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Dibenzoterrylene as a Single Photon Source

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Declaration

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Abstract

Deterministic single photon generation is of huge interest for quantum research and this thesis will begin by outlining the properties of interest for a single photon emitter. I then outline the theory behind the interaction of light and Dibenzoterrylene (DBT), an organic dye molecule that I use for the generation of single photons.

DBT is used in the solid-state, and I present fabrication processes for producing host matrices with DBT embedded. The physical properties of the organic crystals produced by these methods are described, along with the optical properties of the DBT molecules within. The development of a new method for preparing DBT containing polymer encapsulated nanocrystals that show stable single photon emission at cryogenic temperatures is presented.

Interactions between DBT and the vibrations, or phonons, in its host environment are then studied. The effect of thermal dephasing on a DBT molecule will be modelled to predict the probability of excitation as a function of excitation wavelength. Measurements at both room and liquid nitrogen temperatures will verify these predictions. A cryogenically cooled DBT molecule is then used to observe the effects of vibrations on the emitted photons as temperature increases. This allows the temperature dependance of the branching ratio and photon linewidth to be measured.

I use the emission of a single DBT molecule to measure two-photon interference and draw parallels between pulsed and continuous-wave excitation measurements. I find an indistinguishability of 53% using continuous-wave excitation and verify this using pulsed excitation, proving this method works for measuring full photon wavepacket indistinguishability. This is also in line with the expected maximum value given the temperature.

To increase the efficiency of photon collection from DBT molecules I will finish by looking at integration of molecules with nanophotonic devices. Measurements of a 9% coupling of a molecule to a waveguide will be presented, which is the highest cryogenic coupling of a molecule to a waveguide structure measured. Integration of DBT into circular Bragg gratings will also be discussed.

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Abbreviations

Ac	anthracene
AFM	atomic force microscopy
AMA	allyl methacrylate
APD	avalanche Photodiode
BS	beamsplitter
CCD	charge coupled device
cw	continuous wave (laser)
DBATT	dibenzanthanthrene
DBT	dibenzoterrylene
DM	dichoric mirror
FWHM	full width half maximum
hBN	hexagonal boron nitride
HBT	Hanbury Brown and Twiss
HOM	Hong-Ou-Mandel
HOMO	highest occupied molecular orbital
HWP	half wave plate
LPF	long pass filter
LUMO	lowest unoccupied molecular orbital
MMA	methyl methacrylate
MMF	multimode fibre
NA	numerical aperture
NCs	nanocrystals
ND	neutral density (filter)
OBE	optical (Maxwell)-Bloch equations
PAH	polyaromatic hydrocarbon
PBS	polarising beamsplitter
PMF	polarisation maintaing fibre
PMMA	polymethyl methacrylate
PVA	polyvinyl acetate
QD	quantum dot
RMS	root mean squared

SEM	scanning electron microscopy
Si ₃ N ₄	silicon nitride
SMF	single mode fibre
TCSPC	time correlated single photon counting
TLS	two-level system
WS ₂	tungsten sulphide
WSe ₂	tungsten selenide
ZPL	zero phonon line

Symbols

This is likely a non-exhaustive list of symbols used in this thesis. Terms are defined when used in the body of the work.

$\hat{a}$	annihilation operator for mode a
A_n	exponential prefactor
$\hat{a}^\dagger$	creation operator for mode a
α	branching ratio
α_{DW}	Debye-Waller factor
α_{FC}	Franck-Condon factor
β	coupling to photonic structures
$\vec{d}$	molecular transition dipole moment
Δ	laser detuning from transition
$\Delta\nu$	linewidth in frequency
$\Delta\omega$	linewidth in angular frequency
$\Delta\tau$	time delay
$\vec{E}$	electric field
η	efficiency
η_e	excitation efficiency
η_{col}	collection efficiency
F_p	Purcell factor
$g^{(2)}(\tau)$	second-order correlation function measurement
$g_{\perp}^{(2)}(\tau)$	two-photon interference measurement with perpendicular polarisation
$g_{\parallel}^{(2)}(\tau)$	two-photon interference measurement with parallel polarisation
Γ_{mode}	population decay rate into given mode
γ_{isc}	intersystem crossing rate
Γ_1	excited state decay rate
γ_1	excited vibrational state decay rate
Γ_2	coherence decay rate
γ_2	vibrational state coherence decay rate
Γ_2^*	excess (typically thermal) dephasing
I	excitation laser intensity
$\mathcal{I}$	indistinguishability

$\tilde{I}$	driven indistinguishability
I_{sat}	excitation laser intensity at saturation
$\mathcal{M}_{xx}$	matrix element
$\mathcal{M}_i$	photon ‘coherence’, or non-temporally dependant distinguishability
n	refractive index
ν	laser frequency
ν_0	transition frequency
ω	laser frequency (angular)
Ω	Rabi frequency
ω_0	transition frequency (angular)
P	excitation laser power
Φ_f	quantum yield of fluorescence
P_{sat}	excitation laser power at saturation
Q	quality factor
R	measured count rate
r_n/t_n	beamsplitter reflection and transmission coefficients
ρ	density of states
ρ_{00}	ground state population
$\rho_{10/01}$	ground and excited state coherences
ρ_{11} or ρ_e	excited state population
R_∞	maximum count rate
R_n	stimulated excitation or emission rate to or from $S_{1,n}$
S	saturation parameter
S_{flu}	fluorescence spectrum
$S_{m,n}$	singlet electronic state m , with vibrational state n
T_2	coherence time
τ_1	emitter lifetime
τ	time difference (between events)
t	time
T_n	activation energy
T_m	triplet energy level
$\mathcal{V}$	visibility
V	mode volume

1. Introduction to single photon sources

An on-demand single photon source would be an invaluable tool for many quantum technologies [1, 2, 3]. Quantum computing and quantum communication would be enhanced by being able to reliably generate single photons. Linear optical quantum computing [4, 5, 6] uses photons as qubits and can be used to solve problems many, many orders of magnitude faster than a classical (super) computer [7]. Identical photons are required as the quantum gates used for computation are based on two-photon quantum interference, with the success probability depending on photon wavefunction overlap.

Quantum communication uses quantum key distribution (QKD) to create a secure communication channel between remote parties [8]. This process can utilise attenuated laser light, which is a coherent but classical (not quantum) state. However, the Poissonian statistics of this light result in imperfect single photon state generation. The higher the purity of the single photon state [9], the more secure this channel. A useful auxiliary technology for both quantum computing and QKD is that of an optical quantum memory [10]. A quantum memory is a device that is able to store the quantum state of a photon for a period of time, determined by the user in the most powerful cases. The photon is typically stored as an excitation within an atom or across an ensemble of atoms.

There are two distinct approaches to achieving deterministic photon generation. Non-linear processes, such as spontaneous parametric down conversion or four-wave mixing, can be used to probabilistically generate pairs of photons. One of these photons can then be used to herald the presence of the other. Although this is fundamentally a probabilistic method, using multiplexing [7] and switching based on detection this can approach an on-demand system [11].

The alternative is to use the radiative decay from a two-level system (TLS). There is a wide variety of potential physical realisations of the TLS, from free space atoms, to molecules or defects in the solid state [1]. If the excitation is on-demand, such as through a laser pulse, so will the subsequent photoemission as the system relaxes. The following section will discuss the properties of interest of a deterministic TLS single photon source. This will be followed by

an overview of the main deterministic single photon emitters currently used. Our emitter of choice, dibenzoterrylene (DBT) will then be discussed [12]. There will then be a brief look at the theoretical origin of the optical properties of single photon emitters and how they can be experimentally measured. This chapter will then finish with an overview of the rest of the thesis.

1.1. Single photon sources

This section will begin with an overview of the most important properties of a single photon emitter. The benefit of using a solid-state emitter will be briefly covered followed by a discussion of the properties of the emitted photons, and then the more general optical properties of the emitter-host combination.

1.1.1. Single photon source properties

The requirements of an ideal single photon source would vary depending on its intended use, but there are some common properties that can be identified first. To begin with the more practical, physical considerations; a solid-state source is desirable. Atoms or ions in a free-space trap are probably the most obvious realisation of a TLS, with the first experiment of a deterministic single photon source using emission from sodium vapour [13]. More modern experiments have improved upon this significantly by dropping clouds of laser-cooled atoms through an optical cavity to give much greater control over the photon emission [14]. This requires a huge increase in complexity and equipment, making integration into any system seem impractical. The finite trap lifetime, and the time required to refill it, also result in a limited duty-cycle for photon generation.

Instead, a properly designed source should provide long-term stability allowing emission of photons from the same emitter, for an indefinite period of time. This requires the emitter to have a constant energy difference between the two levels and preferably to be localised within a solid-state matrix [1]. The choice of the particular solid-state matrix will depend on compatibility with the single photon emitter. This solid-state matrix should also provide protection from the environment, to prevent bleaching of the emitter due to reaction with oxygen or interaction with nearby impurities. Chapter 2 covers synthesis methods for DBT in a solid-state anthracene (Ac) matrix. The vibrational coupling of the emitter with the solid-state matrix is also an important factor that will be discussed in Chapter 3. For any kind of integration, either into a nanophotonic structure or some wider technology platform, compatibility with the other materials used is also

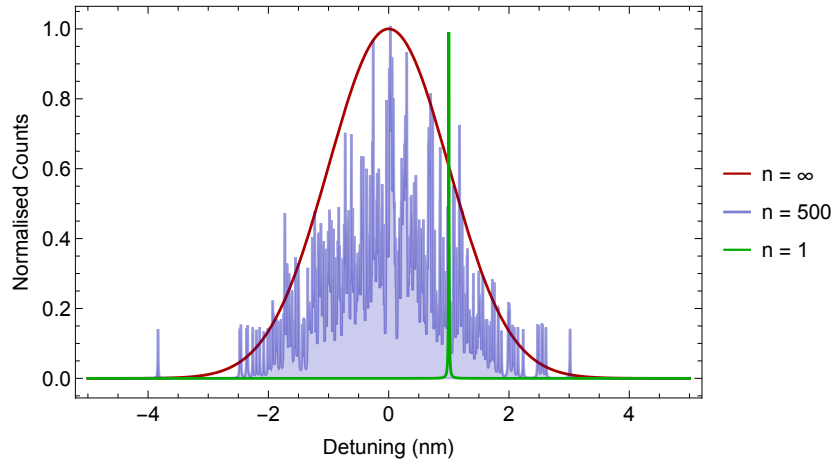


Figure 1.1. – A plot of the showing the normalised emission from an inhomogeneous distribution (of 1 nm) of n single photon emitters, with a linewidth of 0.01 nm. The red line is a Gaussian curve showing the emission in the limit of $n = \infty$ emitters, outlining the inhomogeneous distribution. Blue is the summation the Lorentzian emission of $n = 500$ individual emitters distributed around the central emission wavelength, showing how the inhomogeneous distribution arises from many normally distributed single emitters. Green shows the emission from a single emitter. For DBT, the emitter used in this thesis, the emission wavelength is 785 nm.

an important consideration.

Photon properties

Next, we can begin to consider the optical properties of the emitter, starting with the wavelength of emitted photons. For a TLS photon emitter this will be determined by the energy difference between the two energy levels. For a real system this will be the difference between the highest occupied and lowest unoccupied (and accessible) electronic orbital. A given emitter-host combination will have a range of possible wavelengths for any particular emitter, arising from slight variation in the local environment affecting the energies of these orbitals. This is called inhomogeneous broadening and at cryogenic temperatures the inhomogeneous linewidth can be orders of magnitude greater than the homogeneous linewidth of the emitter. This results in a distribution of possible emission wavelengths for a particular single photon emitter, given the emitter-host combination chosen, as shown in Fig. 1.1.

The optimum wavelength will depend on the intended use, and this will typically dictate the

choice of single photon emitter. Generally, shorter wavelengths are ideal for using high efficiency, readily available single photon detectors [2], whilst longer wavelengths can take advantage of the low-loss transmission through optical fibre in telecommunication systems. Ensuring the solid-state host is transparent at the emission wavelength is also essential for efficient extraction of the photons. Some experiments, such as those with narrowband quantum memories, require interaction with transitions in other quantum systems and as such place more specific requirements on the wavelength [15]. Even with an inhomogeneous broadening centred on the correct wavelength, the probability of an emitter having the exact required wavelength can be very low, as shown when considering the emission from a single emitter in Fig. 1.1. This problem is amplified for uses that require the interference of photons emitted from multiple (identical) emitters, such as quantum optical circuits [16]. There are methods that can be used to tune the emitter wavelength on resonance with the other system, such as Stark tuning or charge-transfer induced tuning [17, 18] or strain induced tuning [19], which use controlled modification of the electrical or physical environment to modify the emitter energy gap. The ratio of tuning range to the inhomogeneous broadening is often of interest here.

Another important consideration is the potential repetition rate of the single photon source. This is determined by the fluorescence lifetime, τ_1 , of the excited state. Fluorescence can be described by an exponential decay, and the excited state lifetime is the inverse of decay rate characterising this; $\tau_1 = 1/\Gamma_1$ where Γ_1 is the population decay rate of the excited state. Figure 1.2(a) shows the normalised excited state population of an emitter with a lifetime of $\tau_1 = 4$ ns as a function of time.

The repetition rate can be set through control of the excitation rate as long as this is slow compared with Γ_1 . A shorter lifetime is therefore desirable for achieving a high repetition rate. It also reduces the opportunity for dephasing by the environment. A specific single photon emitter will have a range of lifetimes dependent on the specific solid-state matrix it lies within. Nanophotonic structures will often enhance the decay rate, and therefore reduce the lifetime, of the emitter in a process called Purcell enhancement [21, 22]. Section 5.1 will discuss this in greater detail. The uncertainty relationship between time and energy gives a minimum width for a given excited state lifetime, hence the designation of lifetime-limited emission. Expressed in frequency, the linewidth of a lifetime-limited emitter is $\Delta\nu = 2\pi \times \Gamma_1$, where Γ_1 is the decay rate of the excited state introduced above. Figure 1.2(b) shows the relationship between the population decay rate and linewidth of the emitted photon.

However, additional dephasing through interaction with the environment can result in a much

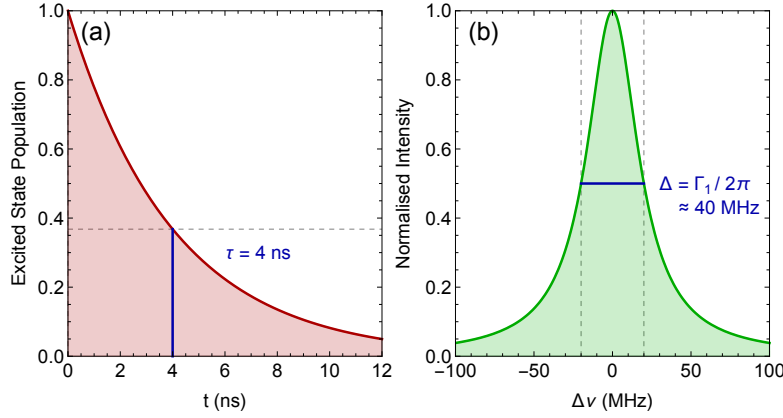


Figure 1.2. – (a) A plot of normalised excited state population versus time for a fluorescing TLS. Curve is an exponential decay of the form $e^{-t\Gamma_1}$ with $\Gamma_1 = 0.25 \text{ ns}^{-1}$. Dashed line is at the $1/e$ excited state population value, allowing a value for the lifetime $\tau_1 = 4 \text{ ns}$ to be seen (blue) [20]. (b) A plot of normalised intensity versus frequency detuning for a lifetime-limited photon emitted by the same TLS as in (a). The Lorentzian curve has a linewidth $\Delta = \Gamma_1/2\pi \approx 40 \text{ MHz}$, shown by the blue line. Dashed lines are at $\pm 20 \text{ MHz}$.

broader photon spectral width. This additional dephasing will be discussed in greater detail in Chapter 3. Any quantum information applications that require interacting indistinguishable photons will want to use a single photon source where dephasing is negligible. A suitable, impurity-free solid-state matrix will leave the only source of dephasing as that caused by local phonons in the matrix around the emitter. This thermal dephasing can then ideally be reduced to zero by operating at cryogenic temperatures, allowing the generation of indistinguishable photons [23, 24]. Chapter 3.3 will discuss the development of an experiment to measure the indistinguishability of photons from DBT.

Source optical properties

The photon purity of emission from a single photon source describes the likelihood that only a single photon is emitted at once. True single photon emission is essential for truly secure quantum communication and error-free quantum computation [6]. This can be quantified through the measurement of the second-order correlation function at zero time delay, $g^{(2)}(\tau = 0)$. The second-order correlation function measures the correlation between the intensity of light emitted

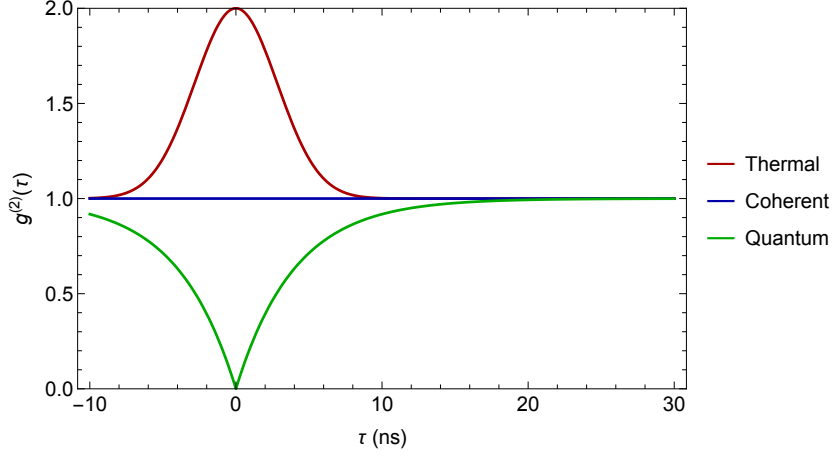


Figure 1.3. – A plot of normalised second-order correlation functions for thermal (red), coherent (blue) and quantum (green) light sources with a lifetime of $\tau = 4$ ns under cw excitation. The thermal light is described by $g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2$ and the quantum light is described by $g^{(2)}(\tau) = 1 - e^{-|\tau|}$ [26].

from a source at time t with the intensity at time $t + \tau$, expressed as

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle^2} \quad (1.1)$$

where $I(t)$ is the intensity at time t . This can be measured by using a Hanbury Brown and Twiss interferometer [25], which records the time intervals between the emission of one photon and the next.

Setting $\tau = 0$ gives you the probability of detecting photons on both detectors simultaneously, and allows three distinct statistical regions to be identified [27]. A thermal light source demonstrates photon bunching and is likely to have more photons at zero delay, giving $g^{(2)}(0) = 2$. A coherent state, such as from a laser beam, has no correlations between photon emission events and will have a $g^{(2)}(0) = 1$. A quantum emitter can only emit one photon at a given time, and as such will give a $g^{(2)}(0) = 0$. Figure 1.3 shows a plot of $g^{(2)}(\tau)$ versus τ for these three cases, for cw pumping. A single photon emitter has a photon purity of $g^{(2)}(0) = 0$, however in an experiment there can be contributions to the collected light from scattered excitation light or other nearby emitters. The second-order correlation function at $\tau \neq 0$ will be discussed later in this chapter.

Another important factor is the efficiency, η , of the single photon emitter. This is the probability that the source produces a photon in a suitable spatial mode on command. This can also be

thought of as the reliability of photon generation. Naturally all use cases for single photons can benefit from greater reliability, and some cases have a fixed lower bound for successful operation [1]. For example, modern optical quantum computing error correction schemes require a ‘photon loss’ $(1 - \eta)$ below 1.5% [28] to 7% [29] to work, depending on the implementation. The efficiency can be expressed as the product

$$\eta = \eta_e \Phi_f \eta_{\text{col}} \quad (1.2)$$

and Fig. 1.4 shows a schematic representation of these three terms. The excitation efficiency of the emitter, η_e , represents the likelihood that the excitation trigger is capable of driving the emitter into the suitable excited state, and will be discussed in Chapter 3.1 [30]. The quantum yield of fluorescence Φ_f is the probability that the emitter relaxes through fluorescence and selection of a suitable emitter and solid-state matrix can give a value of (effectively) unity here. Finally, the collection efficiency, η_{col} , is the probability that the photon is emitted into a useable spatial mode for the experiment. Most single photon emitters can be modelled accurately as a dipole emitter, including quantum dots [31, 32], which typically results in poor overlap with a single mode fibre. Increasing η_{col} is therefore a major focus of research in the field of deterministic single photon emission. This can be achieved both through redirection of emitted light using optics and modification of this emission pattern using nanophotonic structures. Chapter 4 will discuss this in more detail.

A final consideration is the method of excitation to be used. Most single photon emitters are optically excited, using either resonant or blue-detuned light. Resonant excitation requires specific engineering to prevent laser light overwhelming any single photon emission. Many single photon emitters take advantage of energy levels above the excited state, typically with (non-radiative) decay rates much greater than the radiative decay rate, on the order of some ps^{-1} , to allow non-resonant pumping. Laser light can then be efficiently removed using frequency filtering. The excitation method also unsurprisingly has an effect on the excitation efficiency η_e . Depending on whether resonant or blue-detuned excitation is used the system will behave as a two or three-level system. This limits $\eta_e = 0.5$ in the two-level system case as stimulated emission prevents population inversion [30], unless precise π -pulses are used to coherently drive a Rabi oscillation. Blue-detuned pumping instead allows $\eta_e \rightarrow 1$ if the third energy level has fast decay back to the second radiatively decaying level.

Blue-detuned pumping is not always appropriate; for example if Purcell enhancement on the fluorescing transition is used. The enhancement can cause the radiative Γ_1 decay rate to become similar to the fast decay from the third energy level. This causes jitter in the timing of the photons

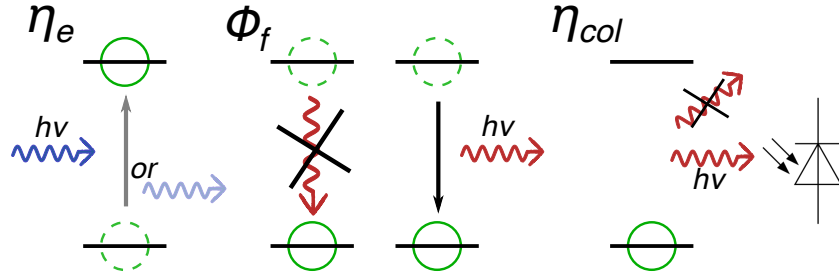


Figure 1.4. – A schematic representation of three terms contributing to the total efficiency, η , of a single photon emitter. The two lines represent the ground (bottom) and excited (top) states of the TLS. The collection efficiency, η_e is the likelihood of excitation from the given excitation method. In this case, this is the probability a photon ($h\nu$) is absorbed and excites the TLS, rather than not interacting. The quantum yield of fluorescence Φ_f is the likelihood the system fluoresces (right), as opposed to relaxing through a non-radiative process (left). The collection efficiency η_{col} is the probability the emitted photon is emitted into a useable spatial mode for the experiment, in this case detection on a photodiode.

comparable to their coherence length [33]. Most practical uses of a single photon emitter would utilise pulsed excitation, with the intention that the input of each laser excitation pulse results in the output of a photon. However, cw excitation is also useful in the laboratory setting for frequency selective excitation in a sample with many emitters in a laser focus or maximising the excitation rate of an emitter. There are also some emitters that can take advantage of electronic excitation [34, 35]. The next section will give an overview of the prominent quantum systems used for single photon generation and their performance in relation to these properties.

1.1.2. State of the art emitters

This section will discuss the most promising and well-developed single photon emitters at the current time; namely quantum dots and organic molecules. 2D materials, a much newer addition to the field, will also be briefly covered.

Quantum Dots

A quantum dot (QD) is a semiconductor ‘artificial atom’, consisting of a region of lower band-gap semiconductor embedded in higher band-gap semiconductor [2]. The lower band-gap centre is on the order of nanometers in size which, upon excitation, results in a localised electron-hole pair with discrete energy levels hence the designation of an artificial atom [31]. There is a wide range of different material combinations that can be used, giving rise to different emission wavelengths and other properties [3]. Fabrication of QDs typically relies on one of two methods: either epitaxial growth on a solid-state semiconductor substrate or in-solution growth of a colloidal QD. Colloidal QDs have shown potential for a large range of applications from solar cells to sensors [36]. They have shown promising photon purities at room temperature [37] and coherent behaviour, although not lifetime-limited, at cryogenic temperatures [38]. However, epitaxially grown QDs are significantly more developed as single photon emitters and they will be the focus of this section.

A highly desirable aspect of QDs is the compatibility that the semiconductor materials have with well developed nanofabrication methods such as electron beam lithography, making the integration of QDs within high quality photonic nanostructures possible. Emission wavelengths from 350 nm to 1550 nm are possible depending on the QD material and size [2, 39, 40], although the most advanced sources are typically in the region of 900 nm [22]. Quantum dots typically have radiative lifetimes of order 1 ns, however integration into a nanostructure with some form of cavity can reduce this lifetime by a factor of 5 to 20 through Purcell enhancement [41]. This corresponds to a Purcell enhanced lifetime-limited linewidth of 160 MHz, to some GHz.

The random nature of epitaxial growth methods results in a large inhomogeneous broadening, typically in the region of 20 nm to 50 nm (roughly 10 THz) for InGaAs based dots [33, 31], although when optimised this can be brought down to the few nm range [42]. This is a large energy range when compared to the homogeneous linewidths above and is a problem if interaction between photons from two (or more) QDs is desired, or when making a nanostructure resonant to a given QD. Strain tuning has been used to tune InAs QDs over the whole inhomogeneous

width [43], requiring deposition of a specific film that could be crystallised *in situ* by a laser, and to enable interaction between photons from two separate InAs samples [44], but these approaches are some way from being integrated into scalable quantum nanophotonic structures. Electrodes for Stark tuning have been incorporated into nanophotonic pillar cavities to tune InGaAs dots onto the cavity resonance [41], however a comparably large tuning range has not yet been demonstrated.

As well as interfering photons from separate sources, subsequent photons from the same source can be time-delayed and interfered with each other. This type of delayed interference permits the measurement of indistinguishability. Modern InGaAs QDs can reach indistinguishabilities of greater than 95 % [22, 41], although there is potential for greater than 99 % with an optimum system [24]. Resonant and non-resonant excitation can be used to excite QDs, with non-resonant excitation generally being simpler and resulting in high count rates [41]. Collection efficiencies of 80 % [45] and photon purities of $g^{(2)}(0) = 0.009$ [46] are possible for non-resonant excitation, although there is typically some trade-off between the two.

For coherent experiments that use Purcell enhancement the timing jitter necessitates resonant excitation [33]. This is due to the enhanced decay rates of the radiative transition becoming comparable to the initial non-radiative decay rate from the higher energy level used in non-resonant excitation, which are on the order of 1 ps^{-1} to 100 ps^{-1} [47]. In these cases a cross-polarised excitation scheme is often used, allowing for extraction efficiencies (of a specific polarisation of photons) around 30 % and photon purities of $g^{(2)}(0) = 0.0092$ [48]. Beyond simply measuring impressive properties, time multiplexing of a resonantly pumped QD coupled to a micropillar has recently performed a 20-input-photon boson sampling experiment [49]. This involved using an array of switches and delay fibres to temporally overlap photons from subsequent QD emissions. To finish this overview it is worth noting that a majority of these results are from QDs coupled out of a sample into free space collection optics which does pose an issue for scalability. As impressive as the 20-input-photon boson sampling experiment is, it is hard to imagine scaling it up to the thousands of photons required for solving problems with practical applications. There are efforts integrating QDs into waveguides to address this, which would not require independent free space optics for each emitter [31].

2D Materials

2D materials are a new approach to single photon generation based on transition metal dichalcogenide [50] and hexagonal boron nitride (hBN) [51, 52] monolayers. Atomically thin layers of

these materials can show localised defects that demonstrate single photon emission. The first demonstrations of these emitters used naturally occurring defects from deposition on substrates [50], some engineered to increase strain [53]. More recent efforts have used additional treatment such as heating, electron beam irradiation [51] or plasma etching [54] to increase the yield of emitters. The exact physics leading to the localisation of charge and therefore the creation of the emitter is not fully understood [55], and there are likely multiple contributing factors.

Flakes of mechanically exfoliated WSe₂ can be placed on surfaces engineered to encourage the formation of emitters, such as rows of dielectric pillars. These induce regular strain in the monolayer causing deterministic formation of emitters localised to specific strained regions [56]. There is a wide inhomogeneous broadening with emission from 720 nm to 780 nm, but it is suggested that multiple layers and pillar engineering could improve this. Emitters in hBN created through thermal annealing followed by plasma etching have been incorporated into tuneable microcavities [55]. The intrinsically thin nature of the hBN allows for easy incorporation into the cavity through coating in a polymer film and a Purcell factor of 2.3 has been measured. A similar production method is also used to create defects that show ZPL narrowing as the temperature is lowered to 7 K [54], although the lifetime limit is not reached. There are also experiments showing electrical excitation of WS₂ [57] and WSe₂ emitters [35].

These results show promise in single photon generation using these materials, especially when considering the potential for deterministic placement and compatibility with nanophotonic devices. With this in mind, there are a number of key issues that need to be solved. Count rates are typically very low when considering the excited state lifetime, in part due to non-radiative decay [55]. Lifetime-limited emission has also only been reported in one instance, where the linewidth strangely showed no temperature dependence [58].

