

Coupling of Single Organic Molecules to Photonic Micro-Structures

A Thesis Submitted to the Department of Physics,
Imperial College London
by

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In Partial Fulfilment of the Requirements for the Degree of
Doctor of Philosophy

2020

Abstract

Dopant molecules in organic crystals can be triggered to create single photons with certainty. This basic principle is currently being leveraged to develop a new generation of photonic components capable of delivering single photons to optical hardware. In turn, these single-photon sources are enabling increasingly sophisticated technologies based on the quantum nature of photons, in areas such as quantum computation and quantum cryptography.

In this thesis, I present my work towards realising an organic single-photon source using dibenzoterrylene (DBT) molecules in anthracene crystals. To realise a deterministic single-photon source with molecules, we have to address two main challenges. First, it is necessary to collect all the photons emitted by a single molecule into a propagating optical mode. To achieve this, I have investigated methods to place single DBT molecules close to the field maximum of single-mode waveguides. I describe our strategy which consists of overlaying microfluidic channels on top of silicon-nitride ridge waveguides. With this geometry, targeted crystallisation of DBT-doped anthracene occurs in small gaps running across the waveguides. We probe the system using coherent single-molecule spectroscopy and estimate that 7 % of the molecular emission is coupled to the waveguide modes for one of our fabricated devices. The second challenge is to turn DBT molecules into coherent two-level systems. The vibrational spectrum of DBT prevents the system from generating indistinguishable single-photons without filtering of the emission. However, the reduction in single-photon efficiency due to filtering can be improved by selectively accelerating the radiative decay of the zero-phonon line. I discuss how such an enhancement is possible using optical cavities and how both challenges can be addressed with this approach. Finally, I introduce a new design for a vertically-emitting cavity with an active layer of DBT-doped anthracene.

Declaration

I declare that all the material in this thesis is my own, unless otherwise stated and referenced.

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List of Publications

1. S. Grandi, M. P. Nielsen, J. Cambiasso, **S. Boissier**, K. D. Major, C. Reardon, T. F. Krauss, R. F. Oulton, E. A. Hinds, and A. S. Clark. “Hybrid plasmonic waveguide coupling of photons from a single molecule”. In: APL Photonics 4.8 (2019), p. 086101. doi: [10.1063/1.5110275](https://doi.org/10.1063/1.5110275)
2. R. C. Schofield, K. D. Major, S. Grandi, **S. Boissier**, E. A. Hinds and A. S. Clark. “Efficient excitation of dye molecules for single photon generation”. In: Journal of Physics Communications 2.11 (2018), p. 115027. doi: [10.1088/2399-6528/aaf09a](https://doi.org/10.1088/2399-6528/aaf09a)
3. S. Grandi, K. D. Major, C. Polisseni, **S. Boissier**, A. S. Clark, and E. A. Hinds. “Quantum dynamics of a driven two-level molecule with variable dephasing”. In: Physical Review A 94.6 (2016), p. 063839. doi: [10.1103/PhysRevA.94.063839](https://doi.org/10.1103/PhysRevA.94.063839)
4. C. Polisseni, K. D. Major, **S. Boissier**, S. Grandi, A. S. Clark, and E. A. Hinds. “Stable, single-photon emitter in a thin organic crystal for application to quantum-photonic devices”. In: Optics Express 24.5 (2016), p. 5615. doi: [10.1364/OE.24.005615](https://doi.org/10.1364/OE.24.005615)

1 Introduction

The concept of quantised light dates back to the origins of quantum mechanics at the start of the twentieth century, when classical physics failed to explain radiation phenomena [1]. But it was not until the early 1980s and the experiments of Aspect that the experimental foundations for quantum optics were laid down [2]. At that time, it was realised that attenuating classical light sources, such as lamps or lasers, is not enough to isolate single-photon quantum states. The previous rationale was that weak classical sources - for which there is on average much less than one photon at any time - could be described as being made from distinct, temporally separated single-photon states. However, this is not strictly true because photon emission events from such sources are random and independent from each other. Regardless of how weak the source is, the probability of finding two photons or more in any time interval is still significant compared to the probability of finding only one. Any experiments based on these sources can be explained by classical theories of light which do not require the concept of a photon.

The paradox is that weak beams of classical light are mostly comprised of single-photon states but still behave classically on average. To access the quantum nature of the underlying photons, we also need to know at which time the single photons are being emitted. During an experiment, it is then possible to restrict the data collection to when single-photon states are travelling through the apparatus. Only then does the quantum nature of light start to appear. To achieve this, the first experiments leveraged the process of radiative cascade in calcium atoms, which generates two photons in quick succession [3]. With photon-pair sources, the detection of one of the photons in a pair heralds the presence of the other and gives the timing information necessary to isolate

it. This has led to beautiful single-photon interference experiments revealing the wave-particle duality of light [4].

Since then, photon-pair sources have been the workhorse of quantum optics. Modern sources of photon pairs are generally based on non-linear processes in the solid state [5], such as spontaneous parametric down-conversion [6, 7] or four-wave mixing [8]. In addition to isolating single-photon states, these sources have been instrumental in fundamental tests of quantum mechanics [9] and have enabled real-world applications of quantum information [10]. Beyond these great advances, quantum sources are now facing the challenge of scaling. For cutting-edge applications that require networks of interacting quantum systems [11–13], sources must emit at known times for the photons to travel through the experiment simultaneously. With current photon-pair sources, the emission time can be measured by detecting one photon of the pair, but that time is still random. The synchronisation of two photons from two different photon-pair sources is therefore probabilistic.

To synchronise single-photon sources, they must be triggered. In most cases, this is achieved using short laser or electronic pulses to initiate the emission process. The figure-of-merit is then the probability of producing a single photon per pulse. For current photon-pair sources, the probability per pulse must be kept low to minimise the chances of emitting more than one photon. To get around this problem, it is possible to combine several pair sources together to increase the probability of one successful emission event. Upon detection of one photon from a successful source, the other photon is routed into the experiment using active optical elements. This method is called multiplexing, and this is an ongoing area of research [14–17].

Another solution is to use a physical process from which one and only one photon is emitted with a high probability. Let us consider the quantised electronic levels of a single charged particle bound to a region of space. For allowed transitions, a short laser pulse can excite the particle to a high energy level, and the laws of spontaneous emission

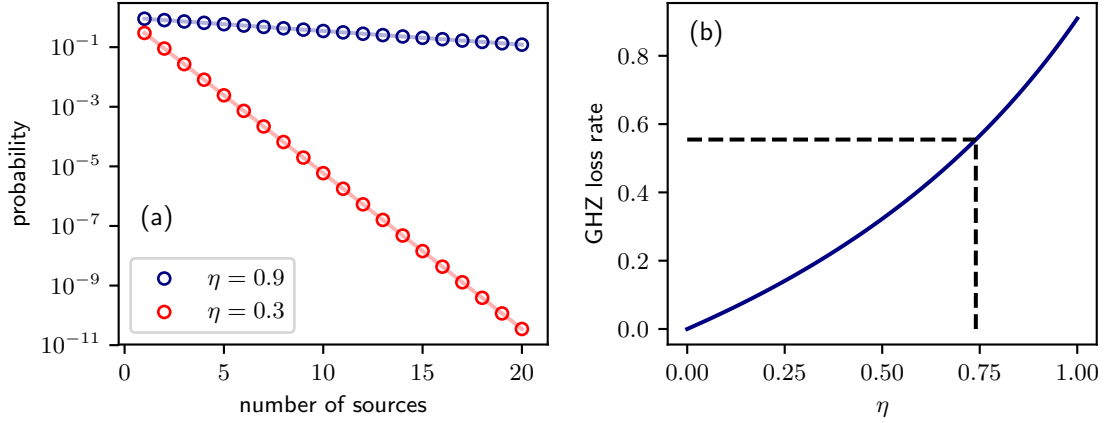


Figure 1.1: The scaling catastrophe. (a) Probability per triggering event of all sources firing simultaneously as a function of source efficiency η . (b) Probability of successfully generating a GHZ state after post-selection with detector efficiency of 90% and as a function of source efficiency. The dashed line represent the minimum source efficiency required to implement linear-optical quantum computation as described in [18].

dictate that only one photon is emitted during the decay to a lower energy state. To this end, many quantum emitters have been isolated [19, 20], which range from atoms and ions, to fluorescent organic molecules, to nano-islands of semi-conductor material, to impurities in diamond. Of course, the single-emitter approach comes with limitations of its own, and the biggest challenge is that of collection. In bulk material, the radiation pattern of these emitters is somewhat isotropic, and designing optical structures to collect every emitted photon is very challenging. If the collection efficiency is not close to unity, these deterministic quantum emitters become probabilistic single-photon sources of their own.

Single molecules in organic crystals were one of the first solid-state quantum emitters to be studied [21, 22]. It was quickly realised that they could form the basis of a triggered source of single photons [23, 24]. However, organic materials are not well suited for the fabrication of sub-wavelength structures, which are necessary for efficient photon extraction. In contrast, emitters such as quantum dots have hugely benefited from established nano-fabrication technology to become the mainstream path towards

deterministic single-photon sources [25–27]. Recently, a renewed interest in organic molecules has emerged, as technology is developing to incorporate organic crystals with inorganic photonic structures in hybrid devices [28–31].

1.1 Single Photons

Light, after matter, has not escaped the fate of quantisation. Dirac, in 1927, was the first to formally quantise the electromagnetic field [32]. But, as mentioned in the previous section, it wasn’t until the 1980s that the field of quantum optics truly began. At that time, experiments could no longer be explained by semi-classical theories, and the modern quantum theory of light had just been developed, notably by Glauber [33, 34]. The rigorous quantisation of the classical Hamiltonian is not given here as it can be found elsewhere [35–38]. However, it is enlightening to present an informal derivation.

1.1.1 Quantisation in Transparent Dielectric Media

Throughout this thesis, we will restrict ourselves to the propagation of light in non-absorbing, dielectric materials and we also ignore dispersion. Structures are therefore well described by a scalar dielectric function $\varepsilon(\mathbf{r})$ which is purely real and positive. In the absence of sources and using the generalised Coulomb gauge (in which the scalar potential $\Phi(\mathbf{r})$ is zero), the electric field $\mathbf{E}(\mathbf{r}, t)$ and magnetic induction $\mathbf{B}(\mathbf{r}, t)$ are related to the vector potential $\mathbf{A}(\mathbf{r}, t)$ as [39]

$$\mathbf{E}(\mathbf{r}, t) = -\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t}, \quad \mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t), \quad (1.1)$$

and the equation of motion for the vector potential is given by

$$\nabla \times \nabla \times \mathbf{A}(\mathbf{r}, t) + \frac{\varepsilon(\mathbf{r})}{c^2} \frac{\partial^2 \mathbf{A}(\mathbf{r}, t)}{\partial t^2} = 0. \quad (1.2)$$

We first consider the spatial dependence of the electromagnetic field. This part is entirely classical and not affected by quantisation. The aim here is to expand the fields into harmonic modes $\mathbf{u}_{k_m}(\mathbf{r}, t)$ for which the spatial and time dependence can be separated as

$$\mathbf{u}_{k_m}(\mathbf{r}, t) = \mathbf{u}_{k_m}(\mathbf{r}) \exp(-i\omega_{k_m} t) . \quad (1.3)$$

The mode profiles $\mathbf{u}_{k_m}(\mathbf{r})$ obey the wave equation

$$\nabla \times \nabla \times \mathbf{u}_{k_m}(\mathbf{r}) - \frac{\omega_{k_m}^2}{c^2} \varepsilon(\mathbf{r}) \mathbf{u}_{k_m}(\mathbf{r}) = 0 , \quad (1.4)$$

and the normalisation relation

$$\int dV \varepsilon(\mathbf{r}) \mathbf{u}_{k_m}(\mathbf{r}) \cdot \mathbf{u}_{k'_m}^*(\mathbf{r}) = \delta_{k_m, k'_m} , \quad (1.5)$$

with appropriate boundary conditions [40, 41]. They are eigenfunctions of the generalised eigenvalue problem $\mathcal{A}\mathbf{u}_{k_m} = k_m^2 \mathcal{B}\mathbf{u}_{k_m}$ with $\mathcal{A} = \nabla \times \nabla \times$, $\mathcal{B} = \varepsilon(\mathbf{r})$ and we label them by the square root of their eigenvalues $k_m = \sqrt{\frac{\omega_{k_m}^2}{c^2}}$. To account for any degeneracy, we can add another label $p \in \{0, 1, \dots\}$ and write $\mathbf{u}_{k_m, p}(\mathbf{r})$. But for simplicity, we ignore any degeneracies in the following treatment. By Fourier analysis, we build any solution to Eq. 1.2 according to

$$\mathbf{A}(\mathbf{r}, t) = \sum_{k_m} \{ A_{k_m} \mathbf{u}_{k_m}(\mathbf{r}) \exp(-i\omega_{k_m} t) + A_{k_m}^* \mathbf{u}_{k_m}^*(\mathbf{r}) \exp(i\omega_{k_m} t) \} , \quad (1.6)$$

with the appropriate set of coefficients A_{k_m} .

The total energy contained in the electromagnetic field is

$$E_R = \frac{1}{2} \int dV \left(\varepsilon_0 \varepsilon(\mathbf{r}) \mathbf{E}(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t) + \frac{1}{\mu_0 \mu(\mathbf{r})} \mathbf{B}(\mathbf{r}, t) \cdot \mathbf{B}(\mathbf{r}, t) \right) , \quad (1.7)$$

with ε_0 the vacuum permittivity, μ_0 the vacuum permeability and $\mu(\mathbf{r})$ the relative

magnetic permeability, which is assumed to be 1 for most materials. After expanding in the basis of the harmonic modes, Eq. 1.7 can be reduced to

$$E_R = \sum_{k_m} \varepsilon_0 \omega_{k_m}^2 (A_{k_m} A_{k_m}^* + A_{k_m}^* A_{k_m}) . \quad (1.8)$$

The quantisation of the electromagnetic field is then performed by associating every harmonic mode with a quantum-mechanical harmonic oscillator [42]. Thus, the Hamiltonian for each mode is given by

$$\hat{\mathcal{H}}_{k_m} = \frac{1}{2} \hbar \omega_{k_m} (\hat{a}_{k_m} \hat{a}_{k_m}^\dagger + \hat{a}_{k_m}^\dagger \hat{a}_{k_m}) , \quad (1.9)$$

with the creation and annihilation operators acting on energy eigenstates as

$$\hat{a}_{k_m}^\dagger |n_{k_m}\rangle = (n_{k_m} + 1)^{1/2} |n_{k_m} + 1\rangle , \quad \hat{a}_{k_m} |n_{k_m}\rangle = n_{k_m}^{1/2} |n_{k_m} - 1\rangle , \quad (1.10)$$

and n_{k_m} is an integer greater than or equal to zero. We also recall the commutation relation

$$[\hat{a}_{k_m}, \hat{a}_{k'_m}^\dagger] = \hat{a}_{k_m} \hat{a}_{k'_m}^\dagger - \hat{a}_{k'_m}^\dagger \hat{a}_{k_m} = \delta_{k_m, k'_m} . \quad (1.11)$$

In contrast with the classical decomposition of Eq. 1.6, where the vector-potential amplitudes can take arbitrary values, each quantum oscillator can only exist in discrete states or a superposition of those states. When a spatial mode $\mathbf{u}_{k_m}(\mathbf{r})$ is in its n^{th} excited state, we say that it contains n photons.

The total Hamiltonian for the electromagnetic field is the sum over all harmonic-oscillator contributions

$$\hat{\mathcal{H}}_R = \sum_{k_m} \hat{\mathcal{H}}_{k_m} = \frac{1}{2} \sum_{k_m} \hbar \omega_{k_m} (\hat{a}_{k_m} \hat{a}_{k_m}^\dagger + \hat{a}_{k_m}^\dagger \hat{a}_{k_m}) , \quad (1.12)$$

and comparison with Eq. 1.8 suggests the following replacement of classical vector-

potential amplitudes with quantum-mechanical operators

$$A_{k_m} \rightarrow \sqrt{\frac{\hbar}{2\varepsilon_0\omega_{k_m}}} \hat{a}_{k_m} , \quad A_{k_m}^* \rightarrow \sqrt{\frac{\hbar}{2\varepsilon_0\omega_{k_m}}} \hat{a}_{k_m}^\dagger , \quad (1.13)$$

which leads to the vector potential and electric field operators being expressed as

$$\begin{aligned} \hat{\mathbf{A}}(\mathbf{r}, t) &= \sum_{k_m} \sqrt{\frac{\hbar}{2\varepsilon_0\omega_{k_m}}} \{ \mathbf{u}_{k_m}(\mathbf{r}) \hat{a}_{k_m} \exp(-i\omega_{k_m} t) + \mathbf{u}_{k_m}^*(\mathbf{r}) \hat{a}_{k_m}^\dagger \exp(i\omega_{k_m} t) \} , \quad (1.14) \\ \hat{\mathbf{E}}(\mathbf{r}, t) &= \sum_{k_m} \sqrt{\frac{\hbar\omega_{k_m}}{2\varepsilon_0}} \{ \mathbf{u}_{k_m}(\mathbf{r}) \hat{a}_{k_m} \exp(-i(\omega_{k_m} t + \pi/2)) + \mathbf{u}_{k_m}^*(\mathbf{r}) \hat{a}_{k_m}^\dagger \exp(i(\omega_{k_m} t + \pi/2)) \} , \end{aligned} \quad (1.15)$$

and we usually write

$$\hat{\mathbf{E}}(\mathbf{r}, t) = \hat{\mathbf{E}}^+(\mathbf{r}, t) + \hat{\mathbf{E}}^-(\mathbf{r}, t) , \quad (1.16)$$

with the positive and negative frequency contributions

$$\hat{\mathbf{E}}^+(\mathbf{r}, t) = \sum_{k_m} \sqrt{\frac{\hbar\omega_{k_m}}{2\varepsilon_0}} \mathbf{u}_{k_m}(\mathbf{r}) \hat{a}_{k_m} \exp(-i(\omega_{k_m} t + \pi/2)) , \quad (1.17)$$

$$\hat{\mathbf{E}}^-(\mathbf{r}, t) = \sum_{k_m} \sqrt{\frac{\hbar\omega_{k_m}}{2\varepsilon_0}} \mathbf{u}_{k_m}^*(\mathbf{r}) \hat{a}_{k_m}^\dagger \exp(i(\omega_{k_m} t + \pi/2)) . \quad (1.18)$$

An inconvenient consequence of quantisation arises when considering the vacuum energy. Even if a mode does not contain any excitations, it still has a finite energy according to

$$\hat{\mathcal{H}}_{k_m} |0\rangle = \frac{1}{2} \hbar \omega_{k_m} |0\rangle , \quad (1.19)$$

and because Eq. 1.12 runs over an infinite number of modes, the total vacuum energy is also infinite. For most applications however, this is not important as any measurement of the light intensity can only detect electromagnetic energy above that of the vacuum [42]. In some cases however, the presence of the electromagnetic vacuum leads to real observations [43–45] including spontaneous emission, which is covered in Sec. 1.3.

1.1.2 Single Photon States

For a relevant subset of modes S , a pure single-photon state is defined as a superposition of fundamental mode excitations

$$|1\rangle = \sum_{k_m \in S} c_{k_m} \hat{a}_{k_m}^\dagger |0\rangle , \quad (1.20)$$

with $\sum_{k_m \in S} |c_{k_m}|^2 = 1$ and $|0\rangle = |0_{k_m}\rangle$, $\forall k_m \in S$, is the vacuum state. A photon state generally cannot be a fundamental excitation of only one harmonic mode, unless the mode is spatially bounded inside a perfect optical cavity. In practice however, even cavity modes are not perfect harmonic modes of a system and have an infinite extent in space [46]. It follows that photons are always a continuum of fundamental mode excitations in the form of a pulse. To encapsulate this idea, we can define a photon-wavepacket creation operator

$$\hat{a}_\xi^\dagger = \sum_{k_m} c_{k_m} \hat{a}_{k_m}^\dagger , \quad (1.21)$$

which describes the creation of a single photon in a wavepacket with spectral, temporal, spatial and polarisation properties given by the infinite collection of $\{c_{k_m}\}$.

It is possible to convert the sum in Eq. 1.21 to an integral with

$$\sum_{k_m} \rightarrow \int D(\omega) d\omega , \quad (1.22)$$

by defining the density-of-states

$$D(\omega) = \sum_{k_m} \delta(\omega - \omega_{k_m}) , \quad (1.23)$$

so that $\int_{\omega}^{\omega+\delta\omega} d\omega' D(\omega')$ is the number of modes which have a corresponding angular

frequency between ω and $\omega + \delta\omega$. If the mode expansion has no degeneracy, we can unambiguously define the continuous-variable creation and annihilation operators as

$$\hat{a}^\dagger(\omega) = \sqrt{D(\omega)}\hat{a}_{k_m}^\dagger, \quad \hat{a}(\omega) = \sqrt{D(\omega)}\hat{a}_{k_m}, \quad (1.24)$$

so that $[\hat{a}(\omega), \hat{a}^\dagger(\omega')] = \delta(\omega - \omega')$. We can then write Eq. 1.21 as

$$\hat{a}_\xi^\dagger = \int_0^\infty \xi(\omega)\hat{a}^\dagger(\omega)d\omega, \quad (1.25)$$

where $\xi(\omega)$ defines the pulse shape. Eq. 1.25 can also be expressed in the temporal domain by $\hat{a}_\xi^\dagger = \int_{-\infty}^\infty \xi(t)\hat{a}^\dagger(t)dt$ where $\xi(t)$ is the Fourier transform of $\xi(\omega)$ and $\hat{a}^\dagger(t)$ is the Fourier-transformed operator

$$\hat{a}^\dagger(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty \hat{a}^\dagger(\omega) \exp(i\omega t) d\omega. \quad (1.26)$$

Finally, a single-photon state can also be a statistical mixture of pure states. The density-operator formalism is best suited to write single-photon states more generally as

$$\hat{\rho} = \sum_i p_i \hat{a}_{\xi_i}^\dagger |0\rangle\langle 0| \hat{a}_{\xi_i}, \quad (1.27)$$

with the normalisation condition

$$\text{Tr}(\hat{\rho}) = \sum_i p_i = 1. \quad (1.28)$$

1.2 The Relevance of Single Photons

Quantum key distribution (QKD) [47, 48] and quantum computation [13] continue to be the main driving forces for the development of single-photons as a quantum system. Both of these technologies would benefit from components that reliably generate and

manipulate single-photon states. Other research avenues include quantum metrology [49] and imaging [50] but are not reviewed here.

1.2.1 Quantum Key Distribution

QKD relies on physical principles instead of computational complexity to communicate encryption keys securely. At the core of QKD is the measurement process in quantum mechanics which is intrinsically random and cannot be done without perturbing the system. Supplemented with the fact that quantum states cannot be copied, quantum measurement allows the implementation of communication protocols in which eavesdropping is easily detectable [51]. QKD protocols depend on the ability of two parties to prepare, send and measure quantum states. This communication of quantum information between distant parties can only be achieved in practice with photons. Indeed, single photons are able to conserve their quantum state over long distances, in optical fibres or in free space. Usually, these communication channels are only limited by the loss of photons due to absorption or beam diffraction [10].

Further along the development of QKD, it was shown that weak laser pulses may be used to communicate keys just as securely as with single photons. Some modern schemes use weak coherent states to emulate single-photon states, and any attack which takes advantage of this approximation can be detected by the use of additional or modified procedures [52, 53]. Other implementations use the quadrature component of a coherent state to encode quantum information in continuous-variable QKD [54]. These protocols were a major step towards the practical realisation of QKD, which could then be implemented using cheap, readily-available laser systems. It has led to the demonstration of QKD over impressive distances using low-loss fibres [55] or satellite-based links [56], and the distance between parties can be scaled up using trusted relays [57]. With the advent of secure protocols with weak laser pulses, true single-photon states will unlikely play an important role in prepare-and-measure QKD technology.

On the other hand, sources of entangled photon-pairs have been instrumental in the development of entanglement-based protocols [58]. Rather than communicating complete quantum states from sender to receiver, these versions of QKD rely on both parties sharing maximally-entangled states. Because of the perfect correlation between measurement results when both parties measure in the same basis, they receive identical random keys and can easily detect eavesdropping [59]. Entanglement-based QKD forms the basis of device-independent QKD (DI-QKD), which removes the assumptions that the quantum states are correctly prepared and measured [60]. In DI-QKD, security is proven solely based on the violation of a Bell inequality and without detailed knowledge of how the QKD devices work. Bell inequality violation ensures that both parties share entangled states, but also rules out the presence of an eavesdropper. It offers the strongest form of secure communication.

The main limitation for DI-QKD is the detection loophole in optical Bell tests. This problem arises because most entangled photons are not measured due to unavoidable losses over long communication distances. The missed events can then be used by an eavesdropper to compromise the security of the protocol [61]. To close the detection loophole, it is imperative to herald the successful distribution of the entangled states, which can be done using qubit amplification [62]. In this context, single-photon states turn out to be a useful resource. By assuming perfect single-photon states for qubit amplification, the heralding efficiency of entanglement distribution is significantly increased, which makes DI-QKD theoretically feasible over dozens of kilometres [63]. In addition, four single-photons could also be used to produce entangled photon-pair states more efficiently [64].

Single photons are also an attractive resource to extend the range of QKD using quantum repeaters [65]. This technique consists of creating a link of entangled photons which are generated at regular intervals along the communication channel. If the entangling operation is successful, a quantum state can be teleported from one end

of the channel to the other, without being affected by propagation losses. Of course, entanglement between spatially separated photons must be mediated by other photons, which do suffer from propagation losses. For quantum repeaters to work efficiently, it is a requirement to have quantum memories at each node to store photons until every entangling operation is successful [66]. Therefore, memories that can store and retrieve photons on demand are currently the limiting technology for quantum repeaters [67]. Assuming quantum memories become readily available, the most efficient protocol for quantum repeaters uses single-photons at each node to create entanglement along the communication channel [68]. True single-photon sources perform better than current photon-pair sources because of the inherent probability of the latter to emit more than one pair of photons at a time.

1.2.2 Quantum Computing

Since Feynman’s 1981 keynote address in which he proposed the idea of a quantum computer [69], an enormous effort has been devoted to attain experimental control over networks of quantum bits. The promise is huge. It is strongly believed, although not proven, that quantum computers can solve a range of computational problems exponentially faster than their classical counterparts [70]. The most notorious example of such speed-up is Shor’s algorithm for factoring large prime numbers [71]. Another important problem is the efficient simulation of quantum phenomena themselves, which was the initial inspiration for Feynman’s pioneering paper. Despite great advances, the computational complexity of quantum computation is still relatively unknown. Consequently, only a handful of large-scale applications have emerged, in fields such as computational chemistry, database searching and optimisation [72]. Quantum computation also has had a great impact on the field of cryptography [73].

One can argue that the best way to explore the power of quantum computers is to build one. Recently, this task has attracted investment from outside academia and a

number of companies have published impressive results. Superconducting circuits [74, 75] are currently the most attractive platform for implementing quantum processors of modest sizes. At the time of writing, IBM and Google are routinely operating universal 20-qubit and 53-qubit processors respectively [76, 77], and a D-Wave system is capable of quantum annealing with around 2000 qubits [78]. While no system has achieved quantum supremacy yet, this will certainly happen very soon [79]. Of course, research into quantum systems is not limited to superconducting qubits. Numerous schemes for the realisation of universal quantum computation have been put forward, each with their own advantages and disadvantages. Other mature architectures include ion traps [80] (which feature exceptionally high gate fidelities [81]), spins in semiconductors [82–84] and integrated quantum photonics [85, 86].

The photonic approach to quantum computing is strikingly different to other methods. Using single photons as qubits is well suited to “one-way” or measurement-based quantum computing (MBQC) with discrete variables (DV) [87, 88]. In this scheme, the quantum information is encoded in discrete degrees-of-freedom of light, such as polarisation or path. To perform a useful computation with MBQC, a large entangled resource state is first created, and the computation then follows with a series of operations and measurements on individual qubits. Recent theoretical improvements have narrowed the prerequisites for photonic DV-MBQC to producing small entangled photon states on a chip, with scaling up to a larger entangled state a relatively easier task [89]. Scalable protocols rely on the ability to produce on-demand the following three-photon entangled state

$$|GHZ\rangle = \frac{|000\rangle + |111\rangle}{\sqrt{2}}, \quad (1.29)$$

named after Greenberger, Horne and Zeilinger [90]. This is the fundamental resource from which arbitrary large cluster states can be created ballistically [89]. In turn, cluster states are used to perform universal quantum computation [87]. To leverage

the scalability of the architecture, the fabrication of deterministic GHZ sources must also be scalable. GHZ states may be generated from a range of more fundamental components, including entangled photon-pair sources and single-photon sources [91]. Currently, the most promising approach is multiplexing of photon pairs produced by spontaneous four-wave mixing in silicon photonics [92–94]. Additionally, photonic DV-MBQC seems to suffer less from stochastic noise than other approaches, but instead has to deal with measurable systematic imperfections and qubit loss [13]. This is a very different, and potentially advantageous, paradigm for the implementation of error correction.

Continuous variables (CV), such as quadrature amplitudes, can also be used to encode and process quantum information with light [95]. In contrast to DV schemes, quantum protocols with CVs can be deterministic, but usually suffer from lower gate fidelities [96]. Another difference is that single-photon technology is not a requirement for quantum computing with CVs, which relies on squeezing instead. Recently, hybrid protocols have also been proposed to combine the strength of both approaches [97].

1.3 Light-Matter Interactions

In Sec. 1.1, we have dealt with the interaction of photons with lossless dielectric-materials by modelling space with a macroscopic dielectric function $\varepsilon(\mathbf{r})$. We will now look at the interaction of photons with atom-like objects, which have quantised electronic states. This quantum interaction of light with matter forms the basis for the deterministic generation of single-photon states.

1.3.1 The Two-Level-System

Consider a simple system with a ground electronic state $|g\rangle$ and an excited electronic state $|e\rangle$. Equating the ground state energy to zero, the Hamiltonian of the isolated

system can be written as

$$\hat{\mathcal{H}}_A = \hbar\omega_0|e\rangle\langle e| = \hbar\omega_0\hat{\sigma}^+\hat{\sigma}^- , \quad (1.30)$$

where $\hbar\omega_0$ is the energy difference between the two states and $\hat{\sigma}^+ = |e\rangle\langle g|$, $\hat{\sigma}^- = |g\rangle\langle e|$ are the emitter's raising and lowering operators respectively.

Inspired by classical electrodynamics, the electric dipole moment $\boldsymbol{\mu}$ - defined as the sum of all particle's positions $\mathbf{r}_\alpha$ times their respective charges q_α - plays a critical role in light-matter interactions. The quantum analogue is the operator

$$\hat{\boldsymbol{\mu}} = \sum_{\alpha} q_{\alpha} \hat{\mathbf{r}}_{\alpha} , \quad (1.31)$$

which is reduced to $\hat{\boldsymbol{\mu}} = -e\hat{\mathbf{r}}$ for our simple model. It is usually assumed that the states $|g\rangle$ and $|e\rangle$ have a specific parity because of mirror symmetry. Therefore the emitter has no permanent dipole moment and we have

$$\langle g|\hat{\boldsymbol{\mu}}|g\rangle = \int dV \psi_g^*(\mathbf{r})\mathbf{r}\psi_g(\mathbf{r}) = 0 , \quad \langle e|\hat{\boldsymbol{\mu}}|e\rangle = \int dV \psi_e^*(\mathbf{r})\mathbf{r}\psi_e(\mathbf{r}) = 0 , \quad (1.32)$$

with $\psi_g(\mathbf{r}) = \langle \mathbf{r}|g\rangle$ and $\psi_e(\mathbf{r}) = \langle \mathbf{r}|e\rangle$. In general, $|g\rangle$ and $|e\rangle$ can have different parities and $\langle g|\hat{\boldsymbol{\mu}}|e\rangle$ and $\langle e|\hat{\boldsymbol{\mu}}|g\rangle$ are not necessarily null. For linearly polarised transitions (although this is easily extended to circularly polarised transitions as well), the transition dipole-moment is real and is given by $\boldsymbol{\mu} = \langle g|\hat{\boldsymbol{\mu}}|e\rangle = \langle e|\hat{\boldsymbol{\mu}}|g\rangle$. The dipole moment operator can then be expressed in terms of $\hat{\sigma}^+$ and $\hat{\sigma}^-$ as

$$\hat{\boldsymbol{\mu}} = \boldsymbol{\mu}(\hat{\sigma}^+ + \hat{\sigma}^-) . \quad (1.33)$$

In the electric-dipole approximation, which holds when the physical extent of the electron's wavefunction is much smaller than the wavevector k_0 associated with ω_0 , the

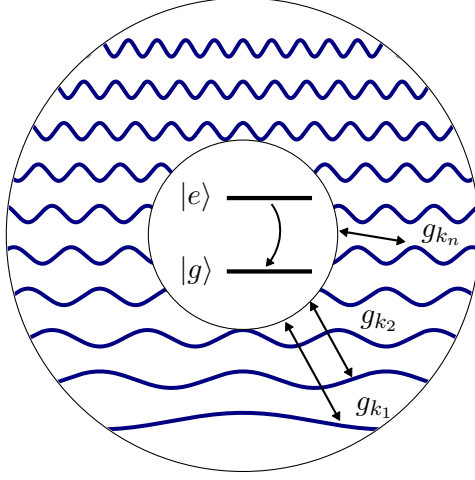


Figure 1.2: Schematic of a dipole coupled to a continuum of optical modes.

complete Hamiltonian of the emitter plus electromagnetic field is [42]

$$\hat{\mathcal{H}}_T = \hat{\mathcal{H}}_A + \hat{\mathcal{H}}_R + \hat{\mathcal{H}}_{\text{ED}} \quad \hat{\mathcal{H}}_{\text{ED}} = -\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}}(\mathbf{r}_0, 0) . \quad (1.34)$$

$\hat{\mathcal{H}}_R$ and $\hat{\mathbf{E}}(\mathbf{r}_0, 0)$ are defined by Eq. 1.12 and Eq. 1.15 respectively. By expanding the electric field operator in terms of harmonic modes $\mathbf{u}_{k_m}(\mathbf{r})$, the interaction Hamiltonian becomes

$$\hat{\mathcal{H}}_{\text{ED}} = \hbar \sum_{k_m} \{ g_{k_m}(\mathbf{r}_0) \hat{a}_{k_m} + g_{k_m}^*(\mathbf{r}_0) \hat{a}_{k_m}^\dagger \} (\hat{\sigma}^+ + \hat{\sigma}^-) , \quad (1.35)$$

with coupling constants

$$g_{k_m}(\mathbf{r}_0) = i \sqrt{\frac{\omega_{k_m}}{2\varepsilon_0 \hbar}} \boldsymbol{\mu} \cdot \mathbf{u}_{k_m}^*(\mathbf{r}_0) . \quad (1.36)$$

We can now invoke the rotating-wave approximation to further reduce Eq. 1.35 to

$$\hat{\mathcal{H}}_{\text{ED}} = \hbar \sum_{k_m} \{ g_{k_m}(\mathbf{r}_0) \hat{a}_{k_m} \hat{\sigma}^+ + g_{k_m}^*(\mathbf{r}_0) \hat{a}_{k_m}^\dagger \hat{\sigma}^- \} . \quad (1.37)$$

The two terms inside the brackets of Eq. 1.37 have a clear physical meaning for the evolution of the system. The term $\hat{a}_{k_m} \hat{\sigma}^+$ represents the destruction of a photon in the

k_m mode accompanied by the excitation of the emitter from state $|g\rangle$ to state $|e\rangle$. The term $\hat{a}_{k_m}^\dagger \hat{\sigma}^-$ represents the inverse process. The strength of both processes depends on the number of photons already present in the mode k_m as characterised by the matrix elements

$$\langle (n-1)_{k_m}, e | \hat{\mathcal{H}}_T | n_{k_m}, g \rangle = \hbar g_{k_m}(\mathbf{r}_0) \exp(i(\omega_0 - \omega_{k_m})t) \sqrt{n_{k_m}} , \quad (1.38)$$

$$\langle (n+1)_{k_m}, g | \hat{\mathcal{H}}_T | n_{k_m}, e \rangle = \hbar g_{k_m}^*(\mathbf{r}_0) \exp(-i(\omega_0 - \omega_{k_m})t) \sqrt{n_{k_m} + 1} , \quad (1.39)$$

which corresponds to stimulated absorption and emission. Even if no photons are present, the state $|e\rangle$ can still decay to $|g\rangle$ through the coupling to vacuum states as

$$\langle 1_{k_m}, g | \hat{\mathcal{H}}_T | 0_{k_m}, e \rangle = \hbar g_{k_m}^*(\mathbf{r}_0) \exp(-i(\omega_0 - \omega_{k_m})t) . \quad (1.40)$$

This is commonly known as spontaneous emission and this process depends solely on the dielectric environment.

Decay of the excited state is always accompanied by the emission of a single photon in the electric-dipole approximation. By considering further terms in the emitter's polarisability, the decay can be mediated by weak non-linear processes such as spontaneous two-photon emission [98]. It is possible to cast these processes in the dipole picture by considering the coupling of $|g\rangle$ and $|e\rangle$ to virtual intermediary states [42]. For states with well-defined parity, second-order processes only couple those which have the same parity. Hence, for dipole-allowed transitions, two-photon emission is usually strongly suppressed, and the next allowed process is an even weaker third-order one. Therefore, the electric-dipole approximation is usually very good in practice.

1.3.2 Spontaneous Emission

Wigner-Weisskopf Decay

For describing spontaneous emission, we assume that the total system only has one excitation, and the quantum state can be expanded as

$$|\Psi(t)\rangle = c_e(t)|0, e\rangle + \sum_{k_m \in S} c_{k_m}(t) \hat{a}_{k_m}^\dagger |0, g\rangle . \quad (1.41)$$

We also require that the emitter starts in its excited state, so that $c_e(0) = 1$ and $c_{k_m}(0) = 0, \forall k_m \in S$. The instantaneous transfer to the excited state can be achieved using a resonant laser-pulse which is much shorter than the time scale associated with the freely evolving probability amplitudes. This laser pulse acts as the trigger which starts the emission process. From $\hat{\mathcal{H}}_T$, the equations of motion for the system can be written as [25, 99]

$$\frac{dc_e}{dt} = - \sum_{k_m} |g_{k_m}(\mathbf{r}_0)|^2 \int_0^t dt' c_e(t') \exp(i(\omega_0 - \omega_{k_m})(t - t')) , \quad (1.42)$$

and

$$\frac{dc_{k_m}}{dt} = ig_{k_m}^*(\mathbf{r}_0) c_e(t) \exp(i(\omega_{k_m} - \omega_0)t) . \quad (1.43)$$

We now introduce the local-density-of-states (LDOS) defined as the density-of-states $D(\omega)$ (Eq. 1.23) weighted by the intensity of each mode's electric field at position $\mathbf{r}$ and in direction $\mathbf{e}$. It is given by

$$\text{LDOS}(\mathbf{r}, \mathbf{e}, \omega) \equiv \rho(\mathbf{r}, \mathbf{e}, \omega) = \sum_{k_m} |\mathbf{e} \cdot \mathbf{u}_{k_m}^*(\mathbf{r})|^2 \delta(\omega - \omega_{k_m}) . \quad (1.44)$$

We can express Eq. 1.42 in terms of the LDOS as

$$\frac{dc_e}{dt} = -\frac{|\boldsymbol{\mu}|^2}{2\epsilon_0\hbar} \int_0^\infty d\omega \omega \rho(\mathbf{r}_0, \mathbf{e}_\mu, \omega) \int_0^t dt' c_e(t') \exp(i(\omega_0 - \omega)(t - t')) . \quad (1.45)$$

where $\mathbf{e}_\mu$ is the unit vector in the dipole direction. In the Wigner-Weisskopf approximation, which holds when $\omega \rho(\mathbf{r}_0, \mathbf{e}_\mu, \omega)$ varies insignificantly over the linewidth of the emitter, Eq. 1.42 is further simplified to

$$\frac{dc_e}{dt} \approx -\frac{\pi|\boldsymbol{\mu}|^2\omega_0\rho(\mathbf{r}_0, \mathbf{e}_\mu, \omega_0)}{2\epsilon_0\hbar} c_e(t) , \quad (1.46)$$

where we neglect the Cauchy principle part, which only contributes to a negligible shift of the transition frequency called the Lamb shift [25]. The solution to the above equation is

$$c_e(t) = H(t) \exp\left(-\frac{\pi|\boldsymbol{\mu}|^2\omega_0\rho(\mathbf{r}_0, \mathbf{e}_\mu, \omega_0)}{2\epsilon_0\hbar} t\right) , \quad (1.47)$$

with $H(t)$ being the Heaviside step function. This leads to an exponential decay of the excited state population $|c_e|^2$ with a rate

$$\Gamma = \frac{\pi|\boldsymbol{\mu}|^2\omega_0\rho(\mathbf{r}_0, \mathbf{e}_\mu, \omega_0)}{\epsilon_0\hbar} . \quad (1.48)$$

In a homogeneous and isotropic medium with refractive index n , we can use plane-wave solutions to Eq. 1.2 with periodic boundary-conditions to show that [41]

$$\rho_{\text{hom}}(\mathbf{r}, \mathbf{e}, \omega) = \frac{\omega^2 n}{3\pi^2 c^3} , \quad \Gamma_{\text{hom}} = \frac{|\boldsymbol{\mu}|^2 \omega_0^3 n}{3\pi \epsilon_0 \hbar c^3} . \quad (1.49)$$

The emission spectrum $S(\omega)$ can be calculated by finding the photon occupation of the modes an infinite time after the start of the process

$$S(\omega) = \sum_{k_m} \lim_{t \rightarrow \infty} |c_{k_m}(t)|^2 \delta(\omega - \omega_{k_m}) . \quad (1.50)$$

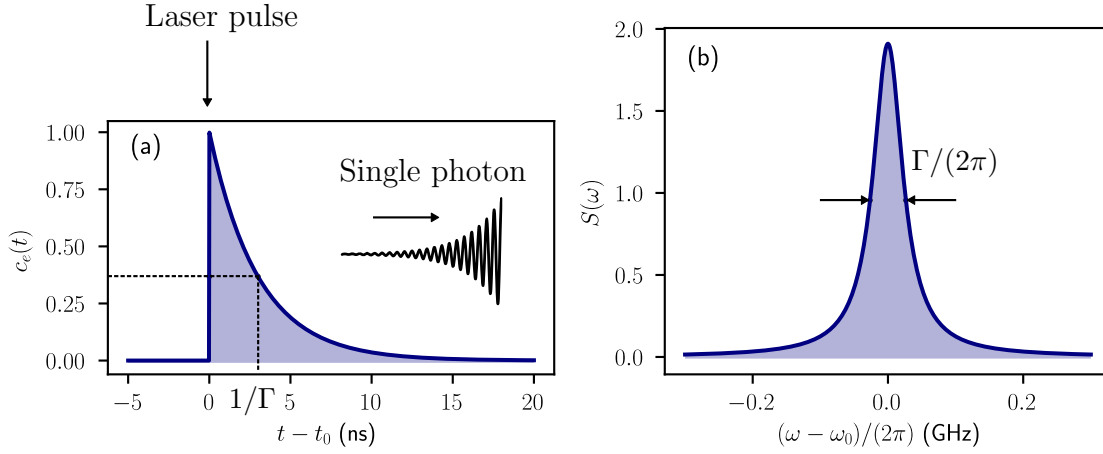


Figure 1.3: (a) Time dependence of excited state probability amplitude for an emitter with lifetime $\tau = 1/\Gamma = 3$ ns. (b) Spectrum of the corresponding single-photon emission

Substituting Eq. 1.47 in Eq. 1.43, we get

$$\frac{dc_{k_m}}{dt} = ig_{k_m}^*(\mathbf{r}_0)H(t)\exp(-\frac{\Gamma}{2}t)\exp(i(\omega_{k_m} - \omega_0)t), \quad (1.51)$$

which can be integrated to find

$$\lim_{t \rightarrow \infty} |c_{k_m}(t)|^2 = \frac{|g_{k_m}(\mathbf{r}_0)|^2}{(\Gamma/2)^2 + (\omega_{k_m} - \omega_0)^2}. \quad (1.52)$$

By using the definition of the LDOS given by Eq. 1.44, together with Eq. 1.48, we get the normalised emission spectrum

$$S(\omega) = \pi^{-1} \frac{\Gamma/2}{(\Gamma/2)^2 + (\omega - \omega_0)^2}. \quad (1.53)$$

In the Wigner-Weisskopf approximation, the emission spectrum is therefore a Lorentzian function with full-width-at-half-maximum equal to Γ .

