonic crystals

**Figure 4.6:** (a) Black curve: intensity ratio for Nile Blue, \( a = 510 \text{ nm} \) taken from Fig. 4.5 for comparison with the spectrally resolved fluorescence decay rates of Nile Blue in the reference (closed triangles) and photonic crystal (open triangles). No significant difference is observed, due to the low quantum efficiency. (b) Black curve as in (a). The open circles indicate the total DOS calculated for a titania inverse opal \( a = 510 \text{ nm} \), divided by \( \omega^2 \) and scaled to match on the low frequency edge.

Inhibiting diffuse light injected by externally incident plane waves. According to diffusion theory, the diffuse intensity escaping in an angular range from \( \alpha \) to \( \alpha + d\alpha \) equals

\[
\frac{1}{2} W(\omega) \cos \alpha [\tau_\omega(\omega) + \cos \alpha [1 - R(\alpha, \omega)]] d(\cos \alpha).
\]

For exit angles outside a stop gap (i.e., \( \alpha \geq 60^\circ \)), the internal reflection coefficient \( R(\alpha, \omega) \) vanishes for all emission frequencies. Hence, the frequency dependence of the measured spectrum at \( \alpha \geq 60^\circ \) is only determined by the angle-integrated emission spectrum \( I(\omega) \), and the so-called extrapolation length ratio \( \tau_\omega(\omega) \). This frequency-dependent parameter is related to the angle and polarization averaged internal reflection coefficient [47, 48], and can be derived from \( R(\alpha, \omega) \) according to Eqs. (7.1.7.17) (see Ref. [47, Eq. (2.22) and (3.5–3.9)])]. We estimate the internal reflection coefficient \( R(\alpha, \omega) \) to be less than 70% for directions within a stop gap [45], and 0% outside. For \( \alpha = 60^\circ \), we find that the extraction efficiency, \( \tau_\omega(\omega) + \frac{1}{2} \), increases by less than 30% as the frequency increases from the red to the blue edge of the L-gap, and linearly decreases by less than 10% as the frequency is increased to the blue edge of the emission spectra. Consequently, the \( \alpha = 60^\circ \) emission spectra are representative of the spectral distribution of diffuse luminescence \( W(\omega) \) in the bulk to within better than 30%. We conclude that the large difference of up to a factor 5 between the \( \alpha = 60^\circ \) emission spectra from the photonic crystals and reference spectra in Fig. 4.4 is due to a large change in the angle-integrated total emission power. Given the low efficiency of the emitters, such a reduced emission reflects the modulation of the photonic LDOS. Detailed analysis shows that the true inhibition of total emission may even exceed the lineshape ratio in Fig. 4.5, due to a slightly enhanced extraction efficiency for \( \alpha = 60^\circ \) for frequencies in the inhibition band.

For comparison with the cw experiment, we have performed time resolved measurements for the Nile Blue doped samples, shown in Fig. 4.6(a). No significant difference is apparent between total decay rates in the photonic crystal and the reference,
4.5. Inhibition of emission and the DOS

neither for frequencies below, or in the range of inhibited radiative decay evident from the spectra. It appears that the low quantum efficiency precludes determination of the radiative decay rate from a dynamic measurement, but allows to extract changes in radiative decay rate from the emitted power. A lengthening of the radiative lifetime according to the inhibition in Fig. 4.5, causes a variation \( \leq 10\% \) of the total lifetime for a quantum efficiency of 10\%. This variation is within the wavelength dependence of the lifetime on individual samples. Furthermore our limited dynamic range, set by the pump pulse repetition rate, does not allow unambiguous observation of lengthened lifetimes. Lacking efficient emitters on semiconductors such as TiO\(_2\) [30], the complementary experiments in which a lengthening of the total lifetime is expected currently remain out of reach. In view of the large magnitude of the inhibition of emission on titania, recently developed silica, zirconia, and alumina air sphere crystals may prove to be sufficiently photonic for such experiments, despite the lower index contrast. These host materials do not cause quenching by electron transfer [33].

Remarkably, the magnitude of the reduction in emitted power, amounting to at least a factor 5 relative to the low frequency edge, exceeds the reduction in total solid angle for light propagation. The reduction in solid angle for light propagation amounts to a factor 2, which is a simple estimate of the reduction of the total DOS [43]. To investigate this further, we have calculated the total DOS using the H-field inverted matrix technique [42, 49], and the fcc Brillouin zone integration scheme [50] explained in Chapter 2. Eigenfrequencies were calculated on a coarse grid of 2480 k-points spanning the irreducible part of the Brillouin zone, using 725 plane waves. To describe the dielectric structure, we used the model presented in Chapter 3, in which close-packed air spheres are assumed, surrounded by shells of titania (\( \varepsilon = 6.5 \)) with cylindrical windows between neighboring spheres. This model predicts reflectivity features in excellent agreement with prior experiments [51], both in the range of first and second order Bragg diffraction (i.e., up to band 9), and is in agreement with structural data. As shown in Fig. 4.6(b), the total DOS, normalized by the quadratic DOS in the reference samples is indeed reduced in a frequency range coincident with the experimentally determined inhibition window. The modulation of the total DOS, however, amounts to even less than the factor of 2 estimated from the reduction in total solid angle of allowed propagation directions. Clearly, a complete understanding of the large reduction of the emitted power requires a full calculation of the local DOS, taking the spatial distribution and dipole orientation of the emitters into account. In the experiment presented here, the spatial distribution of emitters limits the probe volume to those \( \sim 6-12\% \) of the unit cell occupied by titania. Future experiments using, e.g., atomic vapors as emitters, may allow to probe the local DOS over the remaining unit cell volume. Calculating the local DOS averaged over part of the unit cell currently remains a formidable task beyond the scope of this thesis. As yet, the local DOS of realistic three-dimensional structures has only been calculated for a limited number of positions in the unit cell by less than a handful of authors [41, 42, 52]. We note that a time-resolved decay measurement for efficient
Inhibited emission of dye in strongly photonic crystals

fluorescent sources would not show a simple single exponential decay, but would be composed of contributions from sources with different decay times depending on the LDOS at their positions. The first moment of the intensity distribution over time should correspond to the source-averaged reduction in emission power reported in this chapter. In view of the expected complexity of the fluorescence decay of ensembles of sources, it is of prime importance to develop combinations of light sources and photonic crystal materials for which the decay dynamics in absence of LDOS variations is completely understood, and which feature a high quantum efficiency.

4.6 Conclusion

We have observed for the first time inhibition of spontaneous emission in a photonic crystal. This is a first demonstration of the feasibility of creating novel solid state photonic environments that allow experiments shielded from vacuum fluctuations. We have demonstrated that inhibition occurs over a large frequency bandwidth, in accordance with theoretical predictions. The extraordinarily large inhibition compared to the expected variation of the total DOS shows that far reaching spontaneous emission control may even be realized without a full photonic band gap. Central issues to master such control, however, revolve around (i) quantitative knowledge of the local density of states throughout the unit cell, (ii) control over the locations of the emitters, and most importantly (iii) the luminescence quantum efficiency. Each photonic crystal backbone material, usually chosen on the merit of large real and small imaginary dielectric constant, will pose different challenges if efficient emitters are called for. The electron transfer processes occurring on semiconductors like titania simply present an illustrative example of such a specific constraint due to materials issues. Finally, we have shown the relevance of structural disorder in the interpretation of emission experiments.

References

References

Inhibited emission of dye in strongly photonic crystals

Phys. 70, 3884 (1979).
References