Single Molecules

Fluorescence from a single organic molecule embedded in an organic host matrix was first measured from pentacene in a *p*-terphenyl crystal [59, 60]. Since then, a variety of other polycyclic aromatic hydrocarbons (PAH) in a range of organic matrices have been utilised to generate single photons [61]. Many PAHs are fluorescent at visible wavelengths due to the high levels of conjugation lowering the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). As the size of the PAH and therefore the conjugated π -bonding system increases, the fluorescence shifts to longer wavelengths and the quantum yield of fluorescence increases [62], favouring larger emitters. Initial work used

pentacene [60] and terrylene [63] but more recent efforts have focused on dibenzanthanthrene (DBATT) and dibenzoterrylene (DBT). Photons from DBATT under cw excitation, with suitable filtering, have reached an indistinguishability of 97 % [64]. DBT will be discussed in greater detail in the following section.

1.2. Dibenzoterrylene

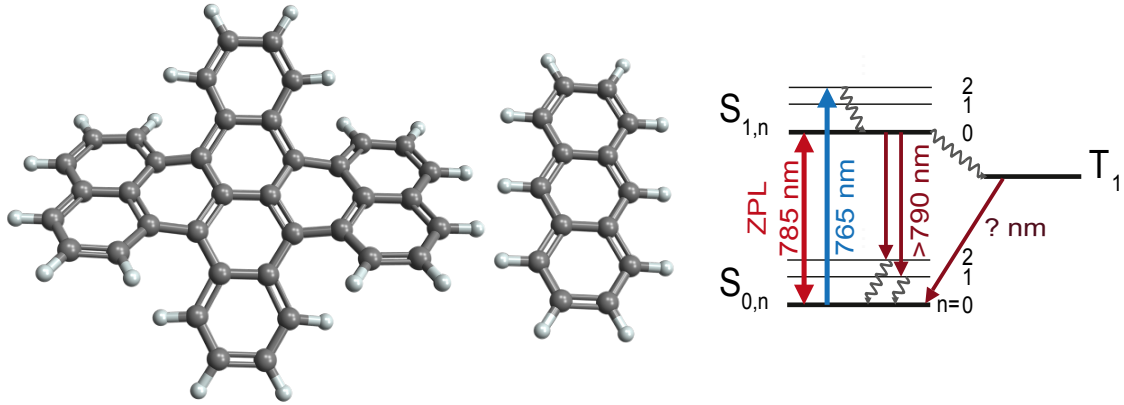


Figure 1.5. – Left: Ball and stick model of dibenzoterrylene (DBT), the quantum emitter of interest. Centre: Ball and stick model of anthracene (Ac), the host material used for DBT. Right: Energy level structure of DBT. The two electronic singlet levels of interest, S_0/S_1 , are shown, along with their vibrational sub-levels, represented with subscript n . The triplet energy level T_1 is also shown; the energy of this transition is unknown. Grey curly arrows represent non-radiative transitions and coloured solid lines represent radiative transitions. Wavelength values are approximate. The energy of the triplet is not known.

Dibenzoterrylene [65], or DBT, is a polycyclic aromatic hydrocarbon (PAH) with formula $C_{38}H_{20}$ and a molecular weight of 476.56. The molecular and electronic structures are shown in Fig. 1.5. Pure DBT appears green as it absorbs both blue and red light; it is the transitions responsible for the red absorption that are of interest for single photon generation. Typically anthracene (Ac) is used as a host for DBT and this will be discussed in more detail in the following chapter.

The electronic transition of interest for single photon generation in DBT is between the ground and excited singlet electronic states, $S_{0,0} \leftrightarrow S_{1,0}$. In an Ac host this transition, called the zero phonon line (ZPL), lies at approximately 785 nm, with a red- (blue-) detuned sideband in emission (absorption) due to transitions to ground (excited) vibrational states, represented by

the $S_{0/1,n}$ levels. When cooled to cryogenic temperatures the ZPL can reach a lifetime-limited width of 40 MHz, corresponding to lifetimes in the region of 4 ns. By contrast, excitation with blue-detuned light to an excited vibrational state is followed by a non-radiative decay from $S_{1,n>0} \rightarrow S_{1,0}$ with a lifetime of a few picoseconds, giving a linewidth on the order of 25 GHz to 40 GHz. Similarly, emission on the red-detuned sideband to an excited vibrational, but ground electronic state, $S_{1,0} \rightarrow S_{0,n>1}$ is also followed by fast non-radiative decay back to $S_{0,0}$. At room temperature thermal dephasing broadens these radiative transitions to approximately 8 THz [30]. The line-broadening causes the ZPL to overlap with the vibrational transitions which strongly affects the excitation efficiency of DBT. This is discussed in greater detail in Section 3.1.

DBT typically has a quantum yield of fluorescence, Φ_f , of near unity [30]. However the multiple radiative decay pathways, $S_{1,0} \rightarrow S_{0,n=0}$ or $S_{1,0} \rightarrow S_{0,n>0}$, need to be considered. There is also a decay to the triplet energy level $S_{1,0} \rightarrow T_1$, however this has a very low probability, as discussed in Section 1.3.3. The ratio of ZPL emission rate Γ_{ZPL} to overall decay rate Γ_1 is described by the Franck-Condon factor, or branching ratio $\alpha_{\text{FC}} = \Gamma_{\text{ZPL}}/\Gamma_1$, which is typically $\alpha_{\text{FC}} = 50\%$ for DBT. Purcell enhancement of the ZPL emission rate Γ_{ZPL} can increase α_{FC} , with values greater than 90 % reported [22]. There is also the possibility of interaction with phonons in the Ac crystal during photon emission and absorption which will be discussed in Chapter 3 [23].

The collection efficiency η_{col} from a DBT molecule in a large Ac crystal is typically poor. Part of this is due to the poor overlap of the dipolar emission pattern with the relevant spatial mode. Waveguides [66] and planar antennas [67] have been used to alter the emission pattern to enhance the overlap with an optical mode. Chapter 4 of this thesis will provide detail on efforts to incorporate DBT into waveguides and circular Bragg gratings, or ‘bullseye’, structures [46]. There is also loss due to internal reflection at the Ac crystal boundary that prevents light from escaping and instead guides it within the crystal. The replication of Ac nanocrystals [68] and development of PMMA coated Ac nanocapsules [69] will be covered in Chapter 2. The small size, on the order of the wavelength of DBT, of these nanocrystals prevents the internal guiding of light and also allows integration into nanophotonic devices with minimal disruption to the structure.

One short term goal for a DBT molecule with high collection efficiency is to investigate the interference of photons from DBT with each other. Although interference between photons from other PAH molecules has been shown, as mentioned previously with DBATT [64], this has not been published for DBT yet. Chapter 3.3 will outline preliminary work in this area. Other research groups are also working towards this. Electrical Stark tuning of DBT has been shown

to work [17] and excitation of a molecule with another molecule coupled to a cavity has been shown [22], paving the way for interactions between photons of two distinct DBT molecules, a building block of linear optical quantum computing. There is also the possibility of using DBT as a differential phase shift for passing photons in a coupled waveguide, another useful tool for quantum information [70].

1.3. Interaction with light

This section will outline the theoretical background of the measurements used to quantify the properties of DBT molecules in the lab. Initially cw resonant excitation from $S_{0,0} \rightarrow S_{1,0}$ will be covered, modelling DBT as a two-level system and solving the associated optical Bloch equations. The relaxation process can involve a third energy level with a radiative decay from $S_{1,0} \rightarrow S_{0,n>0}$ followed by a non-radiative decay $S_{0,n>0} \rightarrow S_{0,0}$. This non-radiative decay is fast compared to the other timescales involved in the system and results in the ground state being repopulated fast enough that it can be approximated as a two-level system [30]. When blue-detuned pumping is used and the molecule is excited from $S_{0,0} \rightarrow S_{1,n>0}$ the vibrationally excited state is similarly short-lived. However, it has a direct effect on the dynamics and this three-level system case will also be modelled later in the section. Finally, this section will finish with a brief look at the key differences when using pulsed excitation light.

1.3.1. Optical Bloch equations

The optical (Maxwell-)Bloch equations (OBEs) provide an ideal starting place for modelling the interactions of light with a DBT molecule [26]. Initially, treating DBT as a two-level system (TLS) with the ground state $|S_0\rangle$ and excited state $|S_1\rangle$ interacting with a coherent light field near resonance gives

$$\begin{aligned}\frac{d\rho_{00}}{dt} &= -\frac{d\rho_{11}}{dt} = \frac{1}{2}i\Omega(\rho_{01} - \rho_{10}) + \Gamma_1\rho_{11} \\ \rho_{00} + \rho_{11} &= 1 \\ \frac{d\rho_{01}}{dt} &= \frac{d\rho_{10}^*}{dt} = \frac{1}{2}i\Omega(\rho_{00} - \rho_{11}) + \rho_{01}(i\Delta - \Gamma_2) \\ \rho_{10} &= \rho_{01}^*.\end{aligned}\tag{1.3}$$

The ground and excited state populations are ρ_{00} and ρ_{11} respectively, whilst ρ_{01} and ρ_{10} are the off-diagonal elements of the density matrix describing the two-level system, sometimes referred to as the coherences. The differentials are with respect to time, t , and ρ^* is the complex conjugate of ρ . The total population is constant, hence $\rho_{00} + \rho_{11} = 1$. Ω is the Rabi frequency

$$\Omega = \frac{1}{\hbar}|\vec{d} \cdot \vec{E}|,\tag{1.4}$$

where $\vec{d}$ is the dipole moment for the transition and $\vec{E}$ is the amplitude of the electric field driving the system. The rotating wave approximation has been made, which neglects the very

non-resonant, counter-rotating part of the electric field. Γ_1 is the radiative decay rate of the excited state¹. This is the sum of the decay rates to each state associated with the ground electronic state, $S_{1,0} \rightarrow S_{0,n}$, but as detailed above the excited vibrational states decay fast enough that they do not need to be considered separately. Γ_2 is the decay rate of the coherence, or transverse decay rate of the emitter, the inverse of the coherence time T_2 . The detuning of the driving light from resonance is given by $\Delta = \omega - \omega_0$, where ω and ω_0 are the electric field frequency and transition frequency respectively.

The OBEs are powerful tools in solving the dynamics of a TLS, as shown later in this section, however many phenomena can be explained by taking the steady state solutions where all time derivatives are set to zero. Doing this and solving the resultant simultaneous equations gives an excited state population ρ_{11}^{ss} of

$$\rho_{11}^{ss} = \frac{1}{2} \frac{\Gamma_2 \Omega^2}{\Gamma_1 \Gamma_2^2 + \Gamma_1 \Delta^2 + \Gamma_2 \Omega^2}. \quad (1.5)$$

Defining a saturation parameter $S = \frac{\Omega^2}{\Gamma_1 \Gamma_2}$, ρ_{11}^{ss} can be rewritten as

$$\rho_{11}^{ss} = \frac{1}{2} \frac{S}{1 + \Delta^2/\Gamma_2^2 + S}. \quad (1.6)$$

This equation allows the calculation of the excited state population of a DBT molecule in the steady state regime. This is true for continuous-wave (cw) excitation which is used for most of the experiments in this thesis.

The detected count rate R from a DBT molecule, or any other TLS, can be expressed as

$$R = \eta_{\text{col}} \Gamma_1 \rho_{11}^{ss} \quad (1.7)$$

where η_{col} is the total collection and detection efficiency and ρ_{11}^{ss} represents the steady state population value. $\Gamma_1 \rho_{11}^{ss}$ describes the total emission rate from our molecule [30]. As η_{col} and Γ_1 will be fixed for a given molecule, Eq. 1.6 and Eq. 1.7 allow one to study the variation of ρ_{11} with Δ or S by recording the count rate R .

Measuring saturation and dephasing

Understanding the saturation behaviour of an emitter in the lab is very useful both for understanding the environment the emitter inhabits, and for choosing the appropriate excitation

¹Because the non-radiative is negligible for DBT in anthracene, Γ_1 is equal to the inverse of the excited state lifetime τ_1

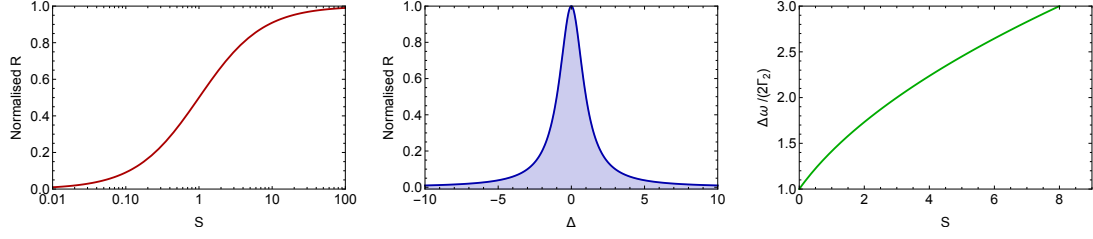


Figure 1.6. – (a) Normalised saturation plot showing the count rate R from a molecule as the excitation intensity, and therefore S , increases at $\Delta = 0$. (b) Lorentzian lineshape seen in the normalised count rate R from a molecule as the excitation frequency is scanned across the emitter frequency at a fixed saturation parameter, $S = 1$ in this case. (c) Power-broadening of the linewidth $\Delta\omega$ of the emitter transition as S increases.

regime for experiments. Ω^2 is proportional to the intensity I of the light field at the emitter, allowing saturation to be expressed as

$$S = \frac{\Omega^2}{\Gamma_1 \Gamma_2} = I/I_{\text{sat}} \quad (1.8)$$

where I_{sat} is the saturation intensity, or intensity required for $S = 1$. This allows for the abstract Rabi frequency to be replaced with the more concrete, and measurable, intensity of incident light. Measurement of I_{sat} can be performed experimentally using the relationship

$$R_{\Delta=0} = R_{\infty} \frac{S}{1+S} = R_{\infty} \frac{I/I_{\text{sat}}}{1+I/I_{\text{sat}}}, \quad (1.9)$$

where $R_{\Delta=0}$ is the molecule count rate at a detuning of $\Delta = 0$ and $R_{\infty} = \eta_{\text{col}} \times \Gamma_1/2$. This comes from setting $\Delta = 0$ in Eq. 1.6 and combining with Eq. 1.7 and Eq. 1.8. Figure 1.6(a) shows an example of the collected photon rate saturating with increasing intensity of illumination. This characteristic is often called a *saturation curve*. Knowing the maximum count rate from an emitter is useful for characterising the change in collection efficiency η_{col} from any modifications to the emitter environment or surrounding photonic structure.

In addition, the dephasing of the emitter can be measured by fixing the saturation parameter and measuring the change in the count rate as the laser frequency ω is scanned across the transition frequency ω_0 . Figure 1.6(b) shows the characteristic Lorentzian lineshape that arises from this measurement. This can be fitted with the equation

$$R = R_{\Delta=0} \frac{\Delta\omega^2/4}{\Delta^2 + \Delta\omega^2/4} \quad (1.10)$$

to measure the linewidth $\Delta\omega$ from a linescan at a known I , but with I_{sat} unknown. The equation

$$\Delta\omega = 2\Gamma_2 \sqrt{1 + I/I_{\text{sat}}} \quad (1.11)$$

is then used to find Γ_2 and I_{sat} , as shown in Fig. 1.6(c) [71], for linescans performed at a range of I values. This is advantageous as it measures both I_{sat} and Γ_2 at the same time, preventing any environmental or experimental variation between experiments. Characterising Γ_2 , and the motivation for this, will be discussed in greater detail in Chapter 3.

1.3.2. Second-order correlation function

The second-order correlation function, $g^{(2)}(\tau)$, is another useful quantity to measure. As discussed earlier, the value of $g^{(2)}(0)$ allows verification that photons are being detected from a single quantum emitter. This is not the only use of a second-order correlation function measurement however, as the shape of the anti-bunching dip about $\tau = 0$ also contains information about the emitter. This section will cover cw excitation $g^{(2)}(\tau)$ measurements, but Section 3.3 will cover pulsed excitation and the use of Hong-Ou-Mandel interferometers for measuring indistinguishability [72].

Using the OBEs outlined above, a general form of the equation describing this function can be derived as shown by Grandi *et al.* [71] by considering the time dependence of the excited state population. More precisely, a $g^{(2)}(\tau)$ measurement is looking at the likelihood of photon emission as a function of time, given a prior photon emission event at $\tau = 0$. The likelihood of photon emission is proportional to the excited state population ρ_{11} as shown in Eq. 1.7, allowing $g^{(2)}(\tau)$ to be expressed as

$$g^{(2)}(\tau) = \rho_{11}(\tau)/\rho_{11}(\infty) \quad (1.12)$$

where $\rho_{11}(\infty)$ is the steady-state value of ρ_{11} and normalises for counts at long times. Therefore, we want to find an equation for $\rho_{11}(\tau)$, given the starting condition of $\rho_{11}(0) = 0$ because of the prior photon emission.

In the case of resonant pumping, $\Delta = 0$, substitution of $\rho_{01} = \frac{1}{2}(u - iv)$ into Eq. 1.3 gives

$$\frac{d\rho_{11}}{dt} = -\frac{d\rho_{00}}{dt} = \frac{1}{2}\Omega v - 2\Gamma_1\rho_{11} \quad (1.13)$$

$$\frac{dv}{dt} = \Omega(\rho_{00} - \rho_{11}) - \Gamma_2 v. \quad (1.14)$$

Here, u and v represent the real and imaginary parts of the coherences respectively. Under resonant pumping, $u = 0$ in these equations. To remove the time differentials here a Laplace transform can be used, and this is described in detail in Appendix A.1.

This allows for $\rho_{11}(\tau)$ to be found, and after normalisation using Eq. 1.12 we find

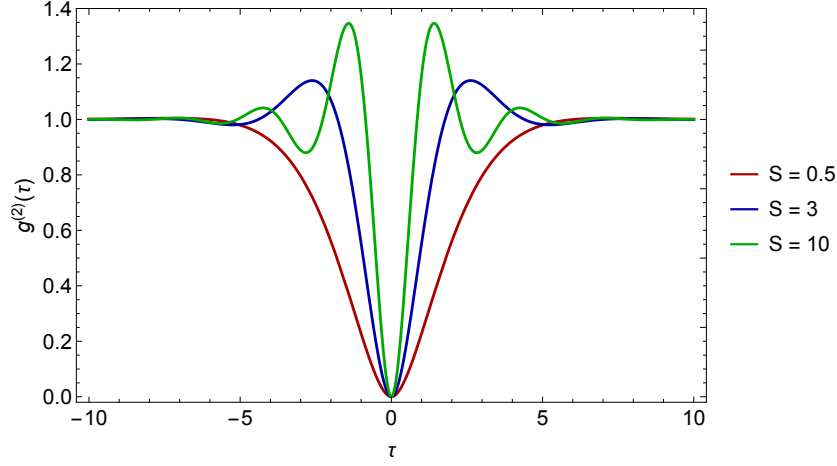


Figure 1.7. – Plots of Eq. 1.15 with saturation values of $S = 0.5$ (red), $S = 3$ (blue), and $S = 10$ (green) showing the onset of Rabi oscillations as intensity of the excitation field increases. $2\Gamma_2 = \Gamma_1$ which corresponds to a lifetime-limited molecule.

$$g^{(2)}(\tau) = 1 - \frac{p+q}{2q}e^{-\frac{1}{2}(p-q)|\tau|} + \frac{p-q}{2q}e^{-\frac{1}{2}(p+q)|\tau|}, \quad (1.15)$$

where

$$\begin{aligned} p &= \Gamma_1 + \Gamma_2, \\ q &= \sqrt{(\Gamma_1 - \Gamma_2)^2 - 4\Omega^2} \\ \Omega &= \sqrt{\Gamma_1\Gamma_2 S}. \end{aligned} \quad (1.16)$$

Figure 1.7 shows Eq. 1.15 plotted for a range of saturation parameters. The low intensity $S = 0.5$ curve in red resembles the previously presented $g^{(2)}(\tau)$ curve in Fig. 1.3 with no coherent effects [26]. However, as the saturation parameter increases the curve begins to narrow and show coherent Rabi oscillations. The strength of these Rabi oscillations is dependant on $S = \frac{\Omega^2}{\Gamma_1\Gamma_2}$, and hence on the intensity of the excitation light [71]. Equation 1.15 provides an alternative way to investigate S , Γ_1 or Γ_2 . This will be shown in Chapters 2 and 3, and is visible in Ref. [23] and Ref. [73] which use $g^{(2)}(\tau)$ measurements to extract parameters.

There is also an inverse relationship between the dephasing rate Γ_2 and strength of Rabi oscillations. Figure 1.8 shows the damping of the Rabi oscillations as Γ_2 is increased, relative to the decay rate Γ_1 . When the dephasing rate is high enough, Eq. 1.15 can be simplified into a single exponential

$$g^{(2)}(\tau) = 1 - e^{-\Gamma_1(1+S)|\tau|} \quad (1.17)$$

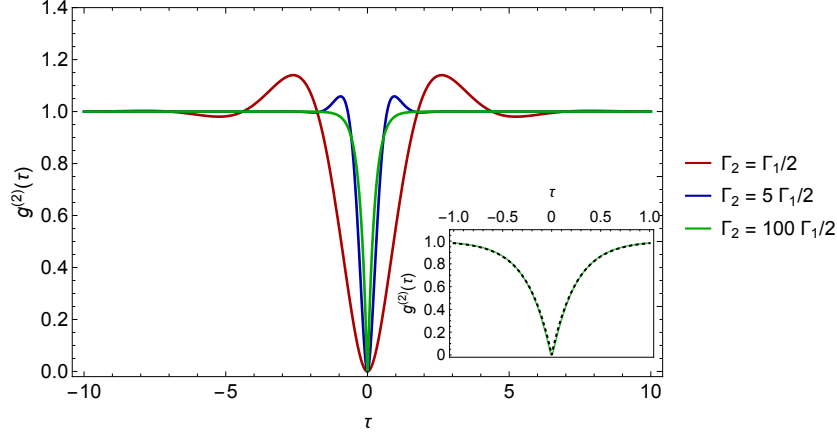


Figure 1.8. – Plots of Eq. 1.15 with $\Gamma_2 = \Gamma_1/2$ (red), $\Gamma_2 = 5\Gamma_1/2$ (blue), and $\Gamma_2 = 100\Gamma_1/2$ (green) showing the damping of coherent Rabi oscillations as the dephasing rate increases. This data is for $S = 3$, the blue curve in Fig. 1.7. Inset: A comparison of the $\Gamma_2 = 100\Gamma_1/2$ curve (green) with Eq. 1.17 (dashed black) with the same parameters showing the close correspondence of the curves.

only dependant on the population decay rate and the saturation [71, 74]. The inset of Fig. 1.8 shows the similarity of Eq. 1.15 and Eq. 1.17 for $\Gamma_2 = 100\Gamma_1/2$. This simplified equation can therefore be used for $g^{(2)}(\tau)$ measurements at raised temperatures where the excitation to the excited state is incoherent. This equation will be derived in the following section for blue-detuned pumping and discussed further.

1.3.3. Three-level system

When blue-detuned pumping is used to excite $S_{0,0} \rightarrow S_{1,n>0}$, the new energy level $S_{1,n>0}$ needs to be considered in the optical Bloch equations [75, 76]. This is labeled by 2, so has state population ρ_{22} . There are several approximations that can be made to simplify this treatment. The non-radiative decay process, with decay rate γ_1 , from $S_{1,n>0} \rightarrow S_{1,0}$ cannot coherently transfer population meaning $\rho_{21} = \rho_{12} = 0$. This additionally means there is no coherence between the excited state $S_{1,0}$ and the ground state $S_{0,0}$, so $\rho_{10} = \rho_{01} = 0$. Further, the non-radiative decay from $2 \rightarrow 1$ is fast compared to the excitation rate from $0 \rightarrow 2$, so $\rho_{22} \ll 1$ and we can neglect stimulated emission from $2 \rightarrow 0$. It is possible to excite the system fast enough that this is not the case, however this would be less efficient and so is not considered here [30].

With these approximations, we find

$$\begin{aligned}
\frac{d\rho_{00}}{dt} &= \frac{1}{2}i\Omega(\rho_{02} - \rho_{20}) + \Gamma_1\rho_{11} \\
\frac{d\rho_{11}}{dt} &= \gamma_1\rho_{22} - \Gamma_1\rho_{11} \\
\frac{d\rho_{22}}{dt} &= \frac{1}{2}i\Omega(\rho_{20} - \rho_{02}) - \gamma_1\rho_{22} \\
\rho_{00} + \rho_{11} + \rho_{22} &= 1 \\
\frac{d\rho_{02}}{dt} &= \frac{1}{2}i\Omega(\rho_{00} - \rho_{22}) - \rho_{02}(i\Delta - \gamma_2/2) \\
\rho_{02} &= \rho_{20}^*.
\end{aligned} \tag{1.18}$$

The Rabi frequency is now defined by the dipole moment for the $S_{0,0} \rightarrow S_{1,n>0}$ transition and $\gamma_2 = \gamma_1/2 + \gamma_2^*$; γ_1 is the population decay rate of $S_{1,n>0}$ and γ_2 is the dephasing rate which includes excess dephasing γ_2^* .

Defining a saturation parameter $S = \frac{\Omega^2}{\Gamma_1\gamma_2}$ relative to the decay rate of the $S_{1,n>0}$ state and setting the time derivatives to zero allows for the steady state solution to be found for ρ_{11}^{ss}

$$\rho_{11}^{ss} = \frac{S}{1 + \Delta^2/\gamma_2^2 + S}. \tag{1.19}$$

This features the same Lorentzian profile seen in Eq. 1.6, however the linewidth is now determined by γ_2 . There is also no $\frac{1}{2}$ term as this three-level system allows population inversion due to the lack of stimulated emission [30]. The saturation and power broadening behaviour discussed above is also seen with blue-detuned excitation. With low excess dephasing, typical at low temperatures as discussed in Chapter 3, this transition will be much wider than the resonant transition and an excitation intensity γ_2/Γ_2 times greater will be needed to achieve the same saturation. However as dephasing increases Γ_2 and γ_2 will both become large and the linewidths will tend to the similar values.

Second-order correlation function

Equation 1.12 can be used to determine the time-dependant behaviour of the three-level system, allowing the form of the second-order correlation function to be found. There are two approaches that can be used here; the dynamics can be solved as in Section 1.3.2 or a simpler rate equation model can be used where the coherence terms related to $\rho_{02/20}$ are replaced with a simple driving

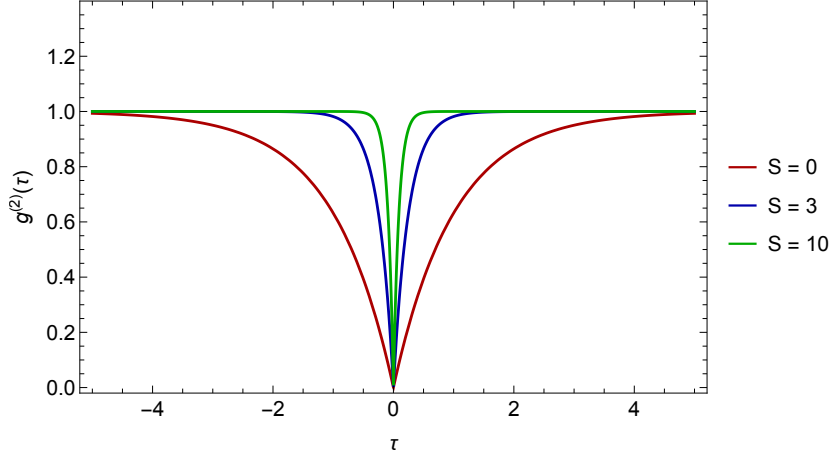


Figure 1.9. – Plots of Eq. 1.17 and 1.23 with $S = 0$ (red), $S = 3$ (blue), and $S = 10$ (green) showing the narrowing of the central feature as saturation increases.

rate [76, 30]. The rate equation model has populations determined by

$$\begin{aligned}\frac{d\rho_{00}}{dt} &= -\Gamma_1 S \rho_{00} + \Gamma_1 \rho_{11} \\ \frac{d\rho_{11}}{dt} &= \gamma_1 \rho_{22} - \Gamma_1 \rho_{11} \\ \frac{d\rho_{22}}{dt} &= \Gamma_1 S \rho_{00} - \gamma_1 \rho_{22}\end{aligned}\tag{1.20}$$

where it is convenient to write the excitation rate as $\Gamma_1 S$. Given the vibrational relaxation rate γ is much (roughly 1000 times) faster than Γ_1 , the $S_{1,n>0}$ energy level population will almost immediately decay into $S_{1,0}$, meaning $\rho_{22} \ll \rho_{00}$ and ρ_{11} . Equation 1.20 can then be simplified back into a two-level system with

$$\begin{aligned}\frac{d\rho_{00}}{dt} &= -\Gamma_1 S \rho_{00} + \Gamma_1 \rho_{11} \\ \rho_{00} + \rho_{11} &= 1.\end{aligned}\tag{1.21}$$

This is easily solved to give

$$\rho_{11}(t) = \frac{S}{1+S} (1 - e^{-\Gamma_1(1+S)t}).\tag{1.22}$$

Eq. 1.19 and 1.12 can then be used, assuming resonant excitation $\Delta = 0$, to give

$$g^{(2)}(\tau) = 1 - e^{-\Gamma_1(1+S)|\tau|},\tag{1.23}$$

which is identical to Eq. 1.17 describing the two-level system with strong dephasing. This function is plotted in Fig 1.9 for a range of saturation parameters. As S increases the central feature begins

to narrow. This is due to the stronger pumping associated with a higher S meaning a molecule is excited after emission faster, which in turn means it emits a second photon faster.

DBT also has a triplet energy level T_1 , with associated intersystem crossing rate γ_{isc} . A similar set of OBEs to Eq. 1.18 can be written to describe the dynamics of the molecule when considering T_1 [77, 76, 75]. The triplet has a lifetime τ_T on the order of microseconds, much longer than τ_1 [65]. This results in the molecule effectively entering a dark state when the intersystem crossing occurs. The associated second order correlation function will show bunching behaviour after photon emission due to a photon emission event indicating the molecule is not in the dark state, and therefore more likely to emit again. However the low intersystem crossing rate of $\gamma_{isc} = \Gamma_1 \times 10^{-7}$ means this has minimal effect, and is not visible on typical measurements. As such it will not be considered further.