By tracing over the radiation degrees of freedom, we obtain the time evolution of

the reduced density matrix for the emitter in the interaction picture [42, 99]

$$\frac{d}{dt}\hat{\rho}_{\text{emitter}} = \frac{\Gamma}{2} (2\hat{\sigma}^- \hat{\rho}_{\text{emitter}} \hat{\sigma}^+ - \hat{\sigma}^+ \hat{\sigma}^- \hat{\rho}_{\text{emitter}} - \hat{\rho}_{\text{emitter}} \hat{\sigma}^+ \hat{\sigma}^-) , \quad (1.54)$$

which is solved using the initial conditions at $t = 0$ with

$$\hat{\rho}_{\text{emitter}} = \begin{bmatrix} \rho_{ee} & \rho_{eg} \\ \rho_{ge} & \rho_{gg} \end{bmatrix} = \begin{bmatrix} H(t) \exp(-\Gamma t) & 0 \\ 0 & H(t) (1 - \exp(-\Gamma t)) \end{bmatrix} . \quad (1.55)$$

Beyond the Macroscopic Picture

So far, we have relied on the assumption that the emitter sits inside a dielectric material which is described macroscopically using $\varepsilon(\mathbf{r})$. However, we would expect that the process of spontaneous emission depends on the microscopic constituents of the dielectric in the vicinity of the emitter [38]. Modelling of the emitter plus its immediate surrounding is a very difficult problem. One approximation assumes that the emitter sits at the centre of a small hole, or virtual-cavity, in the dielectric. This amounts to redefining $\varepsilon(\mathbf{r})$ from which we can derive a new set of harmonic modes and recalculate $\rho(\mathbf{r}_0, \mathbf{e}_\mu, \omega_0)$. For homogeneous media, it is possible to show that, at the position of the emitter, the modes get modified as [35]

$$|\mathbf{u}_{k_m}(\mathbf{r}_0)| \rightarrow \left(\frac{3\varepsilon}{2\varepsilon + 1} \right)^2 |\mathbf{u}_{k_m}(\mathbf{r}_0)| , \quad (1.56)$$

and $\mathbf{u}_{k_m}(\mathbf{r})$ does not need to be renormalised as we assume that the size of the virtual-cavity tends towards 0. This leads to the following modification of the decay rate

$$\Gamma' = \left(\frac{3\varepsilon}{2\varepsilon + 1} \right)^2 \Gamma . \quad (1.57)$$

For inhomogeneous media, the derivation is not as straightforward but if the variation of $\varepsilon(\mathbf{r})$ is small compared to λ_0 , then we can assume that only the bulk dielectric around the emitter is important and

$$\Gamma' = \left(\frac{3\varepsilon(\mathbf{r}_0)}{2\varepsilon(\mathbf{r}_0) + 1} \right)^2 \Gamma . \quad (1.58)$$

It is also possible to abandon the macroscopic quantisation entirely and re-derive a microscopic quantum theory. This leads to other local-field effects and corrections [100, 101] which are beyond the scope of this thesis.

1.3.3 Spontaneous Emission Engineering

Decay Rates

A lot of the physical interpretation is hidden away in the local-density-of-states formalism. It accounts for the strength of the vacuum fluctuations and of the radiation reaction, which both contribute to spontaneous emission [45]. Eq. 1.45 also accounts for the radiation back-action from the reservoir of modes but, in the Wigner-Weisskopf approximation, we assume that this is negligible. Nevertheless, the meaning of Eq. 1.48 is that the decay rate of the emitter depends on its environment, and more specifically on the LDOS. It is therefore possible to engineer the optical surroundings of the emitter to enhance or suppress its spontaneous decay. The modification of the spontaneous emission rate by a dielectric structure is quantified by the Purcell factor defined as

$$F_P(\mathbf{r}, \mathbf{e}_\mu, \omega) = \frac{\Gamma(\mathbf{r}, \mathbf{e}_\mu, \omega)}{\Gamma_{\text{hom}}(\omega)} = \frac{\rho(\mathbf{r}, \mathbf{e}_\mu, \omega)}{\rho_{\text{hom}}(\omega)} , \quad (1.59)$$

where $\Gamma_{\text{hom}}(\omega)$ is the decay rate of the emitter inside its typical dielectric surrounding.

Photonic crystals have been the most successful structures in inhibiting spontaneous emission [40]. They are made from repeating structural patterns to form periodicity in

the dielectric function. Analogous to electronic modes in semi-conductors, the periodicity can lead to gaps in the photonic band-structure of the crystal. This means that, for a range of frequencies and propagation directions, no optical modes exist which satisfy Eq. 1.4. With careful engineering of the periodicity, it is even possible to achieve a complete band gap, for which no modes exist for any propagation direction. In this case, the density-of-states, and therefore the LDOS, both tend to zero and the spontaneous decay is strongly suppressed [102].

To accelerate spontaneous emission, we can use the opposite trick by increasing the density-of-states. For example, this is the case for strongly dispersive structures, such as photonic-crystal waveguides [40]. It can be shown (Sec. 4.1.2), that guided modes have a density-of-states which is proportional to $1/v_g$, where v_g is the group velocity of the light propagating in the waveguide. Hence, by tailoring the mode structure so that light propagates with a slow group-velocity, spontaneous emission can be drastically enhanced [26]. In fact, Eq. 1.49 is a direct consequence of plane waves propagating in a medium of refractive index n with group velocity c/n . This effect is also present in optical cavities which trap radiation between highly reflective mirrors (Sec. 5.1). In this case, the density-of-states is directly proportional to the lifetime of radiation inside the cavity, as measured by the quality factor.

The other way to increase the LDOS is to maximise the electric field of the modes at the position of the emitter. Because of the normalisation condition (Eq. 1.5), $\varepsilon(\mathbf{r})|\mathbf{u}_{k_m}(\mathbf{r})|^2$ has the dimension of inverse volume, and the strength of a mode at one position depends on its full extent in space. To increase the field at $\mathbf{r}_0$, it is possible to constrain $\mathbf{u}_{k_m}(\mathbf{r})$ around that position so that $\int dV \varepsilon(\mathbf{r})|\mathbf{u}_{k_m}(\mathbf{r})|^2$ decreases relative to $|\mathbf{u}_{k_m}(\mathbf{r}_0)|^2$. Reducing the mode volume is achieved by confining modes in two dimensions with waveguides (Sec. 4.1.2) or in three dimensions using cavities (Sec. 5.1).

Radiation Patterns

In the Wigner-Weisskopf approximation, we assume that the response of the environment does not depend on ω across the linewidth of the emitter. To calculate the spatial distribution of the emitted photon, it is therefore sufficient to look at the fields emitted by a classical dipole oscillating at ω_0 . With the usual spherical coordinates system, we place a classical dipole at the origin and orient it in the z-direction. In a homogeneous medium, the far-field radiation pattern of this dipole is [103]

$$\frac{\bar{I}(\theta, \phi)}{\bar{P}_{total}} = \frac{3}{8\pi} \sin^2(\theta) , \quad (1.60)$$

where $\bar{P}(\theta, \phi) = \bar{I}(\theta, \phi)d\Omega$ is the time-averaged power radiated into an infinitesimally small solid angle $d\Omega = \sin(\theta)d\theta d\phi$ and $\bar{P}_{total}$ is the total cycle-averaged power. We see that the bulk of the radiation is emitted perpendicular to the dipole with no dependence on ϕ , as dictated by the symmetry of the problem. In the context of spontaneous emission, we interpret $\bar{P}(\theta, \phi)/\bar{P}_{total}$ as the probability that the emitted photon is detected inside the infinitesimal solid angle. The isotropic nature of the emission illustrates how difficult it is to collect every photon from a quantum emitter embedded in a homogeneous material.

In an inhomogeneous environment, we can break the symmetry to engineer the emitter's radiation pattern. As seen above, the decay rate modification is mode specific, and it is possible to selectively enhance the emission into some modes while others are unaffected or even suppressed. The simplest of examples is when an emitter is placed close to a mirror or even just the interface between two dielectrics [103]. In this thesis, we will usually be concerned about emission into propagating modes, such as waveguides or optical fibres. A guiding mode is defined as having continuous or periodic translational symmetry in the direction of propagation but being confined in the perpendicular plane [104]. The confinement is usually achieved using total-internal

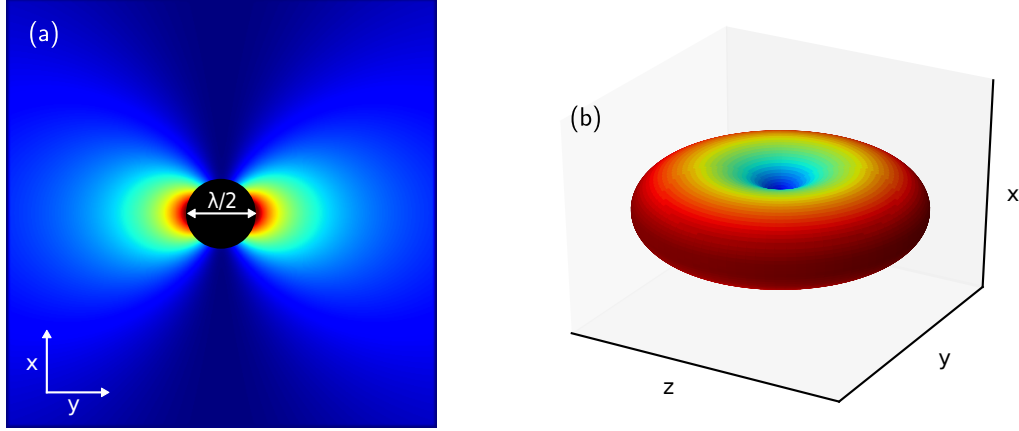


Figure 1.4: (a) Electric energy of a dipole in a homogeneous crystal of anthracene with refractive index 1.8 and orientated in the x-axis. (b) Far-field emission pattern of the same dipole.

reflection from the interface between a high index core and a low index cladding or by scattering from periodic structures.

To quantify how much of the light is emitted into guided modes, we define the coupling efficiency β which is the rate of emission into the guided modes, normalised to the total radiative decay rate

$$\beta(\mathbf{r}, \mathbf{e}_\mu, \omega) = \frac{\Gamma_{\text{guided}}(\mathbf{r}, \mathbf{e}_\mu, \omega)}{\Gamma(\mathbf{r}, \mathbf{e}_\mu, \omega)} = \frac{\rho_{\text{guided}}(\mathbf{r}, \mathbf{e}_\mu, \omega)}{\rho(\mathbf{r}, \mathbf{e}_\mu, \omega)}, \quad (1.61)$$

with

$$\rho_{\text{guided}}(\mathbf{r}, \mathbf{e}, \omega) = \sum_{k_m \in S_{\text{guided}}} |\mathbf{e} \cdot \mathbf{u}_{k_m}^*(\mathbf{r})|^2 \delta(\omega - \omega_{k_m}), \quad (1.62)$$

and S_{guided} the subset of guided modes.

Single-mode waveguides (Sec. 4.1.1) or nanowires [105] are excellent examples of structures which redistribute radiation patterns. When placed in the vicinity of a waveguide or wire, the decay rate of an emitter is usually unchanged, however, the structure funnels a lot of the emission into the guided modes which leads to high β factors. This shows how the emission is redistributed from suppressed out-propagating

modes to the waveguide modes. Going a step further, photonic-crystal waveguides achieve an even faster decay to guided modes due to low mode-areas and slow group-velocities. This is combined with a suppression of the decay to all other modes due to the periodic surrounding. Such waveguides can produce near-unity β factors, coupling almost all the emitted light into guided modes [26].

Cavities (Sec. 5.1) are another way to achieve high β -factors [27, 106]. By confining light in three dimensions, we can engineer small mode-volumes and high density-of-states leading to a large coupling efficiency to the cavity modes. For a good cavity, the photons emitted into the cavity would then leak isotropically from it, and the coupling to out-propagating guided modes would be inefficient. To improve the out-coupling, the cavity should be designed such that the radiation preferentially leaks into chosen modes. Increased leakage into specific modes can only be done at the expense of the coupling to the cavity mode. Therefore, an optimised trade-off has to be made (Sec. 5.1.3).

1.4 Deterministic Single-Photon Sources

At the beginning of the chapter, I stated that deterministic single-photon sources can be built from quantum emitters only if we achieve high collection efficiencies. For most applications, photons have to be collected into guided modes which serve as efficient interconnects between optical elements. In Sec. 1.3.2, we have seen how quantum emitters are indeed able to produce single photons from spontaneous emission. In Sec. 1.3.3, we then discussed how small emitters tend to emit light isotropically unless the landscape of optical modes is modified by photonic structures. Therefore, the only way to fabricate efficient single-photon sources from quantum emitters is by placing them in engineered structures.

I also mentioned that multiplexing of photon-pair sources is another promising way to achieve deterministic single-photon generation. The underlying theory and current

performance of photon-pair sources and multiplexing is beyond the scope of this thesis, but reviews can be found here [15, 16, 107, 108].

1.4.1 Quantifying the Quality of Single-Photon Sources

Assuming guided modes with continuous translational symmetry for simplicity, the guided-mode profiles can be separated as [40]

$$\mathbf{u}_{k_m}(x, y, z) \propto \mathbf{b}_{k_m}(x, y) \exp(ik_m z) , \quad (1.63)$$

where $\mathbf{e}_z$ is the direction of propagation and $\mathbf{b}_{k_m}(x, y)$ represents the cross-section of the mode. We can assume that $\mathbf{b}_{k_m}(x, y)$ does not vary much over the linewidth of the emitted photons and we label $\mathbf{b}$ as a single guided-mode profile. The goal of a single-photon source is to create, at a known time, the state

$$|1_{\mathbf{b},\xi}\rangle = \hat{a}_{\mathbf{b},\xi}^\dagger |0\rangle , \quad (1.64)$$

which is a single-photon in a single guided-mode $\mathbf{b}$ with pulse shape $\xi(\omega)$ (Sec. 1.1.2). For photons spontaneously emitted by an ideal quantum emitter, $|\xi(\omega)|^2$ is a Lorentzian function as described by Eq. 1.53. Of course, photons generated in an experiment will deviate from the ideal state.

Imperfect excitation and collection efficiencies

We have already mentioned that collection efficiency is an important figure-of-merit for a source of single photons based on single emitters. Because we trace over all other optical modes, imperfect collection efficiency simply leads to the mixed state

$$\hat{\rho}_{\mathbf{b},\xi} = (1 - \beta)|0\rangle\langle 0| + \beta|1\rangle\langle 1| , \quad (1.65)$$

which decreases the classical probability of finding a photon in the guided mode.

We also have to consider if the emitter has been perfectly transferred to the excited state at the start of the emission process (Sec. 1.3.2). Imperfect excitation with a resonant laser means that the emitter starts in the state $|\psi_{\text{emitter}}\rangle = \sqrt{1 - \eta_{\text{excit}}}|g\rangle + \sqrt{\eta_{\text{excit}}}\exp(i\alpha)|e\rangle$, where η_{excit} is the excitation efficiency and α depends on the classical phase of the laser pulse. This leads to the coherent photon state [109]

$$|\psi\rangle = \sqrt{1 - \eta_{\text{excit}}}|0\rangle + \sqrt{\eta_{\text{excit}}}\exp(i\alpha)|1\rangle, \quad (1.66)$$

which together with a coupling efficiency gives

$$\hat{\rho}_{\mathbf{b},\xi} = (1 - \beta)|0\rangle\langle 0| + \beta|\psi\rangle\langle\psi|. \quad (1.67)$$

On the other hand, if the excitation scheme is imperfect but incoherent (Sec. 2.2.4), Eq. 1.65 simply gets modified with a reduced efficiency from β to $\eta_{\text{excit}}\beta$.

Finally, it is possible that the excited state of the emitter is coupled to other electronic levels or even decays non-radiatively. We capture this by the generation efficiency η_{gen} so that

$$\eta_{\text{gen}} = \frac{\Gamma}{\sum_i \Gamma_i}, \quad (1.68)$$

with $\sum_i \Gamma_i$ the sum of decay rates over all possible decay paths and Eq. 1.65 is modified by $\beta \rightarrow \eta_{\text{gen}}\beta$.

Background and multi-photon probabilities

In an experiment, it is possible that other light sources leak into the guided mode during the emission process. The largest contribution to this background usually comes from the laser pulse which excites the emitter in the first place. A background of coherent or thermal light reduces the quality of a single-photon source by increasing the multi-

photon probability. It is therefore critical to block the laser light from reaching the guided mode in which the photon is emitted.

To characterise this effect, we typically measure the second-order coherence, or $g^{(2)}$, of the emitted light. The $g^{(2)}(t, t')$ function quantifies the correlation between the intensity of the light at time t and at some other time t' . Classically, it is given by

$$g^{(2)}(t, t') = \frac{\overline{I(t)I(t')}}{\overline{I(t)} \overline{I(t')}} , \quad (1.69)$$

where the barred quantities denotes the cycle-average. Again, assuming that $\mathbf{b}_{k_m}(x, y)$ doesn't vary much over the linewidth of the light, the $g^{(2)}$ can be written in the interaction picture as [42]

$$g^{(2)}(t, t') = \frac{\langle \hat{a}_{\mathbf{b}}^\dagger(t) \hat{a}_{\mathbf{b}}^\dagger(t') \hat{a}_{\mathbf{b}}(t') \hat{a}_{\mathbf{b}}(t) \rangle}{\langle \hat{a}_{\mathbf{b}}^\dagger(t) \hat{a}_{\mathbf{b}}(t) \rangle \langle \hat{a}_{\mathbf{b}}^\dagger(t') \hat{a}_{\mathbf{b}}(t') \rangle} , \quad (1.70)$$

with $\hat{a}_{\mathbf{b}}^\dagger(t)$ defined similarly to Eq. 1.26. We are usually interested in the case where the $g^{(2)}$ is integrated over a period of time $[t_1, t_2]$ which includes the entire pulse. Eq. 1.70 can then be rewritten as

$$g^{(2)} = \int_{t_1}^{t_2} dt \int_{t_1}^{t_2} dt' g^{(2)}(t, t') = \frac{\langle \hat{n}(\hat{n} - 1) \rangle}{\langle \hat{n} \rangle^2} , \quad (1.71)$$

where we define the photon number operator $\hat{n} = \int_{t_1}^{t_2} \hat{a}_{\mathbf{b}}^\dagger(t) \hat{a}_{\mathbf{b}}(t) dt$. The average number of photons in the pulse is then simply given by $\langle \hat{n} \rangle$.

For a single-photon wavepacket like Eq. 1.64, $g^{(2)}$ is equal to 0. However, with a small amount of background light, the $g^{(2)}$ can be approximated as

$$g^{(2)} \simeq \frac{2P(2)}{P(1)^2} , \quad (1.72)$$

where we assume that the probability of finding two photons in the pulse, $P(2)$, is much smaller than the probability $P(1)$ of finding just one. For other sources, such

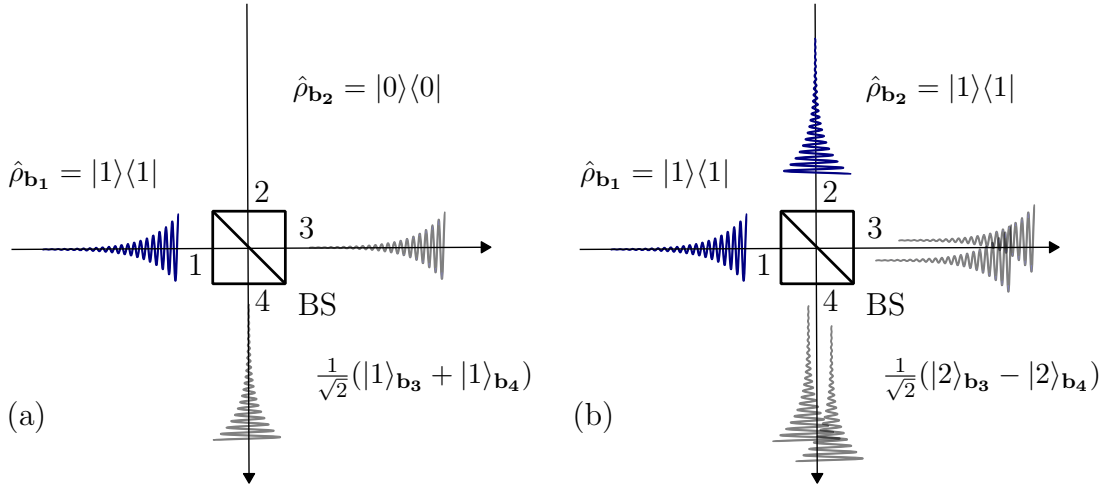


Figure 1.5: Schematic of single photons interfering on a beam-splitter. (a) The state of the photon is split by the beam-splitter but detection can only occur at one of the output ports. (b) A single-photon state arrives at each input port. If the states are identical, bunching occurs at the output ports.

as photon-pair sources based on non-linear processes, a non-negligible multi-photon emission probability is intrinsic to the emission process. This can lead to non-zero $g^{(2)}$ even in the absence of background.

Experimentally, the $g^{(2)}$ is obtained using a Hanbury Brown-Twiss (HBT) interferometer, as shown in Fig. 1.5(a). Here, the pulse of light impinges on an input port of a beam-splitter, and we record the probability of simultaneous detection events at both output ports. If the input pulse only contains a single-photon, wavefunction collapse dictates that the photon can only be detected in one output arm and we observe no simultaneous detection events. This corresponds to $g^{(2)} = 0$. More generally, we have $g^{(2)} \approx \frac{N_c}{N_3 N_4}$, where N_c is the number of coincidence events recorded over the experiment run time and N_3 , N_4 are the total number of detections in each output port of the beam splitter [107].

Indistinguishability

Most applications of single-photons rely on the interference between photons when they are combined on a beam-splitter. This quantum interference, first demonstrated

by Hong-Ou-Mandel (HOM), is illustrated by Fig. 1.5(b) where two photons are simultaneously impinging on separate input ports of a beam-splitter. If the two photons are indistinguishable from one another, we observe that they bunch together and leave from one of the two output ports as a single two-photon state [2]. The interference creates an entangled state, and this mechanism is at the core of quantum information processing and communication with photons [48, 91]. This effect follows from the bosonic nature of photons and only occurs if the impinging photons occupy identical optical modes.

To see interference, it is first required that the photons be in a pure state and not in a statistical mixture of optical modes. The spontaneous emission mechanism presented in Sec. 1.3.2 always leads to the generation of a pure state. However, we have neglected the interaction of the emitter with its local environment. Usually, there is a coupling between the electronic states and the local environment, which causes dephasing and the emission of photons in a mixed-state [110]. The purity of a state can be quantified as

$$\mathcal{P} = \text{Tr}(\hat{\rho}_{\mathbf{b}}^2) , \quad (1.73)$$

where Tr denotes the trace and $\hat{\rho}_{\mathbf{b}}$ is the generalisation of Eq. 1.64.

The purity of the impinging photons, however, is not the only prerequisite to observe interference. It is also a requirement that the two input photon-states are identical. The indistinguishability is measured by

$$\mathcal{I} = 1 - \frac{1}{2} \|\hat{\rho}_{\mathbf{b}_1} - \hat{\rho}_{\mathbf{b}_2}\|^2 , \quad (1.74)$$

with $\|\hat{\rho}_{\mathbf{b}_1} - \hat{\rho}_{\mathbf{b}_2}\|$ the operational distance between two density matrices [111]. For pure single-photon states, this is simply given by

$$\mathcal{I} = |\langle 1_{\mathbf{b}_1}, \xi_1 | 1_{\mathbf{b}_2}, \xi_2 \rangle|^2 = \int_0^\infty \xi_1^*(\omega) \xi_2(\omega) d\omega . \quad (1.75)$$

Combining both criteria together, we obtain the overall figure-of-merit for the indistinguishability

$$\mathcal{V} = \frac{\text{Tr}(\hat{\rho}_{\mathbf{b}_1}^2) + \text{Tr}(\hat{\rho}_{\mathbf{b}_2}^2) - \|\hat{\rho}_{\mathbf{b}_1} - \hat{\rho}_{\mathbf{b}_2}\|^2}{2}. \quad (1.76)$$

$\mathcal{V}$ can take values between zero and one, and is equal to unity only if the photon states are pure and identical. $\mathcal{V}$ is equal to the probability of the photons coalescing at the output ports of the beam-splitter. Experimentally, it is more convenient to measure the probability of finding one photon in each output port of the beam-splitter simultaneously. This quantifies the degree of distinguishability from which we can then deduce $\mathcal{V}$ [27, 112].

1.4.2 State-of-the-Art Implementations

Atoms and Ions

Individual trapped atoms [113] or ions [114] are an obvious candidate for realising an ideal photon-source. From their simple electronic levels, closed two-level systems can be addressed to generate single photons. The biggest advantage is that all atoms (or ions) of the same species are identical and therefore photons emitted by the same source, or by two separate sources, are de facto indistinguishable. However, it is technologically demanding to combine optical trapping and cooling systems with an apparatus capable of collecting the atom's/ion's emission efficiently. Studies are typically limited to cavities with high mode-volumes which therefore require high quality factors to achieve strong light-matter interactions. This is done at the expense of extraction efficiency from the cavity, and β is usually limited to 5-10% [115].

Quantum dots

A more scalable approach consists of optically addressing impurities or defects in a solid-state host. To this end, an ever-growing number of single-photon emitters have been

discovered, including quantum dots, colour-centres in diamond [106, 116] and atomic defects in two-dimensional materials [117]. In particular, quantum dots have become a very successful emitter from which on-chip single-photon sources are being built [25, 118]. Quantum dots are nano-islands of low band-gap semiconductor embedded in a higher band-gap semiconductor. Because of the confinement of the allowed electronic states, the dots have bound quantised states in the conduction and valence bands. By exciting the quantum dot with an optical [119, 120] or electronic [121] pulse, it is possible to promote an electron into the conduction band, leaving a hole in the valence band. The recombination of the bound electron-hole pair, also called an exciton, leads to the emission of a single photon with a high generation efficiency and low $g^{(2)}$ [122]. Quantum dots may also be used to deterministically emit entangled photon-pairs [123] and GHZ states [124].

Quantum dots have benefited from mature nano-fabrication techniques developed for the semiconductor industry. Sophisticated crystal-growth and deposition methods, together with optimised patterning, has made it possible to engineer the dielectric surroundings of quantum-dot emitters with high quality. The coupling of dots to micro-pillar cavities [27, 125] and photonic crystal waveguides [26] have proven successful strategies to enhance the collection efficiency. Recently, the development of deterministic device fabrication has allowed the precise patterning of photonic structures around pre-located quantum dots [126, 127].

To this date, the most successful approach is based on InAs quantum dots in GaAs micro-pillar cavities [128]. Such structures confine a cavity mode vertically with two $\text{Al}_{0.1}\text{Ga}_{0.9}\text{As}$ / $\text{Al}_{0.95}\text{Ga}_{0.05}\text{As}$ Bragg mirrors and laterally by a high refractive index contrast between the pillar and the surrounding air. Between the Bragg mirrors, the cavity length is set to approximately fit one wavelength of light at the typical frequency of the dots, which are grown in the middle of the cavity. The pillars are then patterned in-situ after finding suitable dots using cryogenic photolithography and subsequently

etched with reactive ion etching. To preferentially extract light upwards, the top mirror contains less semiconductor pairs which makes it less reflective. Finally, the mirrors are doped to make p-i-n diodes which can produce vertical electric fields inside the cavity to tune the resonant wavelength of the dots by the dc-Stark effect (Sec. 2.1.5). In this way, the wavelength of the dot can be tuned to match that of the cavity resonance.

The performance of the quantum-dot/micro-pillar sources ultimately depends on how the dot is promoted to its excited state. In this paragraph, I describe the recent results published by Senellart *et al.* [20]. With non-resonant excitation - where the dot is first excited above the band gap of the surrounding semiconductor and then decays into a trapped exciton - the exciting laser can easily be separated from the single-photon emission using filters. For optimised cavities, this has lead to the observation of β factors in the 80% range. However, this excitation scheme suffers from the large time uncertainty induced by the exciton capture, which limited the indistinguishability of successively emitted photons to 75%. To get around this problem, we can use resonant excitation with a cross-polariser scheme to block the pump light. This is done at the expense of β - which was reduced to 33% - because some of the emission has the same polarisation as the pump, and gets filtered out. Nevertheless, the indistinguishability was measured to be 96% using resonant pumping. In both cases, the indistinguishability was improved by the cavity as the radiative decay is sped-up compared to dephasing processes. Other resonant excitation schemes are being developed to increase the coupling efficiency, including side-excitation [129], polarised cavities [130, 131] and dichromatic laser pulses [132].

Finally, open micro-cavities offer another interesting approach [133]. In these structures, one Bragg mirror can be moved independently from the other, which allows precise positioning of the cavity to a dot and adjustment of the cavity length to match the emission wavelength. Control over both the emission wavelength by Stark tuning and of the cavity resonance is necessary to tune the indistinguishability of photons

from two remote sources. In open micro-cavities however, this comes at the expense of a much more complicated apparatus which is less scalable.

1.4.3 Organic-Molecule based Devices

As mentioned at the start of the introduction, dopant molecules in organic crystals can also be a source of triggered single-photons [23, 24]. The optical properties of single organic molecules are unique among all solid-state emitters. In particular, they offer a simple energy structure featuring quantum efficiencies above 95% [134, 135] and a lifetime-limited transition with branching ratio of approximately 33% [136, 137]. In addition, an organic crystal can be highly doped to achieve densities exceeding hundreds of emitters per λ^3 , which can be useful for the study of multi-body systems [138]. However, the patterning of organic materials on the nano-scale requires unconventional techniques [139, 140], and any post-processing of the structures is limited by low melting-points and high sublimation rates. Nevertheless, interesting research has recently been published in the direction of hybrid devices, where doped-organic crystals are grown (or placed) in pre-patterned photonic structures.

One approach consists of placing a doped crystal in an open micro-cavity [29]. In this study by Wang *et al.*, a rounded optical fibre coated with a Bragg mirror is positioned above a flat mirror to form a Fabry-Perot cavity. A large co-sublimated crystal is placed on the surface of the flat mirror to position dopant molecules inside the cavity mode. In this open geometry, precise control of the crystal's thickness is not critical as the cavity can be tuned to the wavelength of the emitter. This allows the coupling of single molecules to low volume and long-lived cavity modes. In addition to modifying the emission pattern, the cavity also acts to turn the molecules into coherent two-level systems. Indeed, organic dopant-molecules usually decay from their excited states to several lower-energy states, and only one of these transitions can produce indistinguishable photons efficiently (see Sec. 2.1.3). By tuning the cavity to that

transition, the decay rate of that transition can be greatly increased compared to the other transitions, which then become insignificant loss mechanisms. In this way, Wang *et al.* report a generation efficiency $\eta_{\text{gen}} = 95\%$ with a coupling to the cavity mode of 93%. However, the geometry did not allow for an efficient out-coupling of the photons from the cavity.

On-chip alternatives have also been developed recently. Coupling of single molecules to ridge-waveguides has been observed at room temperature with $\beta = 42\%$ [141] and at cryogenic temperature with $\beta = 7\%$ [28]. The integration of organic molecules with on-chip planar structures requires a controlled growth (or placement) of a doped-crystal in the vicinity of the optical modes. In [28], a melt-growth technique was used. This method relies on melting a doped-organic powder which fills enclosed structures by capillary forces. When the sample is cooled back to room-temperature, crystallisation of the organic material occurs, yielding high-quality dopant-molecules close to the waveguides. The same technique was used by Rattenbacher *et al.* to couple single dibenzoterrylene molecules to titanium-dioxide ring-resonators [30]. However, the crystallisation is usually not uniform across the photonic structures, which can lead to additional losses and a decrease of the cavity lifetime. A modest coupling to the cavity mode of 23% is reported, leaving some room for improvement.

1.5 Thesis Guide

The rest of this thesis describes my contribution towards fabricating an organic single-photon source of high efficiency. The chapters are organised in the following way. In **Chapter 2**, I introduce the organic quantum-emitter, namely dibenzoterrylene (DBT) molecules in anthracene crystals. I discuss single-photon emission from DBT molecules and the interaction of DBT with an external pump laser. This forms the basis of single-molecule spectroscopy, which is our main characterisation technique. In **Chap-**

ter 3, I describe our experimental set-up and present results from near lifetime-limited DBT in bulk anthracene crystals. In **Chapter 4**, we look at the emission from DBT molecules in the vicinity of single-mode waveguides to efficiently collect photons on a chip. I discuss the design, fabrication and characterisation of such devices. Specifically, I present preliminary results showing the in-waveguide extinction of laser light by resonant scattering of a single molecule. Finally, I investigate the interaction of single DBT molecules with optical cavities in **Chapter 5**. Cavity-assisted spontaneous emission is discussed, and I place lower limits on the performance of cavities to achieve high source efficiencies. I then discuss a vertical-emitting cavity with the potential of turning a single molecule into a near-optimum source of single photons.

2 Fundamentals of Dopant Molecules in Organic Crystals

In the previous chapter, we discussed how to generate single photons from single quantum-emitters and how to modify the emission to build deterministic single-photon sources. We reviewed the current state-of-the-art and seen that dopant molecules in organic crystals form the basis of a new approach which is developing rapidly. In this chapter, I will outline the fundamental principles of single-molecule spectroscopy and describe the main system of interest in this thesis: dibenzoterrylene dopant-molecules in anthracene crystals.

2.1 Dibenzoterrylene in Anthracene

Polycyclic aromatic hydrocarbons (PAH) are organic molecules which are composed of several aromatic rings containing only carbon and hydrogen. Since the early days of single-emitter spectroscopy, it was found that large PAHs such as pentacene [21], terrylene [142], dibenzanthanthrene [143] and dibenzoterrylene [144] can be embedded in crystals of smaller PAH molecules to form stable quantum-emitters in the solid state. The stability of the electronic states depends entirely on how the dopant molecule is inserted in the surrounding host matrix. Provided that it fits tightly in the space created by removing one or several adjacent host molecules, a guest molecule has optical transitions which do not fluctuate in time (spectral wandering), nor disappear (photo-bleaching), when addressed by laser light. These adverse effects are typically more pronounced when PAHs are inserted in polymers [145] or in frozen alkane-chains [146]. Dibenzoterrylene (DBT) molecules in anthracene crystals are a particularly promis-

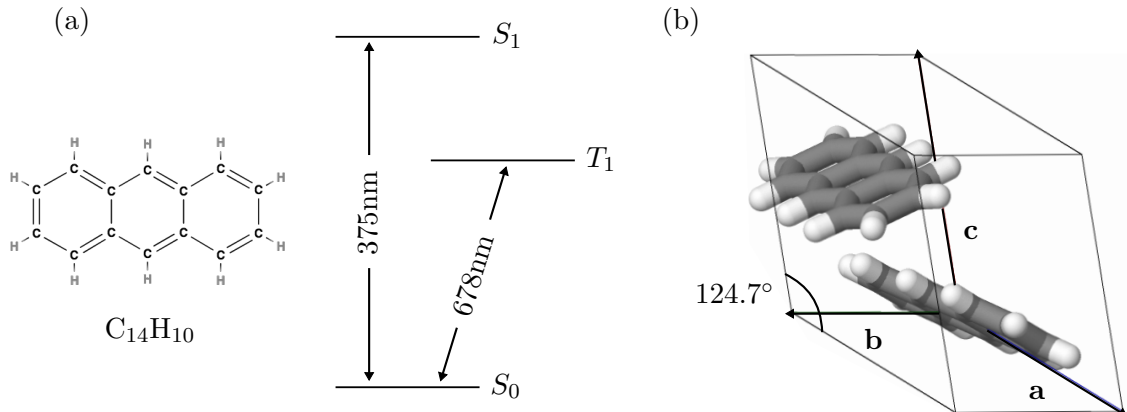


Figure 2.1: (a) Molecular structure of anthracene and energy levels of the outermost electrons of the conjugated π -electron system. (b) Anthracene crystal unit cell.

ing combination for the generation of single-photons [144, 147], because of favourable optical properties which are described in this chapter.

2.1.1 Anthracene Crystals

Anthracene is a small PAH with the chemical composition $C_{14}H_{10}$ whose molecular structure is shown in Fig. 2.1. At room temperature and pressure, anthracene forms a molecular solid held together by weak van der Waals forces, with a relatively low melting point of approximately 217°C and poor electrical conductivity [148, 149]. Anthracene crystals have a base-centred, monoclinic lattice structure, which is also depicted in Fig. 2.1. The lattice constants are 8.56Å, 6.04Å and 11.16Å along the *a*, *b* and *c* axes respectively, and the angle between the *a* and *c* axes is 124.7°[149, 150].

Because of the weak intermolecular forces, the optical properties of organic crystals resemble that of the individual constituent molecules. It is therefore sufficient to know the electronic structure of single anthracene molecules to have a good understanding of bulk crystals. In this thesis, we are only concerned with the spectrum in the visible and near-infrared regions which is dominated by the dynamics of the π -electron pair in

the highest-occupied molecular orbital (HOMO) [149]. The electronic energy levels of the two outer π -electrons are classified by their spins. We denote states with total spin quantum number $s = 0$ as singlet states and $s = 1$ as triplet states. In organic molecules in general, the HOMO is a singlet state which we denote S_0 and is commonly referred to as the ground electronic state. Lying above S_0 in the energy diagram, we find the first three excited triplet states, collectively referred to as T_1 . Above T_1 , we then find the first-excited singlet state S_1 . All these excited states correspond to the promotion of a single outer-most π -electron to a higher energy orbital. The transitions between S_0 and T_1 are spin-forbidden and do not contribute significantly to the absorption and emission spectra of organic crystals. However, the singlet-singlet transition between S_0 and S_1 is dipole-allowed and S_1 is typically regarded as the lowest-unoccupied molecular orbital (LUMO). In organic molecules and crystals, the transition between the HOMO and the LUMO of π -electrons is the lowest energy optical-transition of the system. For anthracene crystals, the energy difference between these two states corresponds to a wavelength of 375 nm [149]. Anthracene is therefore transparent in most of the visible and in the near-infrared regions.

Finally, anthracene has an anisotropic polarisability due to the anisotropy of its molecular and crystal structures. Anthracene crystals are birefringent and we found three orthogonal polarisation axes $\mathbf{n}_x$, $\mathbf{n}_y$ and $\mathbf{n}_z$, where $\mathbf{n}_x$ and $\mathbf{n}_z$ lie in the a-c crystal plane and $\mathbf{n}_y$ is parallel to the b-axis. At 546 nm, the components of the refractive index have been measured as $n_x = 1.57$, $n_y = 1.82$ and $n_z = 2.22$ [151]. However, this study has also shown a strong dependence of the refractive index components on wavelength and crystal thickness.

2.1.2 DBT Doping

In order to isolate a single set of electronic states, it is necessary to introduce a defect in the organic crystal. A particularly successful strategy has been to add guest organic-

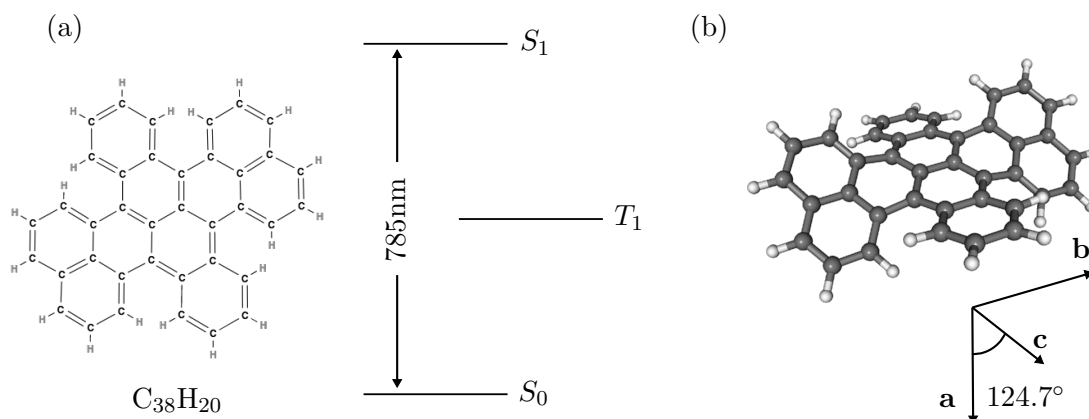


Figure 2.2: (a) Molecular structure of DBT and energy levels of the outermost electrons of the conjugated π -electron system. (b) Orientation of a DBT molecule relative to the crystal axes of anthracene when included in the main insertion site (adapted from [150]). See [147] for a more detailed representation of the main and red insertion sites.

molecules in the crystal by doping. The difference in energy between the HOMO and the LUMO generally decreases with the length of the conjugated π -electron system. Therefore, if the dopant PAH is physically larger than the host PAH, the optical transition of the guest molecule lies outside the absorption region of the crystal, and we can therefore access them optically.