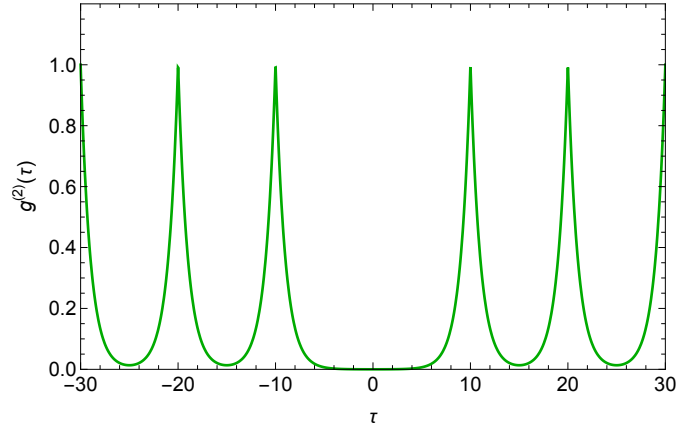


Figure 1.10. – A plot of Eq. 1.24 showing the second-order correlation function $g^{(2)}(\tau)$ for a pulsed single emitter excited using pulsed excitation. The absence of central feature is due to anti-bunching.

1.3.4. Pulsed excitation

Continuous-wave excitation allows for greater spectral selectivity thanks to the narrow linewidth of a cw laser, but if a photon is wanted at a particular time then pulsed excitation is more useful. It is also useful for measuring the emitter lifetime by time-correlated single photon counting experiment and for measuring the pulsed second-order correlation function, as outlined next.

Time-correlated single photon counting

A time-correlated single photon counting (TCSPC) experiment is a simple method of measuring the population decay rate Γ_1 of a quantum emitter. A pulsed laser is used to excite the emitter and a detector (APD) is used to detect emitted photons. Electrical pulses from both a photodiode within the laser system and the APD are connected to a timing card to record the time delay between the excitation pulse and the photon detection event. This can be repeated to obtain a histogram showing the number of detection events as a function from time of excitation pulse. This number is proportional to the excited state population and this allows the plot shown in Fig. 1.2(a) to be recreated, which can then be fitted with an exponential decay to extract the population decay rate.

Second-order correlation function

Pulsed excitation can also be used to measure the second-order correlation function of a single photon emitter. This excitation causes a series of exponential peaks, regularly spaced in time, as shown in Fig. 1.10. The decay constant of these is determined by the population decay rate of the emitter, with

$$g^{(2)}(\tau) = \sum_i \mathcal{V}_i e^{-\Gamma_1 |\tau - i\Delta\tau|} \quad (1.24)$$

where $\Delta\tau$ is the time between lasers pulses and subscript i specify the pulse. For a pure single photon emitter $\mathcal{V}_0 = 0$ as anti-bunching will mean there are no coincidence counts at zero time delay. For the pulses corresponding to $\tau \neq 0$, or non-zero time delay, $\mathcal{V}_{i \neq 0} = 1$. Unlike the cw case shown in Eq. 1.17, there is no saturation dependance. This is true for excitation on either the $S_{0,0} \rightarrow S_{1,0}$ or $S_{0,0} \rightarrow S_{1,n>0}$ transitions, as long as the pulsed length is short relative to the inverse of the population decay rate $1/\Gamma_1$. As pulsed length increases the emitter will start to show behaviour associated with cw excitation.

1.4. Thesis overview

My PhD has been focused around two goals; increasing the efficiency of single photon emission from DBT and understanding the effects of thermal dephasing on the optical properties of DBT. The experiments presented in this thesis are performed with this in mind.

Chapter 2 covers the growth methods for the DBT/Ac emitters used in this thesis. This starts with brief summaries of co-sublimation and melt growth methods developed by other group members. The in-house development of Ac nanocrystals reported in Ref. [68] will then be covered. The small size of these nanocrystals is ideal for increasing the collection efficiency and for integration into nanophotonic devices. The low $g^{(2)}(0)$ values achieved also make nanocrystals ideal for understanding the changes in the properties of a single molecule with temperature. The chapter will finish with the preparation of novel PMMA coated DBT/Ac nanocapsules, which is also presented in Ref. [69].

Chapter 3 is focused on characterising how phonons in the Ac host matrix affect DBT. This begins with considering how thermal dephasing affects the excitation efficiency of a DBT molecule through development of a rate equation model, which is tested at room temperature and 77 K. This work is also presented in Ref. [30]. The increase in thermal dephasing from 4 K to 40 K is then measured, along with the increase in strength of the phonon sideband. This data is also presented in Ref. [23] in a collaborative experimental-theory work to develop a theoretical model explaining the interaction of DBT with phonons. The chapter will finish with an experiment measuring the indistinguishability of photons emitted from a DBT molecule, excited with both pulsed and cw excitation. The parallels between these two measurements are used to develop a method for deriving full photon indistinguishability from a cw measurement.

Chapter 4 will describe current work in modifying the emission properties of DBT to enhance the efficiency for collecting emitted photons. Fermi's golden rule will be discussed, first generally, then for coupling to waveguides and circular Bragg cavities. Data showing coupling of a DBT molecule to a Si_3N_4 waveguide will be discussed, which is also presented in Ref. [66]. In particular, the limitations of this method and how these can be overcome with future work will be focused on. A variety of experiments working towards integrating DBT into circular Bragg cavities will be presented. The thesis will then finish with a summary and an overview of future work.

2. Growth methods

Unlike a free space atom or ion in a vacuum chamber, a solid-state emitter is embedded within a much larger matrix. The choice of solid-state host matrix for a single photon emitter is key in determining its optical and physical properties. The material chosen and the production method both contribute to the final properties of the single photon source. For defect centres in crystals or QDs the material is dictated by the choice of crystal or semiconductor. However, for any given organic molecule emitter there are a large number of potential host matrices [78], with the choice having significant affect on the properties of the emitter [63].

There have been three distinct types of host matrix used for performing spectroscopy on single molecules [78]; Shpol'skii matrices [79], polymers [80] or organic crystals [81]. A Shpol'skii matrix is used as a general term for a host matrix that is liquid or gas at room temperature and freezes the dopant single emitter in place when cooled for spectroscopy. These were used in the first spectroscopic measurements on single PAH molecules, however the transient nature of the host matrix means they are not suitable for producing a robust single photon emitter. A polymer matrix is solid at room temperature, however the long polymers result in a disordered structure, and consequently molecules with broad transitions due to dephasing [80]. Organic crystalline matrices are the preferred host for single photon generation. These use a smaller PAH as a host, which is doped with the larger PAH emitter. The π bonding, in particular π -stacking, between the PAH results in an ordered, crystalline host.

Anthracene has previously been identified as having ideal properties as a host for DBT molecules [65]. It is transparent at the relevant wavelengths, it provides protection from the environment, and DBT is capable of lifetime-limited linewidth emission at low temperatures when hosted within it [82]. The interaction of a DBT molecule with the phonons in the host matrix will be discussed in greater detail in Chapter 3. Instead, this chapter will focus on the fabrication method used to prepare the DBT/Ac matrix. Not all Ac host matrices are equal and to achieve spectrally narrow emission with long-term stability care has to be put into the method of growth. Additionally, different uses for the single photon emission call for different

host properties and sizes.

Co-sublimation [81] and melt [75] growth methods developed by other members of the group, but used for experiments in this thesis, will first be briefly described. This will be followed by work replicating a re-precipitation [68] growth method for producing Ac nanocrystals, which is used in Chapter 3 and 4 and Ref. [23]. Finally, a new nanocrystal polymethyl methacrylate (PMMA) encapsulation technique will be described in detail [69].

2.1. Co-sublimation growth

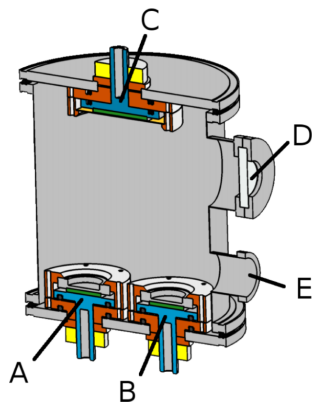


Figure 2.1. – Diagram of a cut-through of the co-sublimation chamber, taken from Ref [81]. A: Ac crucible. B: DBT crucible. C: Growth Plate. D: Viewing port. E: Vacuum Port.

Co-sublimation crystal growth is a mature method within the research group. The development of this technique is detailed in Ref. [83] and the growth chamber construction is also described in Ref. [81]. This section will simply provide brief context as this growth method is used in later experiments. A home-built co-sublimation chamber is used to reliably grow large, flat DBT-doped Ac crystals, on the order of mm tall and wide with sub-micron thickness. The growth chamber is shown in Fig. 2.1, and consists of two independently temperature controlled crucibles and a water-cooled growth plate. The temperature of the Ac crucible affects the growth rate and morphology of the crystals that deposit on the top growth plate. The crystal used later in this thesis had the Ac crucible set to 162 °C. The entire chamber itself is also heated to approximately 80 °C and the growth plate cooled to 50 °C to encourage deposition only on the growth plate.

The temperature of the DBT crucible controls the DBT concentration within the crystals. DBT has a significantly lower vapour pressure than Ac and a temperature of 180 °C resulted in the low-doped crystal used in the later experiment. The vacuum port is used to evacuate air and purge the chamber with nitrogen, preventing oxygen from entering the crystals during growth and causing photo-bleaching of the DBT molecules. A growth typically takes two hours, plus time for heating and cooling the chamber, after which tweezers can be used to remove crystals from the growth plate. These can then be placed on a substrate of choice and spin-coated with ~ 200 nm of PVA to inhibit sublimation of anthracene, protect them from the environment and ensure they remain on the substrate.

2.2. Melt growth

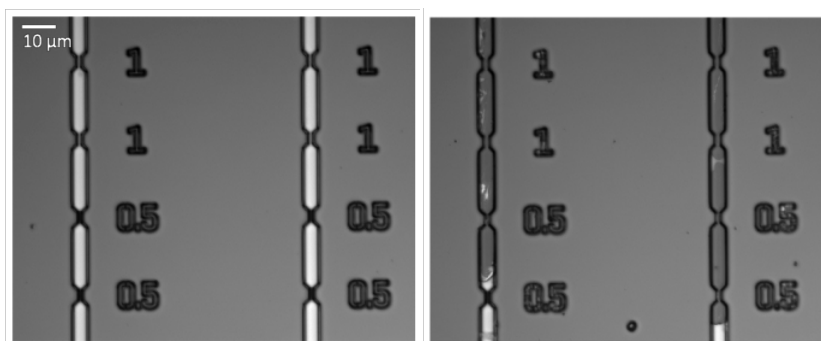


Figure 2.2. – White light images of micro-capillaries running vertically through a SiO_2 layer. Numbers on sample indicate width at the tapered sections in microns. A melt growth technique is used to fill the empty micro-capillaries (left) with a DBT/Ac mixture (right).

Unlike the other growth methods described in this section, melt growth methods typically involve flowing molten DBT-containing Ac onto, or into, a structure, where it can crystallise *in-situ*. This can give greater control over placement of the crystals, however ensuring that the DBT is well included within an ordered Ac matrix requires precise control over growth parameters and the geometry of the structure [84]. This growth method is based on previous work shown in Refs. [85] and [86].

A melt growth technique is used within the group to fill micro-capillaries in Si_3N_4 on SiO_2 on Si. Figure 2.2 shows an example of the filling of micro-capillaries using this method. These micro-capillaries run the width of the chip, with each end open. To fill with DBT/Ac, the chip is clamped to a copper block on a hotplate which is heated to 210°C in a N_2 filled fume cupboard. The N_2 atmosphere is used to prevent O_2 entering the Ac matrix and subsequently causing the DBT molecules to photo-bleach. The DBT/Ac mixture is placed at one end of the capillary to be filled, and capillary action is responsible for filling once the DBT/Ac melts. The hotplate can then be turned off to cool the chip before removal. A Peltier is used for additional heating power when the Ac is near its melting point as Ac sublimates rapidly before it reaches its melting point. If the heating takes place too slowly a majority of the Ac/DBT will sublime before it can melt, and a poor quality filling is seen within the micro-capillaries. Results from this growth method will be discussed in Chapter 4 and can be seen in Ref. [66].

2.3. Reprecipitation growth

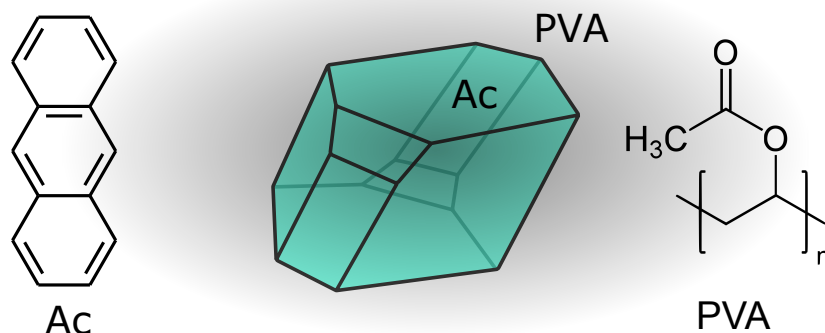


Figure 2.3. – Chemical structures of Ac and PVA with an artist's impression of an Ac nanocrystal in typical crystal habit (green) in a spin-coated PVA layer (grey).

Reprecipitation growth is a method using sonication [87, 68] to produce Ac nanocrystals (NCs) containing DBT. These nanocrystals are typically sub-micron in diameter and once protected with a 200 nm PVA film show stable, narrow DBT emission lines. Figure 2.3 shows the chemical structures of the Ac and PVA along with an artist's impression of a typical Ac nanocrystal in a PVA film. Collection of light from the nanocrystals is typically more efficient than from the co-sublimation crystals as there is minimal internal reflection of light at the crystal boundary. They are also ideal when an isolated single molecule is required, as in the following chapter [23], as they can be doped with DBT to achieve one molecule per crystal (on average). The small size also makes them ideal for integrating DBT into nanophotonic structures [88].

This section will detail the growth method used and characterisation of both the morphology and optical properties of the NCs.

2.3.1. Reprecipitation growth method

Reprecipitation based methods for the formation of organic nanoparticles have been covered in the literature for some time [89], but these were focused on polymers and often result in larger particles with more aggregation. Research on sonication based growth methods show that the acoustic cavities forming during sonication affect the crystal growth [87]. The high frequency of cavity formation and the extreme conditions within are thought to result in a high rate of nanocrystal formation, promoting the growth of a larger number of smaller nanocrystals, ideal for my purposes.

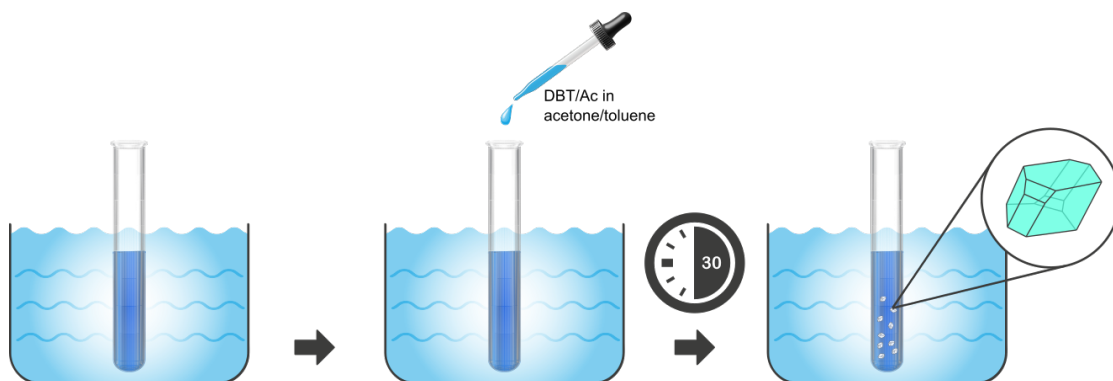


Figure 2.4. – Schematic of the Ac nanocrystal growth procedure. 5 ml of distilled water is degassed in the sonicator. 250 μ l of DBT/Ac in an acetone and toluene solution is added to this. See text for details regarding concentrations. After 30 min of sonication at 37 kHz Ac nanocrystals have formed in solution, as shown by the inset figure. This solution can then be pipetted onto a substrate of choice, where the water will evaporate leaving nanocrystals for analysis.

This growth method uses the general technique described in Ref. [68]. For the following experiments, 10 μ l of a DBT in toluene solution was added to 10 ml of 5 mM anthracene in acetone solution. The concentration of the DBT in toluene solution can be varied to change the final DBT content of the nanocrystals, with some trial and error being initially required to get a useful concentration. 250 μ l of this mixed solution was then added to 5 ml of degassed, distilled water. This was sonicated at 37 kHz¹ for 30 min. Figure 2.4 shows a schematic representation of this growth procedure. Growths used in later experiments maintained the bath temperature at 50 °C to prevent warming during the sonocation.

The NCs can then be used as produced or the growth solution can be passed through a filter to give greater control of the size. The filtering involves pouring the growth solution into a syringe and passing it through a filter of the desired size that attaches to the end of the syringe. Droplets of filtered and unfiltered solution were deposited onto a substrate and left to evaporate before being analysed by atomic force microscopy (AFM). Figure 2.5(a) and (b) show histograms of root mean squared (RMS) side length for unfiltered and 0.45 μ m pore size filtered nanocrystals. Image recognition filters in Mathematica are used to identify individual nanocrystals and extract their surface area. The root mean square side length is then found from the square root of this area. For these calculations large aggregations of NCs were ignored as determining individual

¹One of the limited preset frequencies on the sonicator.

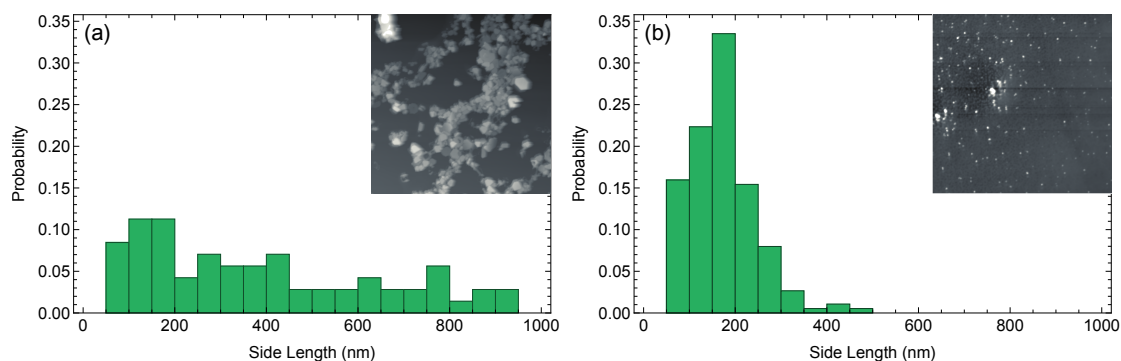


Figure 2.5. – Histogram of RMS nanocrystal side length for unfiltered (a) and 0.45 μm pore size syringe filtered (b) solutions after deposition on silicon nitride. Insets are 20 μm by 20 μm AFM scans used to calculate RMS side length. Colour corresponds to the height of nanocrystal.

component size is impractical. Height is not taken into account as the AFM has a systematic offset across a scan. Filtering reduced mean side length from 550 nm to 170 nm.

Once the NCs have been grown (and optionally filtered) a small droplet, typically 5 μl , can be deposited onto a substrate and left to evaporate. This is then spin-coated with ~ 200 nm of PVA before use. This PVA layer is required to see any stable emission, testing with no PVA or with a reduced thickness of PVA resulted in unstable emission. The following initial characterisation was performed using unfiltered NCs.

2.3.2. Nanocrystal optical properties

This section will cover the characterisation of the optical properties of DBT within the nanocrystals. Initial analysis was performed in a room temperature confocal microscope to determine if DBT was present.

Room temperature confocal microscopy

Nanocrystals containing DBT molecules were observed using the confocal microscope shown schematically in Fig. 2.6. There are a variety of different lasers available to use, this data was taken using an MSquared Solstis Ti:Sapphire laser at 785 nm. The laser light is coupled to the table through a polarisation maintaining fibre (PMF), and is collimated using an aspheric lens (AL). A half wave plate (HWP) and polarising beam splitter (PBS) clean the polarisation of the fibre output, then a second HWP rotates the linear polarisation to lie along the optical transition dipole of the DBT molecule. A neutral density filter (ND) controls the pump power and a filter

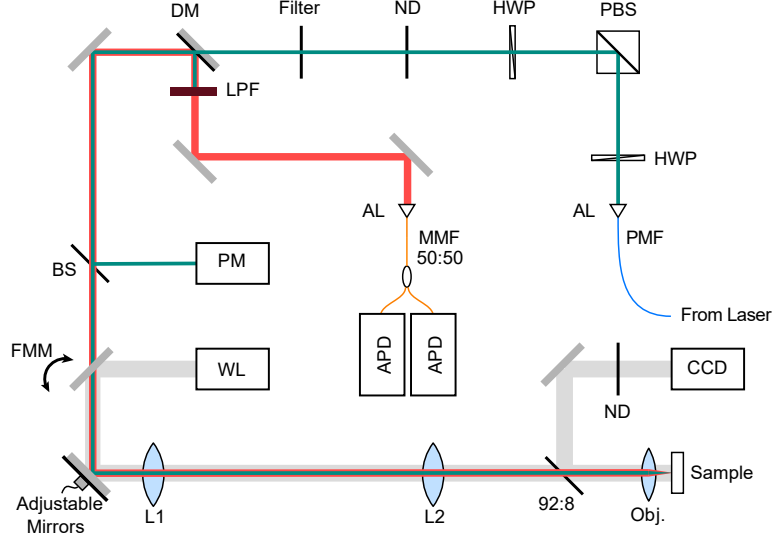


Figure 2.6. – Schematic diagram of the room temperature confocal microscope. Dark green beam indicates the pump light, red is the fluorescence and grey is the white light used for imaging. PMF: polarization maintaining fibre; AL: aspheric lens fibre coupler; HWP: half-wave plate; PBS: polarizing beam splitter; ND: neutral density filter; DM: dichroic mirror; BS: beam sampler; PM: power meter; FMM: flip-mount mirror; WL: white light source; L1: first lens; L2: second lens; Obj: microscope objective lens; CCD: charge-coupled device camera; LPF: 800 nm long pass filter; MMF 50:50: multimode fibre beam splitter; APD: avalanche photodiode.

(Filter) removes any light of unwanted wavelength coming from the laser or from fluorescence of optical components up to this point. For resonant pumping a 780 ± 5 nm bandpass filter is used. After passing through the dichroic mirror (DM) and beam sampler (BS) (used to monitor the forward power), the angle of the beam is scanned by two galvo mirrors. The flip-mount mirror (FMM) is used for white light imaging then flipped down during laser excitation. The beam then passes through lenses, L1 (focal length $f_1 = 75$ mm) and L2 ($f_2 = 250$ mm), in a ‘4f’ arrangement, where the scanning mirrors lie at $2f_1 + 2f_2$ from the back aperture of the microscope objective (Obj, Nikon PlanApo 100x, 0.9NA).

This arrangement allows the galvo mirrors to scan the focal spot on the sample, while always filling the aperture of the objective to produce a Gaussian spot of ~ 720 nm FWHM². The sample in this case was nanocrystals grown with 10 μ l of 0.1 μ M DBT/Toluene solution deposited onto

²Focal spot size from separate calibration grid measurements.

an approx. 1 cm by 1 cm silicon nitride wafer and covered with a 200 nm thick PVA layer, held in place using a vacuum chuck. Red-shifted fluorescence from the DBT molecules travels back to the dichroic mirror, which reflects it through an 800 nm long pass filter (LPF, to block scattered excitation light), and into a multimode fiber (MMF). A 50:50 fiber splitter delivers the light to two avalanche photodiodes (Perkin Elmer, APD) so that the second-order correlation function, $g^{(2)}(\tau)$, can be measured, although this functionality is not used for these measurements.

To verify the presence of quantum emitters, spatial fluorescence scans were recorded by scanning a resonant laser beam across the sample. The polarisation dependence of the emission intensity was measured by repeating these scans as the HWP in the beam path was rotated. A bright point on the scan was selected for analysis. Count rate data for a 6 by 6 pixel area ($1.44 \mu\text{m}^2$) around the bright point was averaged and background subtracted from a neighbouring molecule-free area to provide an estimate for molecule brightness. Figure 2.7(a) shows this data plotted with a $\sin^2 \theta$ curve, showing clear polarisation dependence. This polarisation dependence is due to the varying overlap of the molecule dipole with the polarisation of the excitation light. Although the molecules are expected to have a fixed dipole orientation relative to the Ac crystal axes [81], their small size means the Ac crystals can be pointing in any direction relative to the substrate. An out-of-plane dipole would show imperfect extinction which, along with contributions from scattered laser light and other molecules, could explain Fig. 2.7(a) not dropping to zero. The count rate was also measured for increasing excitation intensity as shown in Fig. 2.7(b). The emitter is clearly saturating as the power increases. These results are indicative of a quantum emitter, assumed to be DBT, and a sample was placed into a cryostat for further analysis.

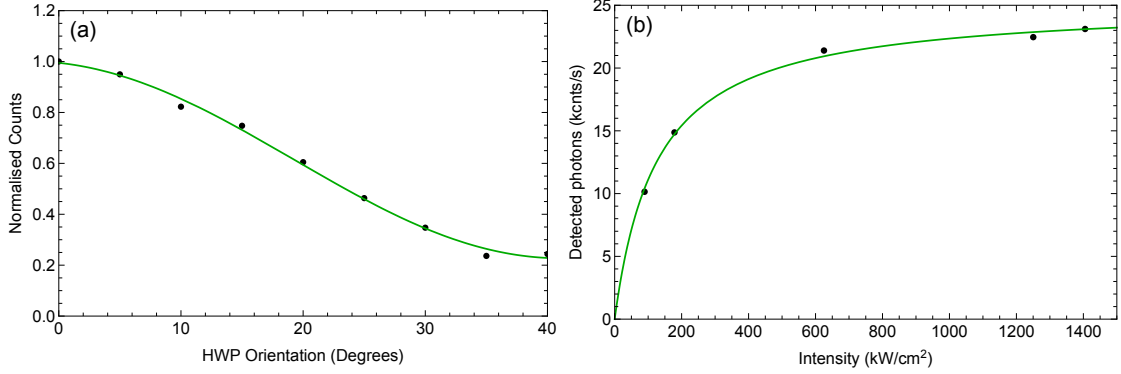


Figure 2.7. – (a) Normalised counts from a molecule as a function of HWP angle θ showing extinction, plotted with a $\sin^2(\theta)$ curve showing approximately 70 % extinction. (b) Average background subtracted counts from a molecule as a function of excitation power. Data is fitted with Eq. 1.9.

Low temperature confocal microscopy

A nanocrystal growth was performed with a thousand times higher DBT concentration. This was again deposited onto a 1 cm by 1 cm silicon nitride wafer protected with 200 nm of PVA and cooled to approximately 4.7 K in a Montana Cryostation cryostat. This is a closed-cycle cryostat featuring a 3-axis Attocube Piezo sample positioning system and objective within the sample chamber. This allows the position to be moved within the cryostat whilst remaining at cryogenic temperatures. A functionally similar confocal microscope, shown in Fig. 2.8, is used to analyse these cold samples. The main difference is the use of a 90 : 10 reflection:transmission beamsplitter instead of a dichroic mirror to separate the excitation and collection pathways, allowing greater combinations of excitation wavelength and collection filtering to be used.

White light imaging with a CCD camera was then used to identify and focus on a nanocrystal. The ‘terascan’ functionality of the SolSTiS laser was then used to scan between 783 nm to 786 nm whilst monitoring APD counts to find the ZPL transition of a molecule. The terascan functionality stitches many resonator scans together to provide a gapless scan of wide wavelength ranges. A sharp increase in counts indicates a molecule is present at that wavelength (and location). The excitation laser is scanned several gigahertz across the molecule ZPL frequency, at a variety of powers, to determine its stability and linewidth. This process was repeated at a number of sites to collect data for 17 identified molecules. Equation 1.10 can then be fitted to find the linewidth $\Delta\omega$; this is described in greater detail later in this section.

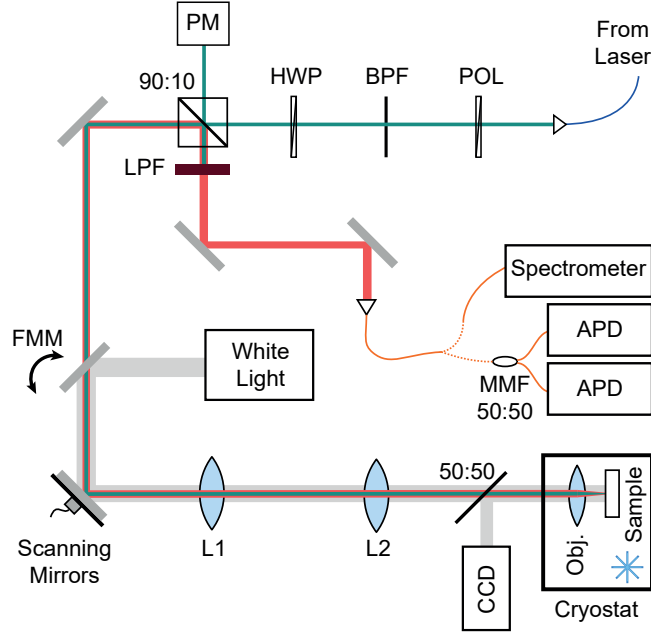


Figure 2.8. – Schematic diagram of the cryogenic confocal microscope. Dark green beam indicates the pump light, red is the fluorescence and grey is the white light used for imaging. Pol: polarizer; BPF: band-pass filter; HWP: half-wave plate; 90:10: 90% reflection, 10% transmission cube beam splitter; PM: power meter; FMM: flip-mount mirror; L1: first lens; L2: second lens; 50:50: 50% reflection, 50% transmission pellicle beam splitter; Obj.: microscope objective lens; CCD: charge-coupled device camera; LPF: long-pass filter; MMF 50:50: 50% reflection, 50% transmission multimode fibre beam splitter; APD: avalanche photodiode.

Defining a stable molecule as one which gives a consistent, Lorentzian response to the laser as it scanned with no drift in ZPL frequency, approximately 50 % of the molecules (10 out of 17) show stable emission. Figure 2.9(a) shows the measured linewidths for these molecules. The linewidth of the stable molecules has a mean of 84 MHz and a standard deviation of 15 MHz. These were measured with an excitation intensity of approximately 1 W cm^{-2} , or $S \approx 1$. Assuming $S = 1$, this would give a power-broadening factor to the width of the ZPL of $\sqrt{1 + S} = \sqrt{2}$. Accounting for this, the low-power linewidth, or $2\Gamma_2$, is approximately 60 MHz. This is higher than the 50 MHz reported by Pazzagli *et al.* [68] and the lifetime limit of 40 MHz [81].

Future growths using high purity zone-refined Ac were able to reduce this linewidth, as seen in the following section, however we are also limited by the base temperature of the cryostat.

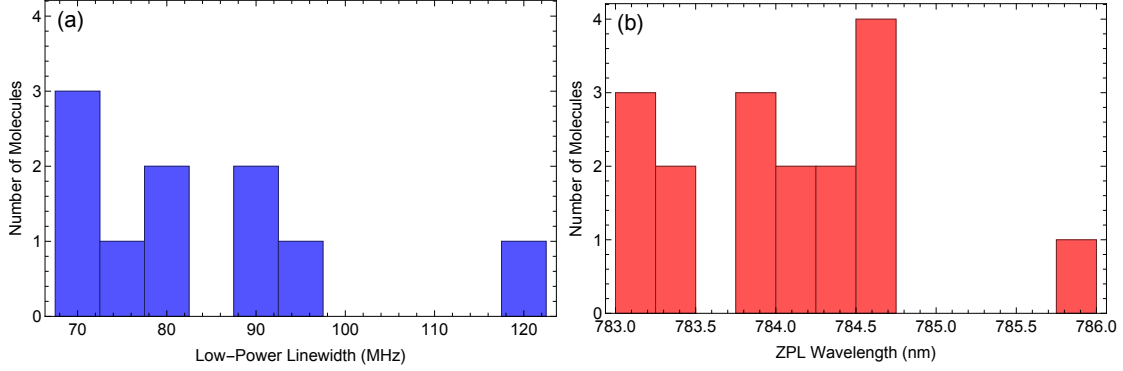


Figure 2.9. – (a) Low-power linewidth for 10 stable DBT molecules in nanocrystals (b) ZPL wavelength for 17 DBT molecules in Ac nanocrystals.

Zone-refining uses spatially controlled crystallisation to concentrate impurities at the edge of an Ac crystal, which can then be removed. To achieve lifetime-limited linewidths the sample would ideally be cooled below 3 K, however this is not possible with the current cryostat due to the limited cooling power. The ZPL wavelengths shown in Fig. 2.9(b) are in line with those of DBT in bulk anthracene, with their inhomogeneous distribution of frequencies. This data indicates there has been no significant change in the properties of DBT when included instead in nanocrystals of Ac.

A stable molecule was chosen for more thorough analysis; Fig. 2.10 shows the data collected for this molecule. The molecule had a ZPL wavelength of 785.80 nm. Figure 2.10(a) shows a scan through the line taken at an intensity of 0.94 W cm^{-2} at the objective lens. A fit to this line using Eq. 1.10 determines the background and the centre frequency. Scans taken at a number of different laser intensities are similarly fitted, allowing the fits to differ in centre frequency because the start frequency of each scan is susceptible to some variation. After removing the backgrounds and aligning the centres, the whole data set is then fitted with

$$R(I, \Delta) = \frac{R_{\infty} S}{\Delta^2 / \Gamma_2^2 + 1 + S}. \quad (2.1)$$

where I is the measured intensity, $S = I/I_{\text{sat}}$, $2\Gamma_2$ is the zero-intensity linewidth, $\Delta\omega$, and Δ is the laser frequency detuning from the ZPL centre frequency [71]. This gives a zero intensity linewidth of $\Delta\omega/2\pi = 73.2 \pm 0.2 \text{ MHz}$ and a saturation power of $I_{\text{sat}} = 1.49 \pm 0.09 \text{ W cm}^{-2}$, before the objective. Additionally, a count rate at infinite intensity of $R_{\infty} = 800 \pm 1 \text{ kcnt s}^{-1}$ is measured. The corresponding power broadening and saturation functions for these values are

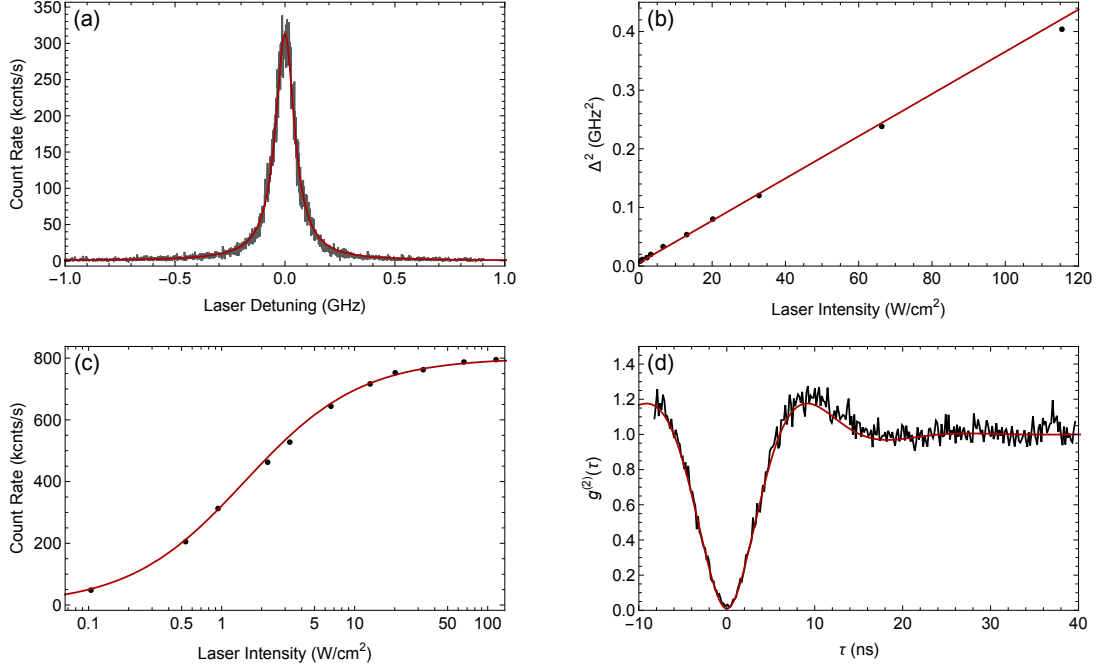


Figure 2.10. – (a) Data is detected fluorescence as a function of excitation laser wavelength showing the Lorentzian shape of a molecule resonance, exciting with $I = 0.94 \text{ W cm}^{-2}$, fitted with Eq. 1.10. (b) Data points are linewidth as a function of pump power taken from fitting Lorentzians to linescans. Fitted line is of the form given in Eq. 1.11, using $\Delta/2\pi = 73.2 \pm 0.2 \text{ MHz}$, $I_{\text{sat}} = 1.49 \pm 0.09 \text{ W cm}^{-2}$ from global fit [71]. (c) Data is count rate as a function of pump power for resonant pumping, taken from fitted linescans (see (a)). Fitted line is of the form Eq. 1.9, with $R_{\infty} = 800 \pm 1 \text{ kcnt s}^{-1}$, $I_{\text{sat}} = 1.49 \pm 0.09 \text{ W cm}^{-2}$ taken from global fit. (d) The black is data from the second-order correlation function measurement exciting with $I = 5.21 \text{ W cm}^{-2}$, showing a characteristic photon anti-bunching dip. Red line is of the form given in Eq. 2.2.

shown in Fig. 2.10(b) and (c) respectively, plotted with data points taken from the individual fits to show the correspondence.

Additionally, the second-order correlation function $g^{(2)}(\tau)$ was measured for this molecule, plotted in Fig. 2.10(d), exciting with 5.21 W cm^{-2} . The coincidence data is normalised and plotted as a function of time delay from a detection event on one detector, τ . This was then fitted with

$$g^{(2)}(\tau) = 1 - \mathcal{V} \frac{p+q}{2q} e^{-\frac{1}{2}(p-q)\tau} + \mathcal{V} \frac{p-q}{2q} e^{-\frac{1}{2}(p+q)\tau}, \quad (2.2)$$

where

$$\begin{aligned} p &= \Gamma_1 + \Gamma_2, \\ q &= \sqrt{(\Gamma_1 - \Gamma_2)^2 - 4\Omega^2}, \\ \Omega &= \sqrt{\Gamma_1 \Gamma_2 S}, \end{aligned} \quad (2.3)$$

which is based on Eq. 1.15, with a visibility term, $\mathcal{V}$, to account for background light and fluorescence from other molecules. This is also convolved with a Gaussian with, 320 ps standard deviation³, to account for the detector jitter. Γ_2 , S are known from above, and the fit gives $\Gamma_1 = 2\pi \times 32.5 \pm 0.2 \text{ MHz}$ and the visibility as $\mathcal{V} = 0.99 \pm 0.01$. This indicates a high photon purity from DBT emission in nanocrystals. The slight increase around $\tau = 8 \text{ ns}$ is due to Rabi oscillations, caused by strong excitation intensity relative to the saturation intensity.

This data indicates that the unfiltered DBT/Ac nanocrystals are working as expected from Ref. [68], and suitable for use. The high $g^{(2)}(\tau)$ visibility is particularly promising for the characterisation of single DBT molecules. This is taken advantage of in Section 3.2, where data from a DBT molecule in a $0.45 \mu\text{m}$ filtered nanocrystal is used.

³Value comes from separate measurement of a laser pulse using the same interferometer, and is line with manufacturer specifications.

2.4. Polymer encapsulation

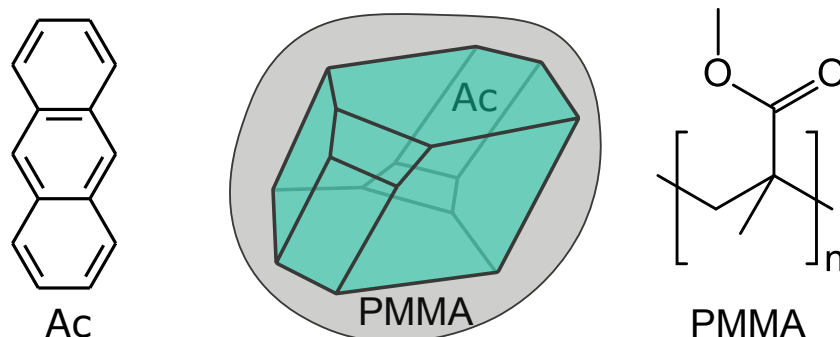


Figure 2.11. – Chemical structures of Ac and PMMA with an artist’s impression of a cut through of a PMMA nanocapsule (grey) containing an Ac nanocrystal in typical crystal habit (green).

This section describes the development of a polymethyl methacrylate (PMMA), commonly known as acrylic, coating for the Ac nanocrystals. The small size of the Ac nanocrystals would initially make them appear to be ideal for incorporation into nanophotonic structures, however, they need to be coated with PVA to exclude oxygen and suppress sublimation, and this limits their use. For example, efforts to use surface tension to infiltrate NCs into holes [90] showed promise, but the inability to then surround the NC in PVA prevented narrow emission from being measured. Figure 2.11 shows the chemical structure of PMMA and an artist’s impression of the nanocapsule structure.

Polymer encapsulation instead provides a protective polymer layer to the nanocrystal itself during the sonication growth using an emulsion polymerisation method [91], resulting in a polymer nano/micro-capsule. The PMMA nanocapsule formation method is based on recipes used for the encapsulation of other hydrocarbon cores [92, 93, 94, 95]. An emulsion of the Ac NCs and MMA monomer in water is made through sonication at a raised temperature. A polymerisation initiator (tert-Butyl hydroperoxide) is then added. As the MMA polymerises to PMMA it becomes less soluble in water. This results in separation and favours the formation of the PMMA capsule around the also immiscible Ac NCs [91]. The polymerisation method will be covered in greater detail in the following section, before the properties of DBT in the nanocapsules are investigated. This work, which I will now describe in more detail, is published in Ref. [69].

2.4.1. Emulsion polymerisation

A similar NC growth technique as previously described, and shown in Fig. 2.4, is used to prepare a nanocrystal growth solution. Figure 2.12 shows this growth procedure. 20 ml of distilled water is sonicated for 5 minutes to deoxygenate it. 5 μ l of DBT (MercaChem) in toluene (VWR) solution is added to 10 ml of 5 mM zone-refined anthracene (Tokyo Chemical Industry UK) in acetone (VWR) solution. The concentration of the DBT in toluene can be varied to change the number of DBT molecules per nanocapsule, a concentration of 1 μ M is typical. 2 ml of this mixed solution is then added to the distilled water and sonicated at 37 kHz and 50°C for 30 minutes. The vial is uncovered for this. The larger ratio of anthracene to water and greater quantity of materials overall are used to increase the fractional precision in measuring the reagents.

The PMMA encapsulation is then performed using an emulsion polymerisation method [95]. 2 μ l of a 10:1 methyl methacrylate and allyl methacrylate solution (both Sigma-Aldrich, with no inhibitor and used as supplied), 7 μ l of a 10 μ M ammonium persulfate ((NH₄)₂S₂O₈, Sigma-Aldrich) and 0.1 μ g of ferrous sulphate heptahydrate (FeSO₄·7H₂O, Sigma-Aldrich) are added to the solution and sonicated for 10 minutes whilst the sonicator heats to 80°C. Unlike the polymerisation methods this is based on, no specific emulsifiers or surfactants are added, as a combination of the sonication, acetone and lower concentration of growth solution means they are not required. Allyl methacrylate is added with the MMA to increase the uniformity of the particles formed [93]. 10 μ l of 10 μ M sodium thiosulphate (Na₂S₂O₇, Sigma-Aldrich) and 0.1 μ l of 70% tert-butylhydroperoxide (tBuOOH, Sigma-Aldrich) are then added to begin the polymerisation. The solution is sonicated at 80°C for a further 2 hours whilst the polymerisation occurs. This solution is then pipetted onto a silicon nitride wafer for analysis, as was done previously with nanocrystals.

Visual analysis

Initial analysis consisted of visible light microscopy to visually determine the presence of polymer nanocapsules. A droplet of the growth solution was pipetted onto a Si wafer and left to evaporate for analysis. Comparison of a 50x magnification image of nanocapsules to a calibration grid (Au, 400 lines per inch) allowed the size distribution to be measured. The measured conversion factor is 7.4 pixels per micron. The image of nanocapsules was imported into Mathematica and the edge detect function was used to select individual nanocapsules. Shape constraints were placed on the aspect ratio/elongation of particles to avoid selecting clusters of nanocapsules, which were

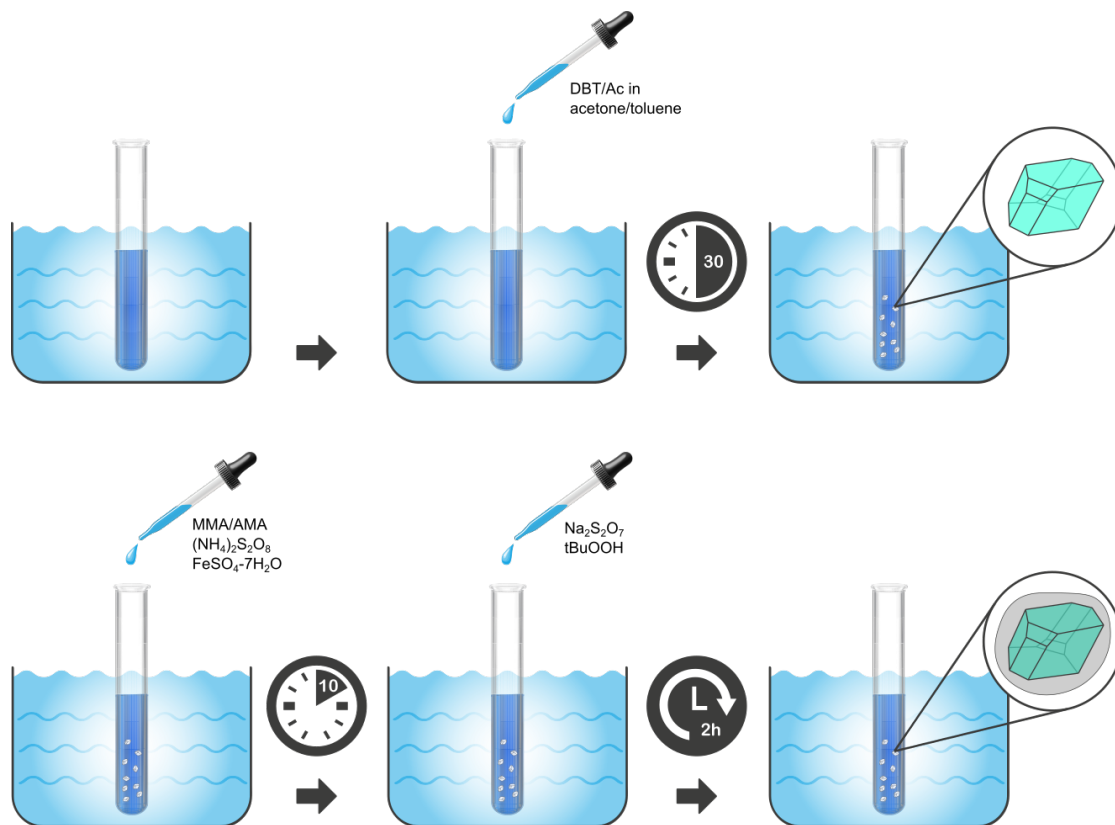


Figure 2.12. – Schematic of the PMMA nanocapsule growth procedure. The first three steps are similar to those shown in Fig. 2.4. 20 ml of distilled water is degassed in the sonicator. 2 ml of DBT/Ac in an acetone and toluene solution is added to this. See text for details regarding concentrations. After 30 min of sonication at 50 °C and 37 kHz Ac nanocrystals have formed in solution, as shown by the inset figure. MMA, AMA, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is then added and sonicated for 10 minutes to mix and heat to 80 °C. The polymerisation of the MMA/AMA is then initiated through the addition of tBuOOH and $\text{Na}_2\text{S}_2\text{O}_7$, and left for 2 h. After this time PMMA nanocapsules have formed in solution, as shown in the inset figure. The growth solution can then be deposited onto a substrate of choice, where water will evaporate leaving the PMMA nanocapsules.

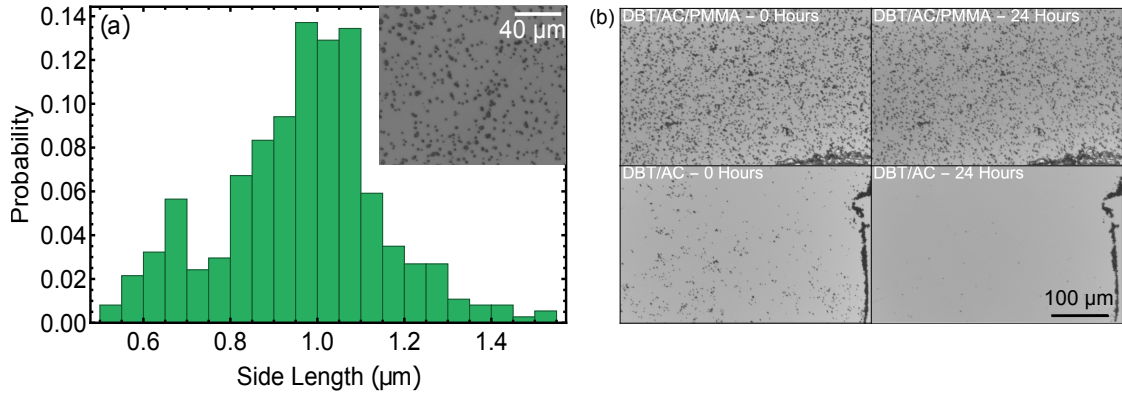


Figure 2.13. – (a) Histogram of single nanocapsule diameters taken from a 50x magnification image. Inset: 50x magnification image used. (b) White light images (20x magnification) of PMMA nanocapsules after deposition (top left) and 24 hours later (top right) and nanocrystals after deposition (bottom left) and 24 hours later (bottom right). Loss of material due to sublimation is clearly visible. Dark scratches on the surface are for orientation and are not included in the analysis.

unlikely to be (nearly) round like the nanocapsules. Fig. 2.13(a) is a histogram displaying the RMS side length of this data, derived from the area of nanocapsules in the inset of Fig. 2.13(a). The assumption that visible particles are actually Ac containing nanocapsules is investigated in the following section.

A mean side length of 960 ± 20 nm with a standard deviation of 180 nm is found. This is considerably greater than the 290 nm diffraction limit of the $NA = 0.8$ microscope objective and matches the result found in Ref. [95]. Using the same processing method on a 50x magnification image of uncoated nanocrystals gives a mean size of 760 ± 20 nm with a standard deviation of 140 ± 20 nm. The reason for the larger size of nanocrystals compared to the data shown in Fig. 2.5 has not been fully investigated, but is likely due to the greater volume of Ac and longer growth times. Addition of PMMA therefore results in a factor $\sim 2.0 \pm 0.2$ increase in particle volume, in line with the two-fold increase expected from the amount of monomer added. This gives a mean PMMA thickness of 100 ± 40 nm.

Filtering with a syringe pore-filter is likely to allow the size distribution to be controlled. 800 nm to 1200 nm filters are commercially available and will likely be investigated in the future. The ratio of MMA to Ac could also be tweaked to control the polymer thickness. The 1:1 ratio currently used is based on the literature which inspired this work [95], however future investigations could look into how thin the nanocapsule polymer could be made without affecting

the protection provided.

To test their longevity the nanocapsule and nanocrystal samples were left exposed for 24 hours. The nanocapsules were then compared to regular nanocrystals grown without polymerisation, as shown in Fig. 2.13(b). The top row of images are of PMMA nanocapsules after deposition (left) and 24 hours later (right). The bottom are images of uncoated Ac nanocrystals, again after deposition (left) and 24 hours later (right). Comparing the surface area covered of the images $\sim 96\%$ of the PMMA nanocapsules are remaining compared to $\sim 10\%$ of the nanocrystals. Visual analysis was also performed for different growth times from 1 h to 4 h to determine the optimal polymerisation time. There was no significant change in visual properties past the 2 h growth sample, however the growth solution began to evaporate dry so this was decided on as the optimal time.

2.4.2. Nanocapsule optical properties

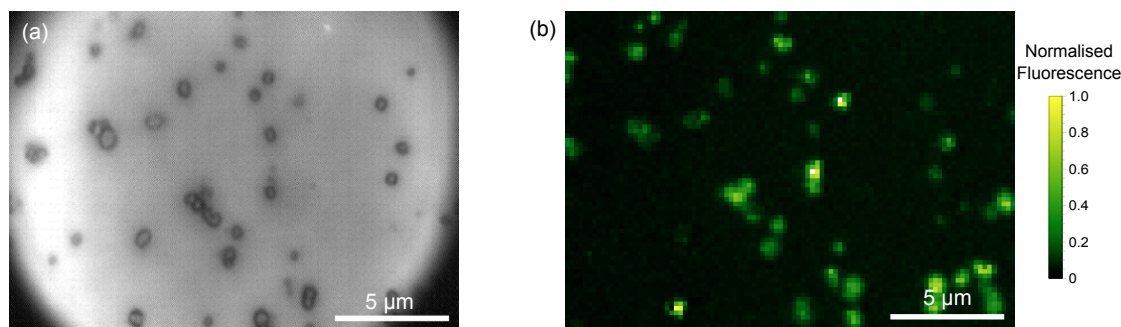


Figure 2.14. – (a) White light image of PMMA nanocapsules taken through the confocal microscope objective. (b) Fluorescence image of the region shown in (a) using 2.6 mW of 767 nm laser light.

Room temperature confocal microscopy

Similarly to the nanocrystal analysis, confocal fluorescence microscopy was initially used at room temperature to verify that DBT was contained within the nanocapsules. Unfiltered nanocapsules were deposited onto a 1 cm by 1 cm silicon nitride wafer and placed into the confocal microscope shown in Fig. 2.8⁴. To start with, the presence of DBT/Ac within the PMMA nanocapsules was confirmed. A Ti:Sapphire laser (Coherent MBR) was tuned to 767 nm and used to perform spatial fluorescence scans. Figure 2.14(a) shows a white light image of an area of the sample taken through the confocal microscope, and Fig. 2.14(b) shows a fluorescence image of the same region. Over 90 % of the visible nanocapsules show fluorescence, indicating that a majority of visible particles were nanocapsules containing DBT.

A well-isolated bright point, seen in the bottom left of Fig. 2.14(b), was selected for analysis. Polarimetry data, shown in Fig. 2.15(a), was recorded by rotating a HWP in the beam path and recording counts from the molecule. There is a clear polarisation dependence arising from the varying projection of the electric field of the light onto the molecular dipole moment. In order to measure the saturation behaviour of the molecule, the count rate is recorded as a function of power. Although this can be measured directly by varying power and recording the count rate that results in uncertainty, about the unknown background component. Instead, spatial fluorescence scans were performed at increasing powers. This involves raster scanning the beam

⁴Although this microscope has cryogenic capabilities, it was used at room temperature for these measurements.

position across the sample using the galvo scanning mirrors and recording the measured count rate at each position. The small size of the molecule relative to the beam means the fluorescence response simply maps out the laser spot. For each laser intensity, the peak fluorescence minus the background is recorded. Fitting this with a saturation curve clearly shows saturation behaviour, shown in Fig. 2.15(b). A similar fitting method, with saturating Gaussians, is used in Section 3.1, and more detail is given there.

A pulsed Ti:Sapphire laser was used to excite the molecule to perform a time correlated single photon counting experiment. Figure 2.15(c) shows the data and fitted exponential decay, giving a lifetime of 3.6 ± 0.2 ns, in line with what is expected from DBT in Ac NCs [68]. Considering these measurements, it can be seen that encapsulation within the PMMA shell has not caused any significant change in DBT properties, compared to DBT in both cosublimated and sonication grown crystals. Additionally, this molecule was consistently excited for many hours at high intensities without any blinking or change in spectral properties, highlighting the stability and protection provided by the PMMA nanocapsules.

To confirm the quantum statistics of the emitted light, the second-order correlation function was measured by splitting the emitted light onto two detectors and recording the delays between photon arrival times. At room temperature the high dephasing rate means Eq. 2.2 is not required to describe this anti-bunching behaviour, and instead the simplified equation shown in Eq. 1.17 can be used [71]. As with Eq. 2.2, the equation is modified to account for visibility, $\mathcal{V}$, giving

$$g^{(2)}(\tau) = 1 - \mathcal{V}e^{-\Gamma_1(1+S)|\tau|}. \quad (2.4)$$

Figure 2.15(d) shows the data and fitting of this measurement, giving $\mathcal{V} = 88 \pm 3\%$, which indicates that the fluorescence comes from a single quantum emitter. The next stage was to cool down a sample to verify if the coherence properties are unaffected.