Dibenzoterrylene (DBT), chemical formula $C_{38}H_{20}$, is a much larger PAH than anthracene (see Fig. 2.2) and is an excellent dopant for single-photon generation. DBT typically includes itself in one of two configurations inside an anthracene crystal [147]. In the “main” insertion site, one DBT molecule replaces three anthracene molecules along the *b*-axis. For this configuration, the transition between the S_0 and S_1 states is situated around 785 nm. In the “red” insertion site, one DBT molecule replaces two anthracene molecules along the *b*-axis and one of their nearest-neighbours along the *a*-axis. The singlet-singlet transition for this configuration corresponds to approximately 794 nm. The main site is usually much more populated than the red site and also suffers less from interactions with the neighbouring anthracene molecules in the crystal

[147]. In the rest of this thesis, we therefore restrict ourselves to the study of the main site.

DBT molecules in the main site are mostly photostable and do not experience severe spectral jumps or diffusion [144]. However, this is strongly dependent on the local crystal environment, which can be different from one dopant molecule to another. Strains in the crystal, caused by structural defects such as dislocations and grain boundaries, can degrade the photostability of dopant molecules. The concentration of defects usually depends on the crystal-growth method and tends to increase towards crystal edges and close to interfaces with different materials [152]. Additionally, the local environment also shifts the energy difference between electronic states from one guest molecule to another. This is known as the inhomogeneous broadening of the spectral lines. In bulk crystals, the inhomogeneous width of the singlet-singlet transition is around 0.3 nm for the main site [144].

In addition to the purely electronic degrees of freedom, we also have to take into account the intra-molecular vibrations of the guest DBT (Fig. 2.3). Each electronic state supports a manifold of quantised vibrational levels, which correspond to relative motions of the nuclei [153]. We label the vibrational states by the electronic levels they are associated with and in ascending order of their energy. For example, the n^{th} excited vibrational state of the S_0 electronic state is denoted as $S_{0,n}$. Optical transitions can occur between any vibrational sublevels of different electronic states and between sublevels of the same electronic state. However, the emission spectrum of dopant molecules is greatly simplified by Kasha’s rule, which states that fluorescence and phosphorescence only occur with high yield from the $S_{1,0}$ and $T_{1,0}$ states, respectively. This is because the excited states in each set of vibrational sublevels are very short lived, as they decay non-radiatively to the ground vibrational state. The fast relaxation is caused by coupling to the surrounding crystal which absorbs the vibration on picosecond time scales [149].

One particularly important feature of DBT is that the energy difference between its S_0 and S_1 states is less than the difference between the S_0 and T_1 states of anthracene. If the opposite were true, we would expect a strong probability of singlet-to-triplet energy transfer from guest to host, followed by a triplet exciton transfer from host to guest [142]. This mechanism would contribute to transitions between the S_1 and T_1 states in DBT which are known as inter-system crossings. In the context of single-photon generation, a high rate of inter-system crossing is undesirable as it would decrease the generation efficiency of single photons from the S_1 state (see Sec. 1.3.3). For DBT in anthracene, the probability of inter-system crossing is very low, on the order of 10^{-7} or lower [144]. The molecule is not completely lost after an inter-system crossing event. Indeed, spin-orbit coupling allows weak, radiative transitions from $T_{1,0}$ back to the $S_{0,n}$ manifold. The lifetime of $T_{1,0}$ is around $40\ \mu\text{s}$ [144], which is much longer than the spin-allowed transitions. Finally, the presence of spin-orbit coupling means that optical transitions between S_0 and T_1 , and between S_1 and T_1 , can in principle be addressed by laser light. To this date however, triplet state spectroscopy has not yet been achieved.

2.1.3 Single Photons from DBT in Anthracene

Efficiency Reduction

The vibrational spectrum of DBT is both an advantage and a disadvantage for single-photon generation. The main limitation is that the molecule can radiatively decay from the $S_{1,0}$ state to any of the $S_{0,n}$ vibrational states. The intensity of each vibrational line is explained by the Franck-Condon principle which takes into account the nuclear wavefunction in the calculation of the transition dipole-moment [153]. In Sec. 1.3.2, we have discussed the evolution of an excited two-level emitter coupled to a continuum of optical modes. This model can be extended to incorporate other vibrational lines by

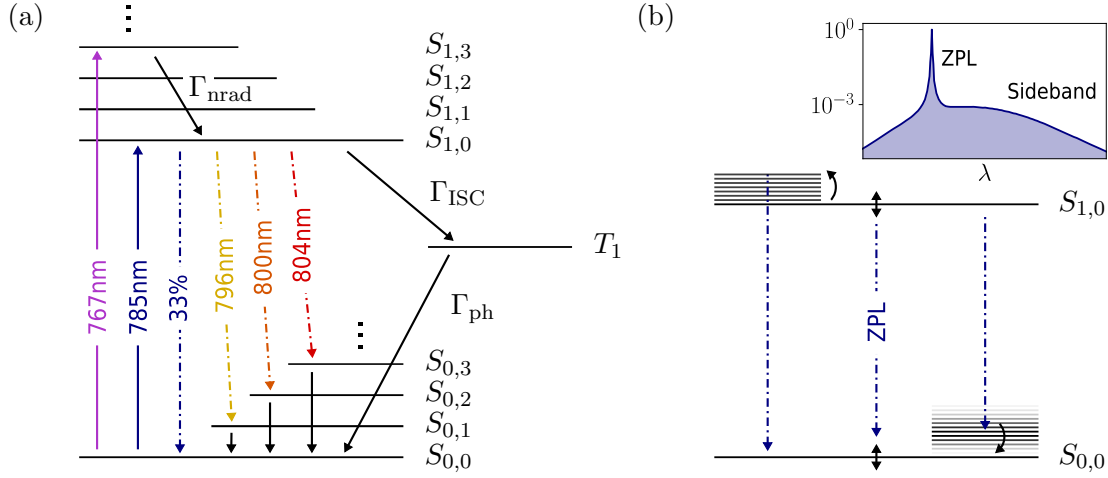


Figure 2.3: (a) Intra-molecular electronic and vibrational energy levels of DBT in anthracene. The system can be pumped resonantly to the $S_{1,0}$, or non-resonantly to $S_{1,n}$ followed by a non-radiative relaxation to $S_{1,0}$ with rate Γ_{nrad} . The molecule radiatively decays back to the $S_{0,n}$ manifold with a rate Γ_1 but also experiences inter-system crossings to the triplet states at a rate Γ_{ISC} . Relaxation from T_1 is likely (but not confirmed) to be dominated by radiative phosphorescence at a rate Γ_{ph} . The wavelengths of the vibrational spectrum and branching ratio of the $S_{1,0} \rightarrow S_{0,0}$ transition are approximate and can vary from one molecule to another. (b) Interaction with the surrounding crystal. Each energy level is dressed with the vibrational modes of the environment. Radiative decays can be accompanied with the absorption or emission of phonons. The presence of phonons also induce random energy fluctuations of the electronic state which cause pure dephasing.

expanding the Hilbert space of the atom so that

$$\hat{\mathcal{H}}_A = \hbar\omega_0|S_{1,0}\rangle\langle S_{1,0}| + \sum_n \hbar(\omega_0 - \omega_n)|S_{0,n}\rangle\langle S_{0,n}|, \quad (2.1)$$

where $\hbar\omega_n$ is the energy difference between the states $S_{1,0}$ and $S_{0,n}$. The dipole-moment operator can be generalised as

$$\hat{\boldsymbol{\mu}} = \sum_n \boldsymbol{\mu}_n|S_{1,0}\rangle\langle S_{0,n}| + h.c., \quad (2.2)$$

with $\boldsymbol{\mu}_n = \langle S_{1,0}|\hat{\boldsymbol{\mu}}|S_{0,n}\rangle$, $h.c$ denotes the Hermitian conjugate and we neglect any interactions between the states $S_{0,n}$ and $S_{0,0}$, for now. The transition dipole-moments $\boldsymbol{\mu}_n$ are real-valued which leads to the emission of linearly-polarised photons [147]. We find that the direction of the dipole-moments is parallel to the b-axis of the host anthracene

crystal. The dynamics of the excited state after pulsed excitation (Eq. 1.47) has to be modified to account for all transitions to vibrational states. Instead, we have

$$c_e(t) = H(t) \exp\left(-\frac{\Gamma_1}{2}t\right) = H(t) \exp\left(-\sum_n \frac{\Gamma_{1,n}}{2}t\right), \quad (2.3)$$

with

$$\Gamma_{1,n} = \frac{\pi |\boldsymbol{\mu}_n|^2 \omega_n \rho(\mathbf{r}_0, \mathbf{e}_\mu, \omega_n)}{\epsilon_0 \hbar}, \quad \Gamma_1 = \sum_n \Gamma_{1,n}, \quad (2.4)$$

and the two-level spectrum (Eq. 1.53) is generalised to

$$S(\omega) = \pi^{-1} \sum_n \frac{\Gamma_{1,n}/2}{(\Gamma_1/2)^2 + (\omega - \omega_n)^2} = \pi^{-1} \sum_n \alpha_n \frac{\Gamma_1/2}{(\Gamma_1/2)^2 + (\omega - \omega_n)^2}, \quad (2.5)$$

which represents a series of Lorentzian lines with FWHM of Γ_1 and weighted by the branching ratios $\alpha_n = \Gamma_{1,n}/\Gamma_1$. For $S_{1,0} \rightarrow S_{0,n>0}$ transitions however, the molecule then decays back to the ground vibrational state $S_{0,0}$ because of a strong mechanical coupling to the surrounding crystal. Hence, this is a two-step decay process and the spectrum of each excited vibrational line is broadened as [154]

$$S_{n \geq 1}(\omega) = \pi^{-1} \alpha_n \frac{(\Gamma_1 + \Gamma_{\text{relax}})/2}{((\Gamma_1 + \Gamma_{\text{relax}})/2)^2 + (\omega - \omega_n)^2}, \quad (2.6)$$

where Γ_{relax} is the relaxation rate from $S_{0,n}$ to $S_{0,0}$, which is assumed to be the same for all $S_{0,n}$ states. In contrast, the $S_{1,0} \rightarrow S_{0,0}$ line does not lead to the emission of intra-molecular phonons and its linewidth is only limited by the lifetime of the $S_{1,0}$ state. For DBT in anthracene, this line is bright and accounts for more than 30% of the emission from $S_{1,0}$. It is therefore the transition of choice for generating single photons. However, the $S_{1,0} \rightarrow S_{0,n>0}$ transitions have to be filtered out to isolate the indistinguishable photons from the $S_{1,0} \rightarrow S_{0,0}$ transition alone. Therefore, the presence of other vibrational lines reduces the generation efficiency of the source to a value α_{FC} , which corresponds to the branching ratio of the $S_{1,0} \rightarrow S_{0,0}$ transition.

Guest molecules also interact with vibrations of the lattice, and optical transitions can be accompanied by the creation or annihilation of phonons in the crystal. For dopant molecules in organic crystals, both the interaction with pseudo-local phonons and the influence of acoustic phonons have to be considered [155–157]. In the emission spectrum, each optical line can be decomposed in two features as seen in Fig. 2.3. The first component is a zero-phonon line (ZPL) which corresponds to the transition with no phonon interaction. In addition, we also observe a broad phonon-sideband which includes all transitions where phonons are created and/or annihilated alongside the emitted photon. The strength of the ZPL depends on the nature of the interaction with localised phonons [157] and on the lattice wavefunction overlap when the molecule is in the ground and excited state (the so-called Debye-Waller factor) [110]. We denote the branching fraction of the ZPL with respect to all $S_{1,0} \rightarrow S_{0,0}$ transitions as α_{DW} . The branching ratio depends on temperature and it is only when the crystal is cooled to cryogenic temperatures that the ZPL becomes the dominant contribution. At low temperatures, the distance in frequency between the $S_{1,0} \rightarrow S_{0,0}$ ZPL and the peak of its phonon sideband is approximately 2 THz [158].

Because of the coupling to the surrounding lattice, photons emitted in the phonon sideband are distinguishable and therefore unwanted in a single-photon source. Combining this with the reduction in efficiency due to intra-molecular vibration, we get an overall single-photon generation efficiency

$$\alpha = \alpha_{\text{FC}}\alpha_{\text{DW}} . \quad (2.7)$$

where - as defined above - α_{FC} is the branching ratio of the $S_{1,0} \rightarrow S_{0,0}$ transition and α_{DW} is the branching ratio of its ZPL. For DBT in anthracene, the overall bulk value for α is generally estimated to be around 33% at liquid-helium temperature [136]. These numbers are likely to fluctuate from one molecule to another because of changes in the local environment. If it were not possible to increase the strength of the $S_{1,0} \rightarrow S_{0,0}$

ZPL, organic molecules in the solid state would not be good single-photon sources compared to other emitters (Sec. 1.4.2). However, as Eq. 2.4 suggests, is it possible to turn the emitter into a coherent two-level system by placing DBT molecules inside structures which change the local density-of-states [29] (Sec. 5.1).

Non-Resonant Excitation

The vibrational spectrum of DBT molecules allows us to efficiently prepare the $S_{1,0}$ state from the ground state using non-resonant laser excitation. This scheme consists of using a short laser pulse which is resonant with one of the $S_{0,0} \leftrightarrow S_{1,n}$ transitions to coherently transfer the population. The molecule then quickly relaxes to $S_{1,0}$, from which it undergoes spontaneous emission back to the ground singlet state, emitting a single photon. Despite this process also being a two-step decay, it is possible to show that the spectrum and the coherence of the single-photon emission are unaffected by the previous phonon decay [159]. Rather, a time uncertainty is added in the preparation of the $S_{1,0}$ state after the pulsed excitation. The $S_{1,0}$ state is long-lived compared to the vibrational relaxation time, with a lifetime of approximately 5 ns (which can vary from one molecule to another). The picosecond-long relaxation therefore does not add a large time uncertainty for the preparation of the $S_{1,0}$ state, and this scheme may be used to trigger indistinguishable photons [160–162]. Because the laser spectrum does not overlap with the single-photon emission, simple filtering can then be used to block any residual pump light. This is the main benefit of the non-resonant excitation scheme.

2.1.4 Dephasing

Over time, the emitter also experiences a loss of coherence due to the interaction with phonons. Together with spontaneous emission, this constitutes an additional form of dephasing. In the simplest approximation, this mechanism can be explained with random energy fluctuations of the system, which are Markovian and stationary [163]. In this

case, the two-level spectrum (Eq. 1.53) still has a Lorentzian form but is homogeneously broadened as

$$S(\omega) = \pi^{-1} \frac{\Gamma_1/2 + \Gamma_2^*}{(\Gamma_1/2 + \Gamma_2^*)^2 + (\omega - \omega_0)^2} , \quad (2.8)$$

where Γ_1 is the radiative rate and Γ_2^* is the pure dephasing rate, which is related to the magnitude of the energy fluctuations. For simplicity, it is convenient to define the total dephasing rate

$$\Gamma_2 = \Gamma_1/2 + \Gamma_2^* . \quad (2.9)$$

Γ_2^* also strongly depends on the temperature T of the surrounding crystal. For dopant-molecules in organic crystals, Γ_2^* obeys an Arrhenius law [156, 157]

$$\Gamma_2^*(T) = A \exp\left(-\frac{E_a}{k_b T}\right) , \quad (2.10)$$

which is the signature of pseudo-localised phonons having a strong influence on the optical transition. In Eq. 2.10, k_b is the Boltzmann constant, E_a is the activation energy associated with the local phonon oscillation and A is a constant that depends on the electron-phonon interaction. For the main site of DBT in anthracene, E_a/k_b is found to be around 40 K [147, 164].

The indistinguishability of the emitted photons depends on the pure dephasing rate. A faster rate of pure dephasing means a stronger coupling to the environment and less-identical photons. In this simple model and assuming that both photons come from the same process, the degree of indistinguishability (as defined in Eq. 1.76) is simply given by [163]

$$\mathcal{V} = \frac{\Gamma_1}{2\Gamma_2} . \quad (2.11)$$

In the presence of pure dephasing, the evolution of the reduced density matrix for

the emitter (Eq. 1.54) in the interaction picture is [42]

$$\begin{aligned} \frac{d}{dt}\hat{\rho}_{\text{emitter}} = & \frac{\Gamma_1}{2} (2\hat{\sigma}^- \hat{\rho}_{\text{emitter}} \hat{\sigma}^+ - \hat{\sigma}^+ \hat{\sigma}^- \hat{\rho}_{\text{emitter}} - \hat{\rho}_{\text{emitter}} \hat{\sigma}^+ \hat{\sigma}^-) \\ & + \frac{\Gamma_2^*}{2} (\hat{\sigma}_z \hat{\rho}_{\text{emitter}} \hat{\sigma}_z - \hat{\rho}_{\text{emitter}}) , \end{aligned} \quad (2.12)$$

where $\hat{\sigma}_z$ is the Pauli z-matrix.

Of course, the pure-dephasing model is incomplete and restrictive. For example, it fails to explain the phonon-wing in the spectrum of solid-state emitters. More sophisticated approaches have been formulated for different emitters [156, 165, 166], which lead to modified results for the indistinguishability of the emitted photons [110, 167]. Exploring those theories in detail is beyond the scope of this thesis.

2.1.5 Stark Tuning

The dc-Stark effect is concerned with the behaviour of electronic states when an external electric field is applied. This typically results in the shifting of spectral lines. Let us denote the static external field as $\mathbf{E}_{\text{Stark}}$, so that the perturbation Hamiltonian is

$$\hat{\mathcal{H}}_I = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E}_{\text{Stark}} . \quad (2.13)$$

By using second-order perturbation theory, the energy E_ψ of a bound electronic state $|\psi\rangle$ is shifted by

$$\Delta E = -\langle\psi|\hat{\boldsymbol{\mu}}|\psi\rangle \cdot \mathbf{E}_{\text{Stark}} + \sum_i \frac{|\langle\psi|\hat{\boldsymbol{\mu}}|i\rangle \cdot \mathbf{E}_{\text{Stark}}|^2}{E_\psi - E_i} , \quad (2.14)$$

where $|i\rangle$ are all other unperturbed states. This can be written more concisely in terms of the permanent dipole-moment $\mathbf{d}$ and the polarisability tensor $\hat{\boldsymbol{\alpha}}$ as

$$\Delta E = -\mathbf{d} \cdot \mathbf{E}_{\text{Stark}} - \frac{1}{2} \mathbf{E}_{\text{Stark}} \cdot \hat{\boldsymbol{\alpha}} \cdot \mathbf{E}_{\text{Stark}} , \quad (2.15)$$

and $\mathbf{d}_{\text{induced}} = \mathbf{E}_{\text{Stark}} \cdot \hat{\boldsymbol{\alpha}}$ is the induced dipole-moment. The two terms in Eq. 2.15 are usually referred to as the linear and quadratic Stark shifts. Finally, the energy difference between a ground state, g , and an excited state, e , is shifted by

$$\Delta\hbar\omega = -\delta\mathbf{d} \cdot \mathbf{E}_{\text{Stark}} - \frac{1}{2}\mathbf{E}_{\text{Stark}} \cdot \delta\hat{\boldsymbol{\alpha}} \cdot \mathbf{E}_{\text{Stark}} , \quad (2.16)$$

with $\delta\mathbf{d} = \mathbf{d}_e - \mathbf{d}_g$ and $\delta\hat{\boldsymbol{\alpha}} = \hat{\boldsymbol{\alpha}}_e - \hat{\boldsymbol{\alpha}}_g$. To second order, the frequency of an optical transition can therefore be tuned using static electric-fields, unless the difference in permanent and induced dipole-moments is zero. For the $S_{0,0} \leftrightarrow S_{1,0}$ transition of DBT in anthracene, $\delta\mathbf{d}$ approximately vanishes and we are left with a purely quadratic Stark shift [147, 168]. This is expected from states with well-defined parity. The $\delta\hat{\boldsymbol{\alpha}}$ tensor has not yet been mapped in all three dimensions but, for electric fields applied in the a-b crystal plane with an angle of 60° with respect to the b-axis, the scalar polarisability was found to be $-0.4 \text{ MHz}/(\text{kVcm}^{-1})^2$ [147]. For electric fields on the order of 10^2 kV/cm , this corresponds to an absolute tunability of approximately 0.4 GHz/V .

2.2 Continuous-Wave Spectroscopy

So far, I have avoided any consideration regarding the interaction of quantum emitters with an external source of light. However, DBT molecules have to be excited by laser pulses to act as triggered sources of single photons. Before resorting to pulsed excitation, the emitter can also be characterised using continuous-wave spectroscopy. This is the main technique that we use to probe DBT molecules in anthracene.

2.2.1 Resonant Spectroscopy

Optical Bloch Equations

With an external source of light, the interaction Hamiltonian (Eq. 1.34) can be written as

$$\hat{\mathcal{H}}_{ED} = -\hat{\boldsymbol{\mu}} \cdot (\hat{\mathbf{E}}_{\text{rad}} + \hat{\mathbf{E}}_{\text{ext}}) , \quad (2.17)$$

by separating the contribution from the quantum vacuum field $\hat{\mathbf{E}}_{\text{rad}}$ and the external field $\hat{\mathbf{E}}_{\text{ext}}$. We will first consider a DBT molecule interacting with a classical source of monochromatic light close to the $S_{0,0} \leftrightarrow S_{1,0}$ transition. Hence, $\hat{\mathbf{E}}_{\text{ext}}(t)$ can be replaced in the Heisenberg picture by

$$\mathbf{E}(t) = \boldsymbol{\mathcal{E}}_0 \cos(\omega_L t) . \quad (2.18)$$

To simplify the problem, we assume that each contribution is acting separately from one another, so that we simply add the rates of variation of $\hat{\rho}_{\text{emitter}}$ which come from the separate couplings. This is known as the independent rates-of-variation approximation [169] and leads to the well-known evolution of $\hat{\rho}_{\text{emitter}}$ given by the optical Bloch equations.

Including the vibrational sublevels of the ground electronic state, $\hat{\rho}_{\text{emitter}}$ is expanded as

$$\begin{aligned} \hat{\rho}_{\text{emitter}} = & \rho_{ee}|S_{1,0}\rangle\langle S_{1,0}| + \rho_{gg}|S_{0,0}\rangle\langle S_{0,0}| + (\rho_{ge}|S_{0,0}\rangle\langle S_{1,0}| + h.c.) \\ & + \sum_n \left(\rho_{nn}|S_{0,n}\rangle\langle S_{0,n}| + (\rho_{gn}|S_{0,0}\rangle\langle S_{0,1}| + h.c.) + (\rho_{ne}|S_{0,n}\rangle\langle S_{1,0}| + h.c.) \right. \\ & \left. + \sum_{n' \neq n} (\rho_{nn'}|S_{0,n}\rangle\langle S_{0,n'}| + h.c.) \right) , \quad (2.19) \end{aligned}$$

where $h.c.$ denotes the Hermitian conjugate and we neglect the small rate of inter-system

crossing to the triplet states. The density matrix can be greatly simplified by realising that the radiative decays from $|S_{1,0}\rangle$ to $|S_{0,n}\rangle$ and the lattice-induced relaxation from $|S_{0,n}\rangle$ to $|S_{0,0}\rangle$ are both incoherent processes. If we assume that the emitter always starts in the $|S_{0,0}\rangle$ state, we therefore have $\rho_{gn} = \rho_{ne} = \rho_{nn'} = 0$ as there is no mechanism to coherently transfer the population to any $|S_{0,n}\rangle$ states in this case. By changing to the frame rotating with the laser field and using the above assumptions, the time-independent form of the optical Bloch equations is [42]

$$\frac{d\rho_{ee}}{dt} = \frac{i}{2}\Omega_0(\tilde{\rho}_{ge} - \tilde{\rho}_{eg}) - \sum_n \Gamma_{1,n}\rho_{ee} , \quad (2.20)$$

$$\frac{d\rho_{nn}}{dt} = \Gamma_{1,n}\rho_{ee} - \Gamma_{\text{relax}}\rho_{nn} , \quad (2.21)$$

$$\frac{d\rho_{gg}}{dt} = -\frac{i}{2}\Omega_0(\tilde{\rho}_{ge} - \tilde{\rho}_{eg}) + \Gamma_{\text{relax}} \sum_n \rho_{nn} , \quad (2.22)$$

$$\frac{d\tilde{\rho}_{ge}}{dt} = \frac{i}{2}\Omega_0(\rho_{ee} - \rho_{gg}) - \left(i\Delta_L + \sum_n \frac{\Gamma_{1,n}}{2} + \Gamma_2^* \right) \tilde{\rho}_{ge} , \quad (2.23)$$

$$\rho_{gg} + \rho_{ee} + \sum_n \rho_{nn} = 1 , \quad (2.24)$$

$$\tilde{\rho}_{eg} = (\tilde{\rho}_{ge})^* , \quad (2.25)$$

where we define the variable $\tilde{\rho}_{ge} = \rho_{ge} \exp(-i\Delta_L t)$. The Rabi frequency $\Omega_0 = \boldsymbol{\mu}_0 \cdot \boldsymbol{\mathcal{E}}_0 / \hbar$ is a measure of the coupling strength between the molecule and the external field, which is detuned from the $S_{0,0} \leftrightarrow S_{1,0}$ transition by an amount $\Delta_L = \omega_L - \omega_0$. Ω_0 is assumed to be real. Here, the laser is resonant with the $S_{0,0} \leftrightarrow S_{1,0}$ transition therefore $\boldsymbol{\mu}_0 = \langle S_{1,0} | \hat{\boldsymbol{\mu}} | S_{0,0} \rangle$. We also assume that the decay rates of the $|S_{0,n}\rangle$ sublevels are all equal to Γ_{relax} .

In the limit that $\Gamma_{\text{relax}} \gg \Gamma_{1,n} \forall n$, the above differential equations are equivalent to

$$\frac{d\rho_{ee}}{dt} = \frac{i}{2}\Omega_0(\tilde{\rho}_{ge} - \tilde{\rho}_{eg}) - \Gamma_1\rho_{ee} , \quad (2.26)$$

$$\frac{d\rho_{gg}}{dt} = -\frac{d\rho_{ee}}{dt} , \quad (2.27)$$

$$\frac{d\tilde{\rho}_{ge}}{dt} = \frac{i}{2}\Omega_0(\rho_{ee} - \rho_{gg}) - (i\Delta_L + \Gamma_2)\tilde{\rho}_{ge} , \quad (2.28)$$

$$\rho_{nn} = 0 , \quad (2.29)$$

$$\rho_{gg} + \rho_{ee} = 1 , \quad (2.30)$$

$$\tilde{\rho}_{eg} = (\tilde{\rho}_{ge})^* , \quad (2.31)$$

and we can discard the vibrational sublevels altogether to recover the typical form of the Bloch equations. However, Γ_1 still includes all the contributions from the $S_{1,0} \rightarrow S_{0,n}$ spontaneous decays.

Solutions

The steady-state solutions to the Bloch equations are well-known and we get the expressions [42, 138]

$$\rho_{ee} = \frac{1}{2} \frac{S}{\left(\frac{\Delta_L}{\Gamma_2}\right)^2 + 1 + S} , \quad (2.32)$$

$$\rho_{gg} = 1 - \rho_{ee} , \quad (2.33)$$

$$\tilde{\rho}_{ge} = -\frac{1}{2} \frac{\Gamma_1}{\Omega_0} \frac{S}{\left(\frac{\Delta_L}{\Gamma_2}\right)^2 + 1 + S} \left(\frac{\Delta_L}{\Gamma_2} + i \right) , \quad (2.34)$$

$$\tilde{\rho}_{eg} = (\tilde{\rho}_{ge})^* , \quad (2.35)$$

where it is useful to define the saturation parameter $S = \frac{\Omega_0^2}{\Gamma_1\Gamma_2}$. By using the cycle-averaged intensity $\bar{I} = \frac{1}{2}\varepsilon\varepsilon_0c|\mathcal{E}_0|^2$, we can express the saturation parameter as

$$S = \frac{\bar{I} \cos^2(\theta)}{\bar{I}_{\text{sat}}} , \quad \bar{I}_{\text{sat}} = \frac{\varepsilon\varepsilon_0c\hbar^2}{|\boldsymbol{\mu}_0|^2} \frac{\Gamma_1\Gamma_2}{2} , \quad (2.36)$$

where θ is the angle between $\boldsymbol{\mu}_0$ and $\boldsymbol{\mathcal{E}}_0$, and ε is the dielectric constant of anthracene.

From Eq. 2.32, it is then possible to calculate the average rate of photon emission from spontaneous decay as

$$R(\Delta_L, S) = \Gamma_1 \rho_{ee} = \frac{\Gamma_1}{2} \frac{S}{\left(\frac{\Delta_L}{\Gamma_2}\right)^2 + 1 + S} , \quad (2.37)$$

which has a Lorentzian form with $\text{FWHM} = 2\Gamma_2\sqrt{1+S}$ and amplitude of $\frac{\Gamma_1}{2} \frac{S}{1+S}$.

In a fluorescence spectroscopy experiment, we would filter out the external light and the $S_{1,0} \rightarrow S_{0,0}$ emission would also be lost. In this case, we only care about the non-resonant fluorescence, and the above results are still valid but we now have $R_{\text{fluor}}(\Delta_L, S) = (1 - \alpha_{\text{FC}})R(\Delta_L, S)$.

2.2.2 Coherent and Incoherent Scattering

Let us first generalise Eq. 2.37 which is only a statistical average over time. Here, it is useful to model the molecule as a simple two-level system, with the non-resonant vibrational lines treated as phenomenological decay paths to the ground state. The total power emitted by the molecule on the $S_{0,0} \leftrightarrow S_{1,0}$ line is given by

$$P_{\text{res}}(t) = \oint d\mathbf{S} \cdot \langle \hat{\mathbf{I}}_{\text{res}}(\mathbf{r}, t) \rangle = r^2 \int d\Omega \langle \hat{\mathbf{E}}_{\text{res}}^-(\mathbf{r}, t) \cdot \hat{\mathbf{E}}_{\text{res}}^+(\mathbf{r}, t) \rangle , \quad (2.38)$$

which is the integral of the Poynting vector over a closed surface around the emitter. The last equality holds for a large sphere of radius r and $d\Omega$ is the solid angle. We can then use the source field expression to write Eq. 2.38 in terms of the atomic raising and lowering operators of the two-level system in the Heisenberg picture [42]

$$P_{\text{res}}(t) = P_{\text{res}}^\infty \langle \hat{\sigma}^+(t) \hat{\sigma}^-(t) \rangle , \quad (2.39)$$

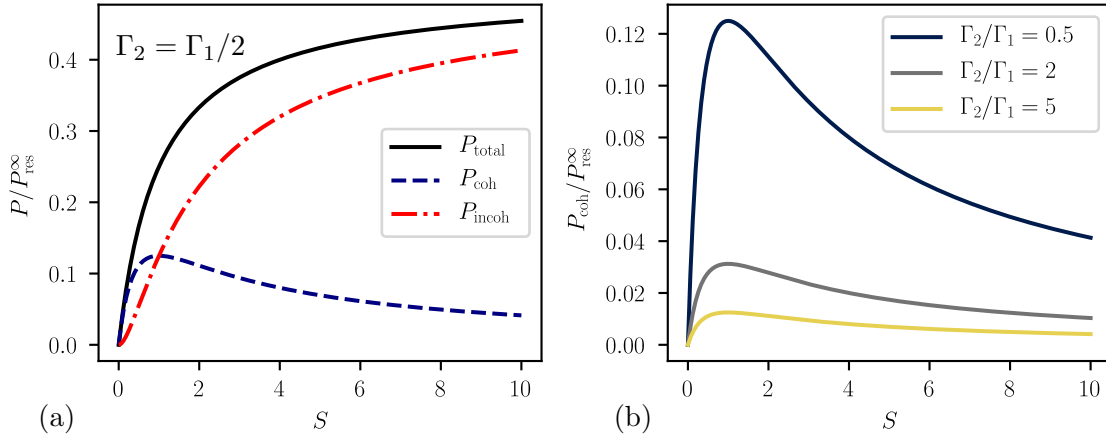


Figure 2.4: (a) Separation of the emitted power into coherent and incoherent parts for no pure dephasing, as given by Eq. 2.42 and Eq. 2.43. (b) Coherent power with an increasing rate of pure dephasing.

where $P_{\text{res}}^\infty = \alpha\Gamma_1\hbar\omega_0$. Now, the atomic operators can be decomposed in terms of their expectation value and instantaneous deviation as

$$\hat{\sigma}^\pm(t) = \langle \hat{\sigma}^\pm(t) \rangle + \delta\hat{\sigma}^\pm(t) , \quad (2.40)$$

with $\langle \delta\hat{\sigma}^\pm(t) \rangle = 0$. Eq. 2.39 can then be rewritten as

$$P_{\text{res}}(t) = P_{\text{res}}^\infty (|\langle \hat{\sigma}^+(t) \rangle|^2 + \langle \delta\hat{\sigma}^+(t)\delta\hat{\sigma}^-(t) \rangle) . \quad (2.41)$$

The emitted power is split in two parts. The first term corresponds to the field emitted by a classical dipole with a well-defined phase relative to the driving field. This corresponds to a coherent scattering process, and the scattered field can interfere with the pump light. The second term corresponds to an incoherent scattering process with a random phase with respect to the driving field.

In the steady-state and for zero detuning, we get

$$P_{\text{res}}^{\text{coh}} = P_{\text{res}}^\infty |\tilde{\rho}_{ge}|^2 = \frac{P_{\text{res}}^\infty}{2} \frac{\Gamma_1}{2\Gamma_2} \frac{S}{(1+S)^2} , \quad (2.42)$$

and

$$P_{\text{res}}^{\text{incoh}} = P_{\text{res}} - P_{\text{res}}^{\text{coh}} = P_{\text{res}}^{\infty}(\rho_{ee} - |\tilde{\rho}_{ge}|^2) = \frac{P_{\text{res}}^{\infty}}{2} \frac{(1+S)\Gamma_2 - \Gamma_1/2}{\Gamma_2} \frac{S}{(1+S)^2} . \quad (2.43)$$

Finally, we can compute the spectrum of the coherent scattering using the Wiener-Khinchin theorem [169]

$$S_{\text{res}}^{\text{coh}}(\omega) \propto \int_{-\infty}^{\infty} d\tau \exp(i\Delta_L \tau) \langle \hat{\sigma}^+(t+\tau) \rangle \langle \hat{\sigma}^-(t) \rangle \quad (2.44)$$

$$= \int_{-\infty}^{\infty} d\tau \exp(i\Delta_L \tau) |\tilde{\rho}_{ge}|^2 \propto \delta(\omega_0 - \omega_L) , \quad (2.45)$$

which is a monochromatic field with frequency ω_L , as expected. The calculation of the incoherent spectrum is more complicated as it involves the Mollow triplet for high pump powers and collisional redistribution of radiation [42]. Finally, it is also worth mentioning that all the power emitted on the non-resonant vibrational lines is incoherent.

2.2.3 Second-Order Correlation Function

In Sec. 1.4.1, we have seen how the second-order correlation function $g^{(2)}$ gives us information about the probability of multiple-photon emission in a pulse. The measurement of $g^{(2)}(\tau)$ under continuous-wave excitation follows the same principles and allows us to further probe the dynamics of the emitter. Let us recall the definition of the second-order correlation function

$$g^{(2)}(t, t') = \frac{\langle \hat{a}_{\mathbf{b}}^{\dagger}(t) \hat{a}_{\mathbf{b}}^{\dagger}(t') \hat{a}_{\mathbf{b}}(t') \hat{a}_{\mathbf{b}}(t) \rangle}{\langle \hat{a}_{\mathbf{b}}^{\dagger}(t) \hat{a}_{\mathbf{b}}(t) \rangle \langle \hat{a}_{\mathbf{b}}^{\dagger}(t') \hat{a}_{\mathbf{b}}(t') \rangle} . \quad (2.46)$$

In contrast with pulsed sources, the statistical properties of the system are stationary under continuous-wave excitation and we can re-write Eq. 2.46 as a function of time

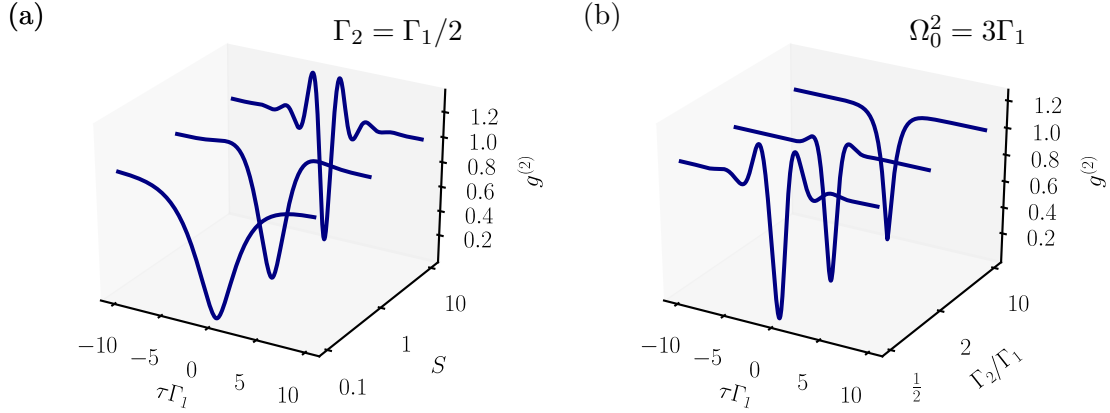


Figure 2.5: Second-order correlation function of the emission from a DBT molecule on resonance with a continuous-wave laser (Eq. 2.51), (a) as a function of the dimensionless parameter $\tau\Gamma_1$ and for increasing saturation levels with no pure dephasing, and (b) for increasing strength of pure dephasing at a constant Rabi frequency.

delay only

$$g^{(2)}(\tau) = \frac{\langle \hat{a}_{\mathbf{b}}^\dagger(t) \hat{a}_{\mathbf{b}}^\dagger(t+\tau) \hat{a}_{\mathbf{b}}(t+\tau) \hat{a}_{\mathbf{b}}(t) \rangle}{(\langle \hat{a}_{\mathbf{b}}^\dagger(t) \hat{a}_{\mathbf{b}}(t) \rangle)^2}. \quad (2.47)$$

For $\tau = 0$, we get a similar result than with pulsed signals

$$g^{(2)}(0) \simeq \frac{2P(2, T)}{P(1, T)}, \quad (2.48)$$

where $P(n, T)$ is the probability of finding n photons in a time interval T given by the resolution of the experiment. T should be small enough so that $g^{(2)}(T/2) \simeq g^{(2)}(0)$.

Under stationary conditions, Eq. 2.47 can be viewed as

$$g^{(2)}(\tau) = \frac{\langle \hat{a}_{\mathbf{b}}^\dagger(\tau) \hat{a}_{\mathbf{b}}(\tau) \rangle_C}{\langle \hat{a}_{\mathbf{b}}^\dagger \hat{a}_{\mathbf{b}} \rangle} = \frac{\langle \hat{N}_{\mathbf{b}}(\tau) \rangle_C}{\langle \hat{N}_{\mathbf{b}} \rangle}, \quad (2.49)$$

where $\langle \hat{O} \rangle_C = \langle \psi_C | \hat{O} | \psi_C \rangle$ and $|\psi_C\rangle$ is the projection of the state upon detection of a photon at time t . Because the molecule is prepared in the ground state when we detect the first photon, $\langle \hat{N}_{\mathbf{b}}(\tau) \rangle_C$ is directly proportional to $\rho_{ee}(\tau)$, which is the solution to Eq. 2.26 for the initial conditions $\rho_{ee}(0) = \rho_{ge}(0) = \rho_{eg}(0) = 0$ and $\rho_{gg}(0) = 1$. In fact,

we have $\langle \hat{N}_{\mathbf{b}}(\tau) \rangle_C = \eta \Gamma_1 \rho_{ee}(\tau) T$ and $\langle \hat{a}_{\mathbf{b}}^\dagger \hat{a}_{\mathbf{b}} \rangle = \eta \Gamma_1 \rho_{ee}(\infty) T$ where η is the efficiency of the set-up. This gives us

$$g^{(2)}(\tau) = \frac{\rho_{ee}(|\tau|)}{\rho_{ee}(\infty)} . \quad (2.50)$$

While $\rho_{ee}(\infty)$ is simply the steady-state population, the transient behaviour requires general solutions to the optical Bloch equations. For $\Delta_L = 0$ and after some analysis, we arrive at the final form [164]

$$g^{(2)}(\tau) = 1 - \frac{p+q}{2q} \exp(-(p-q)|\tau|) + \frac{p-q}{2q} \exp(-(p+q)|\tau|) , \quad (2.51)$$

with

$$p = \frac{\Gamma_1 + \Gamma_2}{2} , \quad q = \sqrt{\left(\frac{\Gamma_1 - \Gamma_2}{2}\right)^2 - \Omega_0^2} . \quad (2.52)$$

At zero delay, we recover $g^{(2)}(0) = 0$ which is what we expect from a single quantum emitter.

2.2.4 Non-Resonant Pumping

As mentioned in Sec. 2.1.3, a useful property of DBT molecules is the ability to promote the molecule to a high vibrational state of the excited singlet-state S_1 . From any $S_{1,n}$ state, we expect a molecule to rapidly decay to $S_{1,0}$, from which single-photons will be emitted with minimal time-uncertainty for indistinguishability. In this scheme, the excitation light, which is blue-detuned with respect to the $S_{0,0} \leftrightarrow S_{1,0}$ transition, can simply be filtered out to isolate the single-photon emission. Typically, the $S_{0,0} \leftrightarrow S_{1,3}$ transition is used because it has the highest transition dipole-moment compared to all other vibrational lines (with the exception of the $S_{0,0} \leftrightarrow S_{1,0}$ line). The wavelength corresponding to this transition is 767 nm. We also note that the rate associated with the $S_{1,3} \rightarrow S_{1,0}$ non-radiative decay, Γ_{nrad} , has previously been measured to be on the order of $2.5 \times 10^{11} \text{ s}^{-1}$, corresponding to a lifetime of 4 ps [136].

This scheme can also be probed using continuous-wave spectroscopy for which we need a modified set of optical Bloch equations. Let us denote the population of the $S_{1,3}$ state as ρ_{33} . Because there is no mechanism to coherently transfer the population between the $S_{1,3}$ and $S_{1,0}$ states and between the $S_{1,0}$ and $S_{0,0}$ state, we have $\rho_{3,e} = \rho_{e,g} = 0$ if we assume that the molecule always starts from the ground state. Hence, the modified Bloch equations with pure dephasing are

$$\frac{d\rho_{33}}{dt} = \frac{i}{2}\Omega_{blue}(\tilde{\rho}_{g3} - \tilde{\rho}_{3g}) - \Gamma_{\text{nrad}}\rho_{33} , \quad (2.53)$$

$$\frac{d\rho_{ee}}{dt} = \Gamma_{\text{nrad}}\rho_{33} - \Gamma_1\rho_{ee} , \quad (2.54)$$

$$\frac{d\rho_{gg}}{dt} = -\frac{i}{2}\Omega_{blue}(\tilde{\rho}_{g3} - \tilde{\rho}_{3g}) + \Gamma_1\rho_{ee} , \quad (2.55)$$

$$\frac{d\tilde{\rho}_{g3}}{dt} = \frac{i}{2}\Omega_{blue}(\rho_{33} - \rho_{gg}) - (i\Delta_L + \Gamma_{2,blue})\tilde{\rho}_{g3} , \quad (2.56)$$

$$\rho_{gg} + \rho_{ee} + \rho_{33} = 1 , \quad (2.57)$$

$$\tilde{\rho}_{3g} = (\tilde{\rho}_{g3})^* , \quad (2.58)$$

with a Rabi frequency $\Omega_{blue} = \langle S_{1,3} | \hat{\boldsymbol{\mu}} | S_{0,0} \rangle \cdot \boldsymbol{\mathcal{E}}_0 / \hbar$ and $\Gamma_{2,blue} = \frac{\Gamma_{\text{nrad}}}{2} + \Gamma_{2,blue}^*$. The steady-state solution for the excited state population is

$$\rho_{ee} = \frac{S_{blue}}{1 + S_{blue}(\frac{2\Gamma_1}{\Gamma_{\text{nrad}}} + 1) + (\frac{\Delta_L}{\Gamma_{2,blue}})^2} , \quad (2.59)$$

where $S_{blue} = \frac{\Omega_{blue}^2}{2\Gamma_1\Gamma_{2,blue}}$. In the limit where $\Gamma_{\text{nrad}} \gg \Gamma_1$, we recover the familiar Lorentzian profile

$$R_{blue}(\Delta_L, S) = \Gamma_1\rho_{ee} = \Gamma_1 \frac{S_{blue}}{1 + S_{blue} + (\frac{\Delta_L}{\Gamma_{2,blue}})^2} , \quad (2.60)$$

which has FWHM $= 2\Gamma_{2,blue}\sqrt{1+S}$. Typically, we also assume that $\Gamma_{\text{nrad}} \gg \Gamma_{2,blue}^*$ at cryogenic temperatures so that FWHM $= \Gamma_{\text{nrad}}\sqrt{1+S}$. A lifetime of 4 ps would therefore correspond to a linewidth of 40 GHz which is the typical value measured

for DBT molecules [136]. With non-resonant excitation, the molecule can reach full population inversion in the limit where $S_{blue} \rightarrow \infty$. However, to achieve the same saturation level as resonant pumping, we must deliver a power which is $\Gamma_{\text{nrad}}/\Gamma_2$ times greater.

The $g^{(2)}(\tau)$ can again be calculated with the transient solution for the excited state when the molecule starts from the ground state. With $\Gamma_{\text{nrad}} \gg \Gamma_1$ and $\Gamma_{\text{nrad}} \gg \Gamma_{2,blue}^*$, it is given by [170]

$$g_{blue}^{(2)}(\tau) = 1 - \exp(-\Gamma_1(1 + S_{blue})|\tau|) . \quad (2.61)$$

3 Experimental Considerations

In this chapter, I describe the experimental details of probing single DBT molecules in anthracene crystals. First, I introduce the optical and cryogenic systems that were used to perform single-molecule spectroscopy. I then present the characterisation of DBT molecules in bulk crystals grown by co-sublimation. The experimental data is compared to the models developed in the previous chapter.

3.1 Signal-to-Background Ratio

The first task was to build an optical microscope capable of single-molecule spectroscopy with a narrow-band, continuous-wave laser. To image a single dopant molecule, we first need to ensure that the intensity of the fluorescence signal is larger than other sources of background light. The largest contribution to this background is elastic scattering of the excitation light. This, we have already discussed in Sec. 2.2.1 and Sec. 2.2.4, where we found that long-pass optical filters can be used to reject the excitation light and let the red-shifted fluorescence through. With this strategy, the signal-to-background ratio simply depends on the ratio of the transmitted fluorescence to the transmitted laser light for the filtering mechanism.

In addition, we must also deal with inelastic scattering of the excitation beam which can be resonant with the emitted fluorescence. This can originate from Raman scattering from the host material but also from other dopant molecules interacting with the pump. Inelastic scattering cannot be distinguished from the signal using wavelength alone and must be kept to a minimum. It is usually reasonable to assume that the intensity of inelastic scattering scales linearly with excitation intensity. Therefore, it is advantageous to cool the sample to low enough temperatures so that Γ_2^* tends to zero

and the saturation intensity reaches a minimum value of

$$\min(\bar{I}_{\text{sat}}) = \frac{\varepsilon\varepsilon_0 c \hbar^2}{|\boldsymbol{\mu}_0|^2} \left(\frac{\Gamma_1}{2}\right)^2. \quad (3.1)$$

Compared to room temperature, a molecule at cryogenic temperatures has the same fluorescence rate for lower pump intensities, which increases the signal-to-background ratio. Finally, for increasing pump intensities, there is a smaller increase of the fluorescence rate compared to the background, due to the saturation behaviour of the molecule. It is therefore best to keep the excitation to a low-saturation regime with $S \leq 1$.

As mentioned above, it is also important to prevent other dopant molecules from interacting with the pump laser. For low levels of doping, such that we find on average less than one DBT molecule per μm^3 of anthracene, it is possible to spatially select single dopant molecules with a tightly focused laser beam. For higher doping concentrations, we have to rely on the inhomogeneous broadening of the optical transitions, which is due to DBT molecules experiencing a slightly different local environment (Sec. 2.1.2). To take advantage of this, it is necessary to work at cryogenic temperatures where the width of the $S_{0,0} \leftrightarrow S_{1,0}$ transition (~ 30 MHz) is much narrower than its inhomogeneous broadening (~ 150 GHz). By using a narrow-band laser, it is then possible to spectrally select individual molecules even if several are present in the focal spot. For non-resonant pumping, this is usually very difficult to achieve as the width of the $S_{0,0} \leftrightarrow S_{1,3}$ transition (~ 40 GHz) is only slightly narrower than the inhomogeneous broadening. This technique also breaks down for very high dopant concentrations when the probability of two molecules with overlapping $S_{0,0} \leftrightarrow S_{1,0}$ transitions is non-negligible.

3.2 Confocal Microscopy

3.2.1 Optical System

Fluorescence confocal microscopy is a well-known technique for single-molecule spectroscopy [171, 172], and I sketch its basic principle in Fig. 3.1. The first component of a confocal microscope is an objective lens which focuses a collimated single-mode laser on the sample. In the focal plane, we can vary the position at which the laser spot hits the sample by either changing the angle at which the beam hits the lens or simply by translating the sample. The response from the sample is then collected through the same objective lens and focused by a second lens on the image plane. Due to selective excitation of the sample alone, the axial (z-axis) and longitudinal (x-y plane) resolutions of the microscope are already small enough to perform single-molecule spectroscopy. Nevertheless, a better axial resolution can be achieved by spatially filtering the response in the image plane using a pinhole or the small aperture of a single-mode fibre or even just with the small pixels of a charge-coupled device [103].

We have developed our own laser-scanning microscope, depicted in Fig. 3.2, which allows us to perform white-light microscopy and single-photon fluorescence imaging. The sample is mounted on top of a 3-axis positioning system (ANP101, attocube) inside a closed-cycle helium cryostat, which is described in more detail in Sec. 3.4. Optical access is provided by a lens (LD EC Epiplan-Neofluar, Zeiss) which sits above the sample, inside the cryostat casing and is held at room temperature by heaters. The objective has an effective focal length of 1.65 mm, with a numerical aperture of 0.75 and a free working distance of 4 mm. For a Gaussian beam, this gives us a theoretical beam waist at the focal plane of

$$w_{focus} = \frac{\lambda f_{obj}}{\pi w_0} \sim 275 \text{ nm} , \quad (3.2)$$

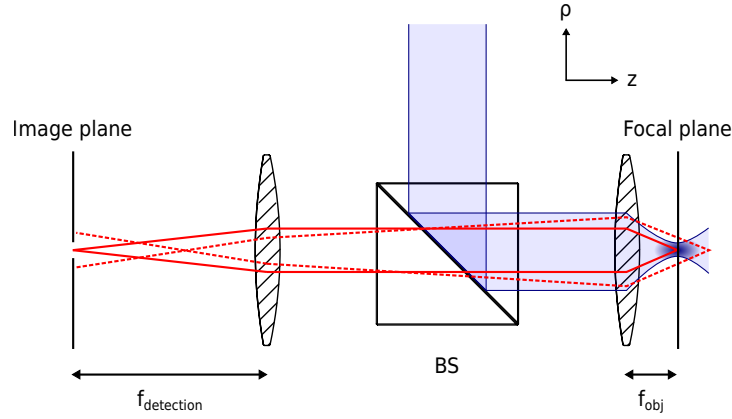


Figure 3.1: Working principle of an infinity-corrected confocal microscope. A collimated single-mode Gaussian beam is focused by a small focal length objective, providing selective excitation of the sample in the focal plane. The response from the sample is collected by the objective and focused by an imaging lens on the image plane. Additional resolution along the optical axis (z -axis) can be achieved by placing a pinhole in the image plane which has the same size as the point-spread function of a single dipole in the focal plane [103].

where w_0 is the beam waist of the collimated laser before the lens, which is approximately equal to 1.5 mm.

Fluorescence microscopy is performed using two confocal light paths which overlap on a 90/10 beam splitter. In one arm, light from a Ti:Sapphire laser (see Sec. 3.3) is collimated from a polarisation-maintaining fibre by an aspheric lens, which gives us a beam with an intensity FWHM of approximately 2 mm. The polarisation of the laser is cleaned using a linear polariser, and a half-wave plate is used to control the polarisation of the beam throughout the rest of the set-up. A band-pass filter (780 nm, 10 nm bandwidth, Chroma Technologies) is used to reject the power in the lower energy wing of the laser emission and any fluorescence or Raman scattering from the fibre. The beam is then sent to a set of steering mirrors (Scanning Galvo Mirror System, Thorlabs), which direct the light into a 4-f lens configuration made of two plano-convex lenses with $f = 250$ mm. The 4-f system allows the beam to hit the centre of the objective lens with varying angle of incidence. For increasing angle, the position of

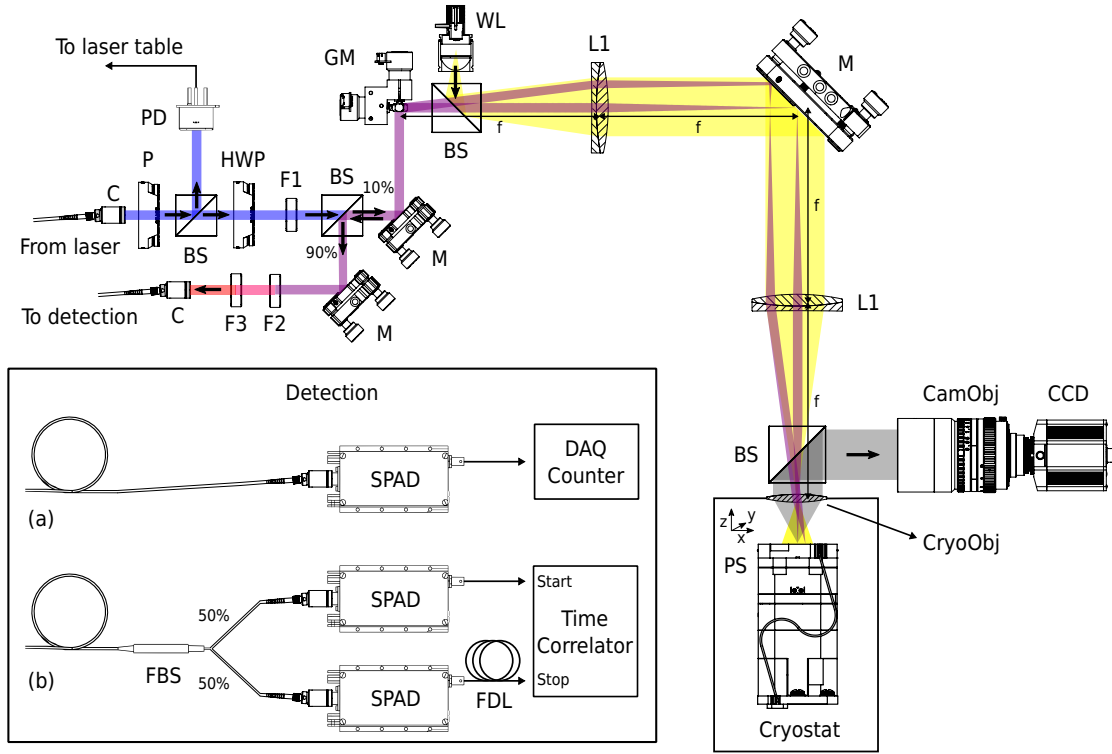


Figure 3.2: Sketch of the fluorescence microscopy optical set-up. BS: Beam Splitter, C: Collimator, CamObj: Camera Objective, CryoObj: Cryo objective lens, F1: Short-pass Filter, F2 & F3: Long-pass Filters, FBS: Fibre Beam Splitter, FDL: Fixed Delay Line, GM: Galvo Mirror, HWP: Half Wave Plate, L1: Achromatic Doublet Lens, M: Mirror, P: Polariser, PD: Photo-Diode, PS: XYZ Position stage, SPAD: Single Photon Avalanche Diode, WL: White Light. (a) Single-photon fluorescence detection. (b) Correlation measurement set-up.

the laser spot in the focal plane gets further away from the optical axis. This allows us to use the steering mirrors to control the position of the laser spot on the sample surface. Emission from the focal spot, which includes scattered/reflected laser light and fluorescence from the sample, is collected by the objective lens and propagates back along the confocal path. After being separated at the beam splitter, the laser light is filtered using two long pass filters (800 nm edge, Chroma Technologies) and focused to a multi-mode fibre with a core diameter of $62.5\ \mu\text{m}$ by an asphere of focal length $f_{\text{collimation}} = 10\text{mm}$. The diameter of the collection fibre is much bigger than the width of the point-spread function of a single dipole in the image plane, which is given

by [103]

$$\Delta x \sim 0.6 \frac{\lambda M}{NA} \sim 4 \mu\text{m} , \quad (3.3)$$

where $M = f_{\text{collimation}}/f_{\text{obj}}$ is the magnification of the microscope and NA is the numerical aperture of the objective lens. Hence, the axial resolution of the microscope almost exclusively comes from selective excitation.

To easily find the focal plane and locate structures on the sample surface, we first use white light microscopy. The source of white light is roughly positioned at the focus of the first lens in the 4-f system and fills a large portion of its aperture. This maximises the illuminated area in the focal plane. Emission is collected by the objective lens, then sent to a variable-zoom lens (AF-S VR Zoom-NIKKOR, Nikkon) and imaged with a charge-coupled device (CCD) camera (Luca R, Andor). The imaging lens is positioned as close to the objective lens as possible to maximise the field-of-view, which has an approximate diameter of 100 μm .

3.2.2 Detection

The light from the collection arm of the confocal microscope can be sent to a variety of detection set-ups. For laser-scanning fluorescence microscopy, the collection fibre is sent to a silicon single-photon avalanche diode (SPCM-AQRH, Perkin Elmer) with a detection efficiency of around 50% at 800 nm. The output of the diode is connected to a counter module on a data acquisition card (USB-6343, National Instruments). To map the fluorescence from the focal plane, the laser spot is moved to successive positions using the steering mirrors and we count the number of detected photons at each position over some exposure time. In this way, we gradually build a two-dimensional raster image of the fluorescence. Additionally, we can also use the positioning system to scan the sample in the z-direction and build a full 3-dimensional image.

For correlation measurements, the collection fibre is coupled to a 50/50 fibre beam-splitter (Thorlabs), and the two outputs are sent to avalanche photo-diodes. The elec-

tronic pulses from one diode are used to trigger the clock of a time-correlator card (Time-Harp 260, PicoQuant), while the outputs of the other diode are delayed and used to stop the clock. This allows us to record the relative time between successive detections at the first and then second diode. The second-order correlation function is not exactly equal to the conditional probability $P_{\text{next}}(\tau)$ of detecting a photon at time $t = \tau$ on the second detector given that a photon is detected at time $t = 0$ on the first detector. In fact, $g^{(2)}(\tau)$ is proportional to the probability of detecting a photon at time $t = \tau$ on the second detector, but which is not necessarily the next one. However, it is possible to show that in the limit of low count rates and/or low multi-photon emission probability, $g^{(2)}(\tau)$ becomes approximately proportional to $P_{\text{next}}(\tau)$ [173, 174].

Finally, the collected light can also be sent to a spectrometer (Shamrock 303i, Andor, not shown in Fig. 3.2) with a resolution of 0.2 nm. The spectrometer is connected to a electron-multiplying CCD camera (Newton 791, Andor) for detection.

3.3 Laser Sources

The laser sources have continuously evolved over the years to perform more sophisticated tasks. Here, I described the main lasers that were used for continuous-wave fluorescence microscopy using the $S_{0,0} \leftrightarrow S_{1,0}$ line around 785 nm.

3.3.1 Distributed Feedback Laser

The main laser used in the early stages of bulk measurements (see Sec. 3.6) was a single-frequency, distributed feedback laser (EYP-DFB-0785, Eagleyard) with a linewidth of approximately 2 MHz, as shown in Fig. 3.3(a). The diode assembly includes a thermoelectric cooler and a monitoring thermistor. The centre wavelength of the emission is 785 nm and can be tuned using either the driving current or the operating temperature of the diode. Fast but small changes in wavelength are achieved using a current con-

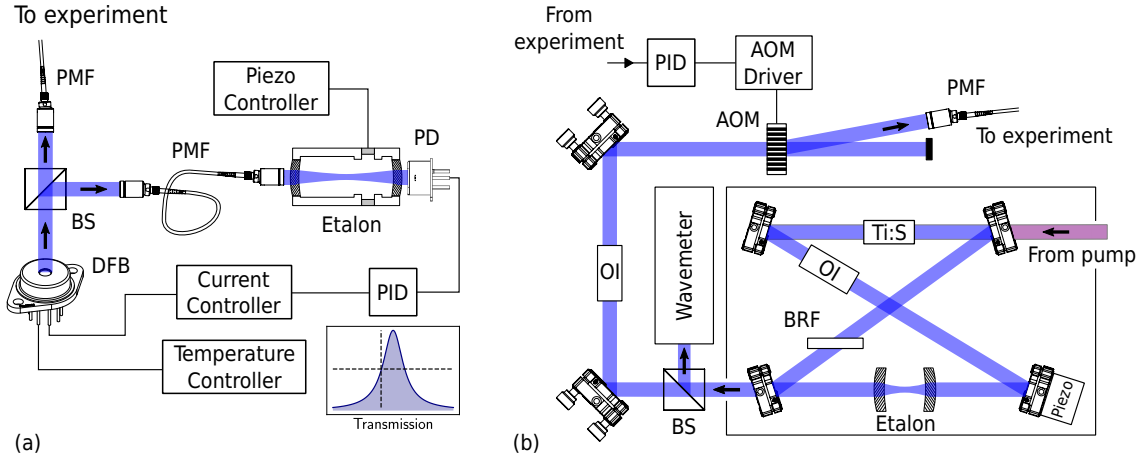


Figure 3.3: Sketch of the laser systems. (a) Distributed Feedback Laser. (b) Tunable Ti:Sapphire Laser. AOM: Acousto-Optic Modulator, BS: Beam Splitter, BRF: Birefringent Filter, DFB: Distributed Feedback Laser, OI: Optical Isolator, PD: Photo-Diode, PID: Proportional-Integral-Derivative controller, PMF: Polarisation-Maintaining Fibre, Ti:S: Titanium-sapphire rod.

troller (LDC205C, Thorlabs), while a larger tunability is possible with a temperature controller (TED200C, Thorlabs) but this requires thermalisation on a longer time-scale. The full wavelength range of the diode is 784 nm to 786 nm.

The diode is frequency-stabilised using a scanning Fabry-Perot interferometer (SA210-5B, Thorlabs). We first pick-off a small percentage of the emitted power which is focused to a polarisation-maintaining fibre. At the output of the fibre, the light is aligned to a Fabry-Perot cavity with a free spectral range of 20 GHz, and we monitor the transmission through the cavity with a silicon photo-diode. The signal from the photo-diode is fed to a Proportional-Integral-Derivative (PID) controller (SIM960, Stanford Scientific) which regulates the current supplied to the distributed feedback laser. The set-point of the PID loop is chosen so that the intensity of the transmission is maintained at half the value of one of the transmission peaks. Additionally, the length of the Fabry-Perot cavity can be scanned using piezo-elements which are driven by a voltage controller (MDT693A, Thorlabs). When locked, the feedback loop causes the emission wavelength to chase that of the cavity mode while it changes with varying cavity length.

In this way, the frequency of the laser can be scanned using the piezo voltage of the cavity. The frequency of the cavity mode is approximately linear with piezo voltage and we record the start and end frequencies of each voltage scan using a high-precision wavemeter (Angstrom, HighFinesse). We find that the scanning rate is approximately 2.3 GHz/V.

3.3.2 Tunable Ti:Sapphire Laser

Later on, the distributed feedback laser was replaced by a commercial Ti:Sapphire laser system (SolsTiS, M Squared) with sub-megahertz linewidth, as shown in Fig. 3.3(b). The SolsTiS consists of a bow-tie cavity geometry with a Ti:Sapphire gain medium. It is pumped by a diode-pumped solid-state laser (Sprout-G, Lighthouse Photonics) which is frequency-doubled to emit at 532 nm. Wavelength dependent intra-cavity losses are controlled with a motorised birefringent filter and an adjustable etalon. These two mechanisms allow for coarse tuning of the emission wavelength over a very broad range (700 nm to 1 μ m). To guarantee single-mode operation, the etalon can be locked to a single longitudinal mode by slightly modulating the etalon spacing using an electronic servo and a feedback loop. For fine tuning of the emission, the length of the bow-tie cavity is adjusted using a piezo-mounted mirror. By varying the piezo voltage, the lasing frequency can be scanned by approximately 25 GHz, while the locking mechanism ensures that the etalon transmission is always centred on the same longitudinal mode. This is referred to as a resonator scan. Finally, the cavity length can be locked to a high-precision wavemeter which tunes the piezo voltage to an absolute frequency reference with a resolution of 2 MHz. The long-term drift of the laser is managed in this way.

The SolsTiS system is fully automated and controlled by dedicated electronics and software, which are accessed with a simple Ethernet connection. In particular, the software is capable of continuously scanning the emission through a large wavelength range, which is only limited by the overall response of the Ti:Sapphire crystal. This is

done by stitching together resonator scans so that the start of the current scan coincides in frequency with the end of the previous one. The automatic gluing of successive scans is achieved using the tunability provided by the birefringent filter, the etalon and the resonator, together with readings from the wavemeter. It is then possible to scan the laser by several nanometres at a constant rate while maintaining single-mode operation. This is referred to as a terahertz-scan or just tera-scan. During the scan, automatic messages are sent to keep track of the start and end of each resonator scan. Live updates of the wavemeter readings are also broadcasted during each scan. This enables coarse syncing of the laser frequency to other data acquisition inputs such as counts from a single-photon detector. Monitoring the piezo voltage of the resonator gives us a more accurate way of measuring the change in laser frequency.

The output of the SolsTiS is directed through an optical isolator and sent to an acousto-optic modulator (AOM) which operates at a centre frequency of 110 MHz (M110-2B/F-GH2, Gooch & Housego). The AOM is driven by a home-built radio frequency driver with a constant frequency but variable amplitude in order to stabilise the laser power. We pick off the first diffracted beam from the AOM which is then coupled to a polarisation-maintaining fibre. On the confocal microscope table, the laser power is monitored at the output end of the fibre after the light is cleaned by a polariser. The output of this silicon photo-diode is fed to a PID controller (SIM960, Stanford Scientific) which modulates the amplitude of the AOM driver, therein stabilising the power entering the confocal microscope.

3.4 Cryogenics

As explained in Sec. 3.1, single-molecule spectroscopy is a much easier task when the crystals are cooled to cryogenic temperatures. Moreover, we only expect the photons emitted by the molecules to be indistinguishable when pure dephasing is negligible

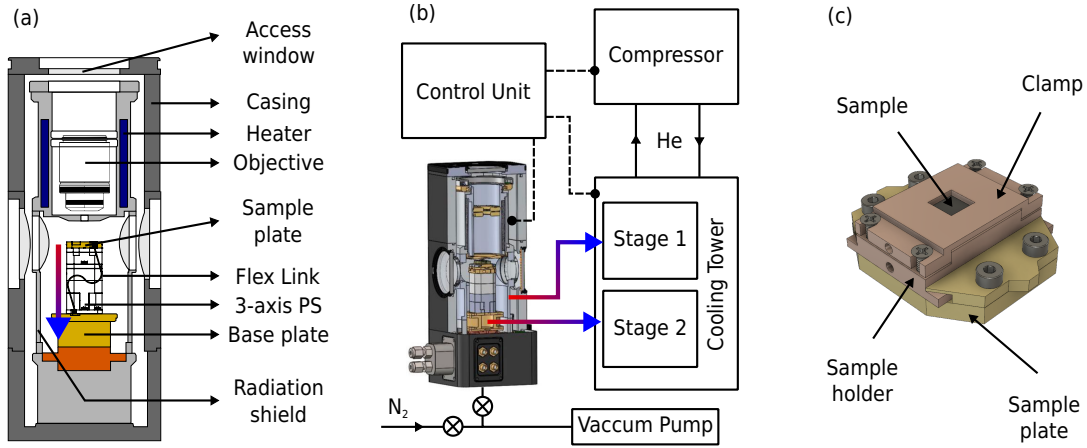


Figure 3.4: Sketch of the cryostat system. (a) Sample chamber assembly with the objective lens integrated in the casing for high numerical aperture imaging. Flexible thermal links connect the base plate and the sample plate which sits on top of the positioning stage (PS). (b) Cryocooler system. The first stage of the cryostat is connected to the radiation shield and the second stage is in direct thermal contact with the base plate in the sample chamber. (c) Schematic of the sample holder and clamping mechanism for optimum thermal contact with the sample plate.

(Sec. 2.1.4) and the excitation linewidth of the $S_{0,0} \leftrightarrow S_{1,0}$ transition has a lifetime-limited value (Sec. 2.2.1). For the main site of DBT in anthracene, these conditions are only met when the sample is cooled to below 4 K [147]. We achieve this by placing the crystals in thermal contact with the cold head of a closed-cycle helium cryostat (Cryostation, Montana Instruments).

The cryostat is a two-stage Gifford-McMahon cryocooler [175] with high-pressure helium gas as the working fluid which is recirculated using a compressor. This system is depicted in Fig. 3.4. The temperature of both stages is monitored using thermometers and can be precisely adjusted with heaters. During normal operation, the first stage is cooled to 30 K while the second stage can reach 2.8 K. The sample chamber is physically separated from the cryocooler and the compressor to reduce mechanical vibrations. Thermal links connect different parts of the sample chamber to the cooling stages on the cryocooler. The first stage is thermally coupled to a radiation shield surrounding the entire chamber to eliminate heating caused by black body radiation. The second stage

is directly connected to the base plate of the cryostat which reaches 3.4 K. Before cool-down, the sample chamber is evacuated using a vacuum pump, and charcoal absorbers connected to the radiation shield maintain a pressure of less than 1 mTorr when the system reaches cryogenic temperatures.

Three piezo stages (ANP101, attocube) are mounted directly on top of the base plate and allow for precise positioning of the sample in all 3 dimensions (10 nm steps at base temperature) with a large scanning range (travel of approximately 5 mm). The sample plate is placed on top of the positioning stage and is thermally connected to the base plate with high-purity copper links. In this way, the sample plate reaches approximately 3.6 K during normal operation, as measured by a thermometer placed inside the plate. For optical imaging, a vacuum-compatible lens (LD EC Epiplan-Neofluor, Zeiss) sits in the casing directly above the sample plate and is held at room temperature using heaters. Optical access to the sample chamber is provided by a 2 mm opening in the radiation shield, aligned with the lens.

The final component of the system is a removable sample holder which is clamped on top of the sample plate. It is made from high-purity copper with a gold coating and allows for quick sample replacement. The majority of our samples are made from intrinsic silicon wafers with a thickness of 0.38 mm. Over the years, we tried several ways to thermally contact the silicon to the sample holder. This is a crucial step as the thermal budget is very tight if we want to cool the top side of our samples to 4 K. The first method we used was to apply a thin layer of silver paint (Agar Scientific) as a cryogenic adhesive between the sample and the holder. Despite some early success, it was hard to achieve predictable and reproducible thermal contact with the paint alone. Hence, I developed a simple assembly to clamp the samples to the holder from the top surface (Fig. 3.4). A small amount of thermally conductive grease (N Grease, Apiezon) is used to fill the small gaps between the clamped surfaces. We observe that clamping is the most effective method to draw heat from the sample to the holder.

3.5 Co-Sublimation Growth

To verify the experimental set-up, we first performed single-molecule spectroscopy with bulk crystals grown by co-sublimation of anthracene and DBT. This is a well-known and popular way of growing doped organic crystals [29, 136, 144, 176]. Crystal growth by co-sublimation consists of heating both anthracene and DBT powders at a low pressure (approximately 200 mbar) to cause simultaneous sublimation of both molecules. The ejected anthracene and DBT are then deposited on a collection plate located directly above the sublimation vessels, and macroscopic DBT-doped anthracene crystals are formed.

A home-built co-sublimation growth chamber was developed by other members of our group before the start of my PhD [177]. As depicted in Fig. 3.5, the chamber body has a cylindrical geometry with two aluminium crucibles at the bottom in which we place anthracene (ReagentPlus 99% purity, Sigma-Aldrich) and DBT (PAH Research Institute, Greifenberg, Germany). The copper collection plate is situated at the top of the assembly, approximately 25 cm away from the crucibles. We control the temperatures of both crucibles and of the collection plate independently, using resistive heaters for coarse tuning and Peltier elements for fine tuning. The body of the chamber is also separately heated to prevent growth on the side walls. Finally, the vacuum port of the chamber is connected to both a roughing pump and a dry-nitrogen supply to control the growth environment.

Crystals are grown following a standard recipe. First, the chamber is pumped and purged three times with dry nitrogen to remove atmospheric oxygen and reduce humidity. After the last purge, the nitrogen pressure is set to an initial value of 225 mbar. The growth process then starts with the heating of the chamber walls to 180°C and of the collection plate to 100°C. Once the temperature of these elements is stabilised, the crucibles are heated up to pre-set growth values. The temperature of the anthracene

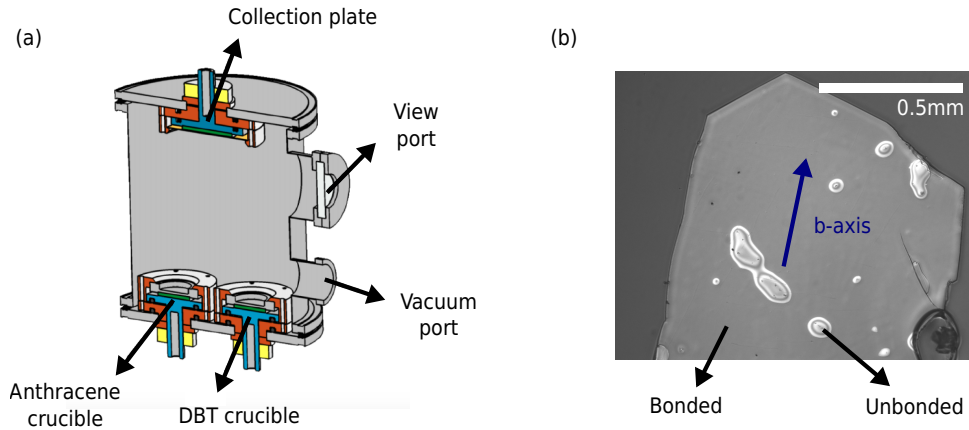


Figure 3.5: (a) Sketch of the co-sublimation chamber. Reprinted with permission from [177]. (b) Typical crystal grown by the co-sublimation method. The crystal is weakly bonded to a flat silicon substrate by van der Waals forces.

powder is always set at 160°C , while the temperature of the DBT can be varied in the range $120\text{-}200^{\circ}\text{C}$ to control the dopant concentration of the final crystals [177]. The duration of the growth is set to one hour after the crucible temperatures are reached, and the pressure is approximately constant at 350 mbar during this time. At the end of the growth, all the elements are gradually cooled back to room temperature.

The crystals produced by this method are hexagonal, approximately $1\text{ }\mu\text{m}$ thick and have a surface area of about 5 mm^2 . The macroscopic geometry of the crystals reflects the fundamental crystal structure and allows us to identify the orientation of the b-axis [150]. In this way, we can determine the direction the molecular dipole moments just from optical microscope images (Sec. 2.1.3). The crystals are large enough to be picked up from the collection plate with tweezers and directly placed on silicon substrates. We observe that the crystals bond well with the substrates due to weak van der Waals forces (as shown in Fig. 3.5), which indicates a good thermal link between the two.

3.6 Bulk Characterisation

3.6.1 Finding a Single Molecule

One such crystal was grown with a high DBT crucible temperature of 200°C to get a large dopant concentration. Because this was an early sample, it was then placed on a silicon substrate which was bonded to the cryostat holder using silver paint. Before cooling the system down, the sample stage was raised to image the surface with white light and confocal microscopy. By using the distributed feedback laser, we took a raster scan of the fluorescence at room temperature as described in Sec. 3.2. The laser wavelength was 785 nm, with a power of approximately 0.2 mW before the objective lens of the cryostat. At room temperature, the pump laser excites every dopant molecule as the excitation spectrum is broadened by dephasing and with phonon-sidebands. A raster scan at room temperature therefore gives us some information about the total concentration of DBT molecules in the crystal. As shown in Fig. 3.6(a), we see that the dopant concentration of this crystal is too high to completely isolate single DBT molecules at room temperature with the spatial resolution of our microscope. This is a good sign for cold spectroscopy. As the transition linewidths narrow down to approximately 30 MHz at 4 K, we would still like to find at least one molecule per field-of-view whose $S_{0,0} \leftrightarrow S_{1,0}$ transition is resonant with the laser. At this stage, we also optimised the polarisation of the laser, as all dipoles should mostly be aligned to the b-axis of the crystal. We adjusted the angle of the half-wave plate to maximise the fluorescence integrated over the whole field of view.

The sample was then cooled down to the lowest temperature achievable by the cryostat, and the temperature of the sample plate was 3.4 K. At cold temperatures, the first task is to find the centre of the inhomogeneous broadening, which can vary for different crystals and for different regions inside the crystal. In this case, the strategy

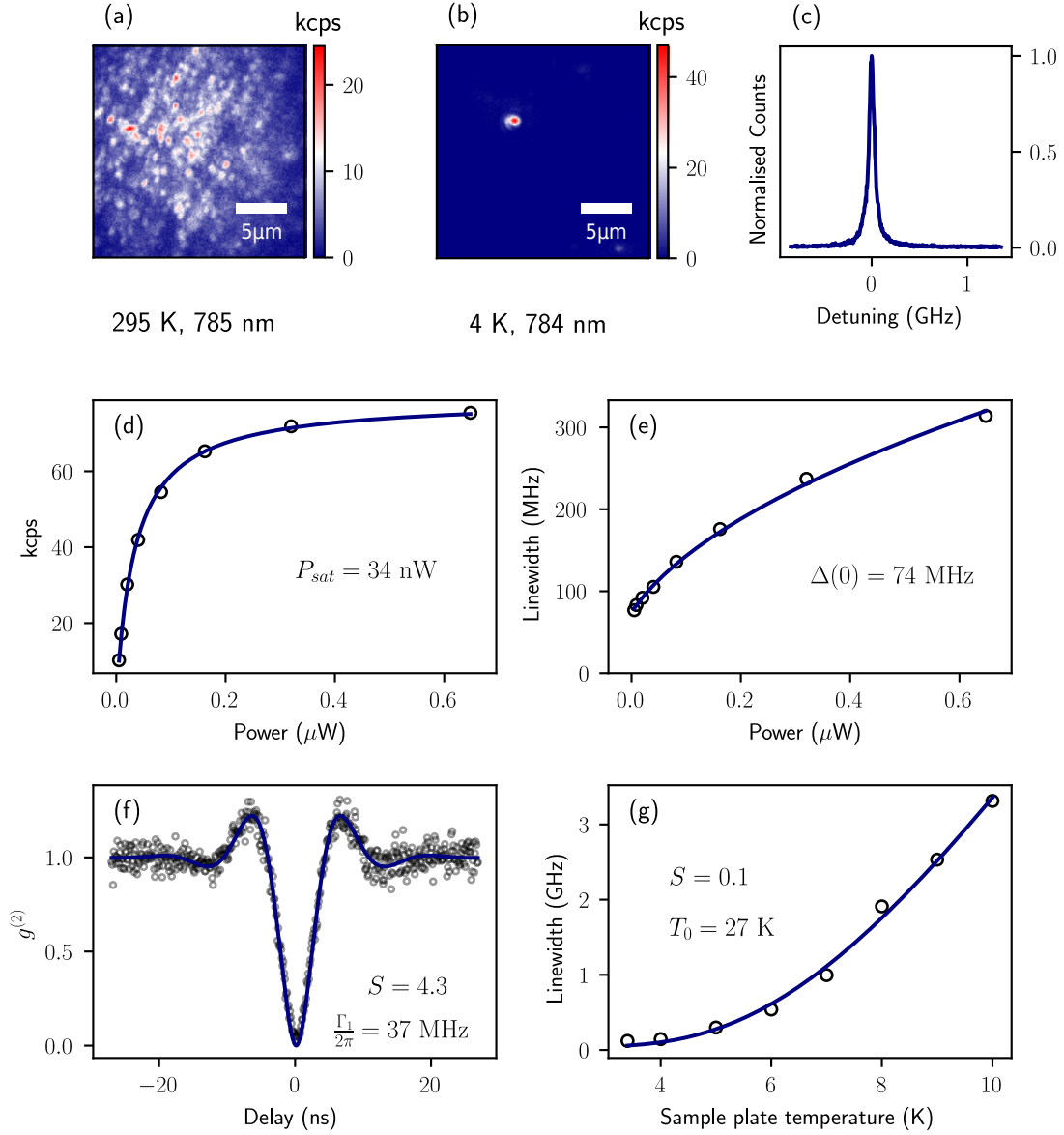


Figure 3.6: (a) Fluorescence raster scan of a co-sublimated crystal at room temperature with an excitation wavelength of 785 nm. (b) Raster scan of the same crystal at cryogenic temperatures showing a single isolated molecule at 784.0 nm. (c) Detected fluorescence count rate from the molecule as a function of laser detuning. The linewidth of the emitter is 74 MHz. (d) Fluorescence intensity at zero detuning as a function of pump power as measured before the objective lens. (e) Power broadening of the fluorescence linewidth. (f) Second order correlation function of the fluorescence at a known saturation and for no detuning. (g) Increase of the linewidth with sample temperature at constant saturation.

was to perform a series of raster scans by stepping the laser by 50 GHz and count the number of bright emission spots in the field of view. Because the saturation intensity decreases with temperature, the power of the laser at the objective was reduced to 0.2 μ W. The centre of the inhomogeneous broadening for this crystal was observed to be around 784.0 nm. Next, we found an isolated molecule (see Fig. 3.6(b)) and optimised the position of the laser spot (both in the x-y plane and in focus) and the angle of the half-wave plate to maximise the collected fluorescence. At this point, the molecule was probed by scanning the laser frequency through the optical transition, and we observed a Lorentzian line shape as predicted by Eq. 2.37 (see Fig. 3.6(c)).

3.6.2 Continuous-Wave Spectroscopy

We then investigated the change in line shape with increasing laser power and observed the saturation behaviour of the fluorescence. Fig. 3.6(d) shows the fluorescence rate for no detuning, which has the form $S/(1+S)$ with $S = I/I_{\text{sat}} = P/P_{\text{sat}}$. We estimate that a power of 34 ± 1 nW before the objective gives a saturation parameter of 1. As a further step, it is possible to calculate I_{sat} from P_{sat} if the beam profile and losses through the cryostat objective are known. This could be useful, for example, to estimate the transition dipole moment $|\mu_0|$ from Eq. 2.36. However, I do not attempt to do this here. We also observed the power broadening of the excitation line as plotted in Fig. 3.6(e). The variation of the linewidth follows the expected function $\frac{\Gamma_2}{\pi} \sqrt{1+S}$, which gives us a second independent measure of the saturation power. From this fit, we get $P_{\text{sat}} = 37 \pm 3$ nW which agrees with the previous value. We can also estimate the total dephasing rate Γ_2 by extrapolating the linewidths to zero power, and for this molecule we find $\Gamma_2/\pi = 74 \pm 2$ MHz. This is larger than what we expect for a lifetime-limited molecule. Indeed, assuming a lifetime of 6 ns, we should have $\Gamma_2/\pi = \Gamma_1/(2\pi) \simeq 26$ MHz [144].

Next, the laser was set to zero detuning and with a power which was at a known value

on the saturation curve. The collected fluorescence was sent to the time correlation set-up (Sec. 3.2), and we measured the $g^{(2)}$ function as approximated by the histogram of start-stop delays. The results for $S = 4.3 \pm 0.4$ are shown in Fig. 3.6(f). We fit the data to Eq. 2.51 with Γ_1 as the last unknown variable. We estimate that $\Gamma_1/(2\pi)$ is 37 ± 1 MHz, which confirms that the molecule is not lifetime limited as $\Gamma_2 > \Gamma_1/2$. The $g^{(2)}$ measurement therefore indicates that the anthracene crystal is not cooled to below 4 K. This can be explained by a large thermal gradient between the sample plate and the crystal. There is no easy solution to this problem as the limiting factor for the sample temperature is the cooling power of the cryostat itself.