Low temperature confocal microscopy

An unfiltered sample of DBT-doped anthracene nanocrystals coated in PMMA with twice the DBT concentration was cooled down to 4.7 K in the cryostat to measure their low temperature properties, using the same confocal microscope. There was no additional polymer coating on the sample, the nanocapsules were being used as-is after evaporation. Spatial fluorescence scans were performed to identify regions of bright emission for further investigation. A stable molecule was identified at 783.484 nm using the ‘teraScan’ functionality between 782 nm to 785 nm. Linescans were performed using resonant excitation at a variety of laser powers whilst measuring the

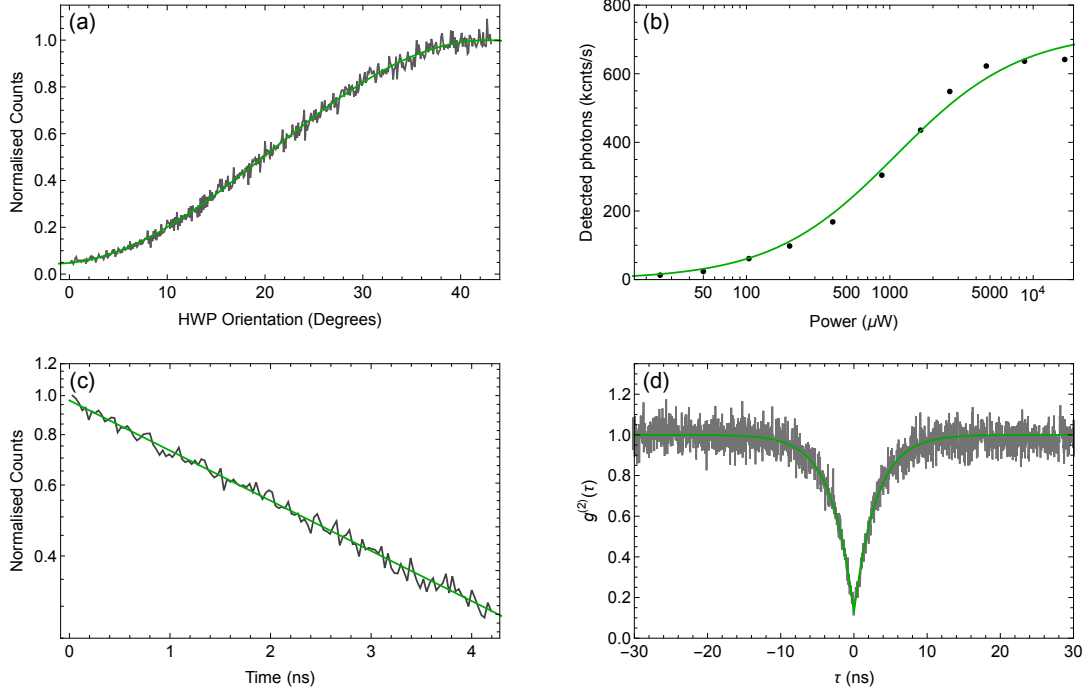


Figure 2.15. – Optical properties of DBT in a PMMA nanocapsule at room temperature. (a) Black is normalised count rate from the selected molecule as the half-wave plate is rotated, fitted a $\sin^2 \theta$ curve in green. (b) Data points are the peak fluorescence count rate measured from spatial scans of the molecule at increasing pump powers. Fitted line is of the form given in Eq. 1.9, giving a maximum count rate of $720 \pm 20 \text{ kcnt s}^{-1}$. (c) Black is data from a TCSPC measurement. Green line is an exponential decay fitted to the tail of the data giving a lifetime of $\tau_1 = 3.6 \pm 0.2 \text{ ns}$. (d) The black is data from the second-order correlation function measurement exciting with $P = 1.26 \pm 0.01 \text{ mW}$, showing a characteristic photon anti-bunching dip. Green fitted line is Eq. 2.4, showing a visibility of $88 \pm 3 \%$.

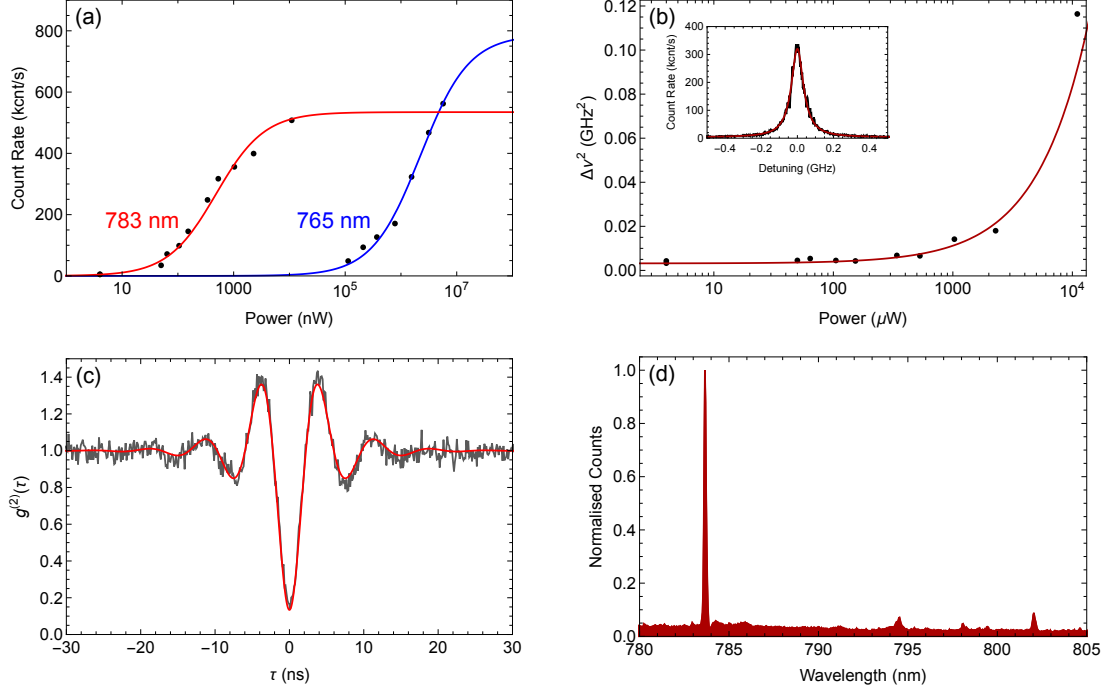


Figure 2.16. – Optical properties of a DBT molecule in a PMMA nanocapsule at cryogenic temperatures. (a) Count rates for resonant (783 nm, points with red curve) and blue-detuned (765 nm, points with blue curve) pumping for different pump powers. Resonant data is taken from fitted linescans (see (b)) and blue-detuned data is from spatial fluorescence scans. Fitted lines are of the form given in Eq. 1.9, giving $R_\infty = 540 \pm 40 \text{ kcnt s}^{-1}$ and $R_\infty = 780 \pm 50 \text{ kcnt s}^{-1}$ for the resonant and blue-detuned cases respectively. (b) Data points are linewidth as a function of pump power taken from fitting Lorentzians to linescans. Fitted line is of the form given in Eq. 1.11. Inset: Example of detected fluorescence as a function of excitation wavelength showing the Lorentzian shape of a molecule resonance, see Eq. 1.10, exciting with $P = 530 \pm 1 \text{ nW}$. (c) The black is data from the second-order correlation function measurement exciting resonantly with $P = 5.49 \pm 0.01 \text{ }\mu\text{W}$, showing a characteristic photon anti-bunching dip. As excitation is resonant, only fluorescence that passes through a 800 nm long pass filter is measured. Red line is of the form given in Eq. 2.2. (d) Fluorescence spectrum of a single molecule.

red-shifted fluorescence. Fitting Lorentzians curves to these allowed the maximum counts and linewidth to be determined. Figure 2.16(a) shows the maximum count rate as a function of power, and a saturation curve (red) fitted to the count rate data gives a $R_{\infty} = 530 \pm 40 \text{ kcnt s}^{-1}$, in line with what is seen for regular nanocrystals. The linewidth as a function of power is shown in Fig. 2.16(b). Fitting the linewidths with a power broadening curve gives a zero-power linewidth of $\Delta/2\pi = 56 \pm 4 \text{ MHz}$. The inset of Fig. 2.16(b) shows an example of the Lorentzian lineshape fitting.

The second-order correlation function, $g^{(2)}(\tau)$, was also measured, with Fig. 2.16(c) showing the characteristic Rabi oscillations from strong resonant pumping [71]. After convolving Eq. 2.2 with a Gaussian describing the 320 ps detector timing-jitter, this equation was fitted to the data. Γ_2 and S are known from the linescans, leaving $\mathcal{V}$ and Γ_1 as free parameters. A visibility of $\mathcal{V} = 87 \%$ was measured. The lower visibility than typical from nanocrystals is thought to be due to this molecule being present in a large nanocapsule with a broadband background from DBT not well included within the Ac core. The fit also gave $\Gamma_1 = 2\pi \times 41 \pm 5 \text{ MHz}$, corresponding to a lifetime of $3.9 \pm 0.4 \text{ ns}$, a typical value for DBT [68]. The increased Δ compared to Γ_1 is thought to arise from thermal dephasing which will be discussed in the next chapter.

To determine if there has been any change in the emission spectrum of DBT due to the nanocapsules the laser was tuned to 765.81 nm, resonant with a transition to an excited vibrational level of the excited electronic state. Spatial fluorescence scans were performed at increasing powers and fitted with Gaussians to give the count rates shown with the blue curve in Fig. 2.16(a). These scans were performed with a $785 \pm 3 \text{ nm}$ filter in collection. This bandpass filter was then replaced with a 770 nm longpass filter and the emission was sent to an Andor spectrometer. This data is shown in Fig. 2.16(d). The strong ZPL is visible at 783.6 nm, along with three vibrational transitions at 794.5 nm, 798.1 nm and 802.0 nm representing emission from $S_{1,0} \rightarrow S_{0,n}$ transitions. These vibrational energy spacings are in line with calculated and measured values for DBT [96, 23].

After verifying that the polymer encapsulation has not negatively affected the properties of this molecule, additional molecules were identified to determine the reliability of this growth method. Resonant linescans were then repeated at varying powers to determine the zero-power linewidth and ZPL frequency for 34 additional molecules, shown in Fig. 2.17. A majority of the molecules are stable, with resonance linewidths near the lifetime limit as shown in Fig. 2.17(a). The inhomogeneous broadening of ZPL wavelengths shown in Fig. 2.17(b) is also in line with expectations. Overall, this data shows that the PMMA encapsulation has no negative effect on

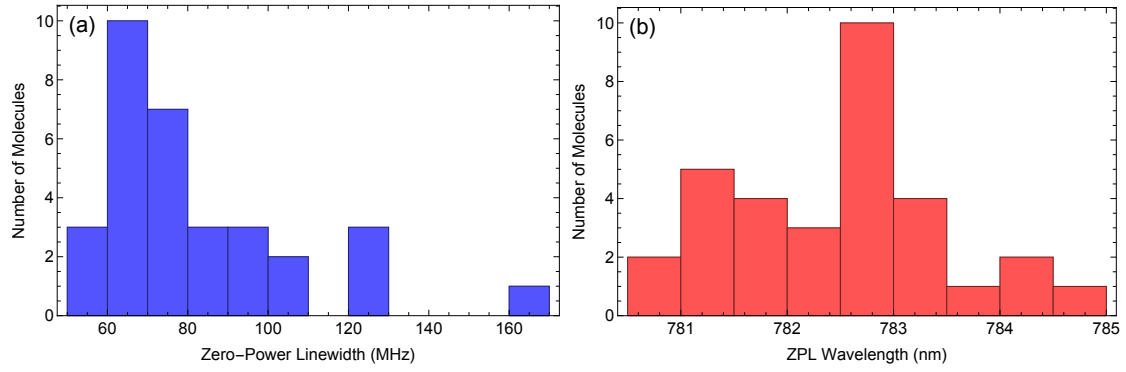


Figure 2.17. – (a) Zero-power linewidths for 35 identified DBT molecules in PMMA nanocapsules.
(b) ZPL wavelength for 35 DBT molecules in PMMA nanocapsules.

the emission properties of the DBT and the capsule does not require further polymer protection, such as with the PVA used on the nanocrystals. The final chapter of this thesis will detail initial efforts to incorporate nanocapsules into nanophotonic structures. However, first I present a detailed study of vibrations and phonon interactions of DBT in anthracene at various temperatures, and how this affects the efficiency of excitation and emission, as well as the coherence properties of the emitted photons.

3. DBT and phonons

Vibrations in the Ac host matrix have a major role in determining the optical properties of a DBT molecule. These vibrations, or phonons as they will be called to distinguish them from the internal vibrational modes of the DBT molecule, broaden the linewidth of spontaneously emitted photons from the lifetime limit by dephasing superpositions of the excited electronic and ground electronic states of the molecule. This reduces the indistinguishability of emitted photons. The linewidth of an emitted photon is twice the dephasing rate, Γ_2 [71], which in turn can be expressed as

$$\Gamma_2 = \Gamma_1/2 + \Gamma_2^*(T). \quad (3.1)$$

Γ_1 is the population decay rate, or the inverse of the excited state lifetime, and is the minimum linewidth possible due to uncertainty. This happens when the thermal dephasing $\Gamma_2^*(T)$ is zero. This term represents the excess dephasing due to interactions of DBT with phonons in the surrounding Ac matrix. The temperature dependance of the population of these phonon modes gives rise to the term thermal dephasing. Figure 3.1 shows a diagram of example emission spectra from DBT as a function of temperature. The solid lines show the increase in emission width with temperature due to an increase in Γ_2^* as the Ac phonon modes become more populated. There is also the possibility of dephasing due to other sources such as hyperfine interactions, however these effects are expected to be significantly smaller than phonon broadening and are not considered in this section.

There are also local phonons - Ac vibrations that are localised in the vicinity of the DBT - and the absorption and emission of these produce bands on each of the main lines (dashed in Fig. 3.1). These become more prominent as the temperature increases, the ratio of zero-phonon line emission to zero-phonon line and phonon sideband emission can be described by the Debye-Waller factor, α_{DW} , as

$$\alpha_{\text{DW}} = \frac{\Gamma_{\text{ZPL}}}{\Gamma_{\text{ZPL}} + \Gamma_{\text{SB}}} = \frac{I_{\text{ZPL}}}{I_{\text{ZPL}} + I_{\text{SB}}}, \quad (3.2)$$

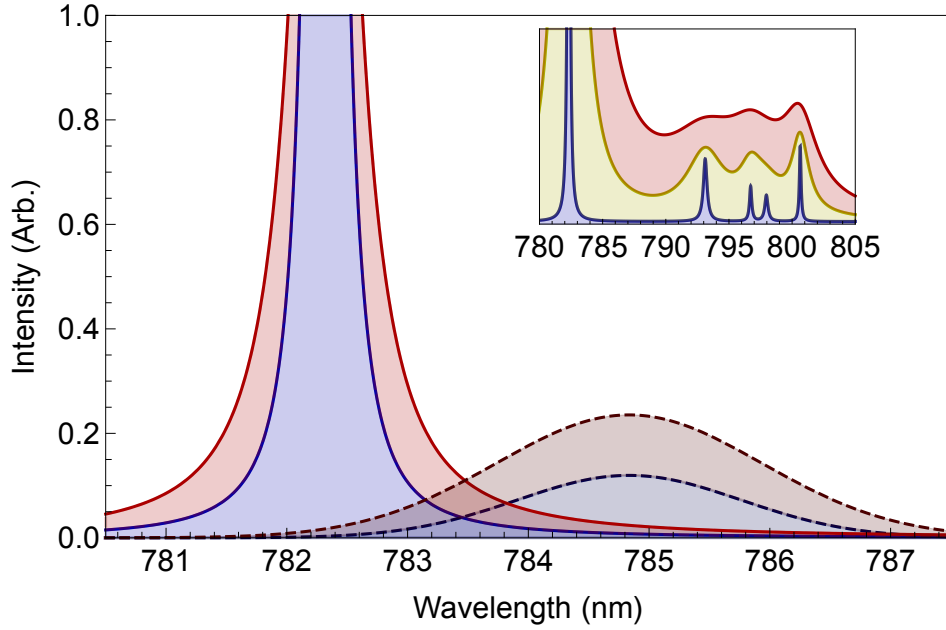


Figure 3.1. – Diagram of DBT emission spectra showing various effects phonons and dephasing have on the fluorescence from DBT. Blue lines represent the cold ZPL (solid) and phonon sideband (dashed) emission. Red lines represent higher temperature ZPL (solid) and phonon sideband (dashed) emission. Increase in temperatures causes broadening of the ZPL and a greater proportion of the emission on the phonon sideband. Inset: Total emission from the ZPL and first four vibrational lines of DBT. Increasing temperature (blue to yellow to red) broadens the transitions and causes them to overlap.

where $\Gamma_{\text{ZPL/SB}}$ are the radiative decay rates on the zero-phonon line and sideband respectively and $I_{\text{ZPL/SB}}$ are the corresponding fluorescence intensities. Transitions that change the vibrational state of DBT are affected by the same phonon coupling and as such, they should have similar α_{DW} between the zero-phonon vibrational line and the corresponding sideband. The effect of local phonons on the Franck-Condon factor α_{FC} , or the ratio of zero-phonon line to vibrational level emission, in DBT has not been investigated prior to this, and will be commented on later.

Furthermore, with sufficiently high dephasing, the zero-phonon line $S_{0,0} \rightarrow S_{1,0}$ begins to spectrally overlap with transitions to the excited vibrational states $S_{0,0} \rightarrow S_{1,n>0}$. This reduces the efficiency with which a molecule can be prepared in the excited state as it becomes impossible to address states individually. The inset in Fig. 3.1 shows the loss of definition between the ZPL and first four vibrational lines of DBT as temperature increases.

This chapter will first present research on the effect of thermal dephasing on the excitation of a single quantum emitter at room temperature. In particular, the effect of spectral broadening on the excitation efficiency of a single emitter will be predicted using an analytical rate-equation model. This general model will then be applied to DBT. Experimental data will be collected to verify the validity of the model, and the effect of cooling to 77 K on restoring this efficiency will be presented. This will be followed by a detailed spectral characterisation of a DBT molecule from 4 K to 40 K. This experimental data is compared to a theoretical model which predicts the line-broadening and phonon sideband strength across this range. This model can be used to make predictions regarding the indistinguishability of emitted photons, a key property for a practical single photon emitter [24, 1].

This data will be used to optimise the filtering and temperature for the experiment to measure the maximum indistinguishability from subsequent photons emitted by a DBT molecule presented at the end of this section. A parallel will be drawn between the measurement of indistinguishability $\mathcal{I}$ from pulsed and cw excitation of a molecule. The section will finish with the development of this experiment and the testing of the interferometer. Preliminary results will be presented.

3.1. Excitation efficiency

The efficient excitation of a single quantum emitter is essential in deterministically generating single photons. At cryogenic temperatures the excitation to $S_{1,n}$ (shown blue in Fig. 1.5) can be clearly resolved [82], allowing the optical pumping to populate the level $S_{1,0}$ with essentially unit certainty. At higher temperatures however phonon-induced line-broadening causes off-resonant excitation of the ZPL transition, and complete population inversion, to become impossible. This section will cover the development of a rate-equation model to determine the excitation likelihood of a molecular single photon emitter as a function of excitation wavelength and intensity, at a given dephasing and therefore temperature.

This model is then applied to DBT in Ac, and experimentally verified at both room temperature and 77 K. A maximum $S_{1,0}$ population of approximately 75 % is found at room temperature and approximately 94 % at 77 K. This population is of particular interest when determining the coupling to nanophotonic device by measuring the count rate of the emitter from the device as shown in Ref. [97]. The model is also used to predict excitation efficiency for another organic dye molecule, terrylene, and compared to published values [98]. This section is also published in Ref. [30].

3.1.1. Modelling excitation efficiency

The diagram inset in Fig. 3.2 illustrates the energy levels of a suitable molecule, such as DBT. The optical excitation $S_{0,0} \rightarrow S_{1,0}$ is followed by stimulated decay back to $S_{0,0}$, and by spontaneous decay in a few ns to the $S_{0,n}$ levels. Any population in $S_{0,n>0}$ relaxes in a few ps to $S_{0,0}$. Alternatively, the molecule may be excited from $S_{0,0}$ to $S_{1,n>0}$. From here the molecule relaxes (again in ps) to the $S_{1,0}$ state, from which it decays spontaneously to the $S_{0,n}$ levels. It is also possible for S_1 to decay to the lowest-lying triplet state, T_1 , but for efficient fluorophores this decay branch is weak [65, 81] and therefore it is neglected in the present discussion. Given that the rate for excitation be much slower than the (THz) rate for relaxation of the vibrational excitations, an excitation to $S_{1,n>0}$ is followed promptly by an incoherent transfer of population to the state $S_{1,0}$, whilst the subsequent decay to $S_{0,n}$ is immediately followed by relaxation to $S_{0,0}$. Writing the populations of $S_{1,0}$ and $S_{0,0}$ as p_e and p_g respectively, it is then a good approximation to consider that $p_g + p_e = 1$ and the excited state population obeys the rate

equation

$$\frac{dp_e}{dt} = p_g \sum_{n=0}^{n_{max}} R_n - p_e(R_0 + \Gamma_1). \quad (3.3)$$

Here R_n is the stimulated transition rate (per molecule) on the transition $S_{0,0} \leftrightarrow S_{1,n}$, and Γ_1 is the spontaneous decay rate (per molecule) of the population p_e . The sum goes up to the highest vibrational level labeled by n_{max} . The excitation term $p_g \sum_{n=0}^{n_{max}} R_n$ is dependent on all excitation rates R_n , however the fast relaxation $S_{1,n>0} \rightarrow S_{1,0}$ means only stimulated emission from the $S_{1,0}$ state, described by R_0 , is relevant for the relaxation term $p_e(R_0 + \Gamma_1)$.

After sufficient time under cw excitation, the populations relax to a steady state, where $\frac{dp_e}{dt} = 0$ and therefore

$$p_e = \frac{\sum_n R_n}{R_0 + \sum_n R_n + \Gamma_1}. \quad (3.4)$$

With strong excitation, such that $R_0 + \sum_n R_n \gg \Gamma_1$, p_e saturates to the value

$$p_{e,\infty} = \left(1 + \frac{R_0}{\sum_n R_n}\right)^{-1}. \quad (3.5)$$

If the only significant excitation is on the ZPL then $R_0 = \sum_n R_n$ and p_e saturates to $\frac{1}{2}$. If instead the excitation is entirely to states $S_{1,n>0}$, then $R_0 = 0$ and p_e saturates to 1. This reproduces the well-known result that the steady state of a driven, damped 3-level system can have a population inversion, whereas the damped 2-level system cannot. From the perspective of building a triggered photon source, it is desirable for the trigger pulse to produce a steady state with the largest p_e it can, and to do so quickly enough that the resulting spontaneous emission delivers a photon with high probability and well-defined timing. This argues for excitation with a sub-nanosecond pulse, and with a low rate R_0 , which requires excitation on the blue side of the ZPL, together with a low enough dephasing rate.

The excitation rates R_n in Eq. 3.5 are found by solving the optical Bloch equations in the steady state to give

$$R_n = \frac{1}{2} \Omega_n^2 \frac{\Gamma_{2,n}}{\Delta_n^2 + \Gamma_{2,n}^2}, \quad (3.6)$$

where Ω_n , Δ_n and $\Gamma_{2,n}$ are respectively the Rabi frequency, laser (angular) detuning from resonance, and dephasing rate for the transition $S_{0,0} \leftrightarrow S_{1,n}$ [26, 71]. In particular, this is based on Eq. 1.5, generalised for more energy levels and without the radiative decay component. The Rabi frequency is

$$\Omega_n = \frac{1}{\hbar} |\vec{d}_n \cdot \vec{E}|, \quad (3.7)$$

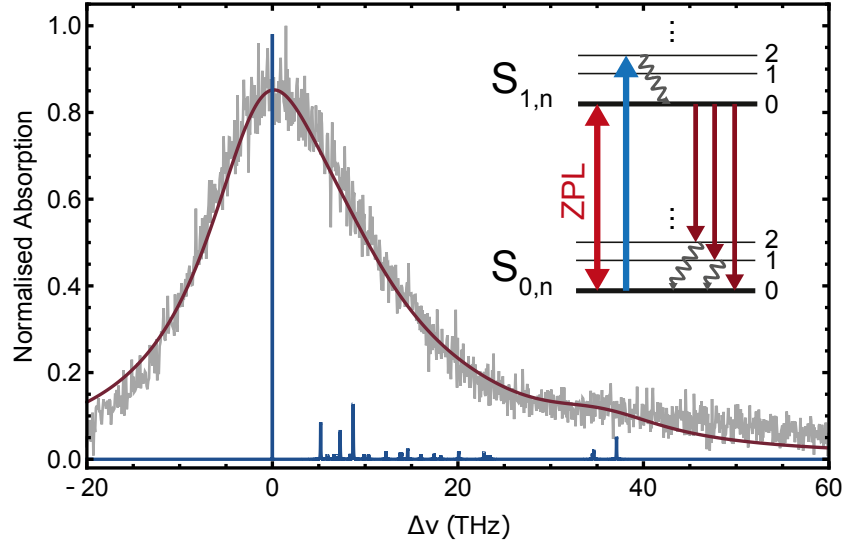


Figure 3.2. – Absorption spectrum of a DBT molecule. The grey line is the spectrum measured at room temperature. An analytical spectrum (see Eq. 3.10) constructed to reproduce the low-temperature emission spectrum in Fig. 1(c) of Trebbia *et al.* is shown in blue [82]. The red line is the same analytical spectrum, but with $\Gamma_{2,n}$ increased to fit the room temperature data. Inset: Generic energy level diagram showing pumping on the ZPL (red double-ended arrow), to a higher vibrational level (blue up arrow), fast non-radiative decays (black curly arrows) and decays to higher vibrational levels of the ground state (maroon down arrows).

where $\vec{d}_n = \langle S_{0,0} | \vec{d} | S_{1,n} \rangle$ is the dipole transition matrix element and $\vec{E}$ is the amplitude of the electric field driving the transition. Since all the transitions are driven by the same component, $E_{\parallel}$, of the light field,

$$R_n = \frac{I}{\epsilon\epsilon_0\hbar^2 c} d_n^2 \frac{\Gamma_{2,n}}{\delta^2 + \Gamma_{2,n}^2}, \quad (3.8)$$

where the effective plane-wave intensity at the molecules, defined as $I = \frac{1}{2}\epsilon\epsilon_0 E_{\parallel}^2 c$, is proportional to the laser light intensity, I_{ext} , incident on the sample. Without needing to know I , Eq. 3.8 allows us to evaluate Eq. 3.5 given the dipole matrix elements, the detunings and the transverse relaxation rates. The following section will evaluate this for DBT.

3.1.2. Modelling dibenzoterrylene

When DBT decays from the $S_{1,0}$ level, there are multiple transitions $S_{1,0} \rightarrow S_{0,n}$ visible, as shown in Fig. 3.2, whose transition moments are $\tilde{d}_n = \langle S_{1,0} | d | S_{0,n} \rangle$. Table 3.1 at the end of this section lists the frequencies ω_n and relative intensities η_n of these lines, taken from the low-temperature fluorescence spectrum in Fig. 1(c) of Trebbia *et al.* [82]. From these we can deduce the relative strengths of the transition moments: $\tilde{d}_n^2 \propto \eta_n / \omega_n^3$. As the excitation of the optically active electron has very little influence on the vibrating bonds the vibrational frequencies and wavefunctions are similar in the upper and lower electronic states [20]. Due to this, the approximation that the Franck-Condon factors are the same for the excitation $S_{0,0} \rightarrow S_{1,n}$ and the decay $S_{1,0} \rightarrow S_{0,n}$, and hence that d_n is equal to $\tilde{d}_n$ is made. This allows for the measured fluorescence spectrum to give a set of (relative) values for the d_n to be used in Eq. 3.8 as

$$d_n^2 \simeq \tilde{d}_n^2 \propto \frac{\eta_n}{\omega_n^3}. \quad (3.9)$$

Turning now to the damping rates to be used in Eq. 3.4 and 3.8, previous measurements [71] give the population decay rate $\Gamma_1/(2\pi) \simeq 40$ MHz, corresponding to a spontaneous decay lifetime of 4 ns, and this remains the same whether at room temperature or at low temperature [76]. The damping rates $\Gamma_{2,n}$ in Eq. 3.8 describe relaxation of the optical coherences $|S_{1,n}\rangle \langle S_{0,0}|$, or using the equivalence of vibrational states in both vibrational manifolds, $|S_{1,0}\rangle \langle S_{0,n}|$. At 4 K, $\Gamma_{2,n}$ is small enough that one can excite a single $S_{1,n}$ level and observe resonance fluorescence proportional to that R_n alone, with a spectral width (FWHM) of $2\Gamma_{2,n}$. Using the strong $n = 3$ line 8.7 THz to the blue of the ZPL (see Fig. 3.2), we measure a value of $\Gamma_{2,3}/(2\pi) = 23 \pm 3$ GHz, corresponding to a decay time for the vibrationally excited population of ~ 4 ps. For simplicity,

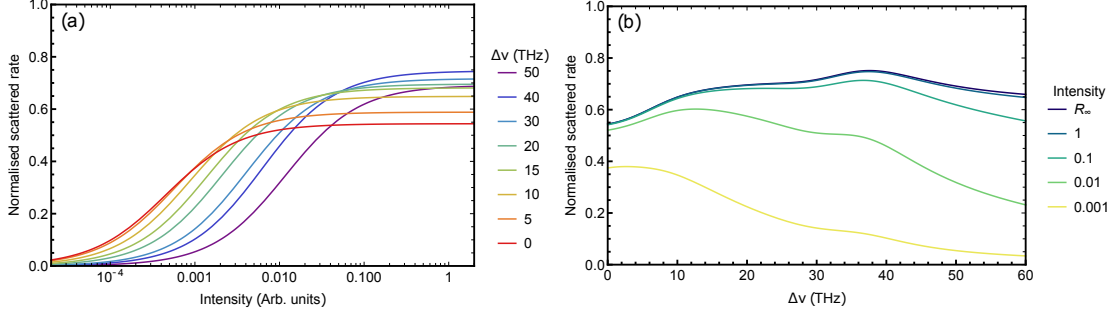


Figure 3.3. – (a) Calculated excited state population for DBT in equilibrium at room temperature versus intensity of excitation laser for several detunings to the blue of the ZPL. (b) The same data plotted against detuning for several values of (arbitrary) pump laser intensity.

it is assumed all the $S_{1,n>0}$ states have similar vibrational relaxation times. The exact values are not essential as these will be broadened significantly by thermal dephasing.

At room temperature the optical coherence is so rapidly dephased by the interaction with thermal phonons that $\Gamma_{2,n}$ is a thousand time larger and the absorption lines are no longer resolved. Indeed, the excitation laser used for this work is unable to scan far enough to measure the width of the room-temperature absorption spectrum directly. Instead, the dispersed fluorescence spectrum is measured while exciting continuously at 730 nm, with the result shown by the grey line in Fig. 3.2. We use this spectrum to determine the room-temperature value of $\Gamma_{2,n}$, as follows. The blue curve in Fig. 3.2 shows the narrow lines of the dispersed fluorescence spectrum, $\mathcal{S}_{flu}$, at 2 K,

$$\mathcal{S}_{flu}(\omega) = \sum_n \eta_n \frac{\Gamma_{2,n}^2}{(\omega - \omega_n)^2 + \Gamma_{2,n}^2}, \quad (3.10)$$

in which ω is the frequency of the emitted light, taking $\Gamma_{2,0} = \Gamma_1/2$ and $\Gamma_{2,n>0}/(2\pi) = 23$ GHz on the assumption that all the vibrational excitations relax at roughly the same rate. The broad spectrum (red line) is obtained by adding a further rate Γ_2^* to these low temperature rates in order to model the dephasing of the optical dipole by thermal phonons. On fitting this curve to the data we obtain the value $\Gamma_2^*/(2\pi) = 8.2$ THz.