Finally, we also investigated the change in line shape as a function of sample temperature. We precisely changed the temperature of the sample plate using heaters connected to the base plate of the cryostat. For each temperature of the sample plate, we took line scans of the molecule at different powers to build a saturation curve. As given by Eq. 2.36, the saturation power is proportional to Γ_2 and therefore increases with temperature. Once the saturation power was estimated, we took a final scan at $S = 0.1 \pm 0.01$. Fig. 3.6(g) shows the increase of linewidths with temperature at constant saturation. We fit the data to $2\Gamma_2(T)\sqrt{1+0.1}$ with $\Gamma_2(T) = A\exp(-T_0/T)$ as given by Eq. 2.10. Here, T_0 is approximately equal to $E_a/k_b - \Delta T$ where ΔT is the temperature difference between the crystal and the sample plate. We generally estimate that ΔT is approximately equal to 0.6 K [170] and we therefore find that $E_a/k_b \simeq 33$ K, which is in good agreement with the lower bound cited in [147]. These results, together with a more detailed investigation of the $g^{(2)}$ with dephasing, were published in Physical Review A [164].

4 Coupling to On-Chip Waveguides

In the previous chapter, I described how we were able to perform continuous-wave spectroscopy of near lifetime-limited DBT molecules. Addressing the electronic levels of an isolated quantum emitter is the first step in the development of a single-photon source. However, it is experimentally challenging to collect all the emission from a dipole which sits in a homogeneous medium, as discussed in Sec. 1.3.3. DBT molecules in bulk anthracene crystals are therefore not good single-photons source due to low collection efficiencies. To enhance the single-photon extraction efficiency to a single optical mode, we have investigated how to grow DBT-doped anthracene directly in the vicinity of single-mode waveguides.

Ridge waveguides are one of the fundamental building blocks of on-chip photonics. They are made from a rectangular slab of high refractive-index material surrounded by a lower index dielectric and/or air. Total-internal reflection from the interfaces confines the light to the high index core and guides its propagation along the structure. Due to adiabatic transmission, waveguides maintain their guiding properties even when slightly curved. In this way, different integrated components can be linked together with low optical losses [178, 179]. More generally, ridge waveguides are the basic structure from which numerous photonic components are designed, such as directional couplers, interferometers, resonators and filters [104, 180]. Coupling the emission from a single molecule directly to a ridge waveguide is therefore advantageous.

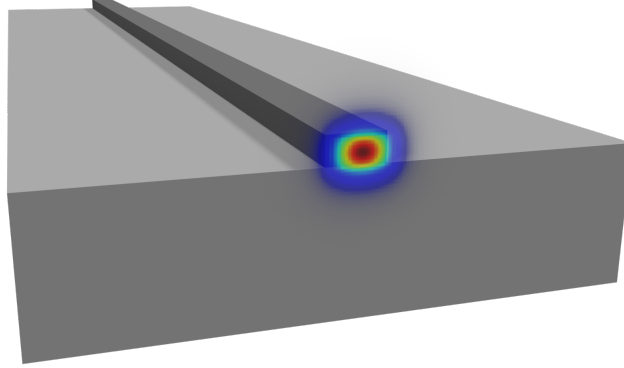


Figure 4.1: Sketch of a ridge waveguide and of the electric field distribution of its fundamental mode.

4.1 Spontaneous Emission Enhancement

4.1.1 Band Structure of Optical Waveguides

Theory

A ridge-waveguide structure has continuous translational symmetry in the direction of propagation. Hence, the harmonic modes (Eq. 1.3) can be separated as [40]

$$\mathbf{u}_{k_m}(x, y, z) \propto \mathbf{b}_{k_m, k_z}(x, y) \exp(ik_z z) , \quad (4.1)$$

where z is the direction of propagation, k_z is the z -component of the wavenumber and $\mathbf{b}(x, y)$ represents the cross-section of the mode. Plugging this solution into the wave equation (Eq. 1.4), we get

$$(ik_z \mathbf{e}_z + \nabla) \times (ik_z \mathbf{e}_z + \nabla) \times \mathbf{b}_{k_m, k_z}(x, y) = k_m^2 \varepsilon(x, y) \mathbf{b}_{k_m, k_z}(x, y) , \quad (4.2)$$

which defines another eigenvalue problem which can be solved to find k_m and $\mathbf{b}_{k_m, k_z}(x, y)$, given a value of k_z . For guided modes, we expect that the wavevector is purely in the direction of the waveguide. Eq. 4.2 is simplified for structures which can be described by a piecewise homogeneous dielectric function. In each separate material, we can use $\varepsilon \nabla \cdot \mathbf{E} = \nabla \cdot \varepsilon \mathbf{E} = 0$ to express Eq. 1.4 as the Helmholtz equation $\nabla^2 \mathbf{u}_{k_m} + k_m^2 \varepsilon \mathbf{u}_{k_m} = 0$, which leads to

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \mathbf{b}(x, y) + (k_m^2 \varepsilon - k_z^2) \mathbf{b}(x, y) = 0. \quad (4.3)$$

In addition, we need to account for the boundary conditions at the interfaces between two materials, which are given by [39]

$$\mathbf{e}_n \times (\mathbf{E}_1 - \mathbf{E}_2) = 0, \quad \mathbf{e}_n \cdot (\varepsilon_1 \mathbf{E}_1 - \varepsilon_2 \mathbf{E}_2) = 0, \quad (4.4)$$

$$\mathbf{e}_n \times (\mathbf{H}_1 - \mathbf{H}_2) = 0, \quad \mathbf{e}_n \cdot (\mathbf{H}_1 - \mathbf{H}_2) = 0, \quad (4.5)$$

where $\mathbf{e}_n$ is the unit vector normal to the interface and $\mathbf{H}(\mathbf{r}) = \mathbf{B}(\mathbf{r})/(\mu_0 \mu(\mathbf{r}))$ is the magnetic field and we assume $\mu(\mathbf{r}) = 1$.

Numerical Solutions

In this thesis, we are mostly concerned with silicon nitride waveguides which are buried in silicon oxide. At 785 nm, the refractive indices of these materials are $n_{\text{SiN}} \simeq 2.01$ and $n_{\text{SiO}_2} \simeq 1.46$ respectively. Hence, the only two remaining parameters are the width w and height h of the waveguide. Even with such a simple structure, there exist no analytical solutions to Eq. 4.3 accounting for all interface conditions, and we have to solve the wave equation numerically. To do so, I use iterative linear-algebra methods to solve Eq. 4.2 for different values of k_z with the MIT Photonic Bands package [181]. Alternatively, it is also possible to formulate an eigenvalue problem to solve for k_z and $\mathbf{b}_{k_m, k_z}(x, y)$ for a fixed k_m . In this way, we can solve for the guided modes at the frequency of the $S_{1,0} \rightarrow S_{0,0}$ transition of DBT in anthracene with $k_m = 2\pi/(785 \text{ nm})$.

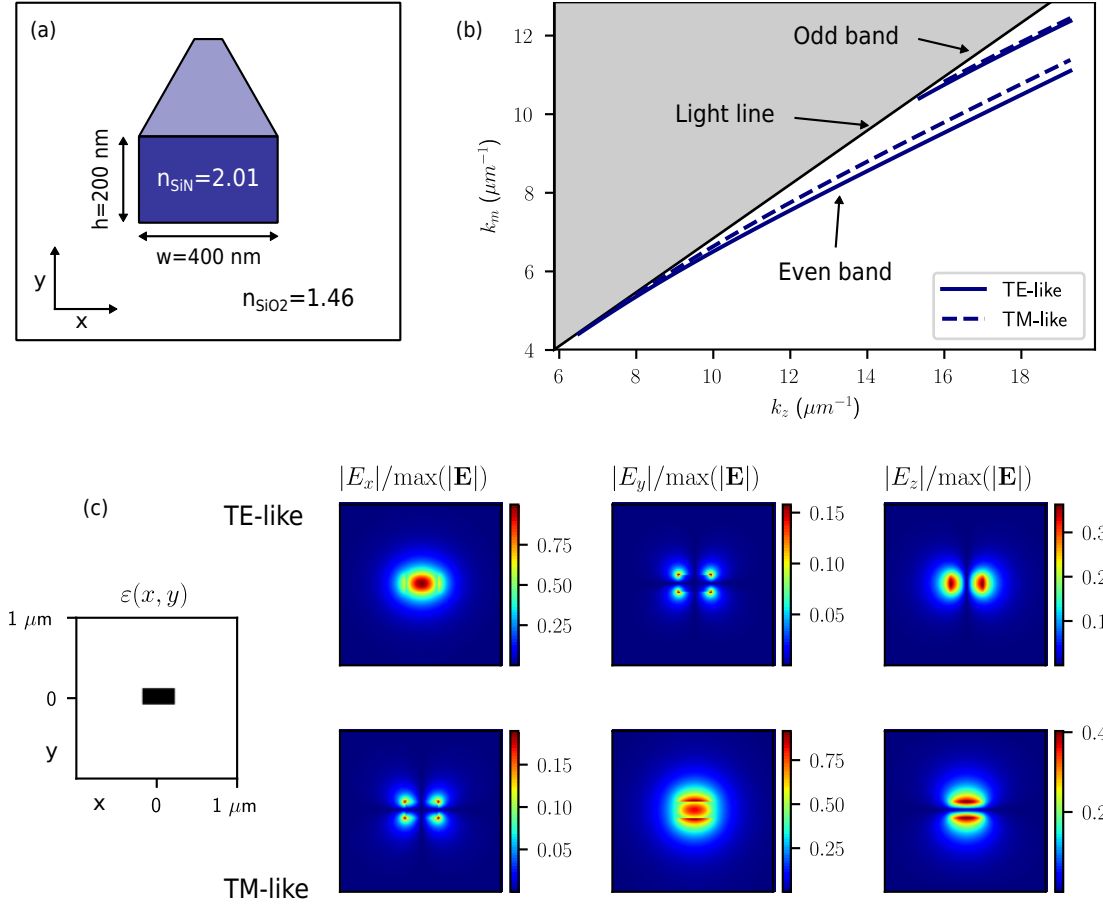


Figure 4.2: (a) Cross section of the waveguide geometry. (b) Band diagram of the waveguide. The modes are classified as TE-like and TM-like with respect to the x - z plane mirror symmetry for $y = 0$. The light-line corresponds to $k_z = n_{\text{SiO}_2} k_m$ for plane waves propagating in the cladding. (c) Electric field distribution for the fundamental TE-like and TM-like modes at $k_m = 2\pi/(785 \text{ nm})$.

To illustrate this, I pick $w = 400$ nm and $h = 200$ nm. I first obtain the band diagram for the waveguide by solving Eq. 4.2 as a function of k_z , and the results are shown in Fig. 4.2(b). We see four distinct modes which we can classify with respect to the mirror symmetries in the $x = 0$ and $y = 0$ planes. The mirror symmetry of the structure in the x - z plane dictates that the fields have to be symmetric or anti-symmetric, and at $y = 0$ the modes can only be transverse-electric (TE) or transverse-magnetic (TM) [40]. TE modes only have the (E_x, E_z, H_y) components of the fields which are non-zero, while TM modes only have non-zero (H_x, H_z, E_y) components. The

TE and TM nature of the fields is not true for any other x-z plane, but the continuity of the fields suggests that the entire modes must be mostly TE-like or TM-like for thin structures. The mirror symmetry in the y-z plane imposes similar constraints for the symmetry of the modes and for the value of the fields at $x = 0$. We label the TE-like modes as even if they are symmetric with respect to the $y = 0$ plane and odd if anti-symmetric. For TM-like modes, we do the same with respect to the $x = 0$ plane. In Fig. 4.2(b), we see the first even-band which consists of the fundamental TE-like and TM-like modes. I plot the absolute value of the electric field components of both modes in Fig. 4.2(c) which are solved for $k_m = 2\pi/(785 \text{ nm})$. For higher values of k_z , the first odd-band appears with another pair of TE-like and TM-like modes.

To simplify the design of subsequent integrated elements, we would like the emission from DBT molecules to be coupled to a single guided-mode. Hence, we first need to ensure that the waveguide only supports the fundamental band at the frequency of the emitter. To check this, I vary the waveguide width while keeping $h = 200 \text{ nm}$ and solve for TE-like guided modes at $k_m = 2\pi/(785 \text{ nm})$. The results are plotted in Fig. 4.3(a) and we see that for $w > 620 \text{ nm}$ the waveguide supports multiple TE-like modes. For each width, I then find the maximum height for which the waveguide still supports only one TE-like mode, as shown in Fig. 4.3(b). This restricts the parameter space for the optimisation of structural parameters.

4.1.2 Radiative Decay of Molecules Near Waveguides

With the band structure solved, we can now look at the decay of a single DBT molecule in the vicinity of a waveguide. From Eq. 1.46, we can separate the decay rate of the $S_{1,0} \rightarrow S_{0,0}$ transition into the following components

$$\Gamma_{S_{1,0} \rightarrow S_{0,0}} = \frac{\pi |\boldsymbol{\mu}_0|^2 \omega_0}{\epsilon_0 \hbar} (\rho_{\text{guided}}(\mathbf{r}_0, \mathbf{e}_\mu, \omega_0) + \rho_{\text{scat}}(\mathbf{r}_0, \mathbf{e}_\mu, \omega_0)) = \Gamma_{\text{guided}} + \Gamma_{\text{scat}} , \quad (4.6)$$

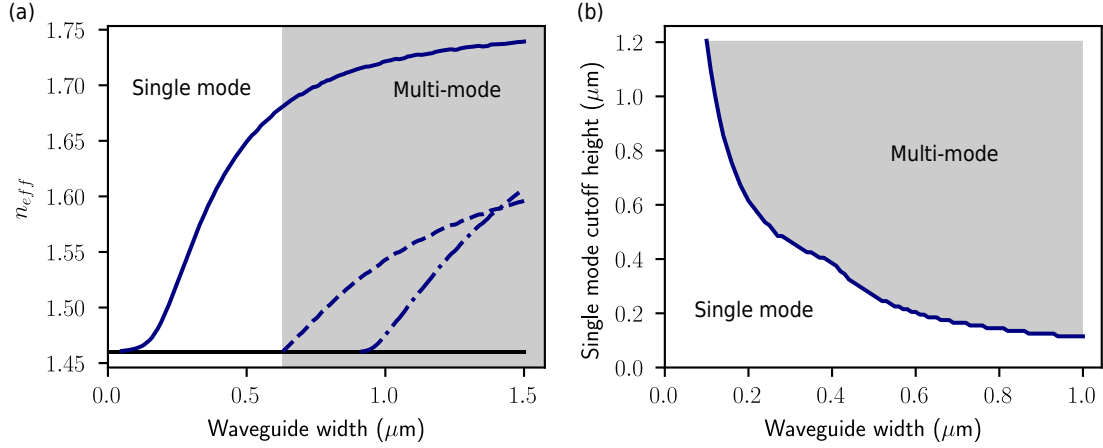


Figure 4.3: (a) Supported TE-like modes at $k_m = 2\pi/(785 \text{ nm})$ for a 200 nm tall waveguide and varying width. The solutions are labelled with $n_{eff} = k_z/k_m$. The black line corresponds to the light-line for plane waves propagating in the cladding. (b) Maximum height for waveguides which support a single TE-like mode as a function of waveguide width.

where ρ_{guided} is the LDOS of the guided modes and ρ_{scat} the LDOS of all other modes. To calculate ρ_{guided} , we first need to normalise the guided modes in the direction of propagation. Let us assume periodic boundary conditions in the z -direction with a period L which tends to infinity. By writing the guided modes as

$$\mathbf{u}_{k_m}(x, y, z) = \frac{1}{\sqrt{L}} \mathbf{b}_{k_m, k_z}(x, y) \exp(ik_z z) , \quad (4.7)$$

we see that the normalisation condition (Eq. 1.5) is satisfied if

$$\int \int dxdy \varepsilon(x, y) |\mathbf{b}_{k_m, k_z}(x, y)|^2 = 1 \quad (4.8)$$

and we assume $\mathbf{b}_{k_m, k_z} \rightarrow 0$ for $x \rightarrow \pm\infty$ and $y \rightarrow \pm\infty$ (which is true for guided modes), so that we don't have to bother with boundary conditions in the x and y directions.

From the definition of the LDOS (Eq. 1.44), we then have

$$\rho_{\text{guided}}(x, y, \mathbf{e}, \omega) = \frac{1}{L} \sum_{k_z} |\mathbf{e} \cdot \mathbf{b}_{k_m, k_z}^*(x, y)|^2 \delta(\omega - \omega_{k_m}) . \quad (4.9)$$

Due to the periodic boundary conditions, the spacing between modes Δk_z is independent of k_z and is equal to $2\pi/L$. Therefore, the density-of-states in k_z -space is $D(k_z) = L/(2\pi)$. In the limit that L goes to infinity we can write

$$\rho_{\text{guided}}(x, y, \mathbf{e}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk_z |\mathbf{e} \cdot \mathbf{b}_{k_m, k_z}^*(x, y)|^2 \delta(\omega - \omega_{k_m}) , \quad (4.10)$$

and with a change of variables

$$\rho_{\text{guided}}(x, y, \mathbf{e}, \omega) = \frac{1}{\pi} \int_0^\infty d\omega_{k_m} \frac{|\mathbf{e} \cdot \mathbf{b}_{k_m, k_z}^*(x, y)|^2}{v_g(\omega_{k_m})} \delta(\omega - \omega_{k_m}) \quad (4.11)$$

$$= \frac{1}{\pi v_g(\omega)} |\mathbf{b}_{k_m, k_z}(x, y)|^2 \cos^2(\theta) , \quad (4.12)$$

with $v_g = d\omega/dk_z$ and θ is the angle between the electric field of the mode and the dipole. Now, $\varepsilon(x, y) |\mathbf{b}_{k_m, k_z}(x, y)|^2$ has units of inverse area because of the normalisation condition of Eq. 4.8. We can add this explicitly by defining the mode area

$$A_{\text{mode}} = \frac{\int \int dx dy \varepsilon(x, y) |\mathbf{b}_{k_m, k_z}(x, y)|^2}{\max \left(\varepsilon(x, y) |\mathbf{b}_{k_m, k_z}(x, y)|^2 \right)} , \quad (4.13)$$

and the absolute scaling of $\mathbf{b}_{k_m, k_z}(x, y)$ does not matter any longer. We can finally write

$$\rho_{\text{guided}}(x, y, \mathbf{e}, \omega) = \frac{1}{\pi v_g(\omega)} \frac{f(x, y) \cos^2(\theta)}{\varepsilon(x, y) A_{\text{mode}}} , \quad (4.14)$$

with

$$f(x, y) = \frac{\varepsilon(x, y) |\mathbf{b}_{k_m, k_z}(x, y)|^2}{\max \left(\varepsilon(x, y) |\mathbf{b}_{k_m, k_z}(x, y)|^2 \right)} , \quad (4.15)$$

which quantifies the mismatch between the position of the emitter and the mode field maximum. Dividing Eq. 4.14 by ρ_{hom} (Eq. 1.49) defines the waveguide Purcell factor

$$F_P^{\text{guided}} \equiv \frac{\Gamma_{\text{guided}}}{\Gamma_{\text{hom}}} = \frac{\rho_{\text{guided}}}{\rho_{\text{hom}}} = \frac{3}{4\pi} \frac{(\lambda/n)^2}{A_{\text{mode}}} \frac{n_g(\omega)}{n} f(x, y) \cos^2(\theta) , \quad (4.16)$$

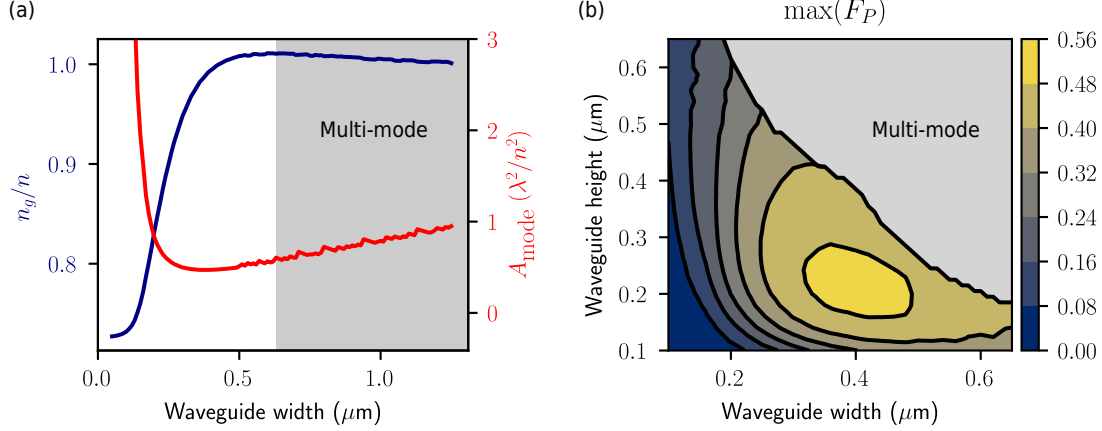


Figure 4.4: (a) Group index and mode area of the fundamental TE-like with a waveguide height of 200 nm and varying waveguide width. (b) Maximum Purcell enhancement due to the fundamental TE-like mode.

where n is the refractive index at the position of the emitter and $n_g = c/v_g$ is the group index. Here, Γ_{hom} is the decay rate of a dipole at the frequency and dipole moment of the $S_{1,0} \rightarrow S_{0,0}$ transition in homogeneous anthracene.

To maximise the decay to the guided mode, Eq. 4.16 tells us that we should decrease the mode area and increase the group index of the guided mode at the frequency of the emitter. We also need to make sure that the emitter sits at the field maximum ($f = 1$) and with the right orientation ($\cos^2(\theta) = 1$). In contrast with photonic-crystal waveguides [26], the group velocity of ridge-waveguide modes is not strongly affected by structural parameters, and the mode area is also relatively constant above a certain threshold. This is shown for $h = 200$ nm in Fig. 4.4(a). Hence, not much optimisation can be done and we typically pick $h = 200$ nm and $w = 400$ nm.

For waveguides with $F_P^{\text{guided}} < 1$, it is usually a good approximation to say that the total decay rate Γ_{total} is equal to the decay rate in a homogeneous medium Γ_{hom} [182]. This means that the power coupled to the waveguide is redistributed from otherwise scattered power, as opposed to a strong rate enhancement from the waveguide itself.

With this approximation, we have

$$\beta \simeq \frac{\Gamma_{\text{guided}}/2}{\Gamma_{\text{hom}}} = F_P^{\text{guided}}/2, \quad (4.17)$$

where β is defined as the fraction of the power which is emitted in only one guided direction.

4.1.3 Design for Maximal Photon Extraction

The coupling of single DBT molecules to optical waveguides was first suggested by Hwang and Hinds [182], and recently implemented by the Toninelli group at room temperature [141] and by the Sandoghdar group at cryogenic temperature [28]. In the above proposal and implementation, molecules are coupled to the evanescent field of the fundamental TE-like mode. The evanescent field is the part of the mode which lives outside of the high refractive index material, with the electric field decaying exponentially away from the waveguide. Evanescent coupling gets around the difficulty of patterning doped-anthracene into waveguide structures directly. Instead, we can crystallise [28] or grow [183] doped-anthracene around a waveguide structure and still expect some coupling to the mode. However, this forces us to compromise. As shown in Fig. 4.2(c), the maximum of the field is generally located in the centre of the waveguide core and we have $f < 1$ in the evanescent tail. To increase f , we need a larger field strength outside the core which leads to an increase in A_{mode} . Additionally, DBT molecules tend to be unstable close to the crystal edges and near the interfaces with different materials (Sec. 2.1.2). It is therefore difficult to find stable molecules close to the waveguide/anthracene boundary where the strength of the evanescent field is at its highest. We note that this is also the limiting factor for our recent demonstration of molecules coupled to hybrid plasmonic waveguides at room temperature [31]. Overall, evanescent coupling is not the optimum solution for photon extraction efficiency.

I propose to solve these problems in the following way. To access the maximum of the electric field, doped anthracene crystals can be grown (or placed) in a small gap etched through the waveguide. Such a gap has to be big enough that the anthracene crystal contains stable molecules away from the waveguide/anthracene interfaces. However, the gap also has to be small enough that the guided mode does not significantly diffract in the homogeneous anthracene, which would increase A_{mode} at the middle of the gap. To fill a gap with doped-anthracene, we use a melt-growth technique which is discussed in more detail in Sec. 4.3. A melt-growth usually results in anthracene crystals which are not optically uniform because of cracks, domain boundaries and different crystal orientations. Hence, it is usually preferable to minimise the footprint of the organic material. To localise the anthracene growth inside the waveguide gap, we fabricate micro-fluidic channels aligned to the gap, which are filled by doped-anthracene (see Sec. 4.3.2). The final structure is sketched in Fig. 4.5(a) and Fig. 4.5(b).

To check the viability of the design, I perform finite-difference time-domain (FDTD) simulations to obtain β . Using the Meep package [184], I estimate the fraction of the power emitted into the waveguide by a classical dipole which is oscillating at the frequency of the $S_{1,0} \rightarrow S_{0,0}$ transition. It is possible to show that this is equivalent to the quantum emitter case [103]. I also estimate the total power emitted by the dipole, which allows us to calculate the total Purcell factor $F_P = \Gamma_{S_{1,0} \rightarrow S_{0,0}} / \Gamma_{\text{hom}}$. As the true refractive indices of anthracene are not known precisely, I approximate the material as an isotropic dielectric with refractive index of 1.8 (see Sec. 2.1.1). In all these simulations, the channel width is set at gap width + 200 nm to allow for the uncertainty of the alignment procedure (see Sec. 4.4.2). The channel height and under-etch are fixed at 1 μm and 150 nm respectively.

Fig. 4.5(c) and Fig. 4.5(d) show the results of selected simulations with the dipole sitting in the middle of the gap, at a height corresponding to the middle of the waveguide and oriented in the x-direction. For $h = 200$ nm and $w = 400$ nm, we see that β

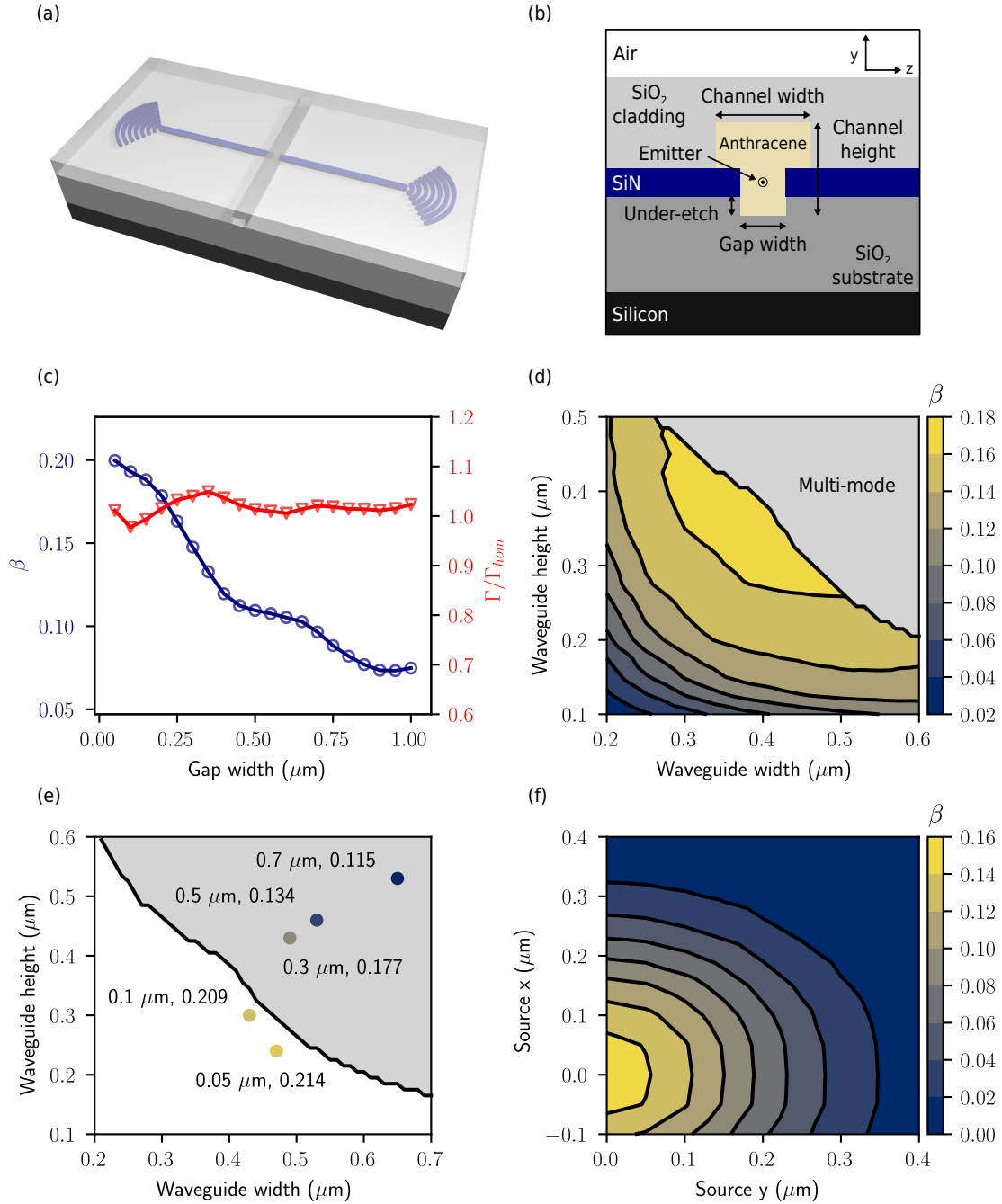


Figure 4.5: (a) & (b) Sketch of the proposed design. (c) Coupling efficiency to the fundamental TE-like mode (circles) and total Purcell factor (triangles) for a dipole oscillating at 785 nm in the middle of the channel and pointing in the x-direction. The waveguide dimensions are $h = 200$ nm, $w = 400$ nm and the channel width is set at gap width + 200 nm for alignment purposes. The channel height is 1 μm with an under-etch of 150 nm. (d) β as a function of waveguide dimensions with gap width = 300 nm. (e) Optimised waveguide dimensions as a function of gap size. Points are labelled as (gap width, β) and the grey area is the multi-mode region. (f) β as a function of dipole position. The waveguide dimensions are $h = 200$ nm and $w = 400$ nm and the gap width is 300 nm.

decreases rapidly with the size of the gap while F_P stays close to 1. Hence, minimising the gap size is critical to maximising the coupling. For a gap width of 300 nm, we also observe that the waveguide dimensions are no longer optimised at $h = 200$ nm and $w = 400$ nm. This can be partially explained by the fact that smaller modes diffract quicker in the homogeneous anthracene, leading to larger mode areas at the position of the emitter. Increasing the waveguide height to ~ 350 nm leads to $\beta \sim 0.17$, which is somewhat larger than numerical simulations for evanescent coupling [182] but for a dipole which sits much further away from any interfaces. This is important in order to increase the probability of finding stable molecules at that position. In Fig. 4.5(e), I plot the waveguide dimensions which maximise β as a function of gap size.

Finally, I vary the dipole position in the x-y plane to estimate the drop in coupling efficiency when the emitter is not placed at the maximum of the mode's electric field. This is plotted for the waveguide dimensions $h = 200$ nm and $w = 400$ nm and a gap size of 300 nm in Fig. 4.5(e). We see that a shift of 100 nm in either direction only decreases β by ~ 0.04 .

4.2 Probing by Extinction Spectroscopy

As explained in Sec. 2.2.2, the power emitted by a molecule pumped by a continuous-wave laser can be decomposed into coherent and incoherent parts. The coherent emission interferes with the pump light, and the visibility of the interference gives us a measure of the coupling efficiency to the waveguide modes. The situation is depicted in Fig. 4.6 where a molecule is coupled to two waveguide-like structures which both extend to infinity in opposite directions. A continuous-wave laser is launched through one of the waveguides, so that the source of light is the fundamental TE-like mode of the unperturbed waveguide with a power P_{pump} . The laser is close to resonance with the $S_{1,0} \leftrightarrow S_{0,0}$ transition. As a result, the molecule scatters light back into the excita-

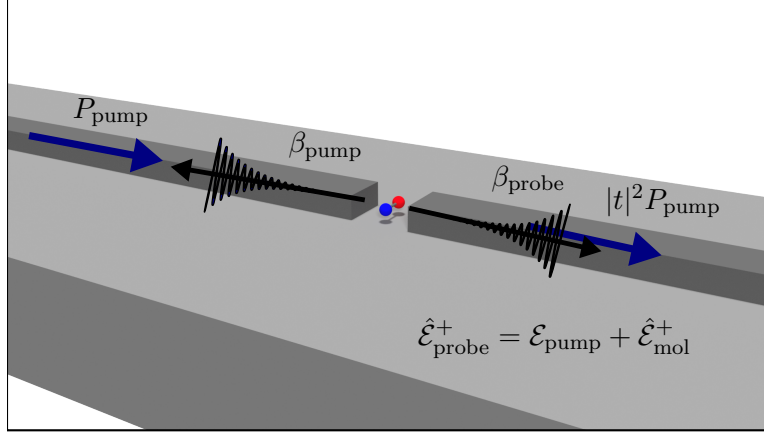


Figure 4.6: Coupling of a dipole to a waveguide structure with a gap.

tion waveguide with a coupling efficiency β_{pump} or emits in the probe waveguide with efficiency β_{probe} . The pump light transmission from the excitation waveguide to the probe waveguide is $|t|^2$.

4.2.1 Reciprocity

First, let us calculate the amount of power emitted by the molecule on the $S_{0,0} \leftrightarrow S_{1,0}$ line, $P_{\text{mol}}^{\text{res}}$, as a function of P_{pump} . From Eq. 2.39 we have

$$P_{\text{mol}}^{\text{res}} = \alpha \Gamma_1 \hbar \omega_0 \rho_{ee} = \frac{\Omega_0^2}{\Gamma_{\text{pump}}} \frac{\alpha \Gamma_1 \rho_{ee}}{\Omega_0^2} P_{\text{pump}}, \quad (4.18)$$

where $\Gamma_{\text{pump}} = P_{\text{pump}}/(\hbar \omega_0)$. I will now use a reciprocity argument to express the coupling of the pump light to the molecule as a function of the spontaneous emission rate to the pump waveguide. To define the source of pump light, we start by imagining a situation where there is no gap nor molecule. In this scenario, we would like to define an equivalent current density $\mathbf{j}_{\text{pump}}(\mathbf{r}, t) = \mathbf{j}_{\text{pump}}(\mathbf{r}) \exp(-i\omega_0 t)$ so that only the fundamental TE-like mode is excited with a power P_{pump} . By using the principle of equivalence, we can define a surface current on an infinite plane which is normal to the

direction of propagation, and the current density satisfies [185]

$$\mathbf{j}_{\text{pump}}(\mathbf{r}) = \mathbf{e}_n \times \mathbf{H}_{\text{mode}}^{\text{f}}(\mathbf{r}) , \quad (4.19)$$

where $\mathbf{e}_n$ is the unit vector in the direction of propagation and $\mathbf{H}_{\text{mode}}^{\text{f}}(\mathbf{r})$ is the cross section of the mode's magnetic field propagating in the forward direction. We can now return to the original scenario, using $\mathbf{j}_{\text{pump}}(\mathbf{r})$ in any normal plane to the left of the gap to emulate the pump source. In this geometry, $\mathbf{j}_{\text{pump}}(\mathbf{r})$ now produces an electric field $\mathbf{E}_{\text{pump}}(\mathbf{r})$, and by reciprocity, we have [103]

$$\int \mathbf{j}_{\text{mol}}(\mathbf{r}) \cdot \mathbf{E}_{\text{pump}}(\mathbf{r}) dV = \int \mathbf{j}_{\text{pump}}(\mathbf{r}) \cdot \mathbf{E}_{\text{mol}}(\mathbf{r}) dV . \quad (4.20)$$

Let us model the molecule as a non-decaying classical dipole and then make the appropriate replacements. We therefore have

$$\mathbf{j}_{\text{mol}}(\mathbf{r}) = -i\omega_0 \boldsymbol{\mu} \delta(\mathbf{r} - \mathbf{r}_0) , \quad (4.21)$$

which we plug into Eq. 4.20 to get

$$\boldsymbol{\mu} \cdot \mathbf{E}_{\text{pump}}(\mathbf{r}_0) = \frac{i}{\omega_0} \int \mathbf{j}_{\text{pump}}(\mathbf{r}) \cdot \mathbf{E}_{\text{mol}}(\mathbf{r}) dV \quad (4.22)$$

$$= \frac{i}{\omega_0} \int \left(\mathbf{e}_n \times \mathbf{H}_{\text{mode}}^{\text{f}}(\mathbf{r}) \right) \cdot \mathbf{E}_{\text{mol}}(\mathbf{r}) dS \quad (4.23)$$

$$= \frac{i}{\omega_0} \int \left(\mathbf{E}_{\text{mol}}(\mathbf{r}) \times (\mathbf{H}_{\text{mode}}^{\text{b}}(\mathbf{r}))^* \right) \cdot d\mathbf{S} , \quad (4.24)$$

where $\mathbf{H}_{\text{mode}}^{\text{b}}(\mathbf{r})$ is the magnetic field of the fundamental mode propagating in the backwards direction and $\mathbf{H}_{\text{mode}}^{\text{b}}(\mathbf{r}) = (\mathbf{H}_{\text{mode}}^{\text{f}}(\mathbf{r}))^*$ for a guided mode.

Next, we can write β_{pump} in terms of the overlap of the emission with the profile of

the fundamental mode as

$$\beta_{\text{pump}} = \frac{|\frac{1}{4} \int (\mathbf{E}_{\text{mol}}(\mathbf{r}) \times (\mathbf{H}_{\text{mode}}^b(\mathbf{r}))^* + (\mathbf{E}_{\text{mode}}^b(\mathbf{r}))^* \times \mathbf{H}_{\text{mol}}(\mathbf{r})) \cdot d\mathbf{S}|^2}{P_{\text{pump}} P_{\text{mol}}}, \quad (4.25)$$

where P_{mol} is the total power emitted by the dipole. By using the Lorentz reciprocity theorem,

$$\oint ((\mathbf{E}_{\text{mode}}^b(\mathbf{r}))^* \times \mathbf{H}_{\text{mol}}(\mathbf{r})) \cdot d\mathbf{S} = \oint (\mathbf{E}_{\text{mol}}(\mathbf{r}) \times (\mathbf{H}_{\text{mode}}^b(\mathbf{r}))^*) \cdot d\mathbf{S}, \quad (4.26)$$

for an infinite box containing the molecule and the surface currents generating $\mathbf{E}_{\text{mode}}^b$ and $\mathbf{H}_{\text{mode}}^b$, Eq. 4.25 is simplified to

$$\beta_{\text{pump}} = \frac{|\frac{1}{2} \int (\mathbf{E}_{\text{mol}}(\mathbf{r}) \times (\mathbf{H}_{\text{mode}}^b(\mathbf{r}))^*) \cdot d\mathbf{S}|^2}{P_{\text{pump}} P_{\text{mol}}}. \quad (4.27)$$

By using Eq. 4.24 and Eq. 4.27, we get

$$\Omega_0^2 = \frac{|\boldsymbol{\mu} \cdot \mathbf{E}_{\text{pump}}(\mathbf{r}_0)|^2}{\hbar^2} = 4\beta_{\text{pump}} \Gamma_{\text{pump}} \Gamma_{\text{mol}}, \quad (4.28)$$

where $\Gamma_{\text{mol}} = P_{\text{mol}}/(\hbar\omega_0)$. We can now replace the classical dipole by its quantum analogue, so that $\boldsymbol{\mu} \rightarrow \langle S_{1,0} | \hat{\boldsymbol{\mu}} | S_{0,0} \rangle$ and we have $\Gamma_{\text{mol}} \rightarrow \alpha\Gamma_1$. Finally, plugging Eq. 4.28 into Eq. 4.18, we arrive at the expression

$$P_{\text{mol}}^{\text{res}} = \frac{\alpha^2 \Gamma_1^2 \rho_{ee}}{\Omega_0^2} 4\beta_{\text{pump}} P_{\text{pump}}. \quad (4.29)$$

We can also write down the power of the non-resonant fluorescence as

$$P_{\text{mol}}^{\text{fluo}} \simeq (1 - \alpha) \Gamma_1 \hbar\omega_0 \rho_{ee} = \frac{\alpha(1 - \alpha) \Gamma_1^2 \rho_{ee}}{\Omega_0^2} 4\beta_{\text{pump}} P_{\text{pump}}. \quad (4.30)$$

4.2.2 Interference

To describe the interference between the transmitted pump light and the coherent emission, we have to look at the relative amplitudes of the electric field contributions. The fundamental TE-like mode of the probe waveguide has the same profile as the pump mode for any normal plane to the right of the gap. In the Markov approximation and far away from the gap, we can write the sum of the two contributions as [186, 187]

$$\hat{\mathbf{E}}_{\text{probe}}^+(\mathbf{r}) = \hat{\mathcal{E}}_{\text{probe}}^+ \mathbf{E}_{\text{mode}}^f(\mathbf{r}) = (\mathcal{E}_{\text{pump}} + \mathcal{E}_{\text{mol}} \hat{\sigma}^-) \mathbf{E}_{\text{mode}}^f(\mathbf{r}) , \quad (4.31)$$

and if we normalise the profile as

$$\frac{1}{2} \int \left(\mathbf{E}_{\text{mode}}^f(\mathbf{r}) \times (\mathbf{H}_{\text{mode}}^f(\mathbf{r}))^* + (\mathbf{E}_{\text{mode}}^f(\mathbf{r}))^* \times \mathbf{H}_{\text{mode}}^f(\mathbf{r}) \right) \cdot d\mathbf{S} = 1 , \quad (4.32)$$

by definition we get

$$|\mathcal{E}_{\text{pump}}|^2 = |t|^2 P_{\text{pump}} , \quad (4.33)$$

$$|\mathcal{E}_{\text{mol}}|^2 \rho_{ee} = \beta_{\text{probe}} P_{\text{mol}}^{\text{res}} . \quad (4.34)$$

Furthermore, comparison with Eq. 4.29 gives us

$$|\mathcal{E}_{\text{mol}}| = \alpha \sqrt{4\beta_{\text{pump}}\beta_{\text{probe}}} \frac{\Gamma_1}{\Omega_0} , \quad (4.35)$$

and we can write, up to a global phase,

$$\hat{\mathcal{E}}_{\text{probe}}^+ = \left(|t| + \alpha \sqrt{4\beta_{\text{pump}}\beta_{\text{probe}}} \frac{\Gamma_1}{\Omega_0} \hat{\sigma}^- \exp(i\phi) \right) \sqrt{P_{\text{pump}}} . \quad (4.36)$$

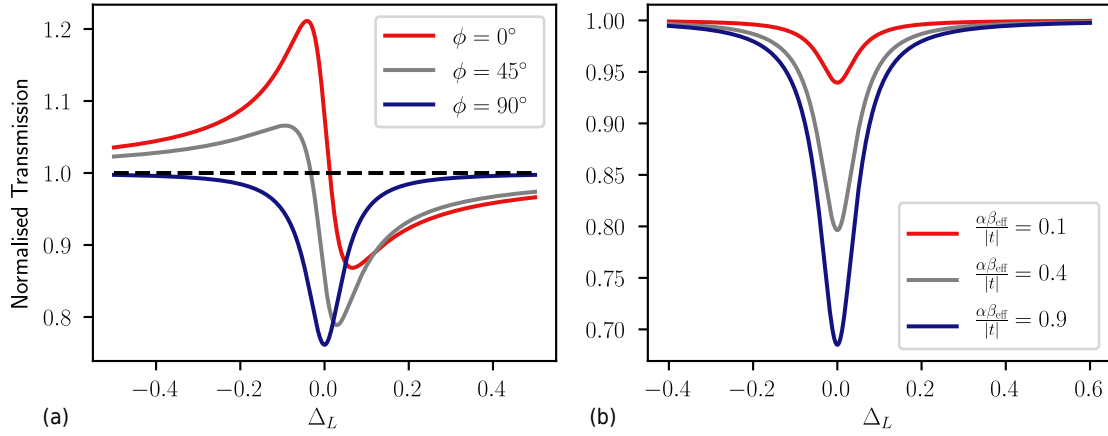


Figure 4.7: Normalised transmission (Eq. 4.40) assuming $\Gamma_1/(2\pi) = 35$ MHz, $\Gamma_2/\pi = 100$ MHz, $S = 0.1$ and: (a) $\alpha\beta_{\text{eff}}/|t| = 0.5$ with varying ϕ , (b) $\phi = \pi/2$ with varying $\alpha\beta_{\text{eff}}/|t|$.