Substituting these values of d_n^2 , $\Gamma_{2,n}$ and $\Gamma_{1,0}$ into Eq. 3.8 and then Eq. 3.4 gives the excited state population p_e prepared by the trigger pulse. Figure 3.3(a) is a plot of p_e at room temperature against the intensity of the pulse, for several blue detunings $\Delta\nu$ of the laser from the ZPL. As anticipated in Eq. 3.5, p_e saturates at various levels $p_{e,\infty}$, the lowest being 0.55 when $\Delta\nu = 0$ and the highest being 0.75 when $\Delta\nu = 40$ THz. Above 40 THz detuning $p_{e,\infty}$ decreases

again because there are only 23 vibrationally excited states in the model; no more have been directly observed experimentally. Thus, it seems likely that $p_{e,\infty} = 0.75$ is the highest achievable at room temperature. Figure 3.3(b) shows the same information, but plotted against detuning for several intensities, indicated by the colour of the lines.

3.1.3. DBT molecule at room temperature

This section describes my experiments to test this theory on a single DBT molecule at room temperature. The room temperature confocal microscope described in Section 2.3 and Fig. 2.6 was used to perform this analysis. The molecule was excited either by a cw tuneable Ti:Sapphire laser (Coherent MBR) or by a pulsed diode laser centred at 781 nm (Picoquant). A 780 ± 6 nm band pass, a 760 ± 6 nm band pass, or a 750 nm short pass filter was used in the excitation path, depending on laser frequency used. The DBT-doped anthracene crystal, shown inset in Fig. 3.4(a), was grown by co-sublimation as described in Section 2.1 [81], then placed on a glass coverslip and protected by a thin, spin-coated layer of polyvinyl alcohol (PVA).

Imaging single molecules

The microscope image in Fig. 3.4(a) shows fluorescence from isolated DBT molecules over a $20 \mu\text{m}$ square area of an anthracene crystal. A single molecule is selected and illuminated with the 781 nm pulsed laser to perform a time-correlated single photon counting (TCSPC) experiment. This gives the histogram shown in Fig. 3.4(b), and fitting the decay curve to a single exponential decay $Ae^{-\Gamma_1 \Delta t}$, shown as a red line, gives an excited state lifetime of $\tau_1 = 3.53 \pm 0.02$ ns. Changing to $\sim 70 \mu\text{W}$ of cw laser light at 780 nm, and using both APD detectors, a $g^{(2)}(\tau)$ is measured, plotted in Fig. 3.4(c). This shows a dip going down to 0.33 ± 0.04 at $\tau = 0$ ns. With the high dephasing rate at room temperature, the $S_{1,0}$ level is populated incoherently, and therefore Eq. 2.4 is used. The green curve in Fig. 3.4(c) is a fit to this function, with Γ_1 fixed at the measured value. This gives $S = 0.5 \pm 0.1$ and $\mathcal{V} = 0.74 \pm 0.04$. Further, there is a background of about 10% of the peak molecule count rate that generates some accidental coincidences. After correcting for that¹, $\mathcal{V} = 0.98^{+0.02}_{-0.04}$ confirming that a single molecule is selected.

¹This is done by considering the ratio of signal to background for this molecule at this pump power, and calculating the number of coincidences this is expected to contribute.

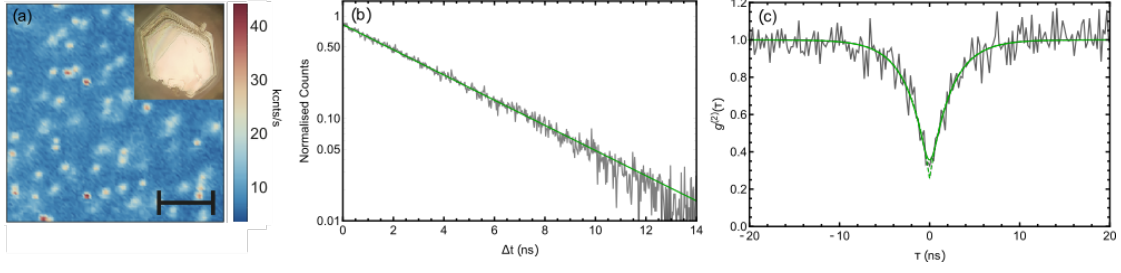


Figure 3.4. – (a) Confocal microscope image showing fluorescence from individual DBT molecules in an anthracene crystal. The scale bar is $5 \mu\text{m}$. Inset: white light image of the crystal, which is $\sim 0.5\text{mm}$ across. (b) Black is data from a TCSPC measurement. Green line is an exponential decay fitted to the tail of the data giving a lifetime of $3.53 \pm 0.02\text{ns}$. (c) The black is data from the second-order correlation function measurement showing a characteristic photon anti-bunching dip. Green fitted line is Eq. 2.4 convoluted with the detector response function, showing a visibility of $74 \pm 4\%$. Dashed line is the deconvolved fit.

Scattering rate at room temperature

Having characterised this particular molecule, the saturation of its scattering rate is investigated by analysing confocal microscope images. The intensity distribution of the laser spot was a slightly elliptical Gaussian with principal axes along the two axes of the scan and with standard deviations σ_x and σ_y . In Eq. 3.4, the rates R_n are all proportional to the laser intensity, so a molecule at position (x_0, y_0) , illuminated by a spot with intensity I_0 centred on (x, y) , gives a signal

$$R(x, y) = R_\infty \frac{S_0}{S_0 + \exp \left[\frac{1}{2} \left(\frac{x-x_0}{\sigma_x} \right)^2 + \frac{1}{2} \left(\frac{y-y_0}{\sigma_y} \right)^2 \right]}. \quad (3.11)$$

Here R_∞ is the fully saturated rate of photons detected from the molecule, $S_0 = I_0/I_{\text{sat}}$ is the saturation parameter when the spot is centred on the molecule and I_{sat} is now defined as $\Gamma_1/(R_0 + \Sigma_n R_n)$. When $S_0 \ll 1$ this gives an image that reproduces the intensity distribution of the laser spot, but as the molecule saturates, the image becomes wider and flatter.

With the excitation laser frequency set at a blue detuning $\Delta\nu$ from the ZPL, microscope images were taken over a range of intensities. These were fitted globally with Eq. 3.11 to obtain a value for R_∞ at that detuning. Each scan was of an area of approximately $20 \mu\text{m}^2$, divided into 75×75 pixels, with an integration time of 5 ms per pixel. The fits were performed on a 15×15 pixel area around the centre of the saturated Gaussian. A comparison of data to the fit is shown

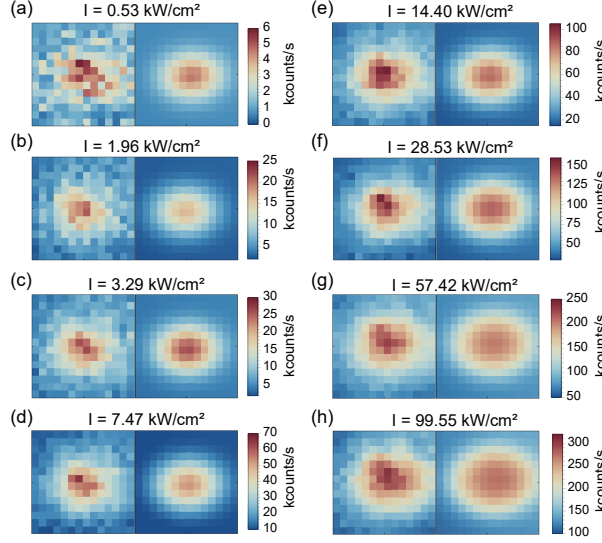


Figure 3.5. – Comparison of confocal microscope images (left) and fitted saturated Gaussian distributions (right) for a pump laser detuning of $\Delta\nu = 19.11$ THz. The intensities listed are obtained from the measured power incident on the sample and the known Gaussian spot size of 770 nm full width half-maximum. Each confocal scan is a $2\ \mu\text{m}$ square.

in Fig. 3.5. This was done for 8 different values of $\Delta\nu$ with the results plotted in Fig. 3.6. It is straightforward to convert these to values of $p_{e,\infty}$ through the relation $R_\infty = \eta_{\text{col}} p_{e,\infty} \Gamma_1$, where η_{col} is the total efficiency for collection and detection. On fitting Eq. 3.5 to the data in Fig. 3.6, with η_{col} as the only free parameter, $\eta_{\text{col}} = 1.03 \pm 0.02 \times 10^{-3}$ for this particular molecule. The correspondence between our data and the theory gives confidence that Eq. 3.5 and 3.8 provide a correct description, and therefore that one cannot expect to achieve more than 75% steady-state excitation at room temperature.

The same data also provide information on the variation of I_{sat} with detuning, as plotted by the data points in Fig. 3.7. Figure 3.3(b) shows how the scattering rate (and hence I_{sat}) should vary with detuning at a fixed laser intensity, but this is not the behaviour in Fig. 3.7. The reason for this is that the intensity I_{ext} incident on the surface of the sample is measured, whereas I in the theory refers to the intensity at the site of the DBT molecule itself. The ratio of these two is frequency dependent because the sample has several parallel dielectric interfaces making a stack of etalons. Modelling the reflection and transmission of light given a PVA spin-coated top layer of 100 nm thickness, an anthracene crystal of thickness to be $7\ \mu\text{m}$, and a $120\ \mu\text{m}$ -thick glass substrate, the I_{ext} blue curve in Fig. 3.7 is found. The PVA thickness is known from spin-coating

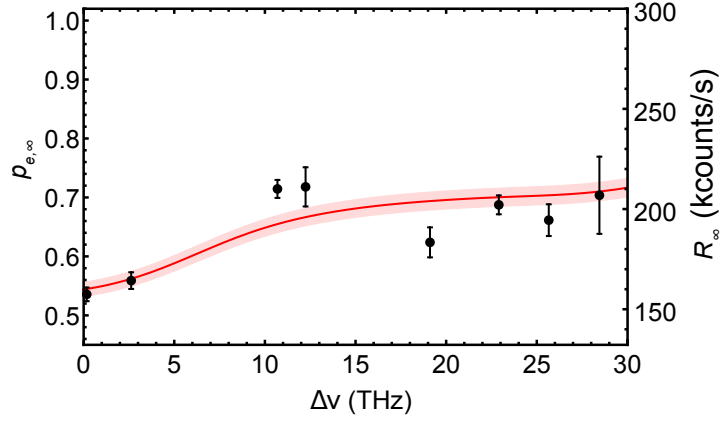


Figure 3.6. – Maximum rate R_∞ of photons detected at room temperature, and corresponding maximum excited state population $p_{e,\infty}$, plotted against blue detuning of excitation laser from ZPL. Red line: room temperature $p_{e,\infty}$ as calculated using Eq.(3.5). Shading: region covered by one standard deviation of the fitted efficiency η_{col} for collection and detection.

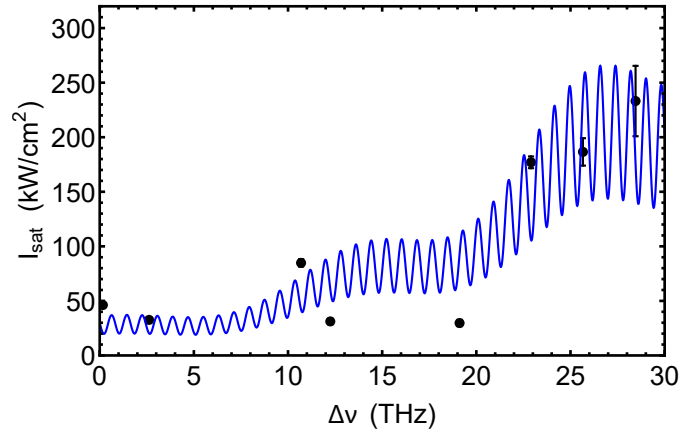


Figure 3.7. – Change in I_{sat} with frequency detuning from experiment (black points) and from the model (blue line) including modulation of intensity inside the anthracene crystal from various boundary reflections and interference between forward and backward going fields.

thickness measurements, the anthracene thickness is calculated from the approximately 10 THz period of intensity modulation (and is in line with expected crystal thickness [81]) and the glass coverslip thickness is from the packaging. Although these are somewhat rough estimates, this seems to explain well the modulation observed in I_{sat} . This effect could also explain the deviation seen in Fig. 3.6, as the collection efficiency of the molecule could be effected by reflection at these interfaces.

3.1.4. DBT molecule at 77 K

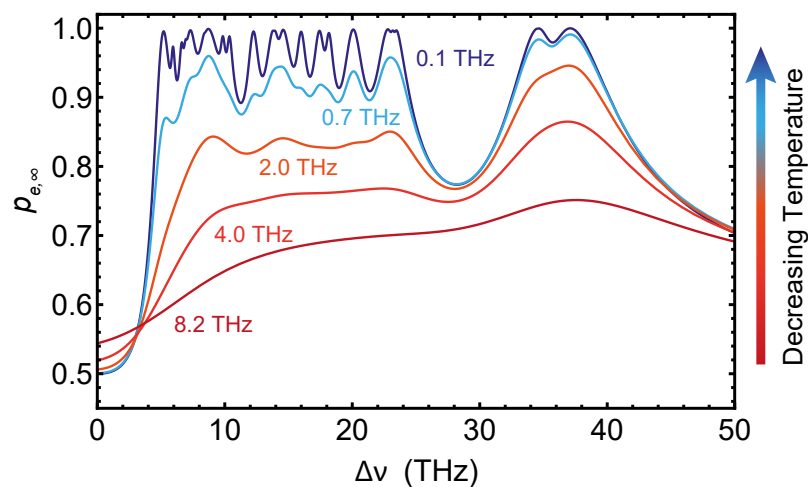


Figure 3.8. – Calculated maximum excited state probability, from infinite excitation intensity, plotted against blue detuning of the excitation laser from the ZPL, for 5 values of $\Gamma_{2,n}$.

The room-temperature limit of $p_{e,\infty} \leq 0.75$ is not high enough to make a good triggered photon source, but a significant improvement is possible if $\Gamma_{2,n}$ can be reduced. Figure 3.8 shows $p_{e,\infty}$ as a function of the blue detuning of the trigger pulse, calculated from Eq. 3.5 for five values of $\Gamma_{2,n}$. The 8.2 THz curve is the same as the red curve in Fig. 3.6, peaking at $p_{e,\infty} = 0.75$ near a detuning of 35 – 40 THz. That peak is improved by reducing the dephasing rate, reaching $p_{e,\infty} = 0.99$ when $\Gamma_{2,n}/(2\pi) = 0.7$ THz. The spectral structure in $p_{e,\infty}$ becomes increasingly evident as $\Gamma_{2,n}$ is reduced because the resonances become narrower, with the dips in $p_{e,\infty}$ corresponding to the regions between resonances, where the effect of the off-resonant R_0 is more significant.

In order to ascertain what level of cooling is required to reach $\Gamma_{2,n} \leq 0.7$ THz, a DBT-doped anthracene crystal was placed in the closed-cycle cryostat (Montana Cryostation) and cooled to

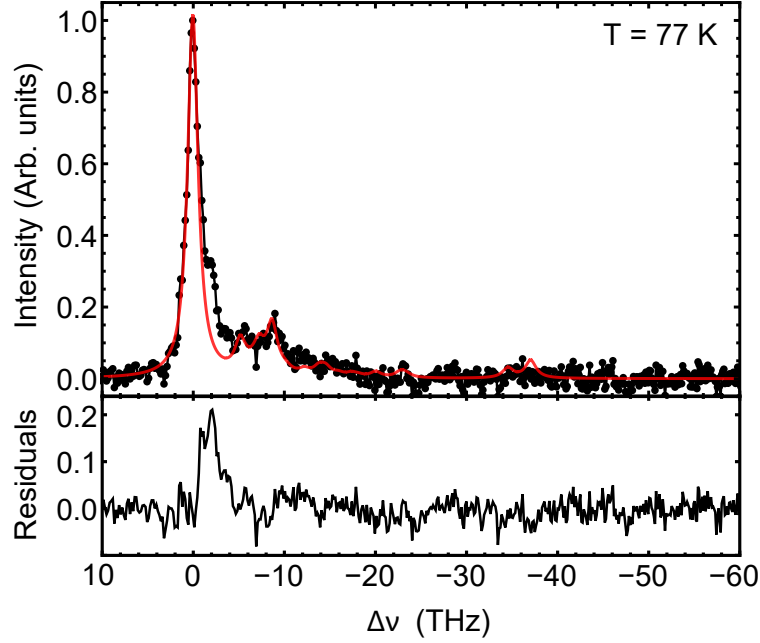


Figure 3.9. – Data points: dispersed fluorescence spectrum of a single molecule measured at a temperature of 77 K. Red line: spectrum given by Eq. 3.10, taking $\Gamma_{2,n}/(2\pi) = 0.7$ THz. Lower panel: difference between data and red line, revealing a sideband 2 THz below the ZPL.

3.5 K. The cryogenic confocal microscopy set-up described in the reprecipitation growth section and Fig. 2.8 was used to identify a single molecule. A low power (35 nW) resonant line scan gave a linewidth of 62 ± 1 MHz, typical for DBT. A low power scan across the $S_{0,0} \rightarrow S_{1,7}$ transition gives a linewidth of 45 ± 6 GHz, corresponding to a $\Gamma_{2,7}/(2\pi) = 23 \pm 3$ GHz [82].

The temperature was then increased to 77 K and the molecule pumped on the $n = 3$ transition 8.5 THz to the blue of the ZPL. The fluorescence was dispersed on a single-photon sensitive spectrometer (Andor Shamrock with a Newton EMCCD). This gave the spectrum shown by the data points in Fig. 3.9, after subtracting a background of light scattered by the anthracene. The main features of this spectrum are well reproduced by the red line, which is a plot of Eq. 3.10, taking $\Gamma_{2,n}/(2\pi) = 0.7$ THz. On the low-frequency side of the ZPL there is a small shoulder that is not reproduced by the red curve. The residuals plotted in the lower panel show that this is a sideband centred at a detuning of ~ 2 THz. This phonon sideband is investigated in greater detail in Section 3.2.

Having established that liquid nitrogen temperature should be cold enough to achieve exceedingly high values of p_e , this was put to the test by recording the saturation of the scattering

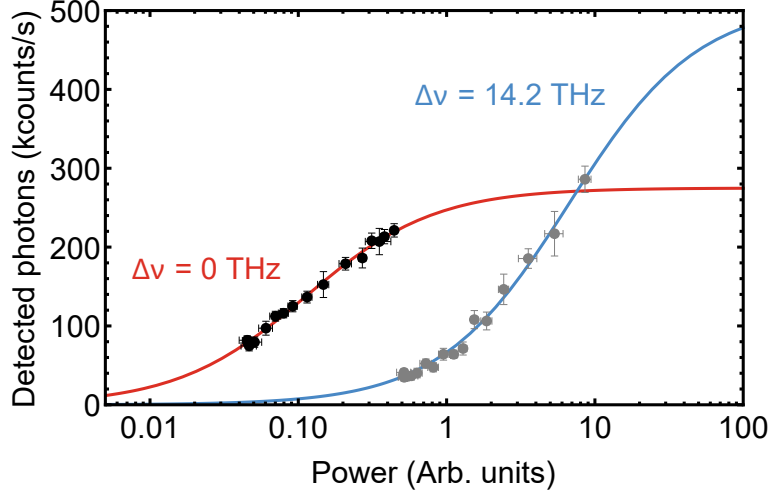


Figure 3.10. – Fluorescence signal *versus* excitation power with the sample cooled to 77 K, with the excitation laser on the ZPL (black dots) and tuned 14.2 THz to the blue. The lines are fits to the form $R_{\infty}S/(1 + S)$

rate, as shown in Fig. 3.10. The grey data points show the photon count rate in the detector as a function of the power incident on the sample, with the excitation laser tuned 14.2 THz to the blue of the ZPL. The blue line is a fit to these points of the function $R_{\infty}S/(1 + S)$, giving $R_{\infty} = 510(4)$ kcounts/s. According to Eq. 3.5, $p_{e,\infty} = 0.94$ when $\Gamma_{2,n}/(2\pi) = 0.7$ THz. To check this, we tuned the excitation to the ZPL, where $p_{e,\infty} = 0.50$. The black data points show the photon count rate in that case, and the red line is a fit giving $R_{\infty} = 275(2)$ kcounts/s. Using this to scale the blue curve, $p_{e,\infty} = 0.93(1)$, which confirms the value 0.94 expected from Eq. 3.5.

$\omega_n/(2\pi)$ (THz)	Relative Weight η_n
382.12	6.596×10^{-1}
387.32	5.410×10^{-2}
388.06	5.419×10^{-3}
388.74	5.414×10^{-3}
389.06	4.836×10^{-3}
389.42	4.199×10^{-2}
390.52	5.402×10^{-3}
390.83	8.346×10^{-2}
391.97	5.104×10^{-3}
392.48	4.812×10^{-3}
394.37	9.696×10^{-3}
395.90	7.669×10^{-3}
396.05	7.380×10^{-3}
396.70	1.429×10^{-2}
398.11	5.349×10^{-3}
399.55	6.203×10^{-3}
400.29	3.029×10^{-3}
402.20	9.928×10^{-3}
404.91	9.044×10^{-3}
405.30	3.280×10^{-3}
405.58	3.854×10^{-3}
416.63	6.074×10^{-3}
416.77	1.212×10^{-2}
419.22	3.198×10^{-2}

Table 3.1. – Frequencies of the lines in the fluorescence spectrum of DBT in anthracene and the relative peak heights, determined from Fig. 1 in J.B. Trebbia *et al.* [82]. We take the zero-phonon line frequency as 382.16 THz.

3.1.5. Modelling other molecules

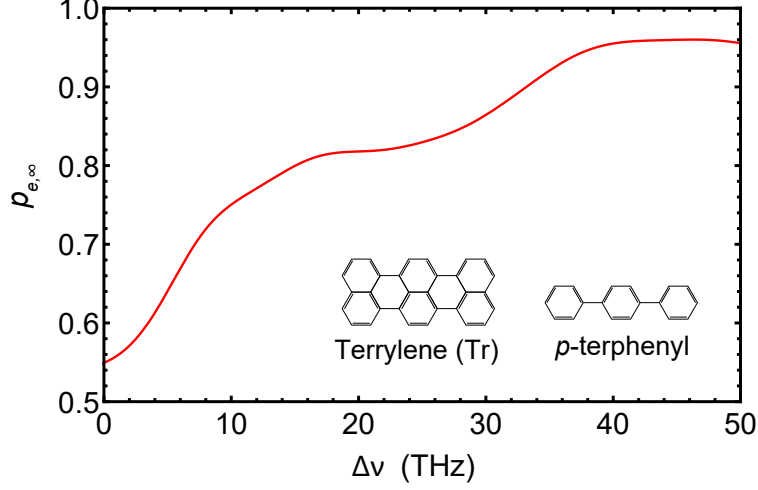


Figure 3.11. – The maximum achievable excited state population $p_{e,\infty}$ of terrylene in p -terphenyl at room temperature. Their molecular structures are inset.

To test the generality of this model, calculations for Terrylene (Tr) in p -terphenyl, another organic molecule emitter-host combination that has been investigated as a potential SPS at both low temperature [99, 78, 100] and room temperature [101, 102, 98]. Using the cold spectra in Fig. 1 and Fig. 2 of Ref. [103], the strengths and frequencies of the fluorescence lines out to 55 THz detuning have been estimated. On broadening these spectra to match Fig. 3 of Ref. [102], a room temperature dephasing rate of $\Gamma_2/2\pi \simeq 6$ THz is found, similar to the 8.2 THz of DBT. Applying the model to Tr gives a maximum excited state population $p_{e,\infty}$ plotted in Fig. 3.11. $p_{e,\infty}$ is higher for terrylene due to the stronger vibrational transitions, relative to the ZPL transition. When the trigger pulse is 40 THz detuned from the ZPL, the steady-state excited population is as high as 96%, which is close to the 99% reported recently by Chu *et al.* [98], when pumping with a detuning of ~ 42 THz. This level of agreement seems to confirm the validity of the theoretical model. I note that there is a down side to having stronger vibration-changing transitions, namely that they result in greater non-ZPL emission as compared to DBT. This has the undesirable effect of making the emitted photons more distinguishable. The higher intersystem crossing rate in terrylene also lowers Φ_f and introduces blinking [98].

3.2. Coherence and dephasing

Coherent, indistinguishable photons are necessary for many quantum technology applications [1]. To begin taking advantage of the coherence properties of the photons emitted by DBT we ideally want to reduce Γ_2 to as close as the lifetime-limit of $\Gamma_2 = \Gamma_1/2$ as possible. In other words, we want to reduce $\Gamma_2^*(T)$ to zero. Excess thermal dephasing Γ_2^* rapidly reduces indistinguishability of the emitted photons and is very difficult to remove through filtering. The effect of temperature on the phonon sideband, in particular the Debye-Waller factor, is also of interest. The broad nature of the sideband does however mean that filtering is a practical method of increasing indistinguishability. Even with perfect filtering, this does still come at the cost of efficiency as rejected photons can no longer be measured, incentivising the understanding and reduction of dephasing.

Minimising the thermal dephasing requires temperatures much lower than the 77 K used previously; DBT in a high quality crystal environment at temperatures around 3 K have previously been shown to achieve this [65]. Unfortunately our cryostat cannot reach this temperature at the sample mount, instead this section will detail the measurement of a DBT molecule from 4 K to 40 K. ZPL power-broadening scans and a spectrum of the same single molecule are recorded at each temperature to allow for measurement of Γ_2 and the Debye-Waller factor.

Analytical analysis of these results will be presented, using a combination of phenomenological models and equations derived by theory collaborators [23]. This data will then be used to predict the temperature required for lifetime-limited emission. The Debye-Waller factor at this temperature will also be predicted. This will be used in the following section to model the effects of filtering on efficiency and indistinguishability of the DBT emission, in preparation for the Hong-Ou-Mandel two-photon interference measurement performed in the next section [72].

3.2.1. Experimental details

Low concentration DBT nanocrystals are desirable for this to ensure spectral isolation of molecules, which is necessary to allow the spectrum recorded to feature emission from only one molecule. Emission from multiple molecules would result in difficulty identifying individual contributions to the expected broad phonon-sideband. The exponential increase in Γ_2 , and therefore linewidth, with temperature means that an isolated sub-100 MHz molecule at 4 K may not be as isolated when 500 GHz at 40 K [71].

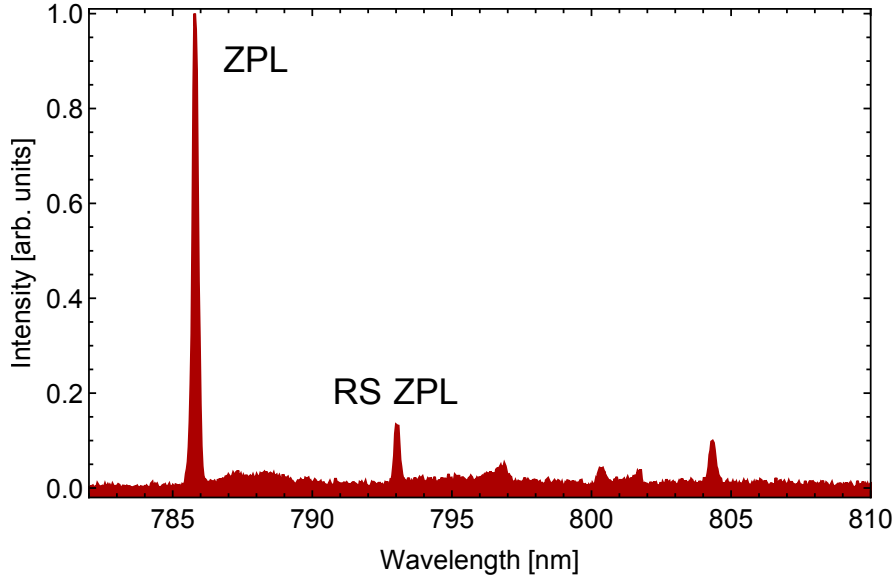


Figure 3.12. – Spectrum from a DBT molecule at 4.7 K with the emission from a second DBT molecule in the red site (RS). The ZPLs of the two molecules are highlighted. The spectrum was taken pumping with 768 nm laser light, which will correspond to excitations to (two different) vibrational states in the DBT molecules.

This can be seen in the DBT spectrum at 4.7 K² shown in Fig. 3.12. A red-site DBT molecule [104] is also excited by the 768 nm laser light, resulting in extra emission peaks in the spectrum due to the spectral overlap of transitions to (different) excited vibrational and electronic states in the two molecules. Red-site DBT molecules have a slightly different orientation within the Ac host, with a inhomogeneous broadening centred around 794 nm, and are not usually used for single photon experiments due to the greater susceptibility to thermal broadening. Unfortunately this was not seen until after a large amount of data for this molecule from 4 K to 40 K was recorded, highlighting the importance of verifying a well-isolated emitter.