The power transmitted to the probe waveguide P_{probe} is then

$$P_{\text{probe}} = \langle \hat{\mathcal{E}}_{\text{probe}}^- \hat{\mathcal{E}}_{\text{probe}}^+ \rangle \quad (4.37)$$

$$= \left(|t|^2 + 2|t|\alpha\beta_{\text{eff}}\frac{\Gamma_1}{\Omega_0} \left(\cos(\phi)\text{Re}(\tilde{\rho}_{ge}) + \sin(\phi)\text{Im}(\tilde{\rho}_{ge}) \right) + (\alpha\beta_{\text{eff}})^2 \frac{\Gamma_1^2}{\Omega_0^2} \rho_{ee} \right) P_{\text{pump}}, \quad (4.38)$$

where $\beta_{\text{eff}} = \sqrt{4\beta_{\text{pump}}\beta_{\text{probe}}}$. Finally, by using the steady-state solutions given by Eq. 2.32 and Eq. 2.35, we get the normalised transmission

$$T_{\text{probe}}^{\text{res}} = P_{\text{probe}} / (|t|^2 P_{\text{pump}}) \quad (4.39)$$

$$= 1 - \frac{\alpha\beta_{\text{eff}}}{|t|} \left(2 \left(\cos(\phi) \frac{\Delta_L}{\Gamma_2} + \sin(\phi) \right) - \frac{\alpha\beta_{\text{eff}}}{|t|} \right) \frac{\Gamma_1}{2\Gamma_2} \frac{1}{\left(\frac{\Delta_L}{\Gamma_2} \right)^2 + 1 + S}. \quad (4.40)$$

To complete the picture, we have to consider another contribution to the transmission signal. Because we are also collecting incoherent red-shifted photons into the guided mode, the dip is further reduced by

$$T_{\text{probe}} = T_{\text{probe}}^{\text{res}} + \frac{\beta_{\text{probe}} P_{\text{mol}}^{\text{fluo}}}{|t|^2 P_{\text{pump}}}, \quad (4.41)$$

which, using Eq. 4.30, leads to

$$T_{\text{probe}} = 1 - \frac{\alpha\beta_{\text{eff}}}{|t|} \left(2 \left(\cos(\phi) \frac{\Delta_L}{\Gamma_2} + \sin(\phi) \right) - \frac{\beta_{\text{eff}}}{|t|} \right) \frac{\Gamma_1}{2\Gamma_2} \frac{1}{\left(\frac{\Delta_L}{\Gamma_2}\right)^2 + 1 + S} . \quad (4.42)$$

4.2.3 The Unperturbed-Waveguide Case

To understand Eq. 4.40 better, let us consider the case of a waveguide without a gap. In this simple picture, we have $\beta_{\text{pump}} = \beta_{\text{probe}} \equiv \beta/2$ and $|t| = 0$. Furthermore, let us select the following simple parameters: no detuning $\Delta_L = 0$, no pure dephasing $\Gamma_2 = \Gamma_1/2$, a perfect two-level system $\alpha = 1$ and low saturation $S \ll 1$. Note that ϕ does not depend on any of these parameters. With the above assumptions, Eq. 4.40 is simplified to

$$T_{\text{probe}}/P_{\text{pump}} = 1 + \beta(\beta - 2 \sin(\phi)) . \quad (4.43)$$

The reflected and scattered power are also easily derived as

$$R_{\text{pump}}/P_{\text{pump}} = \beta^2 , \quad (4.44)$$

and

$$S_{\text{mol}}/P_{\text{pump}} = 2\beta(1 - \beta) . \quad (4.45)$$

To ensure that $T_{\text{probe}} + R_{\text{pump}} + S_{\text{mol}} = P_{\text{pump}}$, we can easily show that ϕ must be equal to $\pi/2$ in this situation. This is the same answer as we would have obtained by considering the eigenmode expansion of the dipole's Green's function [138, 186, 187]. With $\phi = \pi/2$, Eq. 4.42 becomes

$$T_{\text{probe}} = 1 - \alpha\beta(2 - \beta) \frac{\Gamma_1}{2\Gamma_2} \frac{1}{\left(\frac{\Delta_L}{\Gamma_2}\right)^2 + 1 + S} . \quad (4.46)$$

Here, we can identify two contributions to the transmission dip. The first term is due to the coherent emission from the molecule, which has a π phase shift with the pump

light on resonance. The second term is proportional to the total power emitted by the molecule into the waveguide and reduces the visibility of the dip. The term $\alpha\beta(2 - \beta)$ defines the maximum possible visibility for a given system. When pure dephasing cannot be ignored, the visibility is reduced by $\Gamma_1/(2\Gamma_2)$, which is simply the ratio of the lifetime-limited linewidth to the measured linewidth. This is because the share of incoherent emission increases with pure dephasing (see Sec. 2.2.2). Saturation of the emitter also contributes to increasing the incoherent contribution.

The phase shift of the coherent emission is the consequence of two phenomena. Firstly, the dipole oscillation lags behind the driving field by $\pi/2$, which is analogous to a classical dipole. Secondly, the electric field emitted by the dipole into the waveguide lags behind the dipole oscillation by $\pi/2$ as well. The value of the second phase shift is only true for coupling to a translationally-invariant waveguide mode and, therefore, does not apply to the case with a gap.

4.2.4 Phase Shifts in the Presence of a Gap

To investigate the phase shift for the gap geometry, we performed FDTD simulations. In a first simulation, we mapped the electric field generated by a continuous source current matching the TE-like mode of the guide. This allowed us to compute the phase shift of the driving light ϕ_{drive} between the dipole's position and an arbitrary position in the probe waveguide, after the gap. In a second simulation, we simulated the electric field generated by a point current source located at the position of the dipole. This gave us the phase shift ϕ_{mol} between the oscillating current and the electric field at the same arbitrary point in the probe waveguide. Recalling that $\mathbf{j} = -i\omega_0\boldsymbol{\mu}$, we therefore had all the elements to compute ϕ as $\phi = \phi_{\text{drive}} - \phi_{\text{mol}} - \pi/2$.

The results as a function of dipole position in the y-z plane are shown in Fig. 4.8(a) for the following structural parameters: waveguide width 400 nm, waveguide height 200 nm, gap width 400 nm, channel width 1 μm and under-etch 150 nm. We also re-

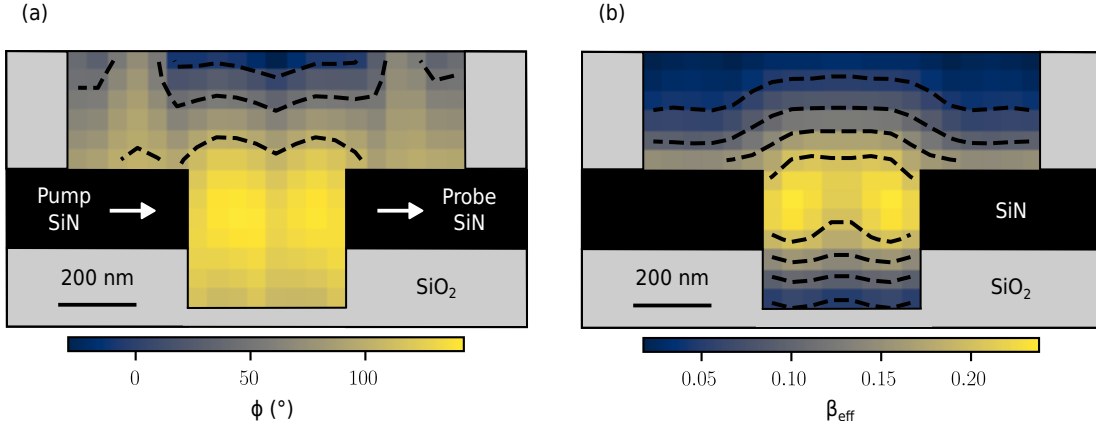


Figure 4.8: (a) Phase shift of the emission relative to the transmitted pump light as a function of source position. The pump light propagates from left to right. The structure parameters are given in the text. (b) β_{eff} as a function of source position inside the anthracene gap structure.

peated the FDTD simulation as explained in Sec. 4.1.3 to compute $\beta_{\text{eff}} = \sqrt{4\beta_{\text{probe}}\beta_{\text{pump}}}$ as shown in Fig. 4.8(b). Due to the lack of translational symmetry, the phase shift is no longer equal to $\pi/2$ for positions that are inside or above the gap. By measuring both ϕ and β_{eff} , we can deduce an approximate position of the emitter using these simulations.

4.3 Micro-Capillary Channels

In the section Sec. 4.1.3, we discussed an optimised geometry to collect the emission from a DBT molecule. The structure relies on the ability to grow doped anthracene crystals in the middle of gaps in the waveguides. To localise the growth to the gaps only, I proposed to fabricate micro-fluidic channels on top of the photonic structures. As shown in this section, it is possible to fill such channels with a mixture of molten anthracene and DBT by capillary forces. When the sample is cooled back to room temperature, crystallisation of the anthracene occurs inside the channels, and this method is known to yield narrow-linewidth DBT molecules. In fact, melt-growth techniques have already been investigated for filling large areas with DBT-doped naphthalene [152], anthracene

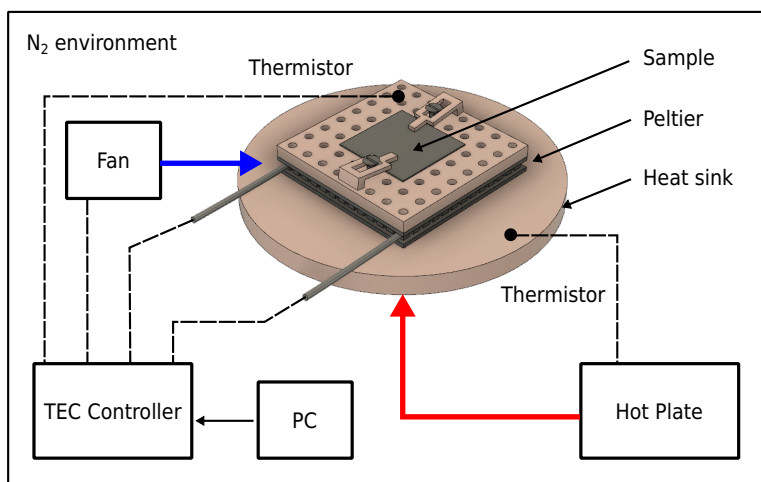


Figure 4.9: Schematic of the heating set-up for melt growths.

[28] and para-dichlorobenzene [30]. In [28], titanium dioxide waveguides are covered in the molten organic mixture which then re-crystallises, allowing the positioning of DBT molecules in the evanescent tail of the waveguides. Similar studies have also explored the filling of small capillaries with DBT-doped naphthalene [188] and para-dichlorobenzene [28]. In those cases, the capillaries were only hundreds of nanometres in diameter so that the organic crystal forms the core of the guiding structures.

4.3.1 Melt Growth Set-Up

For a melt-growth, it is important to control the heating and cooling cycle of the anthracene/DBT mixtures. To achieve this, I have developed a simple set-up to precisely heat up samples above the melting point of anthracene (217°C) and cool them down at a given rate. It is sketched in Fig. 4.9. Active control of the temperature is achieved with a Peltier module (GM200-127-14-10, Adaptive) which is in contact with the sample holder on one side and a heat sink on the other. The Peltier is able to cool or heat up the sample holder depending on the direction of the driving current. At maximum power, the temperature difference between the two sides of the Peltier is approximately 50°C. To reach the melting point of anthracene, we first raise the temperature of the

heat sink to 175°C using a hotplate (Isotemp, Fisher scientific) with an external temperature probe. The sample temperature is then further increased using the Peltier which is regulated by a TEC controller (TEC-1089, Meerstetter Engineering GmbH) with a 200 W power supply (TOP-200, TracoPower). A thermistor measures the temperature on top of the sample holder and serves as the input for the controller. For additional cooling power, the controller also operates a fan which produces an airflow directly across the sample. With this system, we are able to both change the temperature at a fixed rate up to $\pm 5^\circ\text{C}/\text{s}$ and maintain it at a set value within the 125°C - 225°C range.

It is also preferable to do the melt growth in an inert atmosphere to avoid unwanted reactions with oxygen at high temperatures. The melt growth set-up is therefore housed inside a glove box which can be continuously purged with an inert gas. A humidity sensor and an O₂ gas sensor give us information about the growth environment. After a 30 min purge with dry nitrogen, we typically get < 4 % relative humidity and < 0.5 % O₂ concentration.

Finally, this set-up also allows us to prepare anthracene/DBT powders with the correct doping concentration. This is done by heating up pure anthracene (Alfa Aesar) and DBT (New Chem) powders above the melting point of anthracene in an N₂ atmosphere. We observe that DBT is soluble in liquid anthracene which results in a uniformly doped solid when the solution is quickly cooled back to room temperature. At the end of the process, we grind the material to produce a doped-anthracene powder.

4.3.2 Channel Fabrication and Filling

The channels are fabricated on undoped silicon wafers with a 5 μm thermal oxide layer. We spin-coat a 1 μm layer of AZ nLOF 2020 resist (MicroChemicals) which is diluted 4:1 (resist:solvent w/w) with PGMEA (Sigma-Aldrich). The resist is spun at 3000 rpm for 1 min, followed by a soft bake at 100°C for 1 min also. AZ nLOF is a thermally-stable negative-resist, which we pattern into channel structures using electron-beam

lithography (e-Line, Raith) (Fig. 4.10(a)). The patterning is done at an acceleration voltage of 30 kV, a dose of 12 $\mu\text{C}/\text{cm}^2$ and a step size of 10 nm. The resist then needs an additional post-exposure bake at 110°C for 1 min. Finally, we develop the patterns in AZ 826 MIF (MicroChemicals) for 1 min with gentle agitation.

The temperature tolerance of the resist allows us to sputter SiO_2 directly on top of the chip without damaging the structures. We therefore deposit 2 μm of SiO_2 using rf-sputtering with a silica target in an $\text{Ar} + \text{O}_2$ atmosphere (Fig. 4.10(b)). The deposition is done in a custom-made commercial sputterer (Lesker) at a pressure of 1.5 mTorr, with an Ar flow of 4 sccm and an O_2 flow of 1 sccm. The silica target sits in a magnetron sputter gun driven by an rf-power of 200 W. The sample is mounted about 50 cm above the target and rotates at 10 rpm. We monitor the deposition rate using a calibrated quartz crystal. After the sputtering step, we place the sample in a furnace which is heated to 550°C in ambient atmosphere for 2 hours. Under these conditions, we find that the resist is released from the channels without leaving any residue, and we are left with open structures which can be filled with molten anthracene/DBT mixtures (Fig. 4.10(c)).

Next, we place the sample upside-down on a silicon substrate which is then clamped on top of the melt growth set-up (Fig. 4.10(d)). A small amount of DBT-doped anthracene powder is deposited on the cleaved facets to cover both channel entrances. The temperature of the sample is then raised to 220°C to melt the anthracene powder (Fig. 4.10(e)). By capillary forces, the mixture fills both the channels and the space between the silicon substrate and the chip. By using the TEC controller, the sample is finally cooled past the melting point of anthracene at the largest achievable rate of $-5^\circ\text{C}/\text{s}$. As we remove the chip from the substrate, some anthracene is left on the top surface which we clean off using toluene (Fig. 4.10(f)).

An example of a fabricated chip is shown in Fig. 4.11. The channels are nominally 5 μm in width with regions which are tapered to smaller widths. We find that 5 μm

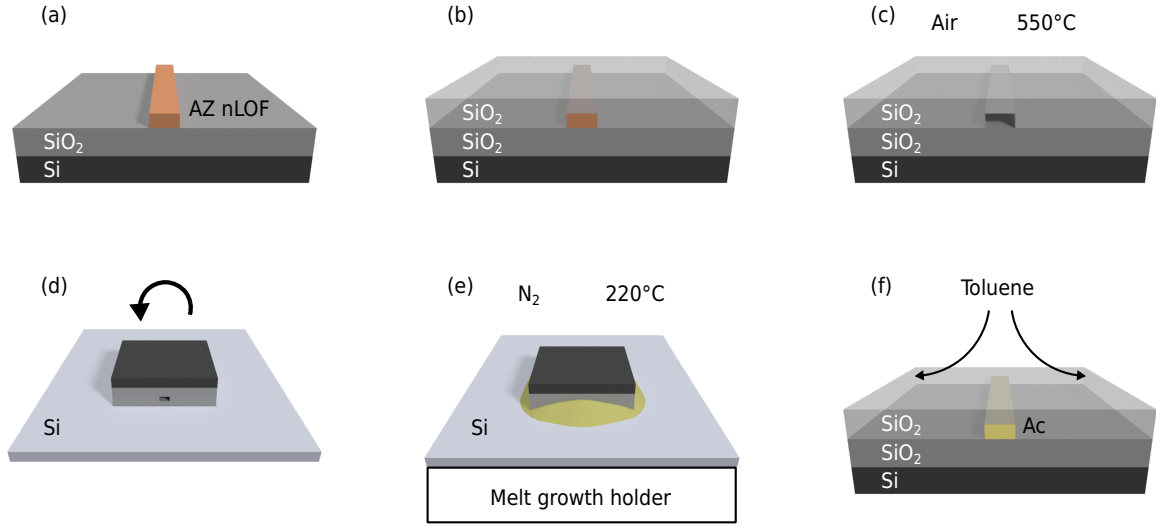


Figure 4.10: Channel fabrication steps. (a) Patterning of the sacrificial resist layer using e-beam lithography. (b) Deposition of the SiO₂ cladding by sputtering. (c) Removal of the resist at high temperatures. (d) The sample is placed upside-down on a silicon substrate. (e) Filling of the channels by melting a doped anthracene powder. (f) Cleaning of residual anthracene on the sample surface.

AZ nLOF rectangles are robust to e-beam patterning errors and do not collapse due to the large aspect ratio. We can therefore fabricate uninterrupted channels millimetres in length across a chip. While the channel fabrication is deterministic, the filling is a more random process. Inside the channels, the crystallisation can result in large unfilled regions which appear randomly along the chip. This can be explained by the formation of multiple seeds at the start of the crystallisation which clog the channels. The growing crystals are therefore not supplied with additional liquid anthracene and voids are created between crystals because the organic material contracts when solidifying. In filled regions, we also observe voids on a smaller scale together with domain boundaries, cracks, etc. Overall, the quality of the filling depends on many parameters such as cooling rate and channel design. Here, the yield (as measured by the number of tapered regions which are filled) was deemed sufficiently high to move on to the next step. But there is still plenty of room for improvement.

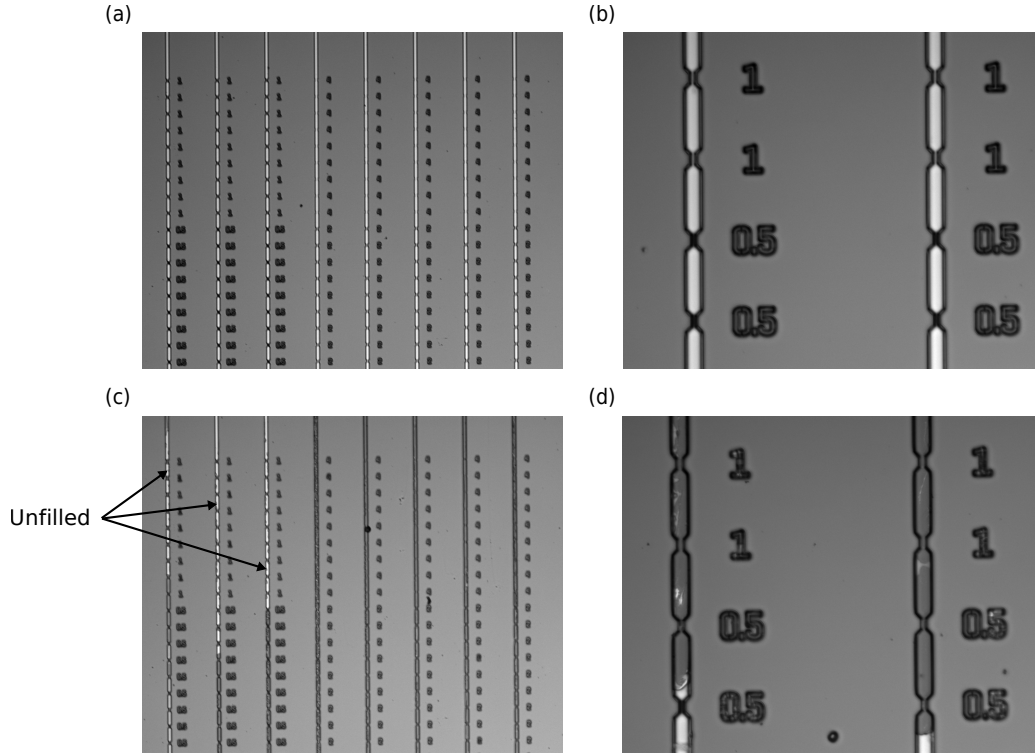


Figure 4.11: (a) & (b) Optical microscope images of unfilled channels after removal of the sacrificial polymer structures. The spacing between channels is $100\text{ }\mu\text{m}$. (c) & (d) Images of the same channels after filling with doped anthracene. The brighter regions correspond to unfilled parts of the channel.

4.3.3 Single-Molecule Spectroscopy

The next step was to check that the anthracene-filled channels contain narrow-linewidth DBT molecules. For this test, we prepared a chip using a 10^{-6} mol/mol doped anthracene powder and placed it in the cryostat. Fig. 4.12(a) shows a white light microscopy image of a filled channel at $\sim 5\text{ K}$. At this point, we had lost some cooling power from the cryostat, as the second stage and sample plate could only reach 3.3 K and 4.2 K respectively. We later realised that the wires for the positioning system had been replaced with thermally conductive material, adding an additional heat load to the base plate. Nominal performance was recovered by changing the wires back to phosphor bronze but all the measurements presented here are at a sub-optimal sample temperature.

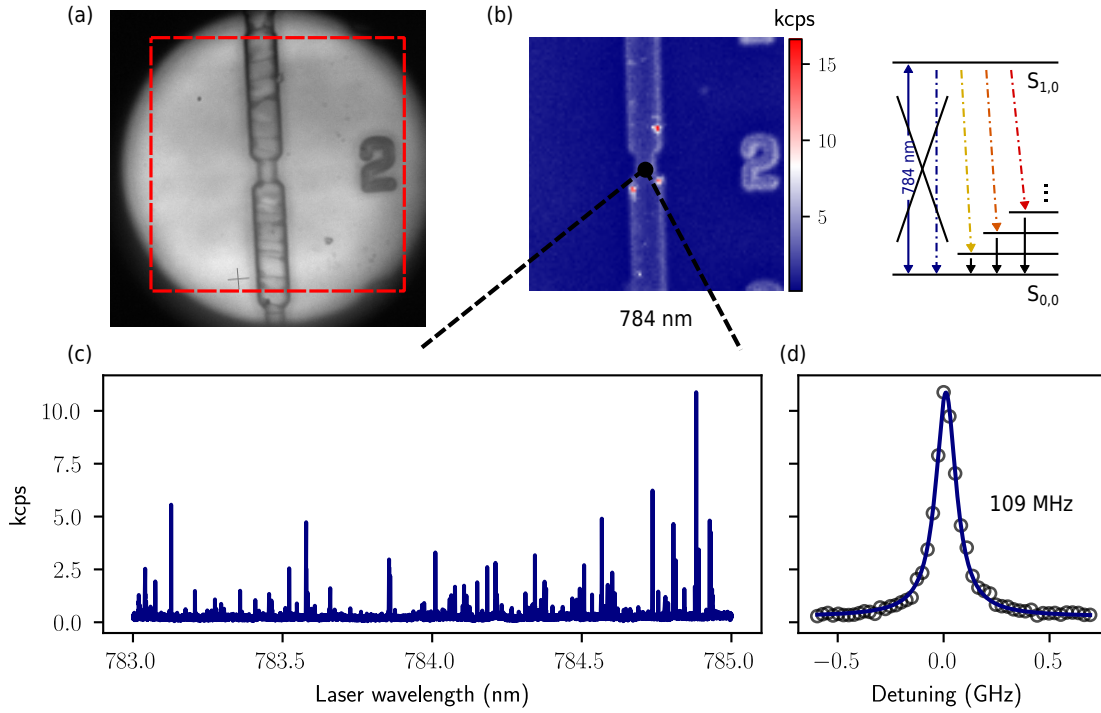


Figure 4.12: (a) White light microscopy image of a filled channel inside the cryostat. (b) Fluorescence microscopy scan of the same channel at ~ 5 K. (c) Excitation spectrum from the centre of the channel. (d) Close-up on a single DBT resonance.

We performed fluorescence confocal microscopy with the Ti:Sapphire laser and two 800 nm long pass filters in the collection path, as described in Sec. 3.2. Fig. 4.12(b) shows the fluorescence from the channel for an excitation wavelength of 784 nm and we can already identify fluorescent centres which likely correspond to single molecules. The laser spot was then positioned at the centre of the $2\ \mu\text{m}$ channel and the laser was continuously scanned from 783 nm to 785 nm. The fluorescence spectrum is plotted in Fig. 4.12(c) and we see a large number of fluorescing molecules within the inhomogeneous broadening of the $S_{0,0} \leftrightarrow S_{1,0}$ transition. A zoom on individual linewidths reveal that the molecules are not lifetime-limited and wider than for the bulk measurements (Sec. 3.6). This is probably due to the poor cryostat performance rather than spectral instability.

To test if the channel dimensions affect the spectral properties of the molecules,

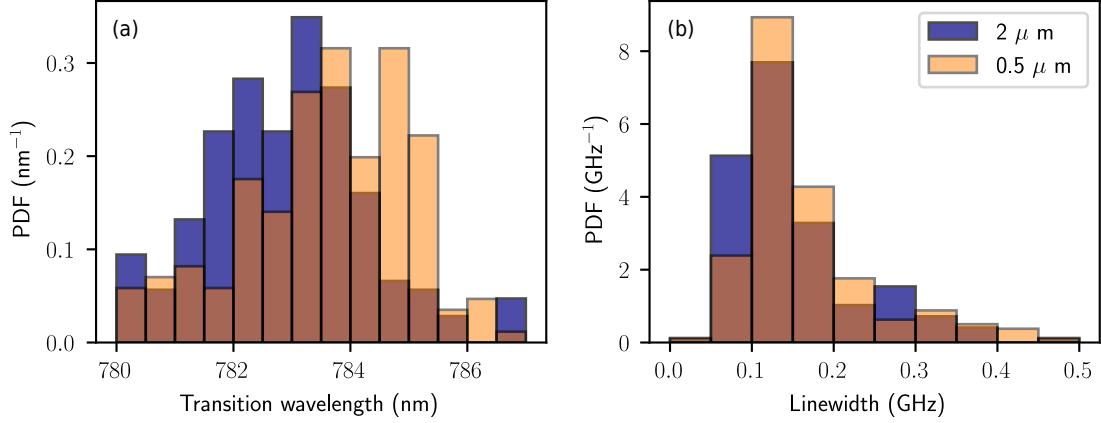


Figure 4.13: (a) Inhomogeneous broadening of 212 and 171 DBT molecules in $2\ \mu\text{m}$ and $0.5\ \mu\text{m}$ channels respectively. (b) Linewidth distribution of the same molecules.

I collected data from the centre of three $2\ \mu\text{m}$ channels and three $0.5\ \mu\text{m}$ channels for comparison. The line scans were done at a low power (150 nW at the objective, $S < 0.1$) so that small power variations at the position of the molecules does not result in significant line broadening. The cumulative statistics are shown in Fig. 4.13. We observe a small shift of the inhomogeneous broadening towards higher wavelengths from $782.9 \pm 0.1\ \text{nm}$ for $2\ \mu\text{m}$ channels to $783.6 \pm 0.1\ \text{nm}$ for $0.5\ \mu\text{m}$ ones, while the standard deviation remains constant at $1.3 \pm 0.3\ \text{nm}$ and $1.4 \pm 0.3\ \text{nm}$. More importantly, we only see a small increase in the mean value of the linewidths from $150 \pm 5\ \text{MHz}$ to $166 \pm 6\ \text{MHz}$. This could suggest the onset of spectral instabilities [152] but, overall, the DBT molecules seem well-behaved even inside small $0.5\ \mu\text{m}$ channels.

Finally, we also did polarimetry on the molecules by varying the orientation of the linearly-polarised pump light using a half-wave plate. Fig. 4.14(a) shows the typical response of a single molecule as a function of laser polarisation for zero detuning. The polarisation scans were done at low power so that $S < 0.1$ and Eq. 2.37 can be approximated by

$$R \propto \cos^2(\theta) , \quad (4.47)$$

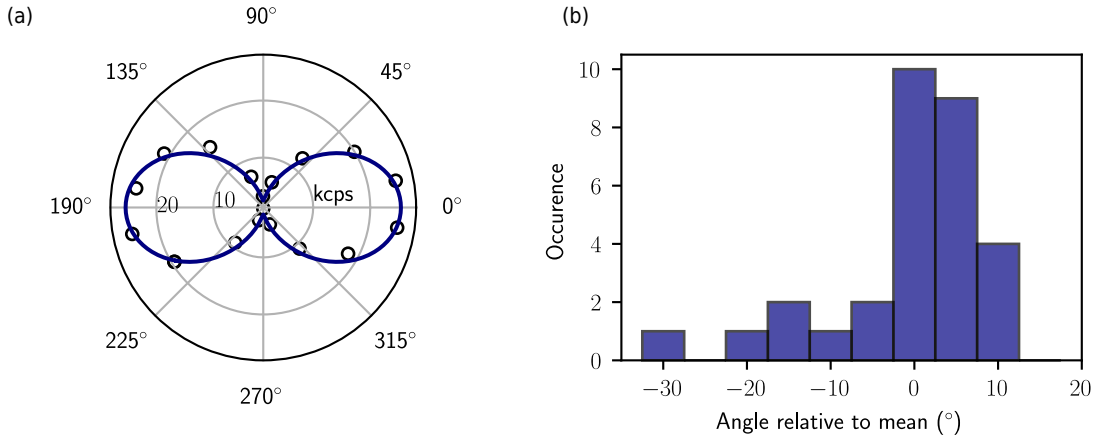


Figure 4.14: (a) Fluorescence of a single molecule inside a $0.5\ \mu\text{m}$ channel as a function of laser polarisation. (b) Histogram of angles between the dipole moment projection in the focal plane and the average orientation. The data is extrapolated from fluorescence excitation spectra of the centre of a $0.5\ \mu\text{m}$ channel.

where θ is the angle between the laser polarisation and the transition dipole-moment of the molecule. In bulk crystals, the orientation of the dipole moment is along the b-axis of the anthracene crystal [147]. We checked if this was true for a $0.5\ \mu\text{m}$ channel by recording its fluorescence excitation spectrum at different laser polarisations. Each molecule in the spectrum is analysed separately and we plot the histogram of dipole moment orientations in Fig. 4.14(b). Within the excitation spot, we see that the DBT molecules preferentially point in one direction which probably corresponds to the projection of the b-axis onto the focal plane. This result, together with the good photostability, suggests that the melt growth produces polycrystalline anthracene inside the channels. Further work should focus on studying the relative orientation of the crystal axes with respect to the channel geometry. This might depend on the structural parameters of the channel as well as on the growth conditions. For optimum coupling to the waveguide mode, the b-axis must be oriented along the channel length.

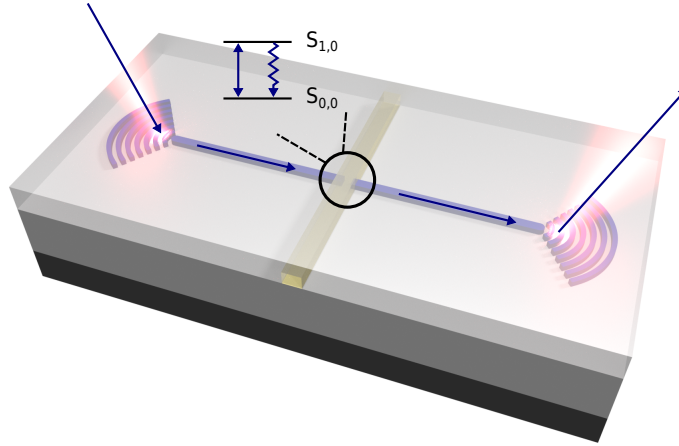


Figure 4.15: Sketch of the full on-chip optical system.

4.4 Experimental Observation of Coupling

In the last section, we showed that the crystallisation of anthracene in micro-capillaries results in a polycrystalline material with narrow-linewidths DBT molecules. With this capability, we can finally fabricate the full chip with micro-capillaries overlaid on top of waveguide structures. The performance of the devices is then characterised using extinction spectroscopy.

4.4.1 Optical System

To complete the design, we use two Bragg gratings to couple light in and out of the waveguides as shown in Fig. 4.15. We base the design on fully etched, concentric couplers with angled sides [189]. The gratings are very compact and optimised for coupling to a Gaussian beam focused by the objective lens of the cryostat. With FDTD simulations, we optimise the grating period and fill factor by calculating the overlap integral of the scattered field with a Gaussian beam focused on the grating plane. The position and angle of the beam are optimised to maximise the overlap integral. Fig. 4.16 plots the efficiency of the out-coupling and the optimised Gaussian beam angle as a

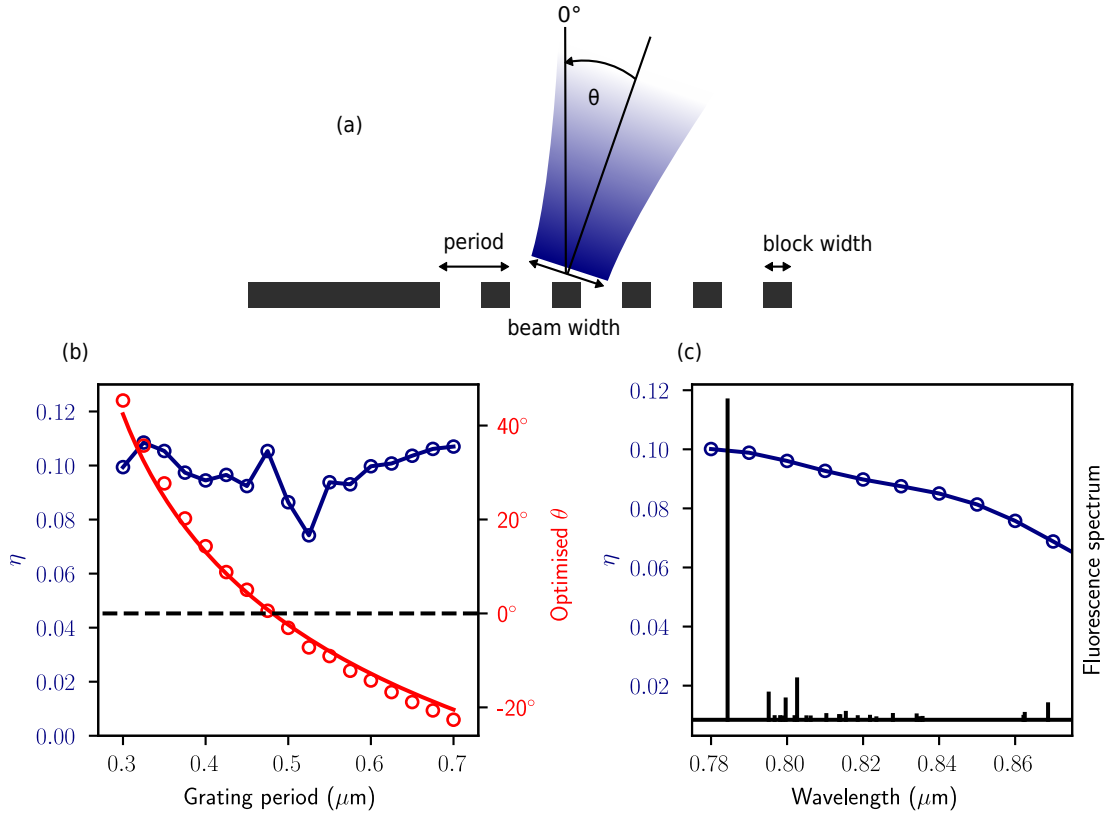


Figure 4.16: (a) Side view of the grating coupler geometry. The structural parameters are the grating period Λ and fill factor = (block width)/ Λ . (b) Coupling efficiency to a Gaussian beam with a waist of 350 nm as a function of grating period. The waveguide is 400 nm wide and 200 nm tall while the fill factor is fixed at 0.4. The angle and position of the beam are optimised for each grating period. We also plot the Bragg law (Eq. 4.48) as the solid red line. (c) Coupling efficiency of a grating with $\Lambda = 0.6 \mu\text{m}$ to a beam with angle $\theta = -14^\circ$ as a function of source wavelength. This is overlaid with the normalised fluorescence spectrum of DBT in anthracene.

function of grating period. We see that the efficiency is somewhat constant at $\sim 10\%$ except with vertical coupling, for which we can expect significant back scattering [190]. The optimised angle obeys a simple Bragg law

$$n_{\text{SiO}_2} \sin(-\theta) = n_{\text{eff}} - \frac{\lambda}{\Lambda}, \quad (4.48)$$

where n_{eff} is the effective index of the guided mode (given by Fig. 4.3) and Λ is the grating period [191]. Fig. 4.16 shows the broadband nature of the grating over the

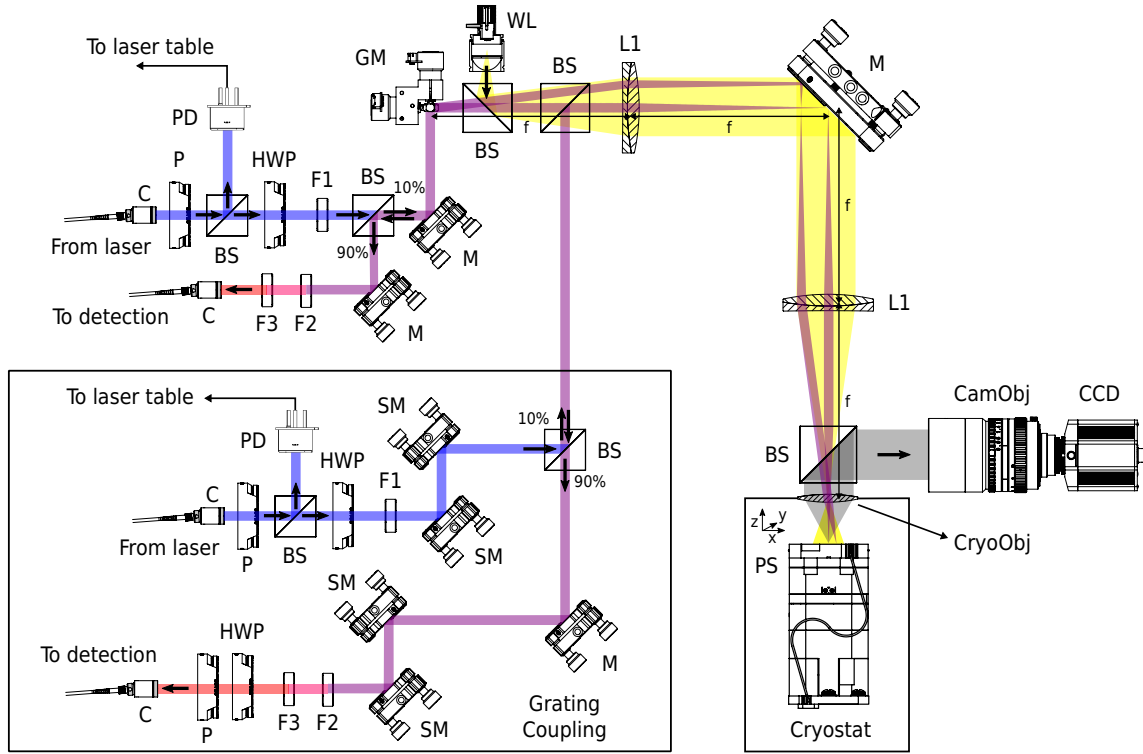


Figure 4.17: Sketch of the fluorescence microscopy set-up with grating arms. BS: Beam Splitter, C: Collimator, CamObj: Camera Objective, Cryo: Cryostat, CryoObj: Cryo objective lens, F1: Short-pass Filter, F2 & F3: Long-pass Filters, FBS: Fibre Beam Splitter, FDL: Fixed Delay Line, GM: Galvo Mirror, HWP: Half Wave Plate, L1: Achromatic Doublet Lens, M: Mirror, P: Polariser, PD: Photo-Diode, PS: XYZ Position stage, SM: Steering Mirror, SPAD: Single Photon Avalanche Diode, WL: White Light.

fluorescence spectrum of DBT in anthracene as measured by Trebbia *et al.* [136]. Here, the angle is not re-optimised for different wavelengths as we are interested in the coupling efficiency of a fixed system optimised for the $S_{1,0} \rightarrow S_{0,0}$ transition.