A nanocrystal growth was performed as detailed in Chapter 2 and Ref. [23], using 5 μ l of 1 μ M DBT in toluene solution. The sonicated solution was filtered through a 450 nm syringe pore filter and 5 μ l was deposited onto a substrate. This was then spin-coated with a 150 nm PVA layer. The substrate was a silica-on-silicon wafer that had a 150 nm layer of gold deposited on the surface, with a 220 nm TiO₂ spacer layer to protect against plasmonic losses. This gold layer acts as a back reflector to alter the emission direction of the emitter through modification of the

²Temperature approximated from sample probe temperature combined with previous calibration measurements accounting for temperature gradient across substrate.

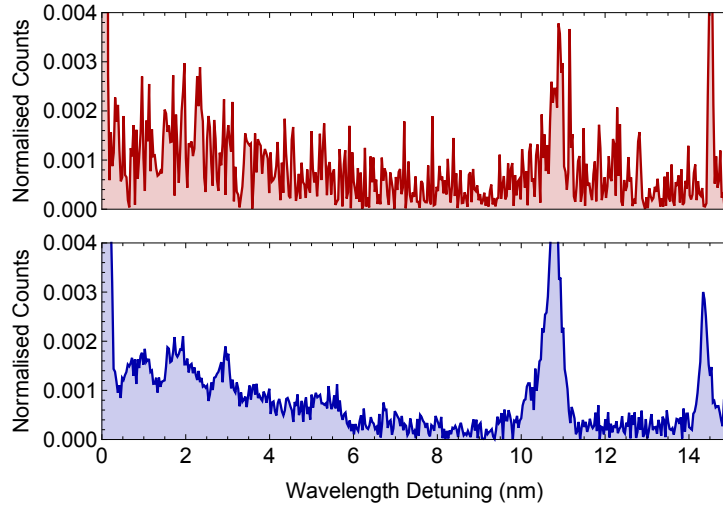


Figure 3.13. – Background subtracted spectra from a SiN coated substrate (top) and a gold back reflector substrate (bottom) at 4 K. Wavelength is detuning from the the ZPL wavelength of both molecules. Normalisation is performed using total counts in each spectra. Higher signal-to-noise ratio in the bottom plot allows for the strength and structure of the phonon sideband (from 0 nm to ~ 4 nm) to be distinguished.

local photonic environment [67]. The physics behind this will be discussed in a later chapter, for the following experiment this is for the purpose of increasing the collection efficiency of photons emitted by the DBT molecules.

This increase in collection efficiency, combined with long integration times, is useful for achieving a good signal-to-noise ratio on emission in the weak, broad phonon sideband. Fig. 3.13 shows a spectrum at 4 K from a previous sample without a back reflector compared to a spectrum with a back reflector. The phonon sideband is much harder to distinguish from the noise in this initial case which prevented detailed analysis by our collaborators, requiring the measurements to be repeated [23].

3.2.2. Measurements

The nanocrystal sample on a gold reflector was placed into the cryostat and cooled to 4.7 K. Measurements were performed using the confocal microscope shown in Fig. 2.8. Terascanes from 782 nm to 785 nm were performed on nanocrystals identified through the white light imaging whilst recording the red-shifted fluorescence, filtering with a long-pass 800 nm filter. A nanocrystal containing a single DBT molecule at 782.32 nm was identified. Linescans were performed at

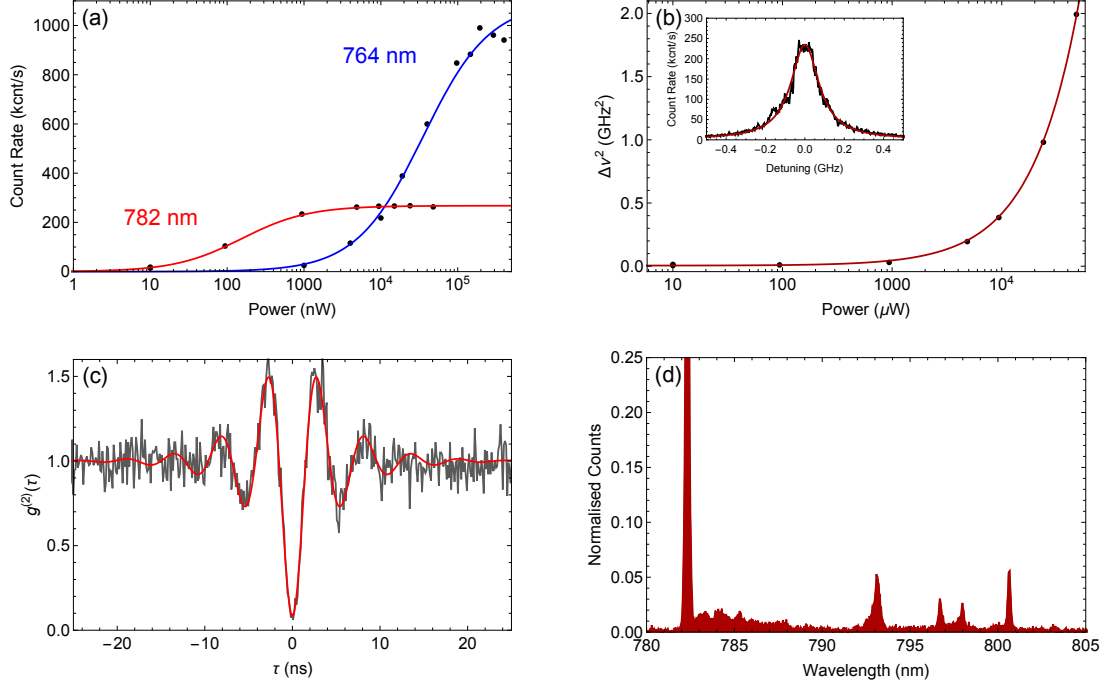


Figure 3.14. – (a) Count rates for resonant (782 nm, points with red curve) and blue-detuned (764 nm, points with blue curve) pumping for different pump powers. Resonant data is taken from fitted linescans (see (b)) and blue-detuned data is from spatial fluorescence scans. Fitted lines are of the form $R = R_{\infty} \frac{S}{1+S}$, giving $R_{\infty} = 267 \pm 2 \text{ knt s}^{-1}$ and $R_{\infty} = 1100 \pm 30 \text{ knt s}^{-1}$ for the resonant and blue-detuned cases respectively. (b) Data points are linewidth as a function of pump power taken from fitting Lorentzians to linescans. Fitted line is of the form given in Eq. 1.11. Inset: Example of detected fluorescence as a function of excitation wavelength showing the Lorentzian shape of a molecule resonance exciting with $P = 940 \pm 10 \text{ nW}$. (c) The black is data from the second-order correlation function measurement exciting with $P = 2400 \pm 10 \text{ nW}$, showing a characteristic photon anti-bunching dip. Red line is of the form given in Eq. 2.2. (d) Fluorescence spectrum of a single molecule. Counts are normalised to the height of the ZPL.

increasing powers to give saturation and power-broadening data, as shown in Fig. 3.14(a) and (b) respectively. Fitting Fig. 3.14(a) for the resonant pumping gives a count rate of $R_\infty = 267 \pm 2 \text{ kcnt s}^{-1}$ and a saturation power of $P_{\text{sat}} = 155 \pm 6 \text{ nW}$. Figure 3.14(b) gives a zero-power linewidth of $70 \pm 20 \text{ MHz}$ is found, corresponding to $\Gamma_2/(2\pi) = 35 \pm 10 \text{ MHz}$. A TCSPC measurement gives a lifetime of $\tau_1 = 4.31 \pm 0.01 \text{ ns}$. This lifetime corresponds to a decay rate of $\Gamma_1 = 1/\tau_1 = 2\pi \times 36.9 \pm 0.1 \text{ MHz}$. Using these values for Γ_1 and Γ_2 in Eq. 3.1 an excess dephasing of $17 \pm 10 \text{ MHz}$ is found. Ideally we would reduce this to zero, but we are limited by the cooling power of our cryostat.

A $g^{(2)}(\tau)$ measurement at $P = 2400 \pm 10 \text{ nW}$ was then made to verify a single-emitter had been identified, shown in Fig. 3.14(c). After convolution of Eq. 2.2 with the gaussian detector jitter function a visibility of $\mathcal{V} = 0.97 \pm 0.03$ is found, clearly showing the quantum nature of the emitted light.

The laser wavelength was then changed to 764.8 nm to excite a $S_{0,0} \rightarrow S_{1,n>0}$ transition. The filtering was changed to a 780 nm long-pass filter to collect all the fluorescence. Spatial fluorescence scans were performed at increasing power to find the saturation power, shown in Fig. 3.14(a). Fitting gives $R_\infty = 1100 \pm 30 \text{ kcnt s}^{-1}$ and a saturation power of $P_{\text{sat}} = 35 \pm 4 \text{ }\mu\text{W}$. A $g^{(2)}(\tau)$ measurement confirmed that a single molecule was still being interrogated. The spectrum was then recorded using a shorter, 770 nm long-pass filter, to avoid any modification of the spectrum from the tail of the filter edge. A background spectrum, taken far from the molecule was subtracted to give the spectrum shown in Fig. 3.14(d).

These measurements were repeated at 10 K , 20 K , 31 K and 40 K . The first stage in analysis is to verify that the molecule remains spectrally isolated for all the measurements. Figure 3.15 shows resonant and blue-detuned pumping $g^{(2)}(\tau)$ measurements at each temperature. The Rabi oscillations visible in the resonant pumping at 4.7 K are damped by dephasing in the other measurements. This is due to either the excess thermal dephasing at higher temperatures in the resonant case and to the inherent dephasing from the short lifetime of the vibrational state in the blue-detuned pumping case [71]. All the measurements have high visibilities above $\mathcal{V} = 0.9$, with most being greater than $\mathcal{V} = 0.95$, indicating that the emission is captured primarily from a single emitter.

The single-molecule emission spectra at the same five temperatures are plotted in Fig. 3.16 against the detuning from the strong ZPL at $792.32 \pm 0.01 \text{ nm}$. These spectra are background subtracted and normalised to the maximum count rate. As temperature increases the broadening of the spectral features can be seen. The relative strength of the phonon sideband from $\sim$

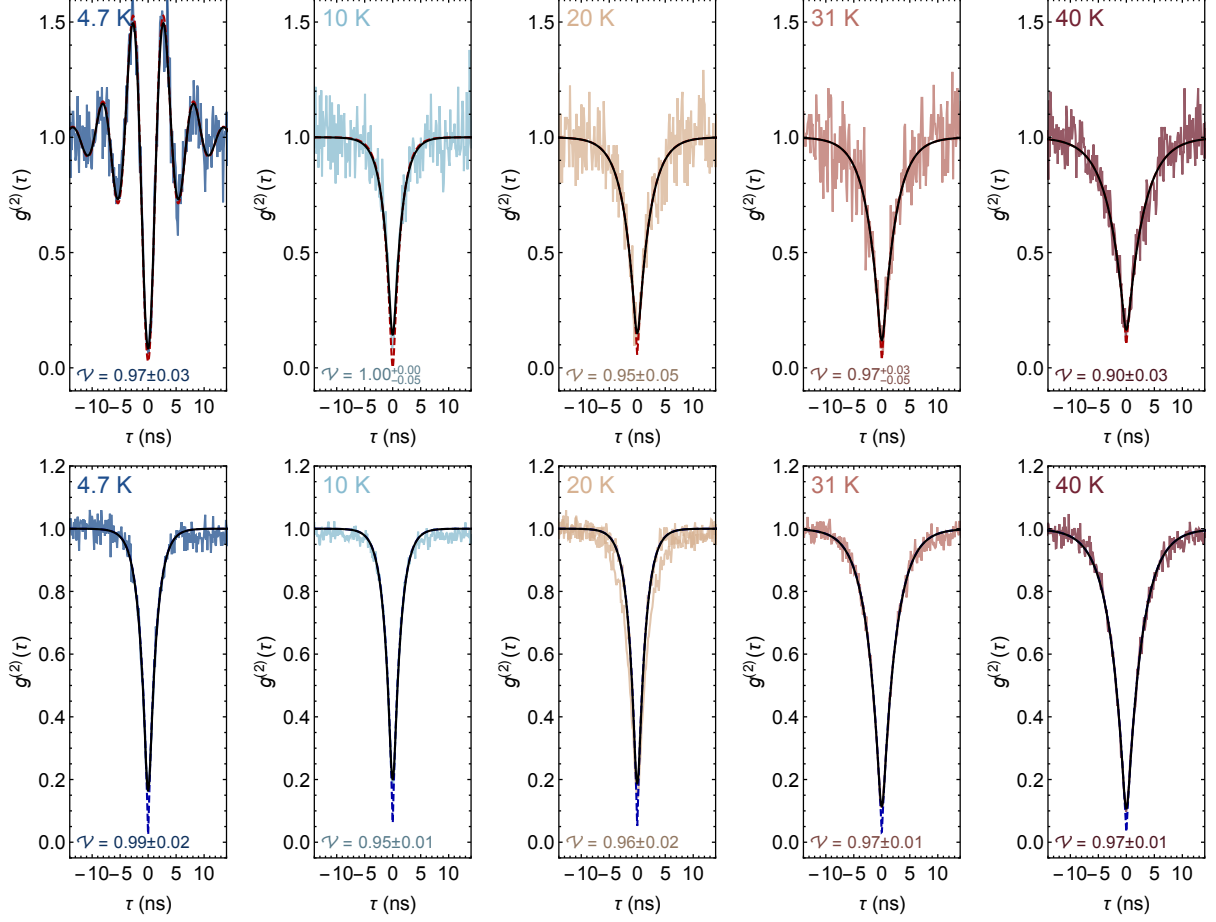


Figure 3.15. – Second-correlation function measurements at 4.7 K, 10 K, 20 K, 31 K and 40 K for resonant (782 nm, top row) and blue-detuned (764 nm, bottom row) excitation. Data is normalised to counts at high (compared to the lifetime) τ values. All $g^{(2)}(\tau)$ show a strong antibunching dip at $\tau = 0$ ns. Solid curves are fitted with a convolution of a Gaussian for detector jitter with either Eq. 2.2 or an exponential decay. Dashed curves are the deconvolved forms to show the high visibilities, $\mathcal{V}$, which are given below the curves. Rabi oscillations are visible in the 4.7 K measurement but thermal dephasing dampens these at higher temperatures [71].

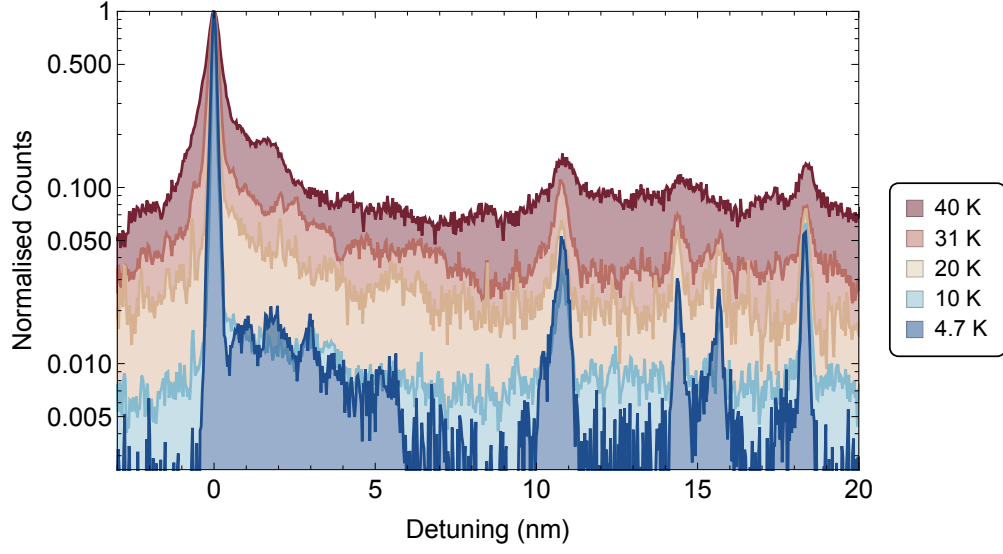


Figure 3.16. – Background subtracted spectra from DBT taken at 4 K, 10 K, 20 K, 31 K and 40 K. Data is normalised to the maximum counts in ZPL. ZPL broadening and the increase in the strength of the phonon sideband is clearly visible. The spectrometer resolution dominates the width of spectral features at low temperatures.

–1 nm to 5 nm also increases. Four other features are visible at 10.80 ± 0.01 nm, 14.40 ± 0.01 nm, 15.64 ± 0.02 nm, and 18.32 ± 0.01 nm corresponding to $S_{1,0} \rightarrow S_{0,n>0}$ transitions. These all correspond to known vibrational transitions in DBT [23, 96].

3.2.3. Analysis

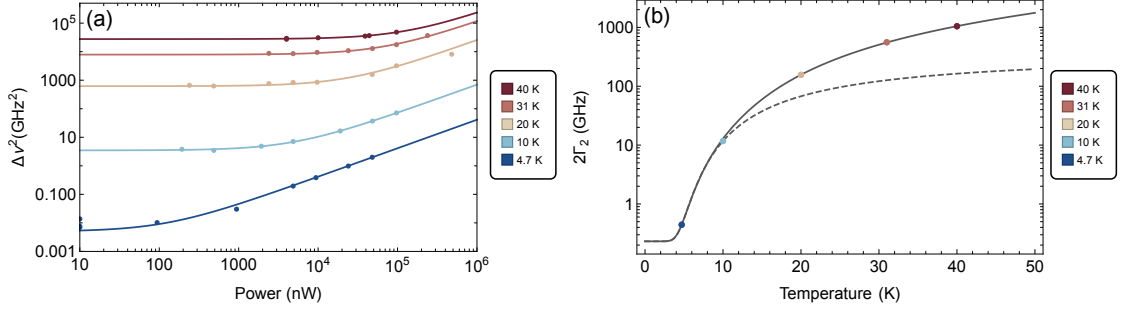


Figure 3.17. – (a) Linewidth-squared $\Delta\nu^2$ as a function of excitation power for the molecule at 4.7 K to 40 K, fitted with Eq. 1.11. The 4.7 K data is also presented in Fig. 3.14(b). (b) The Γ_2 values from the power-broadening data in (a) as a function of temperature. Fitted lines are exponential fits accounting for the coupling to phonons, with the dashed line using a single phonon mode and the solid line using two phonon modes. See text for details.

The results of power-broadening measurements from 4.7 K to 40 K are shown in Fig. 3.17(a). This is the same data presented in Fig. 3.14(b), but for all temperatures. The zero-power linewidths $\Delta\omega = 2\Gamma_2$ from these measurements as a function of temperature are shown in Fig. 3.17(b). Previous research into the thermal dephasing has found an Arrhenius law dependence on temperature [104, 71]. This follows from the likelihood of interaction with a phonon being dependant on the population of the phonon mode [105]. In particular, the increase in linewidth due to thermal dephasing is a result of an interruption of the phase between ground and excited electronic states. This interruption is due to phonon scattering, which occurs more frequently as temperature increases the phonon population. This population increase, and therefore broadening, has been described by an equation of the form

$$2\Gamma_2 = \Gamma_1 + A e^{-T_0/T} \quad (3.12)$$

where A is a prefactor depending on electron-phonon coupling and T is the activation temperatures for the local phonon mode. The lifetime measurement performed using TCSPC gives a lifetime-limited linewidth of $\Gamma_1 = 2\pi \times 36.9 \pm 0.1$ MHz.

Previous research covered low temperatures up to 4 K [104] and 10 K [71]. Fitting the 4.7 K and 10 K data points with an exponential gives an activation energy of $T_0 = 35 \pm 2$ K, in line with the previously reported values of $T_0 = 39 \pm 2$ K [71] and shown by the dashed line on the plot.

This approach is supported by previous research into thermal dephasing in pentacene finding a single phonon mode responsible for broadening under 20 K [105].

Accounting for the high temperature measurements requires a different equation than Eq. 3.12, as this is only valid for $T_0 \gg T$. Instead, the broadening can be described by [106]

$$2\Gamma_2 = \Gamma_1 + A \frac{e^{T_0/T}}{(e^{T_0/T} - 1)^2}, \quad (3.13)$$

which simplifies to Eq. 3.12 for low T , and gives the same activation energy T_0 within error, for the low temperature (4 K and 10 K) measurements. However, using a single phonon mode to account for the thermal dephasing at higher temperatures results in a poor fit. Adding a second phonon mode with activation energy T_1 results in a better fit shown by the solid black line in Fig. 3.17, with $T_1 = 78 \pm 2$ K. Further research would be required to test the validity of this phonon mode activation energy, however the prediction of lifetime-limited emission below 3 K is supported by the literature [71, 65, 23].

Analysing the spectral data allows the Debye-Waller and Franck-Condon factors to be calculated, and their temperature dependences investigated. The Franck-Condon factor α_{FC} , or branching ratio, is the proportion of emission on the ZPL, compared to the total emission of the molecule. Unfortunately only four vibrational transitions are visible in the spectra across the full temperature range, and previous spectroscopy has shown that there are more than 15 [65]. Additionally, although the phonon sideband of the ZPL is clearly distinguishable, the phonon sideband for the vibrational lines are not but these are expected to have similar α_{DW} . These factors prevent an absolute value for α_{FC} being determined, however is still possible to investigate how the temperature affects the strength of the ZPL relative to the total fluorescence that was measured. Figure 3.18 shows that ratio obtained by fitting Lorentzians to each of the features and then integrating over the spectra. The inset shows the data and fits at 20 K. There is no evident temperature dependence here. It is possible that the mean positions of the atoms in the DBT are shifted as the temperature of the Ac increases. This in turn would alter the overlap of the vibrational wavefunctions in the excited and ground states, thereby changing the Franck-Condon factors. However, this does not seem to be a significant effect.

A similar analysis can determine how temperature affects the ratio of the ZPL emission to that of the ZPL plus its phonon sideband. This is the Debye-Waller factor α_{DW} , plotted against temperature in Fig. 3.19. In order to determine the values plotted, the Γ_2 values shown in Fig. 3.17 are used to make the expected ZPL Lorentzian emission spectrum at each temperature. The resolution of the spectrometer is then accounted for by using a Gaussian blur with 0.07 nm

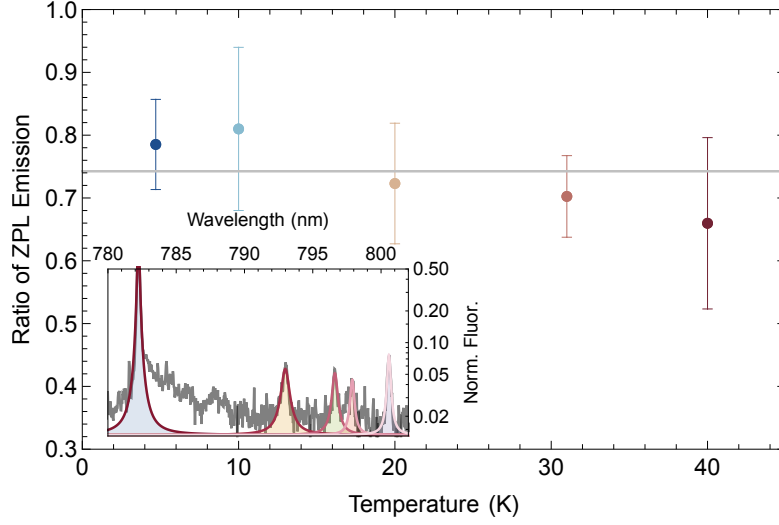


Figure 3.18. – A plot of the ratio of ZPL emission to total emission as a function of temperature. Data is found by fitting the ZPL and four vibrational transitions and integrating the area under these curves. Error bars are from error in height of features. The grey line is the error-weighted average value. Inset: An example of this fitting at 20 K.

standard deviation, based on independent measurements, to recreate the ZPL in the spectrum. The integral of this ZPL is then divided by the integral of a background-subtracted interpolation function of the entire ZPL and sideband, as in Eq. 3.2, to give the data in Fig. 3.19. This shows a clear decrease of α_{DW} as the temperature increases.

Unlike the thermal broadening of the ZPL, there is no simple formula for the change in the phonon sideband. The line in Fig. 3.19 is evaluated using the formula derived in Ref. [23]

$$\alpha_{\text{DW}} = \exp \left(- \int_0^\infty a \omega e^{-\omega^2/\xi^2} \coth(\beta\omega/2) d\omega \right). \quad (3.14)$$

The integral is over all the possible frequencies ω of the thermal phonon bath. A high-frequency cutoff $\xi = \sqrt{2}v/d$ accounts for the suppression of coupling to phonons with wavelengths smaller than the size d of the DBT molecule, where v is the speed of sound in Ac. a is the coupling strength between the TLS and the phonon bath and $\beta = 1/k_bT$. This measurement gives a maximum Debye-Waller factor of 72 %.

The total coherent emission from this molecule when lifetime-limited, below 3 K, will be the product of the Debye-Waller and Franck-Condon factors. Using this measured maximum α_{DW} value of 72 % and the widely accepted α_{FC} value of 50 % gives 36 %, in line with literature [22]. Filtering can increase the amount of coherent emission, at the cost of reducing efficiency [24],

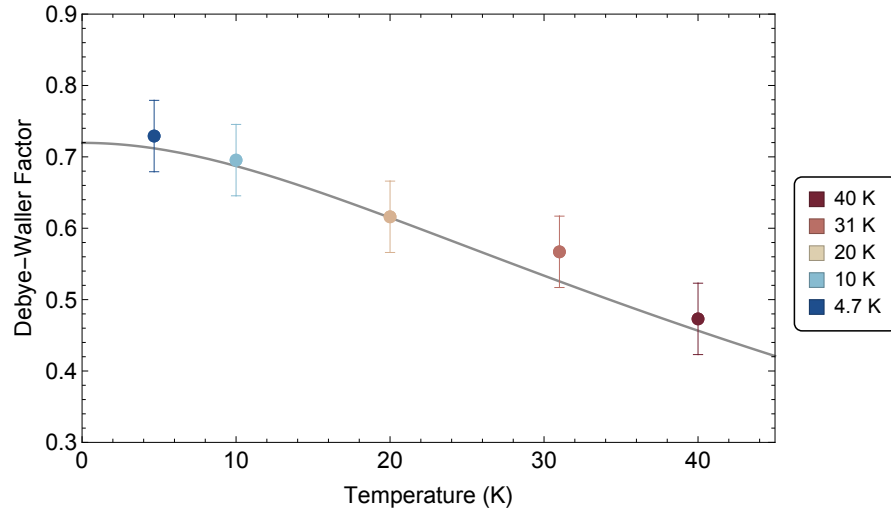


Figure 3.19. – A plot of the Debye-Waller factor α_{DW} , or ratio of ZPL emission to total emission of the ZPL and phonon sideband as a function of temperature. The grey line is Eq. 3.14, see text or Ref. [23] for details.

and this will be discussed in the following section.

4. Indistinguishability

This section will describe the development of an experiment to maximise the indistinguishability of photons emitted by DBT. Although there are published results showing two-photon interference from DBT molecules under cw excitation [107] and interaction between two DBT molecules [108, 22], no one has yet shown pulsed Hong-Ou-Mandel interference [72] between photons from DBT. This tests indistinguishability, which is a key property for many quantum information purposes as detailed in the Chapter 1 and experimental proof of this from DBT will be an important step in establishing DBT as a useful single photon emitter.

This section will start with the theory behind two-photon interference and how this can be measured using a single quantum emitter. The outcome of the measurement is dependent on whether pulsed or continuous-wave (cw) laser excitation is used and the differences between these two approaches will be discussed. Pulsed excitation is commonly used to find the full photon wavepacket indistinguishability $\mathcal{I}$ [109, 110] and the calculation will be outlined here. For cw excitation, measurements have been limited to discussing the ‘visibility’ of the effect [111, 107, 64, 112]. The exact definition of this depends on the measurement in question, however it does not define the probability of two-photon interference across the entire photon wavepacket. Based on comparisons of the pulsed and cw excitation results we will suggest a method of extracting true indistinguishability $\mathcal{I}$ from cw excitation of an emitter. There will then be a brief discussion of the effects of imperfect experimental setup.

The effects of filtering on the Debye-Waller factor and $\mathcal{I}$ will then be discussed. Only the coherent ZPL photons are capable of interfering with each other and as such blue-detuned pumping to an excited vibrational level $S_{1,n>0}$ will be used [23]. This allows convenient spectral filtering of excitation and emission light. The spectral data from the previous section will allow the design of notch filtering to increase the proportion of coherent emission collected.

Experimental data taken using cw and pulsed excitation of DBT molecule will then be presented. There is clear two-photon interference in both measurements. This data will then be used to verify the extraction of $\mathcal{I}$ from cw pumped measurements through comparison to the

value of $\mathcal{I}$ from the well-understood pulsed case.

4.1. Theoretical background

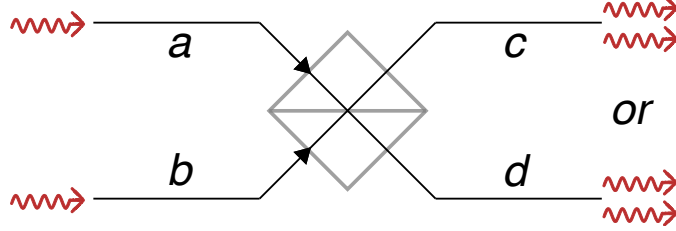


Figure 4.1. – A schematic representation of a 50:50 beamsplitter with input modes a and b and output modes c and d . When identical photons enter both input ports at the same time, they must both leave through the same output port.