In the confocal microscope set-up, we added two paths for excitation and collection from grating couplers (see Fig. 4.17). The two grating arms combine on a 90/10 beam splitter and are sent through the 4-f lens system. To vary the position and angle of the paths with respect to the gratings, we use scanning mirrors to change the angle and position of the beam relative to the cryostat objective. The excitation and collection paths are both coupled to single-mode fibres with identical collimators in order to have symmetric in/out coupling. The diameter of the beams is 1.5 mm after collimation

which gives us a beam waist of approximately 350 nm at the focal point of the cryostat objective.

4.4.2 Device Fabrication

The full chip fabrication starts with the patterning of the silicon nitride waveguides. Optimistically, the first batch had waveguide dimensions optimised for smaller gap widths. We therefore began with silicon nitride (200 nm) on silicon oxide ($2\text{ }\mu\text{m}$) on silicon (0.38 mm) wafers. The patterning was done by collaborators at the University of Münster using a negative e-beam resist and reactive ion-etching¹. We over-etched the silicon nitride by 150 nm so that the middle of the waveguide sits 250 nm away from the bottom surface. Again, this is because we want the position of maximum coupling to be away from any interfaces. The waveguides on the chip had a width of 400 nm and varying gap widths from no gap to 400 nm. Fig. 4.18(a) shows a patterned waveguide with a 400 nm gap before etching. We also varied the period of the gratings (from 500 nm to 650 nm) to achieve acute scattering angles while avoiding the coupling dip at $\theta = 0^\circ$.

Next, we patterned the micro-fluidic channels as described in Sec. 4.3.2 and the channel width was varied from 500 nm to $2\text{ }\mu\text{m}$ for every gap width. To overlay the tapered channels on top of the waveguide gaps, we used local markers etched in the silicon nitride layer. The markers are clearly visible in Fig. 4.18(d), which shows an optical microscope image of the sample after SiO_2 deposition. The alignment error is estimated as approximately $\pm 35\text{ nm}$ by the e-beam manufacturer. By using the melt-growth set-up, we then filled the channels with anthracene as explained in Sec. 4.3.1. We note that baking the sample at 400°C allows us to remove the anthracene from the channels without affecting the structures. Therefore, if the melt-growth is not satisfactory, the process can be repeated again using the same chip.

¹Contact Prof. Wolfram Pernice for full process details (wolfram.pernice@uni-muenster.de).

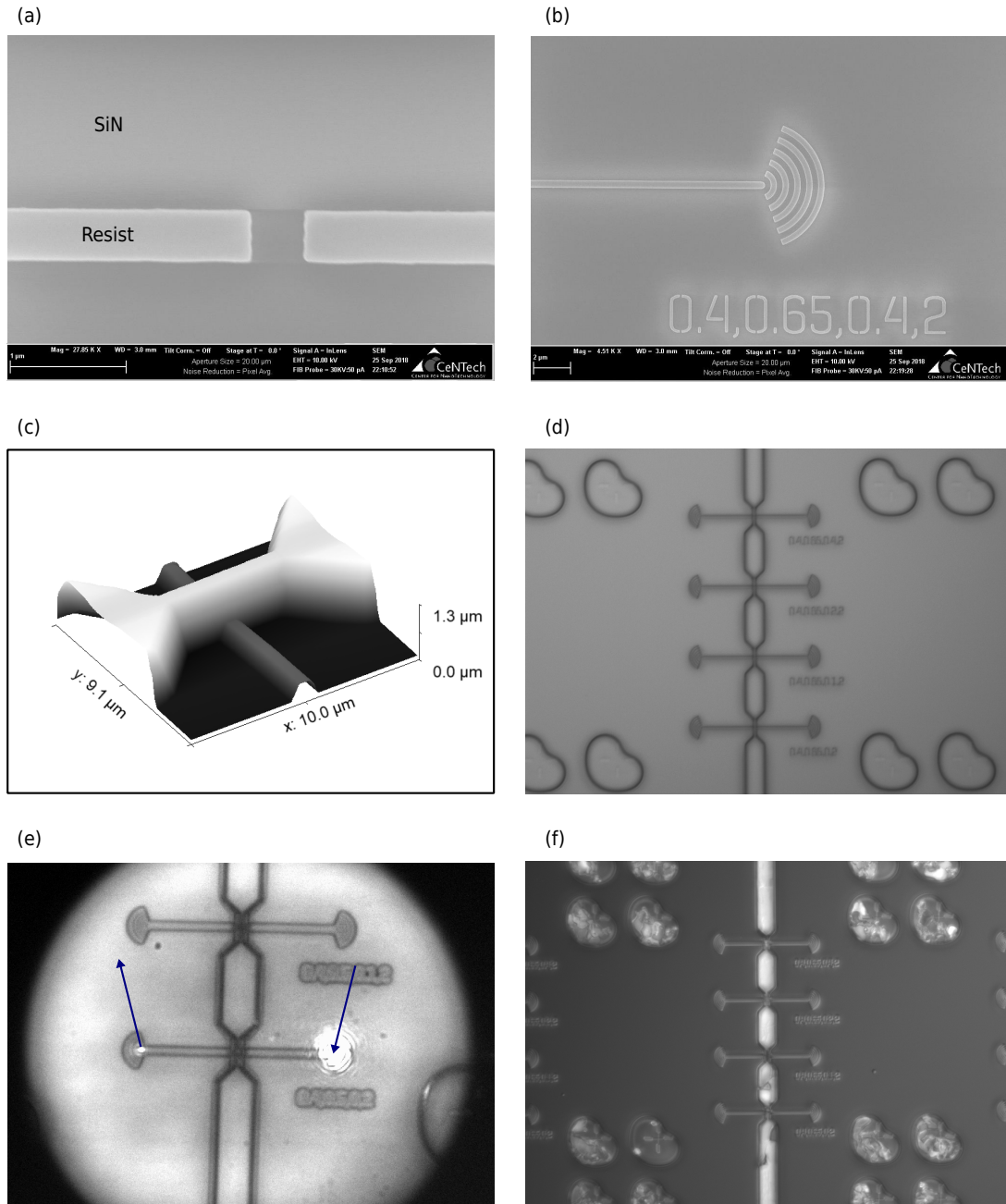


Figure 4.18: (a)&(b) Scanning electron microscope images of a 400 nm waveguide gap and grating coupler patterned in the resist. (c) Atomic force microscopy of the sacrificial resist layer overlaid on top of a waveguide gap. (d) Optical microscopy of an empty micro-fluidic channel spanning multiple waveguides. For reference, the length of the waveguides is 50 μ m. (e) White light image showing the coupling of light to a device in the cryostat set-up. (f) Optical microscope image of a filled channel with cross-polarised light illumination.

4.4.3 Resonant Spectroscopy

Finding a Coupled Molecule

By using a 10^{-4} mol/mol doped anthracene powder, we prepared a micro-fluidic waveguide chip which was put inside the cryogenic set-up. The concentration is about a hundred times higher than for the channel tests so that we can expect to have a few hundred DBT molecules per $(100\text{ nm})^3$ of anthracene. Inside the gaps, the density of photostable molecules in the main site will only be a fraction of the doping density, which is why a high starting point is necessary. Again, the cryostat was only able to cool the sample plate to 4.2 K.

Once the cryostat had reached its base temperature, we characterised the devices according to the following procedure. First, we image the waveguides using the confocal microscope. This step allows us to centre the confocal collection on the gap of the waveguide being characterised. By using the steering mirrors, we then align the grating paths of the microscope to couple the pump light in and out of that waveguide (Fig. 4.18(e)). Pumping through the waveguide, we record both the fluorescence spectrum of the gap as collected by the confocal microscope and the transmission through the waveguide. This is done at low power so that $S \sim 1$ and we scan the laser wavelength across the inhomogeneous broadening. For each peak in the fluorescence spectrum, we then do a slower scan across the resonant frequency at an even lower power. Each peak does not necessarily correspond to a molecule well coupled to the waveguide. Some molecules which sit inside the channel, but above the waveguide, can still be excited by scattered pump light. To find a coupled molecule, we therefore look for a dip in the transmission spectrum as explained in Sec. 4.2.

On the first attempt (and only one so far), we had no success finding molecules which were well coupled to the waveguide in the 100 nm and 200 nm gaps. This could be because these structures confine the crystal to a volume which is too small for

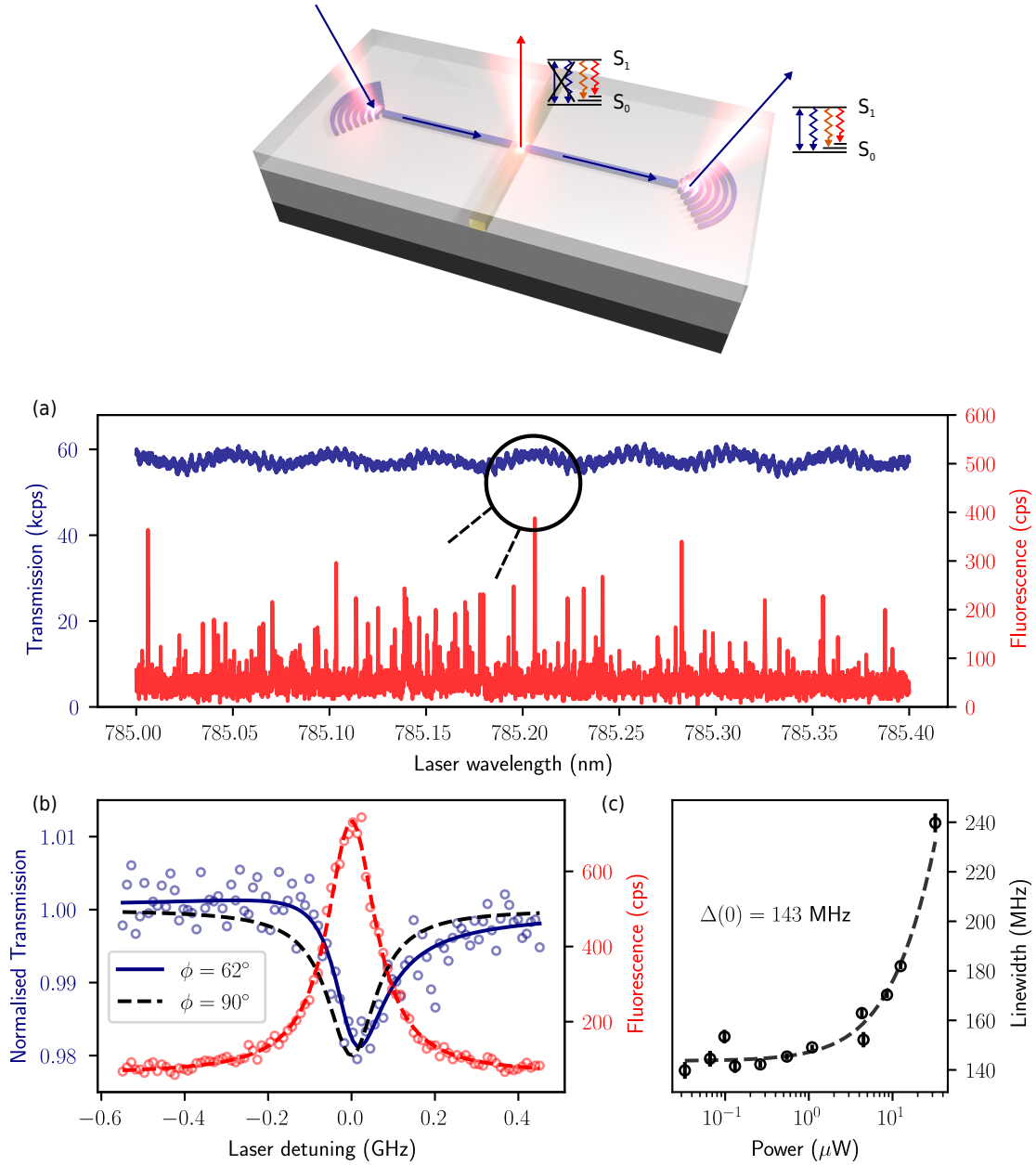


Figure 4.19: (a) Fluorescence excitation spectrum of a 400 nm gap with a 1 μm wide channel (red) and transmission through the waveguide (blue) with a weak pump laser. (b) Close-up on one of the resonances which shows a dip in transmission due the coupling of the molecule to the waveguide. Fit to Eq. 4.40 assuming $\Gamma_1 \sim 33$ MHz and $\alpha = 0.33$ (blue) and Eq. 4.40 with the best fit parameters but setting $\phi = \pi/2$ for comparison (dashed black). (c) Power broadening with increasing pump power. The power is measured before the objective lens of the cryostat.

stable molecules to exist. In contrast, we had better results with the 400 nm gaps, as illustrated in Fig. 4.19 for a device with a channel width of $1\text{ }\mu\text{m}$. Fig. 4.19(b) shows the fluorescence and transmission spectra for the maximum extinction signal measured with this device. The low-power linewidth of the emitter is $143 \pm 1\text{ MHz}$ which indicates that the molecule is not lifetime-limited due to high cryostat temperatures. In addition, the molecule also experienced some spectral diffusion when illuminated on resonance for a few seconds. To measure the spectra, we therefore performed many fast scans which were then summed, instead of slow scans with long exposure times.

Fit to the Theoretical Model

We then investigated the shape of the transmission dip as a function of detuning. Firstly, we assumed that the detection efficiency of the red-shifted photons (including waveguide coupling, grating efficiency, propagation through the set-up and detection) is approximately equal to that of the $S_{1,0} \rightarrow S_{0,0}$ photons, meaning that we should use Eq. 4.42 instead of Eq. 4.40. For small values of β_{eff} , however, there is only a small difference between the two models. Next, we extracted the linewidth $\gamma = 2\Gamma_2\sqrt{1+S}$ and the resonant wavelength of the emitter from the fluorescence spectrum. In addition, Γ_2 was estimated from the low-power linewidth of the emitter. Lastly, Γ_1 and α are the only remaining parameters that we need to fit the extinction data. Unfortunately, the spectral diffusion prevented us from acquiring both a g^2 and a spectrum of the emission. So we used the values of $\Gamma_1 \sim 33\text{ MHz}$ and $\alpha = 0.33$, which are the average values in bulk [136, 144]. With all these assumptions, a fit to the transmission model gives us $\phi = 62 \pm 3^\circ$ and $\beta_{\text{eff}}/|t| = 0.129 \pm 0.009$.

We then measured the transmission through the waveguide by comparison to the transmission we get for an identical device which has no gap. Assuming that the optimised coupling for both sets of gratings is the same, the only additional source of loss is caused by scattering from the gap. In this way, we get $|t|^2 \simeq 0.33$. This is much

lower than the value we get from FDTD simulations $|t_{\text{sim}}|^2 = 0.64$, which suggests that $|t|^2$ should only be treated as an approximate value. Here, a statistically significant measure of transmission is required for more accurate estimates. Nevertheless, we can use this preliminary experimental result to deduce $\beta_{\text{eff}} \sim 7\%$. This conclusion is encouraging as the coupling efficiency is comparable to that measured by Türschmann *et al.* for evanescent coupling [28]. However, further experimentation is still necessary to validate this result.

4.4.4 Summary and Outlook

In this chapter, we have looked at the coupling single molecules to single-mode waveguides. I have proposed a new design based on the integration of photonic structures with micro-fluidic channels, for localised anthracene crystallisation. To account for the unusual gap geometry, I have developed resonant spectroscopy theory to extract the coupling efficiency from extinction measurements. While the fabrication of the devices was successful, the characterisation is still a work in progress. We are mainly limited by two factors: the phononic broadening of the $S_{0,0} \leftrightarrow S_{1,0}$ line and the photostability of the molecules inside the gaps. We are currently working on improving the cryostat performance and sample mounting to mitigate the first problem. The second factor is an inherent issue with growing doped organic crystals in confined geometries. Future work should focus on gathering more data with different melt-growth conditions to see if the method can yield photostable molecules in smaller gaps. Nevertheless, we have observed the in-waveguide extinction of a weak pump light by the coherent scattering of a single molecule. This is an encouraging start for the optimisation of the structure.

Looking forward, there are clear steps which can be taken to improve the coupling efficiency. Knowing that smaller gaps are unlikely to yield stable molecules, we can increase the waveguide dimensions to optimised the geometry for larger gaps (see Fig. 4.5). Better still, we could use a waveguide material with a higher refractive index. Titanium

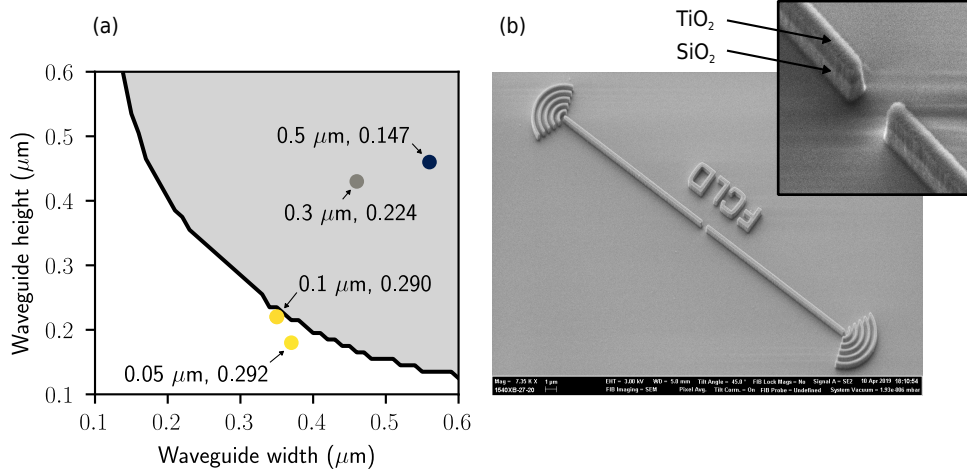


Figure 4.20: Preliminary results for TiO_2 waveguides. (a) Optimised waveguide dimensions as a function of gap size. Points are labelled as (gap width, β). (b) Scanning electron microscope image of an over-etched TiO_2 waveguide.

dioxide is an obvious choice as it is transparent at 785 nm with a refractive index of 2.35 [192]. Fig. 4.20(a) shows FDTD results for TiO_2 waveguides and we see that coupling efficiencies of more than 20 % are possible with gap sizes of 300 nm. Fig. 4.20(a) shows a TiO_2 waveguide fabricated at Imperial College. Another small improvement comes with a more pronounced over-etching of the structures. Compared to SiN waveguides, we are now aiming for a 300 nm over-etch to keep the interface even further away from the position of maximum coupling. This should hopefully help with photostability.

Even with these improvements, we only expect the maximum achievable efficiency of $\alpha\beta \sim 0.33 \times 0.2 \sim 6\%$, which is very far from being a good single-photon source. In essence, this is because the ridge-waveguide structure only helps to collect otherwise scattered photons and does not strongly modify the local density-of-states at the position of the emitter. Instead, we can use optical cavities (as discussed in the next chapter) or photonic-crystal waveguides to significantly increase both α and β . So the question is: can we use the microfluidic-channel/waveguide geometry as a basis for a high-Q cavity or low- v_g guide? On first inspection, it seems unlikely. Of course, nano-beam cavities have been very successful for other emitters [139] but these are fragile

cavity modes which suffer from even the smallest scattering centres [193, 194]. The addition of a micro-fluidic channel on top of a nano-beam cavity therefore does not seem like a viable path forward.

One can also think about using anthracene as the lower index part of the cavity structure. For example, this has already been done with some success for ring resonators [30]. Maybe a structure consisting of dielectric rods [40, 195] embedded in anthracene could be developed. Another approach might be a slotted photonic crystal waveguide [196] with its gap filled with anthracene. However, the homogeneous crystallisation of anthracene around complex structures would have to be tested. Another unknown would be the photostability of the DBT molecules inside the confined regions where the cavity/waveguide modes exist. In light of these issues, I have decided to take a different approach which is described in the next chapter.

5 Coupling to Vertical Cavities

As described throughout this thesis, DBT molecules in bulk anthracene are limited single-photon sources due to two factors: a small collection efficiency β and a non-unity branching ratio α for the zero-phonon line of the $S_{1,0} \rightarrow S_{0,0}$ transition. The properties of the emitter, however, do not fundamentally constrain the quality of a single-photon source built using the emitter. In this chapter, I will first describe an engineering solution to the branching ratio problem and then show how the collection efficiency issue is also solved in the process.

To increase the branching ratio, the rate of emission $\Gamma_{S_{1,0} \rightarrow S_{0,0}}$ must be sped up compared to all other transition rates. This can be done by placing the molecules in a photonic environment so that the local density-of-states at the $S_{1,0} \rightarrow S_{0,0}$ transition frequency is much larger than at any other transition frequencies (see Sec. 2.1.3). Optical cavities are a well-known example of a structure with a local density-of-states spectrum which is both narrow-band and intense. Here, I present a vertical-emitting cavity which is compatible with the melt-growth method for preparing DBT doped anthracene crystals.

5.1 Radiative Decay of Molecules in Cavities

5.1.1 Cavity Modes

In Sec. 1.1.2, I stated that no mode can be localised to a finite region of space and therefore that photons are never created in a single mode. But optical cavities aim to confine light in a standing wave pattern between mirrors. Let us recall that modes are defined as solutions to the wave equation Eq. 1.4 with suitable boundary conditions. In

the last chapter, we applied periodic boundary conditions to define the guided modes of an infinite waveguide structure. For dielectric cavities, it is best to use the Silver-Müller radiation condition [46] and pick the physical solution which dictates that the scattered field coming from the cavity must be propagating outwards. This choice of boundary conditions transforms Eq. 1.4 into a non-Hermitian eigenvalue problem, and we find a discrete spectrum of quasi-normal modes with complex frequencies $\tilde{\omega} = \omega + i\kappa/2$, where κ is the decay rate of a photon out of the cavity mode.

The quasi-normal modes are fundamentally different from the modes we encountered in the last chapter and we cannot compute their contribution to the local density-of-states using Eq. 1.44. Instead, the Green's function formalism can be used to write the LDOS for a single cavity mode as [25, 46]

$$\rho_{\text{cavity}}(\mathbf{r}, \mathbf{e}, \omega) = \frac{2}{\pi} \frac{\omega^2 \kappa}{(\omega_c^2 - \omega^2)^2 + \omega^2 \kappa^2} \frac{f(\mathbf{r})}{\varepsilon(\mathbf{r}) V_{\text{mode}}} \cos^2(\theta) , \quad (5.1)$$

where ω_c is the real part of the mode frequency and θ is the angle between the electric field of the mode and the dipole. V_{mode} is the cavity mode volume and satisfies

$$V_{\text{mode}} \simeq \frac{\int d\mathbf{r} \, \varepsilon(\mathbf{r}) |\mathbf{u}_c(\mathbf{r})|^2}{\max \left(\varepsilon(\mathbf{r}) |\mathbf{u}_c(\mathbf{r})|^2 \right)} , \quad (5.2)$$

where $\mathbf{u}_c(\mathbf{r})$ is the cavity mode solved using the Hermitian eigenvalue problem with fixed or periodic boundary conditions, and spatial cutoffs are applied to the integration volume [46]. Similarly to Eq. 4.15,

$$f(\mathbf{r}) = \frac{\varepsilon(\mathbf{r}) |\mathbf{u}_c(\mathbf{r})|^2}{\max \left(\varepsilon(\mathbf{r}) |\mathbf{u}_c(\mathbf{r})|^2 \right)} , \quad (5.3)$$

which quantifies the mismatch between the position of the emitter and the mode field maximum.

The well-known cavity Purcell factor is then computed by dividing Eq. 5.1 by ρ_{hom}

(Eq. 1.49). At zero detuning between the emitter and the cavity, we have

$$F_P^{\text{cav}} \equiv \frac{\Gamma_{\text{cavity}}}{\Gamma_{\text{hom}}} = \frac{\rho_{\text{cavity}}}{\rho_{\text{hom}}} = \frac{3}{4\pi^2} \frac{Q}{V_{\text{eff}}} f(\mathbf{r}) \cos^2(\theta) , \quad (5.4)$$

where $V_{\text{eff}} = V_{\text{mode}}/(\lambda/n)^3$ with n the refractive index at the position of the emitter and $Q = \omega_c/\kappa$ is the cavity quality factor.

5.1.2 The Jaynes-Cummings Model

The Wigner-Weisskopf theory of spontaneous emission considers a two-level system coupled to a reservoir of continuous modes (Sec. 1.3.2). When the emitter is also coupled to a single cavity mode, we can extend the theory to account for the full dynamics of both the emitter and the quasi-normal mode. This is captured by the dissipative Jaynes-Cummings model.

The Master Equation

Let us model DBT molecules as two-level systems consisting of the $S_{0,0}$ and $S_{1,0}$ states with an energy difference of $\hbar\omega_0$, with the red-shifted fluorescence treated as phenomenological decay paths. The spontaneous emission is split between resonant and red-shifted fluorescence, with rates equal to $\Gamma_{\text{res}} = \alpha_{\text{FC}}\Gamma_1$ and $\Gamma_{\text{red}} = (1 - \alpha_{\text{FC}})\Gamma_1$ respectively (see Sec. 2.1.3). For DBT molecules in bulk anthracene, the rates are given by $\Gamma_{\text{res}}^{\text{hom}} = \alpha_{\text{FC}}^{\text{hom}}\Gamma_1^{\text{hom}}$ and $\Gamma_{\text{red}}^{\text{hom}} = (1 - \alpha_{\text{FC}}^{\text{hom}})\Gamma_1^{\text{hom}}$, where $\alpha_{\text{FC}}^{\text{hom}} \simeq 0.33$ and $\Gamma_1^{\text{hom}}/(2\pi) \simeq 35$ MHz. We start by considering the cavity/molecule system in isolation. By applying the rotating-wave approximation, the Hamiltonian is given by

$$\hat{\mathcal{H}}_{\text{JC}} = \hbar\omega_0\hat{\sigma}^+\hat{\sigma}^- + \hbar\omega_c\hat{a}_c^\dagger\hat{a}_c + \hbar(g(\mathbf{r}_0)\hat{a}_c\hat{\sigma}^+ + g^*(\mathbf{r}_0)\hat{a}_c^\dagger\hat{\sigma}^-) , \quad (5.5)$$

which corresponds to Eq. 1.34 for the case where the molecule is interacting with a single mode. By using the definition of the coupling constant from Eq. 1.36 and Eq. 1.49, we

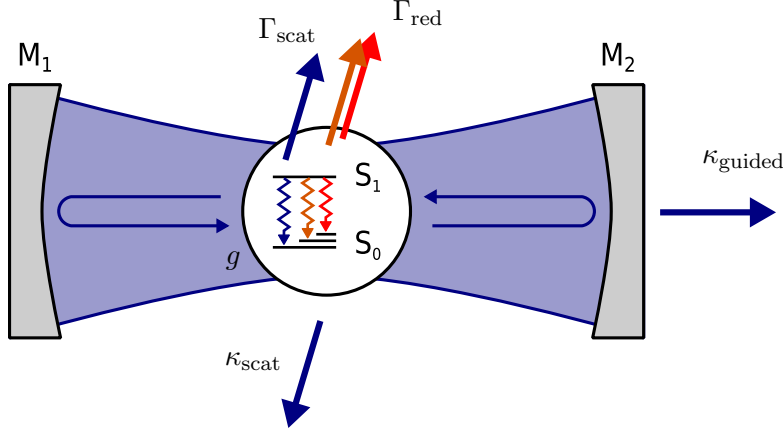


Figure 5.1: Sketch of the DBT/cavity system. The cavity consists of a perfectly reflective mirror M_1 and a lower reflectivity mirror M_2 . Its mode is resonant with the $S_{0,0} \leftrightarrow S_{1,0}$ transition which causes light-matter interaction with a coupling strength g . The molecule can also scatter light into the environment at a rate Γ_{scat} and emit red-shifted fluorescence at a rate Γ_{red} . Finally, photons decay out of the cavity because of scattering and leakage from the M_2 mirror, with rates κ_{scat} and κ_{guided} respectively.

have

$$|g(\mathbf{r}_0)|^2 = \frac{3}{16\pi^2} \frac{\alpha_{\text{FC}}^{\text{hom}} \Gamma_1^{\text{hom}} \omega_0}{V_{\text{eff}}} f(\mathbf{r}_0) \cos^2(\theta) . \quad (5.6)$$

In the interaction picture, Eq. 5.5 is written as

$$\hat{\mathcal{H}}_{\text{JC}}^{\text{int}}(t) = \hbar(g(\mathbf{r}_0)\hat{a}_c\hat{\sigma}^+ \exp(i\Delta_e t) + g^*(\mathbf{r}_0)\hat{a}_c^\dagger \hat{\sigma}^- \exp(-i\Delta_e t)) , \quad (5.7)$$

where $\Delta_e = \omega_0 - \omega_c$ is the emitter-cavity detuning. In the Jaynes-Cummings picture, the cavity losses can be modelled by introducing an artificial coupling of the cavity mode to a memoryless reservoir of radiation modes [197]. The master equation for the cavity/molecule system is then given by

$$\frac{d}{dt}\hat{\rho}_{\text{total}} = -\frac{i}{\hbar} [\hat{\mathcal{H}}_{\text{JC}}^{\text{int}}, \hat{\rho}_{\text{total}}] + \frac{\kappa}{2} (2\hat{a}_c\hat{\rho}_{\text{total}}\hat{a}_c^\dagger - \{\hat{a}_c^\dagger\hat{a}_c, \hat{\rho}_{\text{total}}\}) , \quad (5.8)$$

with $[\cdot, \cdot]$ and $\{\cdot, \cdot\}$ corresponding to the commutator and anticommutator respectively. In practice, it is challenging to engineer the dielectric environment such that

only one quasi-normal mode exists. The emitter therefore couples to scattering modes with a decay rate Γ_{scat} for resonance fluorescence and Γ_{red} for red-shifted photons. Pure dephasing of the emitter can also be included in this model (see Eq. 2.12) and we get the full master equation [25]

$$\begin{aligned} \frac{d}{dt}\hat{\rho}_{\text{total}} = & -\frac{i}{\hbar} \left[\hat{\mathcal{H}}_{\text{JC}}^{\text{int}}, \hat{\rho}_{\text{total}} \right] + \frac{\kappa}{2} (2\hat{a}_c\hat{\rho}_{\text{total}}\hat{a}_c^\dagger - \{\hat{a}_c^\dagger\hat{a}_c, \hat{\rho}_{\text{total}}\}) \\ & + \frac{\Gamma_{\text{scat}} + \Gamma_{\text{red}}}{2} (2\hat{\sigma}^-\hat{\rho}_{\text{total}}\hat{\sigma}^+ - \{\hat{\sigma}^+\hat{\sigma}^-, \hat{\rho}_{\text{total}}\}) + \frac{\Gamma_2^*}{2} (\hat{\sigma}_z\hat{\rho}_{\text{total}}\hat{\sigma}_z - \hat{\rho}_{\text{total}}) \end{aligned} \quad (5.9)$$

Now, let us assume that the system only has one excitation or none at all. In this case, we only have to keep track of the states $|1\rangle = |e\rangle \otimes |0_c\rangle$, $|2\rangle = |g\rangle \otimes |1_c\rangle$ and $|3\rangle = |g\rangle \otimes |0_c\rangle$. Furthermore, we choose g to be real by fixing the absolute phase of the cavity mode. This gives us the following equations of motion

$$\frac{d\rho_{11}}{dt} = -ig(\tilde{\rho}_{21} - \tilde{\rho}_{12}) - (\Gamma_{\text{scat}} + \Gamma_{\text{red}})\rho_{11} \ , \quad (5.10)$$

$$\frac{d\rho_{22}}{dt} = ig(\tilde{\rho}_{21} - \tilde{\rho}_{12}) - \kappa\rho_{22} \ , \quad (5.11)$$

$$\frac{d\tilde{\rho}_{12}}{dt} = ig(\rho_{11} - \rho_{22}) - \left(i\Delta_e + \frac{\Gamma_{\text{scat}} + \Gamma_{\text{red}} + \kappa}{2} + \Gamma_2^* \right) \tilde{\rho}_{12} \ , \quad (5.12)$$

$$\frac{d\tilde{\rho}_{13}}{dt} = -ig\tilde{\rho}_{23} - \left(\frac{i\Delta_e + \Gamma_{\text{scat}} + \Gamma_{\text{red}}}{2} + \Gamma_2^* \right) \tilde{\rho}_{13} \ , \quad (5.13)$$

$$\frac{d\tilde{\rho}_{23}}{dt} = -ig\tilde{\rho}_{13} - \frac{\kappa - i\Delta_e}{2} \tilde{\rho}_{23} \ , \quad (5.14)$$

with $\tilde{\rho}_{12} = \rho_{12} \exp(-i\Delta_e t)$, $\tilde{\rho}_{23} = \rho_{23} \exp(i\Delta_e t/2)$ and $\tilde{\rho}_{13} = \rho_{13} \exp(i\Delta_e t/2)$.

Weak Coupling

For zero detuning and no pure dephasing, we can write analytical solutions to the first three equations when the emitter is initiated in the $|1\rangle$ state at $t = 0$ [25]. In the weak-coupling regime where $g \ll |\Gamma_{\text{scat}} + \Gamma_{\text{red}} - \kappa|/4$ and if the cavity decay rate is

much larger than the emitter scattering, $\Gamma_{\text{scat}} + \Gamma_{\text{red}} \ll \kappa$, we have

$$\begin{aligned} \rho_{11}(t) &\simeq \exp \left(- \left(\Gamma_{\text{scat}} + \Gamma_{\text{red}} + \frac{4g^2}{\kappa} \right) t \right) \\ &= \exp \left(- \left(\Gamma_{\text{scat}} + \Gamma_{\text{red}} + F_P^{\text{cav}} \alpha_{\text{FC}}^{\text{hom}} \Gamma_1^{\text{hom}} \right) t \right) . \end{aligned} \quad (5.15)$$

Eq. 5.15 leads to the simple interpretation that the emitter decays exponentially by three paths, which correspond to resonant scattering, non-resonant fluorescence and emission into the cavity mode. The fraction of photons emitted into the cavity is then

$$\beta_c = F_P^{\text{cav}} \alpha_{\text{FC}}^{\text{hom}} \Gamma_1^{\text{hom}} \int_0^\infty dt \rho_{11}(t) = \frac{F_P^{\text{cav}}}{F_P^{\text{cav}} + s_{\text{scat}} / \alpha_{\text{FC}}^{\text{hom}}} , \quad (5.16)$$

where $s_{\text{scat}} = (\Gamma_{\text{scat}} + \Gamma_{\text{red}}) / \Gamma_1^{\text{hom}}$ is the scattering suppression factor. We can also compute the modified branching ratio of the $S_{1,0} \rightarrow S_{0,0}$ transition which is given by

$$\alpha_{\text{FC}} = \frac{F_P^{\text{cav}} + \Gamma_{\text{scat}} / (\alpha_{\text{FC}}^{\text{hom}} \Gamma_1^{\text{hom}})}{F_P^{\text{cav}} + s_{\text{scat}} / \alpha_{\text{FC}}^{\text{hom}}} . \quad (5.17)$$

Typically, cavity structures do not modify the coupling to the rest of the environment and we can assume $s_{\text{scat}} \simeq 1$. By using the bulk value for $\alpha_{\text{FC}}^{\text{hom}}$, we finally get

$$\beta_c \simeq \frac{F_P^{\text{cav}}}{F_P^{\text{cav}} + 3} , \quad (5.18)$$

$$\alpha_{\text{FC}} \simeq \frac{F_P^{\text{cav}} + 1}{F_P^{\text{cav}} + 3} . \quad (5.19)$$

By adding a cavity mode to the dielectric environment of the molecule, we are therefore able to increase the branching ratio of our chosen transition. We see that both β_c and α_{FC} tend to 1 for large values of F_P^{cav} , which can only be achieved with cavities with small mode volumes and high quality factors.

5.1.3 How Good Must the Cavity Be?

Extraction Efficiency

For single-photon sources based on cavities, the coupling to the cavity mode β_c alone is not a good measure of performance. Ultimately, we also need to out-couple the photon from the cavity to a single guided-mode. In light of this, we split the decay rate out of the cavity in two terms

$$\kappa = \kappa_{\text{scat}} + \kappa_{\text{guided}} , \quad (5.20)$$

corresponding to the decay into non-guided and guided modes respectively. Furthermore, material absorption also contributes to photon loss and it is well described in the quasi-normal mode formalism by adding the absorption rate κ_{absorb} to the total decay rate [46, 198]. In terms of quality factors, we therefore have

$$\frac{1}{Q} = \frac{1}{Q_{\text{guided}}} + \frac{1}{Q_{\text{scat}}} + \frac{1}{Q_{\text{absorb}}} = \frac{1}{Q_{\text{guided}}} + \frac{1}{Q_{\text{loss}}} . \quad (5.21)$$

Hence, the probability that a photon is emitted into the outgoing guided modes is given by

$$\beta = \left(1 - \frac{Q}{Q_{\text{loss}}}\right) \frac{\frac{3}{4\pi^2} Q / \tilde{V}_{\text{eff}}}{\frac{3}{4\pi^2} Q / \tilde{V}_{\text{eff}} + s_{\text{scat}} / \alpha_{\text{FC}}^{\text{hom}}} , \quad (5.22)$$

where we define $\tilde{V}_{\text{eff}} = V_{\text{eff}} / (f(\mathbf{r}) \cos^2(\theta))$. Eq. 5.22 tells us that, in addition to increasing the branching ratio, a good cavity can also enhance the directionality and collection efficiency of our source.

Full Solution

So far, our derivation is restricted to the weak-coupling regime and when κ is much larger than $\Gamma_{\text{scat}} + \Gamma_{\text{red}}$. More generally, we can solve the master equation to get the full time dependence of ρ_{22} when the system is initiated in the $|1\rangle$ state at $t = 0$. For

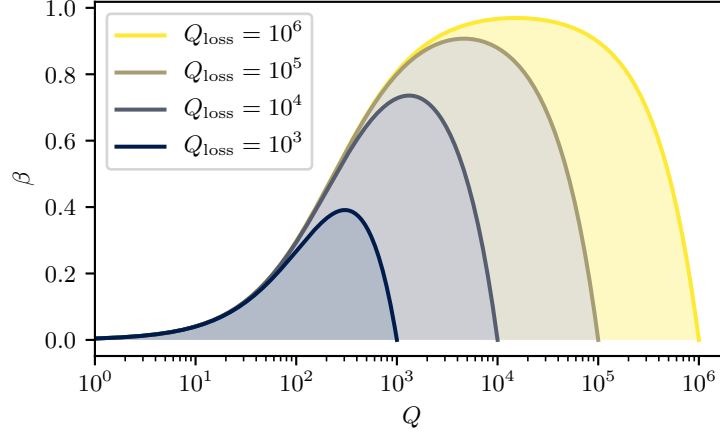


Figure 5.2: Collection efficiency as a function of quality factor for different cavity loss rates. The mode volume is set to $7(\lambda/n)^3$ and $s_{\text{scat}}/\alpha_{\text{FC}}^{\text{hom}} = 3$.

zero detuning and no pure dephasing, we get

$$\rho_{22}(t) = \frac{2g^2}{\Omega_R^2} \exp\left(-\frac{\Gamma_{\text{scat}} + \Gamma_{\text{red}} + \kappa}{2}t\right) (\cosh(\Omega_R t) - 1), \quad (5.23)$$

with

$$\Omega_R = \sqrt{\frac{(\Gamma_{\text{scat}} + \Gamma_{\text{red}} - \kappa)^2}{4} - 4g^2}, \quad (5.24)$$

and κ now also includes the absorption losses. The exact extraction efficiency is hence given by

$$\beta = \kappa_{\text{guided}} \int_0^\infty dt \rho_{22}(t) \quad (5.25)$$

$$= \frac{\kappa_{\text{guided}}}{\Gamma_{\text{scat}} + \Gamma_{\text{red}} + \kappa} \frac{F_P^{\text{cav}}}{F_P^{\text{cav}} + s_{\text{scat}}/\alpha_{\text{FC}}^{\text{hom}}} \quad (5.26)$$

$$= \left(1 - \frac{Q}{\tilde{Q}_{\text{loss}}}\right) \frac{F_P^{\text{cav}}}{F_P^{\text{cav}} + s_{\text{scat}}/\alpha_{\text{FC}}^{\text{hom}}}, \quad (5.27)$$

with

$$\frac{1}{\tilde{Q}_{\text{loss}}} = \frac{1}{Q_{\text{loss}}} + \frac{\Gamma_{\text{scat}} + \Gamma_{\text{red}}}{\omega_c}, \quad (5.28)$$

and we recover a similar solution for β which is valid in all coupling regimes.

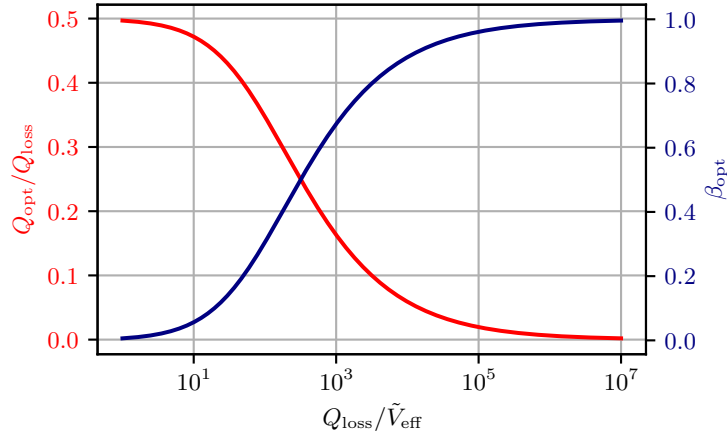


Figure 5.3: Optimum collection efficiency (blue) and fraction of the emission lost to cavity scattering (red) as a function of the figure-of-merit for cavity performance.

Quality Factor Optimisation

During fabrication, the mirror reflectivities can be set independently of each other to optimise the cavity structure. For single-photon generation, one of the mirrors should be perfectly reflective while the second one leaks into a single guided-mode. With real structures however, some scattering will occur even if both mirrors are perfectly reflective, and we can also expect some transmission losses from the highly reflective mirror. These factors all contribute to reducing Q_{loss} . As we can see in Fig. 5.2, there exists an optimum Q which maximises coupling efficiency for a given $\tilde{V}_{\text{eff}}$ and Q_{loss} . It is given by

$$Q_{\text{opt}} = \frac{4\pi^2}{3} \tilde{V}_{\text{eff}} \frac{s_{\text{scat}}}{\alpha_{\text{FC}}^{\text{hom}}} \left(\sqrt{\frac{3}{4\pi^2} \frac{Q_{\text{loss}}}{\tilde{V}_{\text{eff}}} \frac{\alpha_{\text{FC}}^{\text{hom}}}{s_{\text{scat}}} + 1} - 1 \right), \quad (5.29)$$

and the optimised coupling efficiency is

$$\beta_{\text{opt}} = 1 - 2 \frac{Q_{\text{opt}}}{Q_{\text{loss}}}. \quad (5.30)$$

The leaky mirror should therefore be such that its reflectivity gives us Q_{opt} . We can also ask ourselves what the minimum $Q_{\text{loss}}/\tilde{V}_{\text{eff}}$ should be in order to achieve a given

β_{opt} . This can be computed as

$$\left(\frac{Q_{\text{loss}}}{\tilde{V}_{\text{eff}}} \right)_{\text{min}} = \frac{16\pi^2}{3} \frac{s_{\text{scat}}}{\alpha_{\text{FC}}^{\text{hom}}} \frac{\beta_{\text{opt}}}{(\beta_{\text{opt}} - 1)^2} \simeq 16\pi^2 \frac{\beta_{\text{opt}}}{(\beta_{\text{opt}} - 1)^2} . \quad (5.31)$$

For example, if we require a single-photon source efficiency of at least 90%, $Q_{\text{loss}}/\tilde{V}_{\text{eff}}$ must be 1.4×10^4 or more. This illustrates the main design requirement for single-photon sources based on cavities and DBT molecules. It is not sufficient to achieve a high $Q/\tilde{V}_{\text{eff}}$ per se, instead, the important figure-of-merit for extraction efficiency is $Q_{\text{loss}}/\tilde{V}_{\text{eff}}$.

On a final note, the light coming out of the leaky mirror might not be perfectly mode-matched to the outgoing mode. In this case, the coupling efficiency is further reduced by the overlap integral of the two mode profiles which is given by

$$\eta_{\text{overlap}} = \frac{|\frac{1}{4} \int (\mathbf{E}_{\text{mode}} \times (\mathbf{H}_{\text{guided}}^{\text{b}})^* + (\mathbf{E}_{\text{guided}}^{\text{b}})^* \times \mathbf{H}_{\text{mode}}) \cdot d\mathbf{S}|^2}{\frac{1}{2} \int \Re(\mathbf{E}_{\text{mode}} \times (\mathbf{H}_{\text{mode}}^{\text{b}})^*) \cdot d\mathbf{S} \frac{1}{2} \int \Re(\mathbf{E}_{\text{guided}} \times (\mathbf{H}_{\text{guided}}^{\text{b}})^*) \cdot d\mathbf{S}} , \quad (5.32)$$

where S is the surface where the guided mode starts.

Caveat

So far, our discussion has excluded the phonon sideband of the $S_{1,0} \rightarrow S_{0,0}$ transition. However, the coupling of the molecule to phonons is unavoidable, even at cryogenic temperatures. This should be a very similar problem to that of the vibrational spectrum of DBT. The reason why we cannot simply replace $\alpha_{\text{FC}}^{\text{hom}}$ by $\alpha^{\text{hom}} = \alpha_{\text{FC}}^{\text{hom}} \alpha_{\text{DW}}^{\text{hom}}$ is the close proximity of the sideband with its zero-phonon line in frequency. The cavity may or may not resolve the two contributions, depending on the sharpness of its local density-of-states (Eq. 5.1). Worse still, some of the phonon sideband overlaps with the zero-phonon line. This problem has already been tackled for quantum dots, which has put bounds on the indistinguishability of cavity-assisted quantum-dot emission [110]. For DBT in anthracene, the situation is subtly different, as the coupling to the lattice

is also mediated by local phonons [156, 157]. This could lead to different bounds for the indistinguishability but I do not attempt to solve this problem here.

5.2 Gaussian Isophase Cavities

To engineer a high-performance single-photon source, we therefore need to find a cavity structure with a small mode volume and very low scattering losses. To make the most of the cavity, the maximum of the electric field must reside inside the anthracene medium which is doped with the DBT emitters. Additionally, the confinement of the anthracene crystal has to be minimised without compromising on mode volume. This is critical for the stability of the DBT molecules. Finally, unless every component of the photonic system can be integrated with high yield on a chip, the useful efficiency for an end-user is typically measured at the output of a single-mode fibre. To satisfy all these requirements, I have developed a vertical emitting geometry with anthracene as an active medium.

5.2.1 A Vertical Emitting Cavity

Gaussian Beams

In a homogeneous medium, the wave equation for harmonic modes (Eq. 1.4) is reduced to the Helmholtz equation

$$\nabla^2 \mathbf{u}_{k_m} + \varepsilon k_m^2 \mathbf{u}_{k_m} = 0 . \quad (5.33)$$

By using the paraxial approximation, which holds true when the mode is slowly varying in the direction of propagation, Eq. 5.33 is further simplified to [104]

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \mathbf{u}_{k_m} + 2i n k_m \frac{\partial \mathbf{u}_{k_m}}{\partial z} = 0 , \quad (5.34)$$

where z is the direction of propagation. The solutions to Eq. 5.34 can be written in terms of the Hermite-Gaussian functions which form a complete orthonormal set. Here, we are mostly interested in the fundamental solution which, using cylindrical coordinates, is given by [104]

$$\mathbf{u}_{\text{Gauss}}(r, z) = \frac{A}{\sqrt{1 + z^2/z_0^2}} \exp\left(-\frac{r^2}{w(z)^2}\right) \exp\left(ink_m\left(z + \frac{r^2}{2R(z)}\right)\right) \exp\left(-i\phi(z)\right) \hat{\mathbf{x}}, \quad (5.35)$$

with a spot size

$$w(z) = w_0 \sqrt{1 + \frac{z^2}{z_0^2}}, \quad (5.36)$$

radius of curvature

$$R(z) = z \left(1 + \frac{z_0^2}{z^2}\right), \quad (5.37)$$

Gouy phase

$$\phi(z) = \arctan\left(\frac{z}{z_0}\right), \quad (5.38)$$

and where the Rayleigh range is $z_0 = w_0^2 nk_m/2$. A is a normalisation constant and $\mathbf{x}$ is the polarisation axis.

Isophase Surfaces

To create a low-loss cavity from a Gaussian mode, we must arrange two highly reflective mirrors such that the field profile is unchanged after one round trip of the cavity. This imposes tight restrictions on the surface profile of the mirrors and on their separation, because the phase should only accumulate an integer number of 2π per round trip. For our geometry, we choose this integer to be equal to 2 for reasons that will become clear later.

Let us start by propagating a fundamental Gaussian beam from a planar reflecting surface positioned at $z = 0 \mu\text{m}$. On axis, the mode acquires a phase 2π after a

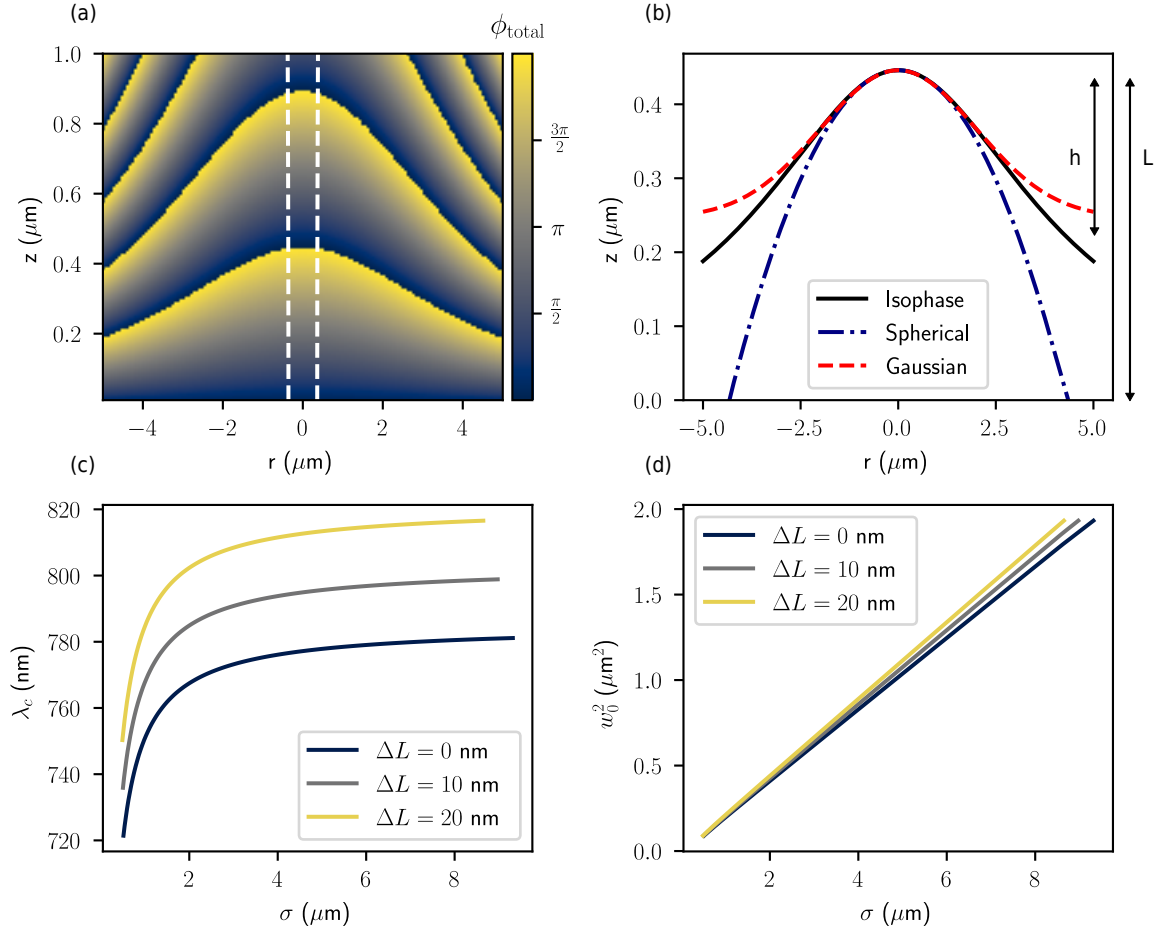


Figure 5.4: (a) Phase of a Gaussian beam propagating in anthracene and focused at $z = 0 \mu\text{m}$ with a waist $w_0 = 0.65 \mu\text{m}$. The mode has a free space wavelength of 785 nm. The dashed white lines represent the $1/e$ electric field amplitude fall-off. (b) 2π isophase surface of the same beam with its spherical and Gaussian approximations. The spherical line has a radius-of-curvature equal to that of the isophase on-axis. For the Gaussian profile, we perform a weighted fit to the isophase line to determine σ . The height of the Gaussian is set at $h = 200 \text{ nm}$. (c) Free space wavelength of the mode vs fitted σ for a range of waists and different cavity lengths $L = \lambda_c/n_{\text{ac}} + \Delta L$. (d) Linear dependence of the fitted σ with the square of the mode waist.

propagation distance $L_{2\pi}$ which satisfies

$$L_{2\pi} = \frac{\lambda_c}{n_{ac}} \left(1 + \frac{\phi(L_{2\pi})}{2\pi} \right), \quad (5.39)$$

where n_{ac} is the refractive index of anthracene and $\lambda_c = 2\pi/k_m$ is the free space wavelength which corresponds to the energy of the mode. We would like the cavity to be resonant with the $S_{1,0} \rightarrow S_{0,0}$ transition, so $\lambda_c \simeq 785$ nm. Placing a reflecting surface at this position allows the light to acquire a phase 4π after one round trip, excluding the phase change due to reflection (which is either 0 or π per mirror). Off-axis, however, we have to take into account the divergence of the beam, and the profile of the reflective surface must match the 2π isophase surface of the propagating Gaussian mode [199, 200]. In doing so, the curvature of the mirror is matched to that of the wavefront and the mode is perfectly reflected back onto itself. The 2π isophase in the paraxial approximation is plotted in Fig. 5.4(b) for $\lambda_c = 785$ nm, $n_{ac} = 1.8$ and $w_0 = 0.65$ μ m.

It is usually sufficient to have a mirror profile which is approximately equal to the isophase surface. For example, spherical profiles are usually a good substitution for the parabola surfaces dictated by the paraxial wave equation (excluding the Gouy phase) [29, 133]. We also note that spherical mirrors are in fact the optimum solution when non-paraxial propagation is included [201]. In the following sections, I will be focusing on a different approach, in which the isophase surface is approximated by the Gaussian function

$$z(r) = (L_{2\pi} - h) + h \exp\left(-\frac{r^2}{2\sigma^2}\right), \quad (5.40)$$

where h is the height of the profile and its full-width at half maximum is $\text{FWHM} = 2\sqrt{2\log(2)}\sigma$. Gaussian approximations have already been found to support low-loss modes [200, 202], even at very short cavity lengths [203]. Furthermore, this profile is easily parametrised and remains smooth for all radial displacements, which is important for the mirror fabrication process [199].

To fit the Gaussian profile to the isophase surface, we set h and do a maximum-likelihood estimation of σ with the data points weighted by the strength of the electric field. We found that the fitted σ is approximately linear with the square of the beam waist, as shown in Fig. 5.4(d). This is expected as the mode waist for short plano-concave cavities is given by [202]

$$w_0 \simeq \sqrt{\frac{\lambda_c}{\pi n}} (LR)^{1/4} , \quad (5.41)$$

where R is the radius-of-curvature of the curved mirror. For a Gaussian profile, the on-axis radius-of-curvature is $R = \sigma^2/h$ and we have

$$w_0^2 \simeq \frac{\lambda_c}{\pi n_{ac}} \sqrt{\frac{L_{2\pi}}{h}} \sigma . \quad (5.42)$$

The Cavity Mode

We now turn to the issue of designing the high-reflectivity mirrors. Here, we can choose between metallic or dielectric mirrors. Metallic mirrors have the advantage that only a thin layer is needed to achieve optimum reflection, which simplifies the design. Moreover, they are very broadband and relatively insensitive to angle of incidence. However, metallic thin-films have absorption losses, which ultimately limit their reflectivity. On the other hand, dielectric Bragg mirrors can achieve much higher reflectivities at the cost of a narrow bandwidth.

Distributed Bragg reflectors (DBR) consist of alternating low and high refractive index layers. The many reflections from the interfaces interfere constructively if the optical thickness of the layers is equal to $\lambda_c/4$. This is due to the π phase change of reflection at the transition from a low refractive-index medium to a high index one. Because the light is only partially reflected at the interfaces, the field penetrates into the multilayer stack. For the curved and planar mirrors, this means that each interface

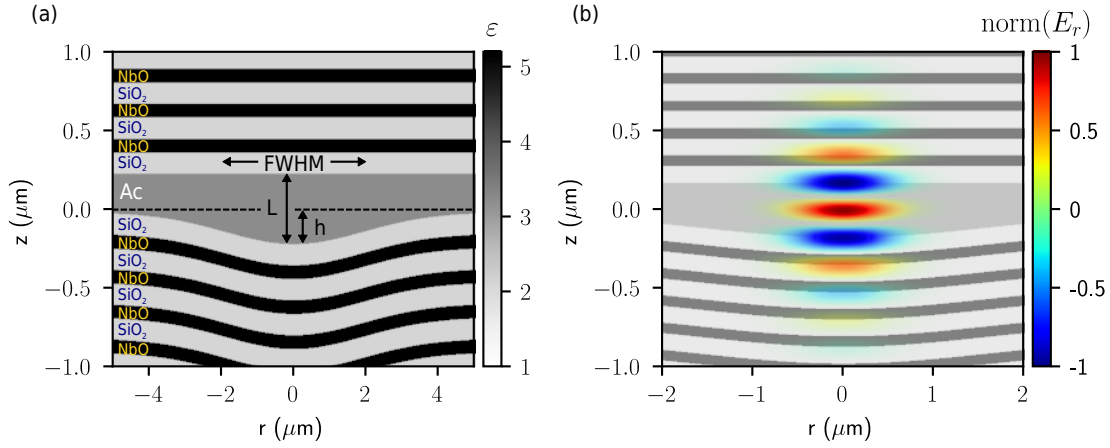


Figure 5.5: (a) Dielectric structure of the proposed Gaussian cavity. (b) Normalised E_r field distribution of the fundamental cavity mode obtained by 3D FDTD simulations with cylindrical symmetry [184].

should follow their respective isophase surface to form a good cavity. Thankfully, this is not a strict requirement as the cavity mode will adapt to the geometry to satisfy the wave equation [199, 200]. However, such deviations can lead to a shift in resonance frequency as well as a decrease in quality factor due to diffraction losses. Finally, we can tune the reflectivity of a dielectric mirror by varying the number of layers in the DBR, which is important for the quality factor optimisation.

To investigate the full cavity structure, we perform 3D finite-difference time-domain (FDTD) simulations with cylindrical symmetry. The dielectric geometry is sketched in Fig. 5.5(a). It consists of a planar and Gaussian DBR with an anthracene cavity medium. Both DBRs are made of alternating layers of silica ($n_{\text{SiO}_2} = 1.46$) and niobium oxide ($n_{\text{Nb}_2\text{O}_5} = 2.28$) with an optical thickness of $\lambda_c/4$. We parametrised the curved mirror according to Eq. 5.40 with Gaussian height h and waist σ . Anthracene fills the space between the DBRs, and the on-axis DBR separation is set to $L = \lambda_c/n_{\text{ac}} + \Delta L$, where ΔL accounts for the Gouy phase. As the refractive index (and birefringence) of anthracene is not known precisely (see Sec. 2.1.1), we set $n_{\text{ac}} = 1.8$.

Fig. 5.5(b) shows the profile of the fundamental mode extracted from an FDTD

simulation with $\Delta L = 10 \text{ nm}$, $h = 200 \text{ nm}$ and $\sigma = 2 \mu\text{m}$. We clearly see that the structure is capable of supporting a cavity mode. Moreover, it is now evident that accumulating a round-trip phase of 4π is a good design choice. In this configuration, the maximum of the electric field sits in the middle of the anthracene medium, far away from any interfaces. Moreover, the cavity length is approximately 450 nm on axis, which is more than enough to expect photostable DBT molecules in the middle.

5.2.2 Structure Optimisation

ΔL and σ as Critical Parameters

We start the structure optimisation by investigating the cavity mode as a function of ΔL and σ . From the isophase-surface picture, we know that varying ΔL will linearly shift the resonant frequency. We also expect that σ is approximately linear with the square of mode waist and therefore also linear with mode volume.

Fig. 5.6(a) plots the simulated quality factor and resonant free-space wavelength as a function of ΔL . The Gaussian height h and waist σ are set to 200 nm and $2 \mu\text{m}$ respectively, and both DBRs have 15.5 pairs of alternating silica and niobium oxide layers. The simulations confirm that the resonant wavelength is linear with ΔL and we get $\lambda_c = 785 \text{ nm}$ for $\Delta L \simeq \phi(L_{2\pi})/k_m = 10 \text{ nm}$, as expected. When this condition is satisfied, the structure features a quality factor of approximately 2.5×10^6 . To clarify whether Q is limited by the mirror reflectivities or diffraction losses, it is useful to compare this number to the expected Q for no scattering losses. With mirror reflectivities R_1 and R_2 , it is given by [204]

$$Q_{\text{theory}} = \frac{2L_{\text{eff}}}{\lambda_c/n_{\text{ac}}} \frac{\pi(R_1 R_2)^{1/4}}{1 - (R_1 R_2)^{1/2}} , \quad (5.43)$$

where L_{eff} is the effective length of the cavity, which takes into account the penetration depth of the mode in the DBRs. L_{eff} can be estimated by dividing the mode volume

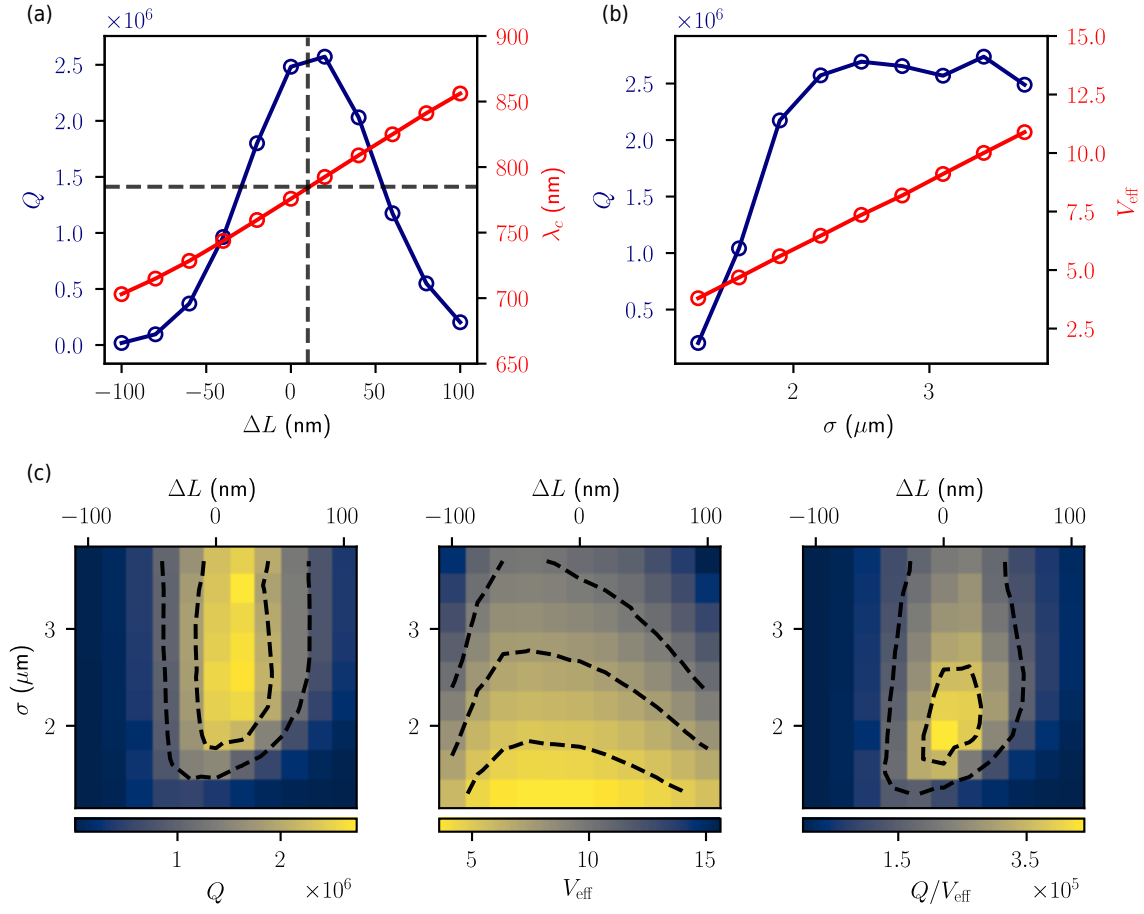


Figure 5.6: (a) Simulated quality factor and resonant free-space wavelength of Gaussian isophase cavities as a function ΔL . The other parameters are set to $h = 200$ nm, $\sigma = 2 \mu\text{m}$. (b) Quality factor and effective mode volume as a function of σ with $\Delta L = 10$ nm and $h = 200$ nm. For $\sigma < 2.2 \mu\text{m}$, the Gaussian profile is no longer a good approximation of the isophase surface, leading to diffraction losses. (c) Q , V_{eff} and Q/V_{eff} as a function of σ and ΔL with $h = 200$ nm.

by the mode area at the centre of the cavity and we get $L_{\text{eff}} = 2.35(\lambda_c/n_{\text{ac}})$. R_1 and R_2 are calculated using the characteristic matrix approach [205]. The curved mirror is deposited on a silicon substrate and has a calculated reflectivity $R_{\text{curved}} = 0.9999974$, while the flat mirror terminates in air and has $R_{\text{flat}} = 0.9999904$. We therefore get $Q_{\text{theory}} = 2.4 \times 10^6$ which shows that the cavity is mostly limited by mirror losses. Additionally, we see that Q decreases when the resonant wavelength deviates from 785 nm, which is due to the small bandwidth of the DBR reflectivity.

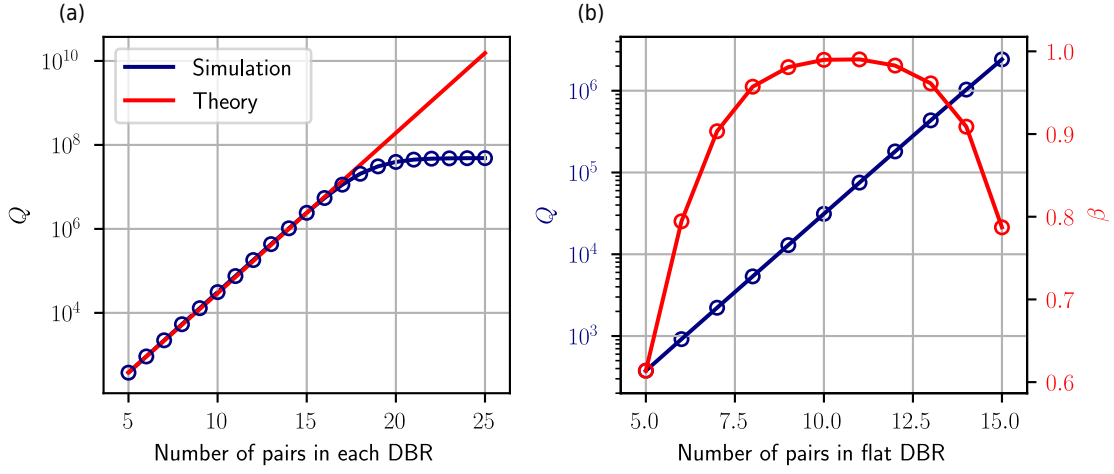


Figure 5.7: (a) Simulated quality factor of the optimum geometry as a function of number of pairs in each DBR (blue line). The results fit well from the predicted value from mirror reflectivities (red line), with any departure due to the finite time of the simulations. (b) Quality factor as a function of number of pairs in the flat DBR, with the number of pairs in the curved mirror set to 15 (blue line). Assuming the cavity is limited by mirror losses alone, so that Q is only limited by the mirror reflectivities, we can estimate β with Eq. 5.22 (red line).

Next, we set $\Delta L = 10 \text{ nm}$ to extract the quality factor and mode volume as a function of σ . These results are shown in Fig. 5.6(b). We see that the mode volume increases linearly with σ , which agrees well with the Gaussian isophase theory. To maximise the strength of the light-matter interaction, it is therefore preferable to choose a small Gaussian waist. However, we also see a sharp drop-off in quality factor for $\sigma < 2.2 \mu\text{m}$, which is likely due to an increased mismatch between the DBR profiles and the isophase surfaces. The combination of the surface mismatch at small waists and an increasing mode volume for larger waists means that there is an optimum σ_{opt} that maximises Q/V_{eff} . This is illustrated in Fig. 5.6(c) and for a Gaussian height $h = 200 \text{ nm}$, σ_{opt} is approximately equal to $2 \mu\text{m}$, which gives $Q/V_{\text{eff}} \simeq 4 \times 10^5$.

Now that we have found the optimum parameters, we vary the number of DBR pairs in each mirror to confirm that the quality factor is limited by mirror losses. The results are plotted in Fig. 5.7(a) and we see that Q is well described by Eq. 5.43 alone. The saturation behaviour of the simulated quality factor is due to the finite time of

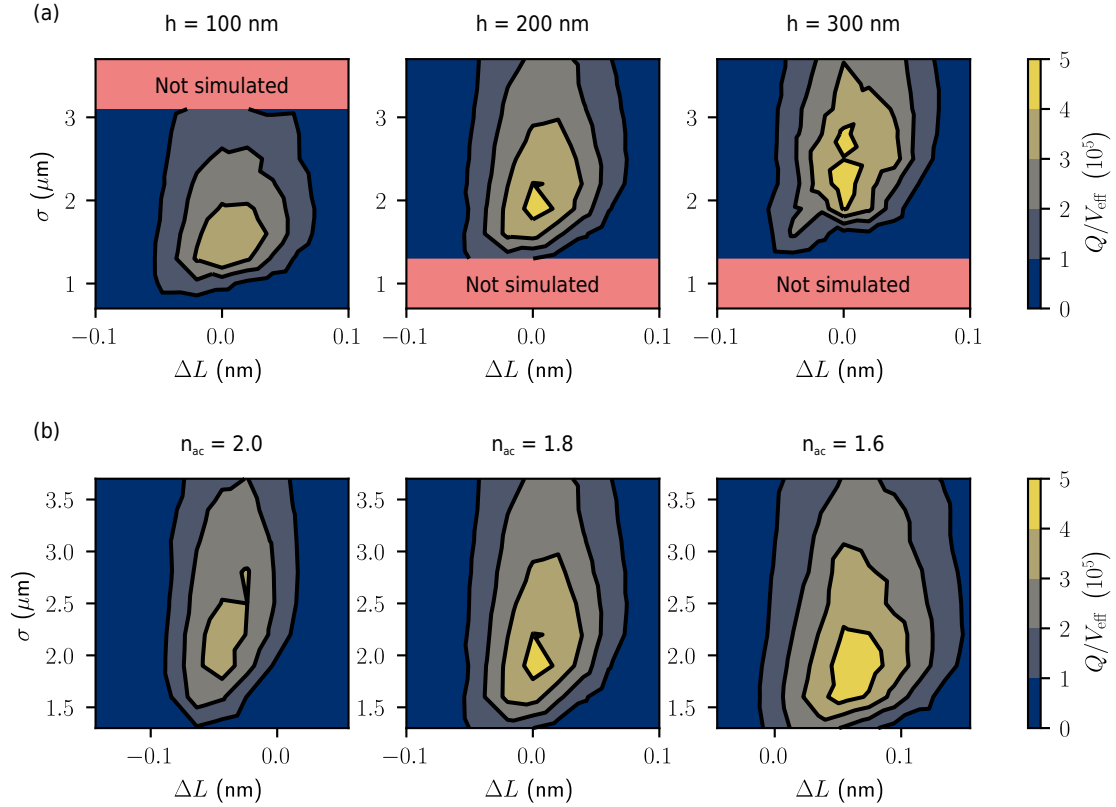


Figure 5.8: (a) Q/V_{eff} as a function of σ , ΔL and h with $n_{\text{ac}} = 1.8$. (b) Q/V_{eff} as a function of σ , ΔL and n_{ac} with $h = 200$ nm.

the simulation rather than diffraction losses. We note that, for real mirrors, the quality factor will likely be limited by material absorption [198] and/or scattering due to surface roughness [206, 207]. Nevertheless, our analysis suggests that we do not have to worry about diffraction losses. Finally, Fig. 5.7(b) illustrates how β can be maximised by using the number of pairs in the flat DBR to tune the quality factor, and we get $\beta_{\text{opt}} = 98\%$. To choose the optimum number of layers for a real cavity however, we would first have to estimate Q_{loss} experimentally.

Sensitivity to h and n_{ac}

We now focus on the last two parameters: h and n_{ac} . From Sec. 5.2.1, we expect the Gaussian profile to become a better approximation of the isophase surface for larger

heights. To check this, we perform simulations similar to Fig. 5.6(e) for different values of h and with $n_{ac} = 1.8$. The results for Q/V_{eff} are plotted in Fig. 5.8(a). Between 100 nm and 300 nm, we observe that the structure is rather insensitive to h . Indeed, the optimum Q/V_{eff} only increases slightly for larger h and we see a limited shift in σ_{opt} towards higher values. This is good for the required tolerance of the fabrication process.

On the other hand, n_{ac} is a problematic parameter as it cannot be controlled experimentally and we do not know its value accurately. Unfortunately, knowing n_{ac} is critical to set the correct cavity length for a resonance at 785 nm (Eq. 5.39). However, we can vary ΔL between devices on the same chip to fine tune the cavity length. With this approach, it would be convenient if σ_{opt} were the same irrespective of n_{ac} so that σ would not have to be varied too. Setting $h = 200$ nm, we run the simulations again for varying n_{ac} . The results are plotted in Fig. 5.8(b) and we see that σ_{opt} is approximately independent of n_{ac} in the range of interest. This finalises our design strategy for the Gaussian isophase cavities. For cavity resonances around 785 nm, we pick $\sigma = 2 \mu\text{m}$, $h = 200$ nm, $L = 785/1.8$ nm and vary ΔL to account for the Gouy phase, the uncertainty in n_{ac} and fabrication imperfections.

5.2.3 Proposed Fabrication Steps

I conclude this chapter by presenting a possible route for the fabrication of the Gaussian isophase cavities. The fabrication steps are sketched in Fig. 5.9. We start with an undoped silicon substrate which is patterned to create the Gaussian profile. The machining can be done using a variety of methods such as focused ion-beam milling [199], CO₂ laser ablation [208] and isotropic etching [209]. With a focused-ion beam, the milling process benefits from full shape control. This would allow us to etch a uniform layer of thickness ΔL in addition to patterning the curve. Next, we deposit a layer of silver followed by the SiO₂/Nb₂O₅ DBR with N_{curved} pairs and a final SiO₂

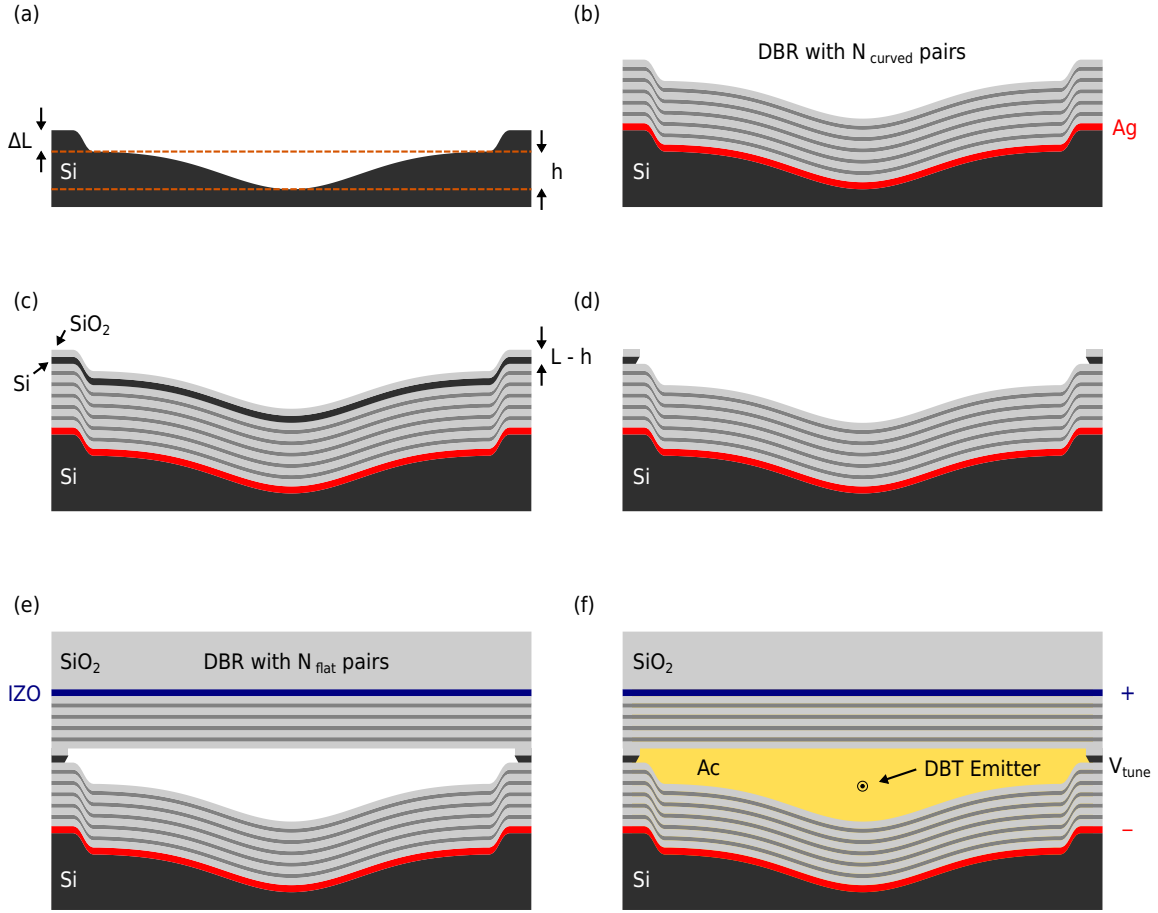


Figure 5.9: (a) FIB milling of the Gaussian profile and fine tuning of the cavity spacing. (b) Deposition of the metallic electrode followed by the DBR. (c)&(d) Deposition and patterning of the silicon and silicon oxide layers which define the coarse cavity spacing. (e) Bonding of the bottom substrate with the flat DBR with a transparent IZO electrode. (f) Filling of the cavity spacing with molten DBT-doped anthracene followed by crystallisation.

layer. The silver layer forms the first plate of a capacitor to create vertical electric fields inside the cavity medium. It also contributes to increasing the reflectivity of the curved mirror. We then deposit a layer of silicon followed by another layer of SiO_2 , whose combined thickness determines the value of $L - h$ for the chip. The top layers are then patterned using reactive ion-etching, with an isotropic etch of the silicon layer to avoid roughening of the surface.

In parallel, a DBR with N_{flat} pairs is deposited on a flat SiO_2 substrate coated with

a layer of indium-zinc-oxide (IZO). The transparent IZO layer forms the second plate of the capacitor. Both chips are then planarised using chemical-mechanical polishing and covalently bonded at room temperature [210, 211]. Finally, the cavity medium is filled with DBT-doped anthracene using the melt-growth method (Sec. 4.3). Because of fabrication imperfections, it is unlikely that the cavity mode will be resonant with an optimally-positioned DBT emitter. However, we can use the capacitor to Stark tune the $S_{1,0} \rightarrow S_{0,0}$ transition frequency with vertical electric fields (Sec. 2.1.5). By scanning the capacitor voltage, we hope to tune into resonance a DBT molecule which is located at the electric field maximum of the mode.

5.3 Outlook

In this chapter, we have discussed the theory of cavity-assisted single-photon emission, and I have outlined a microcavity geometry designed for the efficient production of photons from DBT molecules. We have simulated the proposed cavity mode and shown that, in principle, a device efficiency of more than 95% is achievable. To achieve this we require very low loss cavities. Firstly, the mirrors must be extremely smooth to limit scattering losses. The surface roughness of dielectric coatings on patterned substrates can be as low as 0.2 nm rms [208, 209] but this requires exquisite control of the patterning and deposition methods.

Secondly, we need optically good and flawless anthracene crystals. On the microscopic scale, material absorption and refractive index are not well characterised at 785 nm yet. On the macroscopic scale, it is not known if the anthracene will crystallise homogeneously in the cavity spacing. The existence of cracks and/or crystal boundaries on the scale of our devices would have a detrimental effect on the quality factor. Additionally, birefringence is another issue that we have ignored so far. Anthracene is a biaxial material, which makes the design of the cavity non-trivial. It is possible that

the constrained melt-growth results in crystals with optical axes pointing in predictable directions. If the b-axis lies in the r plane, then our above analysis holds. If not, then the cavity mode needs to be studied as a function of crystal orientation [212]. In the general case, we can expect elliptically polarised modes characterised with an effective refractive index. However, because σ_{opt} is independent of n_{ac} , we can imagine that it is still possible to recover low-loss modes by varying ΔL . This deserves a thorough investigation.

Despite these challenges, the structure solves some key design issues. In contrast with the waveguide geometries, the anthracene is an integral part of the cavity structure and not added as an inconvenient necessity. Moreover, the dimensions of the cavity are such that we can disregard spectral stability as a major issue. Of course, open-access microcavities also have these benefits, in addition to full control of the mirror position and cavity frequency [29]. However, they require a bulky positioning apparatus and are susceptible to vibrations. The cavities presented here are fabricated on a single chip and could provide a scalable route towards multiple integrated single-photon sources.

6 Summary and Conclusions

In this thesis, I explored the coupling of single DBT molecules to photonic microstructures, with the goal of engineering a deterministic single-photon source. DBT molecules in anthracene crystals are known to be good sources of triggered photons [23, 160, 161], and recent work has focused on enhancing both the spectral and spatial properties of the emission [28–31]. In **Chapter 2**, I reviewed the properties of DBT-doped anthracene and discussed the interaction of single molecules with a continuous-wave laser. In **Chapter 3**, I then described our spectroscopy set-up and presented results from DBT in bulk crystals, including absorption linewidths and second-order correlation functions. As expected, we found that the data fits well to the optical Bloch equations, with pure dephasing mediated by localised phonons.

In **Chapter 4**, I presented a new design to efficiently couple the emission to single-mode waveguides. As opposed to evanescent coupling, our strategy relies on the growth of DBT-doped anthracene in small gaps running across waveguides. This design tries to reconcile the conflicting objectives of maximising the collection efficiency and separating the DBT emitters from material interfaces for photostability. With FDTD simulation, I showed that the waveguide structures can collect up to 35% of the emission from a DBT emitter located 150 nm away from the closest interface. I then demonstrated that the crystallisation of molten anthracene in micro-fluidic channels produces photostable DBT molecules and enables high-yield device fabrication. Finally, we were able to show the coupling of a single DBT molecule to a single-mode waveguide with an efficiency of 7 %. This value was extracted from the in-waveguide extinction of a weak pump light by the molecule’s resonant fluorescence, but requires further experimentation to be validated.

The coupling to simple ridge waveguides does not provide the necessary performance to build a near-deterministic source of single photons. The mode confinement is not strong enough, and the group velocity not slow enough, for the waveguide emission to compete with scattering. In addition, the coupling is broadband and does not selectively enhance the $S_{1,0} \rightarrow S_{0,0}$ emission. In **Chapter 5**, I laid down the foundations to show how future experiments using optical cavities can tackle both these challenges. With cavity-assisted emission, the source efficiency tends towards unity for large values of Q_{loss}/V , where Q_{loss} depends on the cavity loss rate and V is the cavity mode volume. To achieve this, I introduced an integrated vertical-emitting cavity for coupling to DBT emitters. Our design is a plano-concave microcavity with doped-anthracene as the cavity medium. Because the mode order is only equal to 2, the mode volume can be as small as $V \simeq 7(\lambda/n)^3$ for optimised parameters. For these same parameters, we have also showed that the cavity quality factor is only limited by mirror losses. With high-quality dielectric mirrors, we can therefore expect source efficiencies close to unity, turning single DBT molecules into near-optimum sources of single-photons. Finally, I outlined the steps we are currently exploring to fabricate such a device.

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