This section will begin by briefly introducing the mathematics behind coalescence of photons at a beamsplitter [72]. Take a 50:50 beamsplitter with two input modes a and b , shown in Fig. 4.1, with an identical photon present in each mode $|1_a, 1_b\rangle$. This can be expressed in terms of the creation operators for these modes, $\hat{a}^\dagger$ and $\hat{b}^\dagger$, as

$$|1_a, 1_b\rangle = \hat{a}^\dagger \hat{b}^\dagger |0_a, 0_b\rangle. \quad (4.1)$$

The beamsplitter transforms the input modes into the c and d output modes. The creation operators transform as

$$\hat{a}^\dagger \rightarrow \frac{1}{\sqrt{2}}(\hat{c}^\dagger + \hat{d}^\dagger) \text{ and } \hat{b}^\dagger \rightarrow \frac{1}{\sqrt{2}}(\hat{c}^\dagger - \hat{d}^\dagger), \quad (4.2)$$

where $\hat{c}^\dagger$ and $\hat{d}^\dagger$ are the creation operators for the output modes. Applying the transformation to the input state

$$\hat{a}^\dagger \hat{b}^\dagger |0_a, 0_b\rangle \rightarrow \frac{1}{2}(\hat{c}^\dagger + \hat{d}^\dagger)(\hat{c}^\dagger - \hat{d}^\dagger)|0_c, 0_d\rangle. \quad (4.3)$$

Expanding this gives

$$\frac{1}{2}(\hat{c}^{\dagger 2} + \hat{d}^\dagger \hat{c}^\dagger - \hat{c}^\dagger \hat{d}^\dagger - \hat{d}^{\dagger 2})|0_c, 0_d\rangle. \quad (4.4)$$

The output mode creation operators commute, allowing for the cancelling of the cross terms.

This results in

$$\frac{1}{2}(\hat{c}^{\dagger 2} - \hat{d}^{\dagger 2})|0_c, 0_d\rangle = \frac{1}{\sqrt{2}}(|2_c, 0_d\rangle - |0_c, 2_d\rangle) \quad (4.5)$$

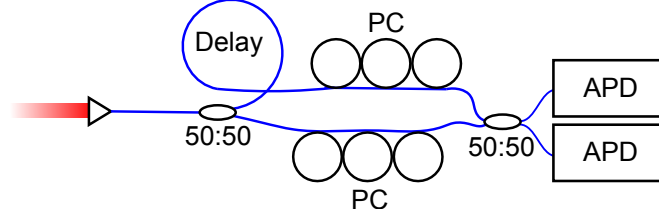


Figure 4.2. – Schematic diagram of the HOM interferometer. Red is the fluorescence and the blue is single mode fibre. 50:50: 50% reflection, 50% transmission fibre beam splitter; Delay: delay fibre; PC: polarisation controller; APD: avalanche photodiode.

giving a result with no single photon states; both photons must coalesce and leave in the same output mode.

For this coalescence to occur with 100 % probability the two photons have to be identical across all degrees of freedom; namely, the temporal and spatial overlap, wavelength, bandwidth and polarisation. When there is some mismatch between the two photons the coalescence probability is the square of the overlap of the two quantum states, which will be referred to as the indistinguishability $\mathcal{I}$. This can be measured by sending the emission of a single emitter, such as a DBT molecule, through a HOM interferometer and performing a $g^{(2)}(\tau)$ measurement on the output.

Figure 4.2 shows the experimental setup for this. The fluorescence is coupled into a single mode fibre and split on a 50:50 fibre beamsplitter. One path, designated ‘short’, leads straight to the second beamsplitter where interference will take place. The other path, designated ‘long’, features a length of fibre to delay the first photon so that it will reach the beam splitter at the same time as a later one. The time difference between the short and long paths is $\Delta\tau$. For pulsed pumping $\Delta\tau$ should ideally be a multiple of the inverse of the pulse repetition rate. There are also polarisation controllers (PC) to account for any polarisation mismatch between interferometer arms. In theory only a single PC is required to match the two arms, however a second polarisation controller is useful in practice. Initially one of the APDs is replaced by a PBS and the two polarisation controllers are adjusted to maximise one of the PBS outputs. This ensures the best polarisation overlap. The PBS is then removed and the APD attached. In order to maximise the excitation efficiency and simplify laser rejection, blue-detuned pumping will be used.

The expected results of pulsed and then cw excitation measurements will now be discussed. Initially, only thermal dephasing will be considered as a source of distinguishability as the ex-

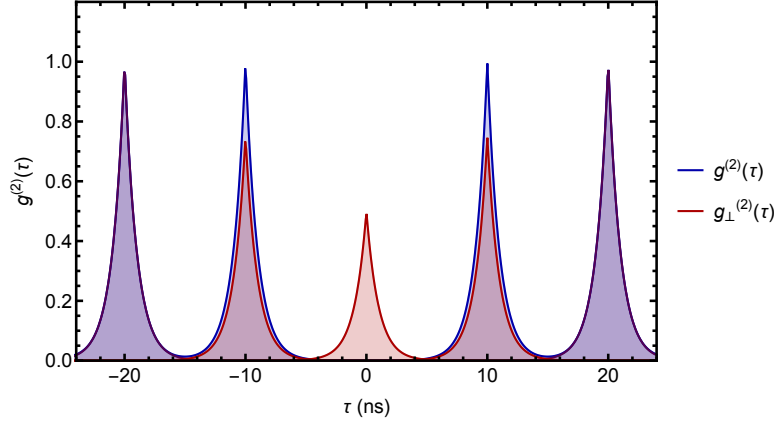


Figure 4.3. – Ideal measurements on a single photon emitter with pulsed excitation. Blue: a standard single beamsplitter $g^{(2)}(\tau)$ measurement. Red: an orthogonal polarisation HOM interferometer $g_{\perp}^{(2)}(\tau)$ measurement. Pulses are $t = 10$ ns apart and the emitter has a lifetime of 1 ns. The peaks corresponding to correlations between pulses greater than $\tau = \pm 10$ ns apart are unaffected by the interferometer.

perimental setup allows for the other photon properties to be controlled. These will be discussed later, along with the experimental parameters of the HOM interferometer set-up in the lab and the equations accounting for all of these factors.

4.1.1. Pulsed excitation

For simplicity let us assume perfect 50:50 beamsplitters, a time delay equal to the repetition rate of the pulses, and initially, no detector jitter. Considering the pulsed-pumping case first; for a standard pulsed $g^{(2)}(\tau)$ measurement, blue in Fig. 4.3, the central $\tau = 0$ ns peak drops to zero for a pure single photon source. However, in a HOM interferometer with different path lengths, the emitted photons do not always take the same time to reach the detectors, some will take τ and some will take $\tau + \Delta\tau$. This will allow successive photons to reach the second beam splitter at the same time.

The probability of this can be found by first considering a randomly selected emitted photon from a continuous stream of photons entering the interferometer. Half of the time it will take the non-delayed path and half of the time it will take the delayed path, for a balanced initial beam splitter. If it takes the non-delayed path and the prior photon had been delayed, which occurs with probability 50 %, they will both reach the final beam splitter at the same time. Alternatively, if a delayed photon is chosen and the subsequent photon takes the non-delay path

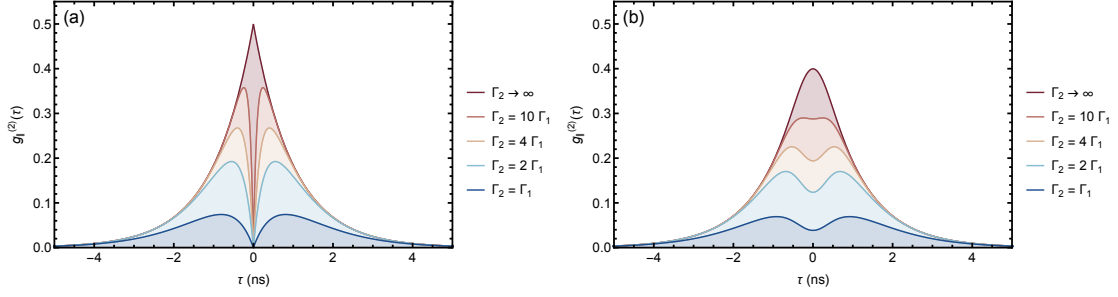


Figure 4.4. – (a) A zoom in on the central feature of a pulsed $g_{\parallel}^{(2)}(\tau)$ HOM interference measurement for values of pure dephasing. As Γ_2 approaches the lifetime-limit of $\Gamma_2 = \Gamma_1/2$ the function flattens. (b) The same function values convolved with a 300 ps detector jitter to give the physically measurable form.

they will also both reach the final beam splitter at the same time. This also has probability 50 %. Either of these options can happen, giving a $0.5 * 0.5 + 0.5 * 0.5 = 50\%$ chance that two photons reach the final beam splitter simultaneously. With perpendicular polarisations, the second-order correlation function value at $\tau = 0$ is $g_{\perp}^{(2)}(0) = 0.5$. There is also a reduction in the second-order correlation function at $\tau = \pm\Delta\tau$ to $g_{\perp}^{(2)}(\pm\Delta\tau) = 0.75$. This is due to photons that would have caused coincidences at these times being shifted to the central $g_{\perp}^{(2)}(0)$ feature.

Figure 4.3 shows a comparison of standard single beamsplitter HBT $g^{(2)}(\tau)$ with a HOM interference measurement of $g_{\perp}^{(2)}(\tau)$. This can be described by

$$g_{\perp}^{(2)}(\tau) = \sum_n (1 - \mathcal{V}_n) e^{-\Gamma_1 |\tau - n\Delta\tau|} \quad (4.6)$$

where $\Delta\tau$ is both the time between lasers pulses and the delay length, $\tau_1 = 1/\Gamma_1$ is the emitter lifetime and $\mathcal{V}_n$ is the visibility of the n^{th} correlation peak. For balanced beam splitters $\mathcal{V}_{-1} = 0.25$, $\mathcal{V}_0 = 0.5$, $\mathcal{V}_1 = 0.25$, as described above. This equation is similar to Eq. 1.24, modified to account for the interferometer. The effect of beamsplitter ratios on $\mathcal{V}_n$ will be looked at later in this section.

If the polarisations are set to be parallel, so that the photons are now indistinguishable ($g_{\parallel}^{(2)}(\tau)$) photons incident simultaneously on the final beamsplitter will coalesce. There will no longer be coincidences on the APDs and the central $\tau = 0$ ns feature will entirely disappear. For photons with some dephasing this suppression of the central feature will be incomplete. This can be

described by [113, 39]

$$g_{\parallel}^{(2)}(\tau) = \mathcal{V}e^{-\Gamma_1|\tau|}(1 - e^{-2|\tau|\Gamma_2^*}) \quad (4.7)$$

$$= \mathcal{V}\left(e^{-|\tau|\Gamma_1} - e^{-|\tau|2\Gamma_2}\right). \quad (4.8)$$

The visibility is $\mathcal{V} = \mathcal{V}_0 = 0.5$. The temporal profile of this suppression is perhaps unexpected, with the value at $\tau = 0$ always falling to zero (for no detector jitter) with a narrow central dip having a width inversely proportional to Γ_2 [39]. Figure 4.4(a) shows this dip for a selection of Γ_2 values. This behaviour occurs even with arbitrarily shortened coherence times, as there is still an arbitrarily short time period where the photons are indistinguishable.

The indistinguishability $\mathcal{I}$ can be found with [39, 114]

$$\mathcal{I} = \frac{\int \delta\tau g_{\perp}^{(2)}(\tau) - \int \delta\tau g_{\parallel}^{(2)}(\tau)}{\int \delta\tau g_{\perp}^{(2)}(\tau)} \quad (4.9)$$

with the integrals being taken over the temporal range of the central feature. This expression gives the difference in areas, or count rates, of the parallel and orthogonal $g_{\perp/\parallel}^{(2)}(\tau)$ measurements and normalises to the $g_{\perp}^{(2)}(\tau)$ case to give a probability of photon coalescence. This is valid for both the $g_{\perp/\parallel}^{(2)}(\tau)$ functions and the normalised coincidence count rate data. Where dephasing is the only source of distinguishability this simplifies to $\mathcal{I} = \Gamma_1/(2\Gamma_2)$.

Convolution of Eq. 4.7 with our Gaussian detector jitter gives Fig. 4.4(b). The sharpness of the function is reduced and $g^{(2)}(0)$ is no longer zero. However, the integral of the two functions is the same, meaning this measurement is still equally valid for determining indistinguishability $\mathcal{I}$. If the pulse rate is slow enough compared with Γ_1 , so that the pulses are temporally distinct, as in Fig. 4.3, this integral is simply the total area of the central feature.

4.1.2. cw excitation

A similar analysis can be performed for blue-detuned cw excitation. Figure 4.5 shows a comparison between a typical single beamsplitter $g^{(2)}(\tau)$ measurement and a HOM measurement using perpendicular polarisations on the two interferometer arms. A modification of Eq. 1.23 describes the result of this HOM measurement

$$g_{\perp}^{(2)}(\tau) = 1 - \sum_{n=-1}^1 \mathcal{V}_n e^{-\Gamma_1(1+S)|\tau-n\Delta\tau|} \quad (4.10)$$

where terms are as defined for Eq. 4.6. The same temporal movement of photons described in the pulsed case also applies here, and results in $g_{\perp}^{(2)}(0) = 0.5$ and $g_{\perp}^{(2)}(\pm\Delta\tau) = 0.75$, with the corresponding visibilities $\mathcal{V}_{-1} = 0.25$, $\mathcal{V}_0 = 0.5$, $\mathcal{V}_1 = 0.25$.

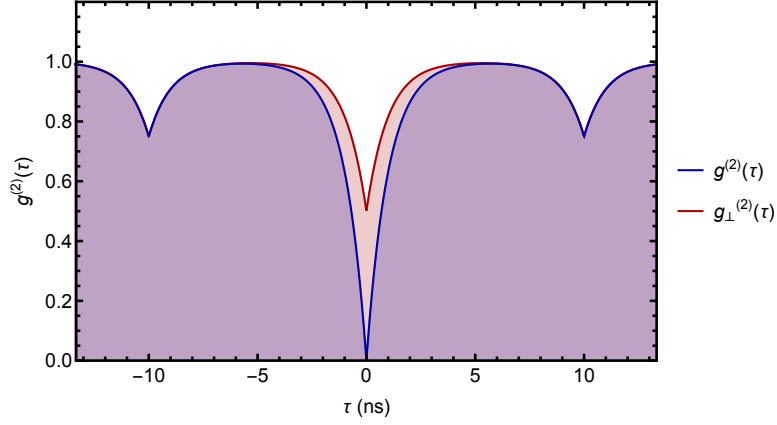


Figure 4.5. – Ideal measurements on a single photon emitter with cw excitation. Blue: a standard single beamsplitter $g^{(2)}(\tau)$ measurement. Red: an orthogonal polarisation HOM interferometer $g_{\perp}^{(2)}(\tau)$ measurement. The delay fibre has a delay of $\Delta\tau = \pm 10$ ns and the emitter has a lifetime of 1 ns.

As with the pulsed case, when the photons are polarised identically the $g_{\parallel}^{(2)}(0)$ value drops to zero as photons will coalesce on the final beamsplitter. This is formed from two exponential decays, one from anti-bunching with a width dependant on the lifetime and a second from indistinguishability causing photon coalescence. We will begin by considering the limiting case of weak driving $S \ll 1$ [64]

$$\lim_{S \rightarrow 0} g_{\parallel}^{(2)}(\tau) = 1 - \mathcal{V}e^{-|\tau|\Gamma_1} - \mathcal{V}e^{-2|\tau|\Gamma_2} \quad (4.11)$$

$$= 1 - \mathcal{V}e^{-|\tau|\Gamma_1} - \mathcal{V}e^{-2|\tau|(\Gamma_1/2 + \Gamma_2^*)}. \quad (4.12)$$

The visibility is $\mathcal{V} = \mathcal{V}_0 = 0.5$. Figure 4.6(a) shows this function plotted for a range of Γ_2 values including the lifetime limit of $\Gamma_2 = \Gamma_1/2$. The $g_{\parallel}^{(2)}(0)$ value always reaches zero, however the dip itself narrows as dephasing increases and coherence time decreases. At high dephasing the separate anti-bunching and indistinguishability components of the function become clear.

Convolution with the 300 ps detector jitter Gaussian gives Fig. 4.6(b). Similar to the pulsed case, the smoothing effect of the detector jitter means that $g_{\parallel}^{(2)}(0) > 0$. This increase in the $g_{\parallel}^{(2)}(0)$ value depends on a combination of the dephasing rate Γ_2 and the width of the Gaussian detector jitter, which means it alone is not a good metric for indistinguishability. Instead, an equation similar to Eq. 4.9 would be useful here, although a search of literature has not provided one. Directly integrating the $g_{\parallel}^{(2)}(\tau)$ or $g_{\perp}^{(2)}(\tau)$ will give infinity as can be seen on Fig. 4.6. However, $1 - g_{\parallel/\perp}^{(2)}(\tau)$, does give a finite integral. Subtracting Eq. 4.12 from 1 and comparing

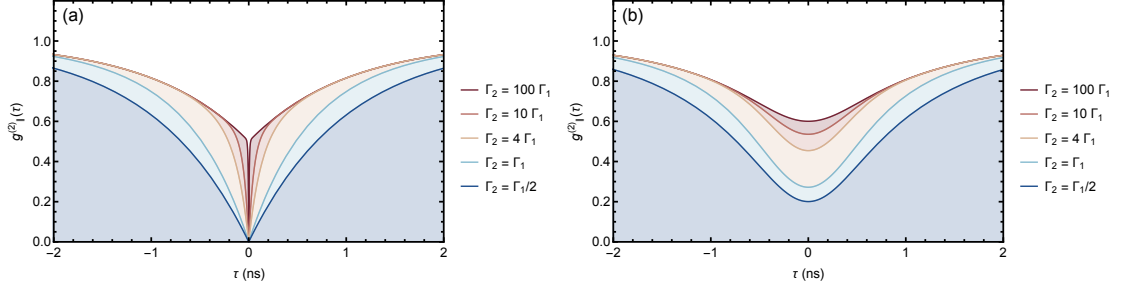


Figure 4.6. – (a) A zoom in on the central feature of a cw HOM interference measurement for values of pure dephasing. As Γ_2 approaches the lifetime-limit of $\Gamma_2 = \Gamma_1/2$ the function approaches a standard $g^{(2)}(\tau)$ function. (b) The same function values convolved with the 300 ps detector jitter to give the profile expected in practice.

that to Eq. 4.7, the only difference is the sign between the Γ_1 and Γ_2 terms. In other words, in the cw case the two exponentials are added and in the pulsed case they are subtracted. This is shown in Fig 4.7.

Taking advantage of this similarity, we postulate that in the case of cw pumping, the indistinguishability is given by the expression

$$\mathcal{I}_{cw} = \lim_{S \rightarrow 0} \frac{\int \delta\tau (1 - g_{\parallel}^{(2)}(\tau)) - \int \delta\tau (1 - g_{\perp}^{(2)}(\tau))}{\int \delta\tau (1 - g_{\perp}^{(2)}(\tau))}. \quad (4.13)$$

In the case of dephasing being the only source of distinguishability, Eq. 4.10 and Eq. 4.12 give in the limit of $S \ll 1$

$$\int \delta\tau (1 - g_{\perp}^{(2)}(\tau)) = \int \delta\tau \frac{1}{2} e^{-|\tau|\Gamma_1} = \frac{1}{\Gamma_1}, \quad \text{and} \quad (4.14)$$

$$\int \delta\tau (1 - g_{\parallel}^{(2)}(\tau)) = \int \delta\tau \left(\frac{1}{2} e^{-|\tau|\Gamma_1} + \frac{1}{2} e^{-2|\tau|\Gamma_2} \right) = \frac{\Gamma_1 + 2\Gamma_2}{2\Gamma_1\Gamma_2}. \quad (4.15)$$

This recovers the result $\mathcal{I} = \Gamma_1/(2\Gamma_2)$, agreeing with the pulsed case of Eq. 4.9. As with the pulsed case, the integral of the convolved form of Eq. 4.12 is the same as the regular form, meaning Eq. 4.13 can still be used to determine $\mathcal{I}$. With stronger driving, Γ_1 is replaced by $\Gamma_1(1 + S)$ as seen in Eq. 1.23. However the reduction in coherence time due to excess dephasing Γ_2^* is not expected to be affected by the driving rate. This gives rise to the result

$$\tilde{\mathcal{I}}(S) = \frac{\int \delta\tau (1 - g_{\parallel}^{(2)}(\tau)) - \int \delta\tau (1 - g_{\parallel}^{(2)}(\tau))}{\int \delta\tau (1 - g_{\parallel}^{(2)}(\tau))} = \frac{\Gamma_1(1 + S)}{\Gamma_1(1 + S) + 2\Gamma_2^*} \quad (4.16)$$

with $\lim_{S \rightarrow 0} \tilde{\mathcal{I}}(S) = \mathcal{I}$.

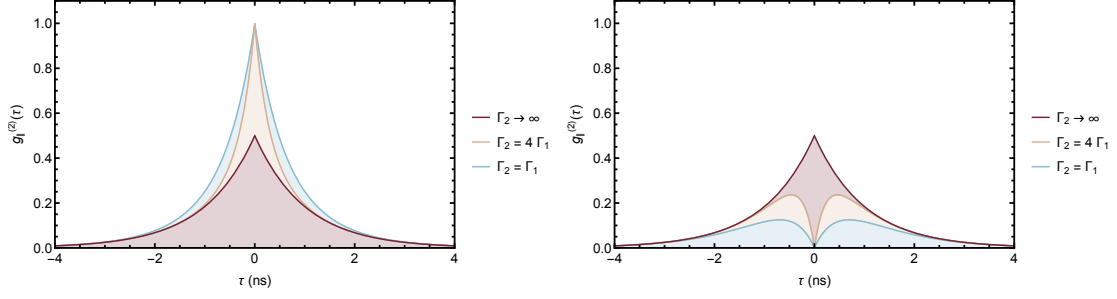


Figure 4.7. – Left: plot of $1 - g_{\perp}^{(2)}(\tau)$ given by Eq. 4.12 for cw excitation. Right: plot of $g_{\perp}^{(2)}(\tau)$ given by Eq. 4.7 for pulsed pumping.

Section 3.3.3 will describe cw $g_{\parallel/\perp}^{(2)}(\tau)$ measurements at known S values to determine $\tilde{\mathcal{I}}(S)$ using Eq. 4.16, which can then be extrapolated to $S = 0$, equivalent to $\mathcal{I}_{\text{cw}}$. This method will be compared with pulsed measurements of $\mathcal{I}$ based on Eq. 4.9. The strengths and limitations of both of these measurement regimes will also be discussed. However, I first conclude this section by considering the contributions of other sources of distinguishability and presenting equations that can be used on experimental data. There will also be a section on optimising the filtering of the molecule.

4.1.3. Other considerations

Up to now we have considered an ideal HOM interferometer and an ideal source, apart from the dephasing, for which $\mathcal{I} = \Gamma_1/(2\Gamma_2)$. In practice, neither one is ideal and several new factors therefore enter into the value of $\mathcal{I}$ deduced from the HOM measurement. First, the source can emit photons on the vibrational sidebands which are completely distinguishable from the ZPL photons. The probability that a photon is not on one of these sidebands is the Franck-Condon factor α_{FC} . Next, there are $\Delta v = 0$ photons emitted in the phonon sideband, which are close in frequency to the ZPL but still distinguishable from ZPL photons. The probability of a $\Delta v = 0$ photon being on the ZPL is given by the Debye-Waller factor α_{DW} . Then, there can be an angle θ between the polarisation directions of the two photons entering the final beam splitter of the HOM interferometer because of error in the relative orientation of the fibre axes. Finally, there can be a mismatch Δt in the arrival times of the two photons at the beam splitter. With all these factors taken into account, the indistinguishability measured by the HOM interferometer becomes

$$\mathcal{I} = \frac{\Gamma_1}{2\Gamma_2} \alpha_{FC}^2 \alpha_{DW}^2 \cos^2(\theta) e^{-\Gamma_1 \Delta t} = \frac{\Gamma_1}{2\Gamma_2} \mathcal{M}. \quad (4.17)$$

All of these factors can be grouped together in a modal overlap $\mathcal{M}$ term. These factors have no τ dependence, and will instead cause a constant reduction [64]. The Franck-Condon and Debye Waller factors are squared here because the HOM interference required two ZPL photons, each having the probability $\alpha_{FC}\alpha_{DW}$ [24, 23]. We neglect the possibility of interference between a pair of sideband photons as it is exceedingly small. The timing overlap between photons arriving at separate times is given by $e^{-\Gamma_1\Delta t}$ [113].

Spectral wandering, or jitter in the ZPL frequency over longer timescales significantly greater than τ_1 , has minimal effect on $\mathcal{I}$. This measurement of consecutive photon interactions is only sensitive to change on the order of τ_1 . Some experiments account for this by comparing $\mathcal{I}$ for variable delays [115]. If interaction between photons from two or more photon sources is desired this spectral wandering will become a much greater issue as this will greatly reduce, or totally remove, any spectral overlap. Although during this PhD no experiments have been directly performed to measure the spectral wandering of DBT, there have been many experiments involving long periods of cw excitation with no change in counts or broadening from excitation [23].

4.1.4. Full equations for measurement

This section reproduces the full equations that describe the cw and pulsed $g_{\parallel/\perp}^{(2)}(\tau)$ measurements. These account for the transmission/reflection coefficients of the beam splitters as well as the factor $\mathcal{M}$ introduced in Eq. 4.17. These equations are based on the supplementary material of Ref. [64], combined with the saturation discussed above. For cw excitation

$$g_{\parallel/\perp}^{(2)}(\tau) = 1 - \frac{\mathcal{V}}{(r_1^2 t_0^2 + r_0^2 t_1^2)(r_0^2 r_1^2 + t_0^2 t_1^2)} \left(r_1^2 t_1^2 (r_0^4 + t_0^4) e^{-\Gamma_1(1+S)|\tau|} \right. \\ \left. + \mathcal{M} 2 r_0^2 r_1^2 t_0^2 t_1^2 e^{-(\Gamma_1(1+S)+2\Gamma_2^*)|\tau|} \right. \\ \left. + r_0^2 r_1^4 t_0^2 e^{-\Gamma_1(1+S)|\tau-\Delta\tau|} \right. \\ \left. + r_0^2 t_1^4 t_0^2 e^{-\Gamma_1(1+S)|\tau+\Delta\tau|} \right), \quad (4.18)$$

where t_0 and r_0 are the transmission and reflection coefficients of the first beamsplitter, and t_1 and r_1 are for the second interference beamsplitter. The visibility $\mathcal{V}$ is now a single value for all features, with the ratio between them determined by the particular reflection and transmission coefficients. There are four exponentials; the first is the $\tau = 0$ anti-bunching dip, the second is the reduction in coincidences due to indistinguishability. The third and fourth are the side dips due to the redistribution of anti-bunching at $\pm\Delta\tau$. Equation 4.18 is for cw excitation, however

replacing the 1 with a series of exponential peaks and removing the saturation dependance, gives

$$g_{\parallel/\perp}^{(2)}(\tau) = \sum_i e^{-\Gamma_1|\tau-i\Delta\tau|} - \frac{\mathcal{V}}{(r_1^2 t_0^2 + r_0^2 t_1^2)(r_0^2 r_1^2 + t_0^2 t_1^2)} \left(r_1^2 t_1^2 (r_0^4 + t_0^4) e^{-\Gamma_1|\tau|} \right. \\ \left. + \mathcal{M} 2 r_0^2 r_1^2 t_0^2 t_1^2 e^{-2\Gamma_2|\tau|} \right. \\ \left. + r_0^2 r_1^4 t_0^2 e^{-\Gamma_1|\tau-\Delta\tau|} \right. \\ \left. + r_0^2 t_1^4 t_0^2 e^{-\Gamma_1|\tau+\Delta\tau|} \right). \quad (4.19)$$

This can be used to describe a pulsed measurement as long as the interferometer delay and pulse repetition rate are close enough to be considered equal.

The parameters measured for our interferometer are $t_0 = \sqrt{0.501(1)}$, $r_0 = \sqrt{0.499(1)}$, $t_1 = \sqrt{0.482(1)}$ and $r_1 = \sqrt{0.518(1)}$. Performing a pulsed $g^{(2)}(\tau)$ measurement with the pulsed laser gives peak spacings of 12.515 ± 0.005 ns. This corresponds to a repetition rate of 79.9 MHz, close to the ‘advertised’ repetition rate of 80 MHz. The delay fibre is currently 24.83 ns, which is only 0.19 ns less than the time between even-numbered laser pulses. The measured timing jitter for the interferometer is 420 ps, which means Eq. 4.19 is suitable to use.

4.2. Filtering design

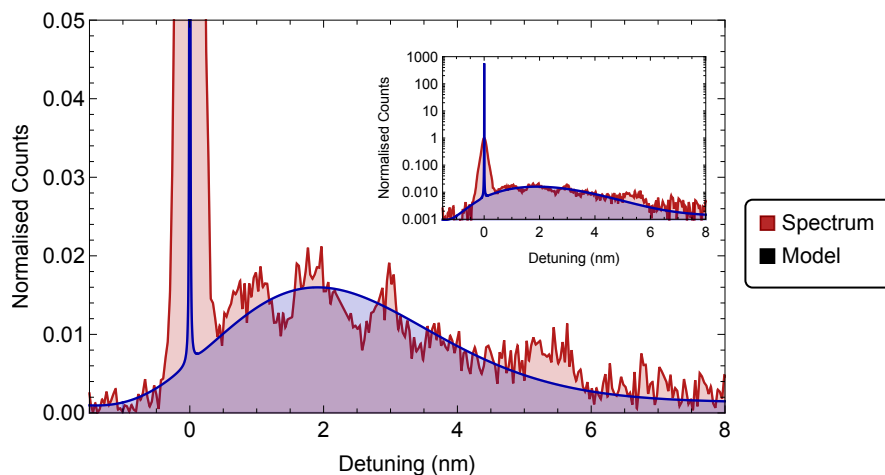


Figure 4.8. – A plot comparing the measured spectrum and a fitted model consisting of a 40 MHz Lorentzian and a Poissonian sideband. The functions are scaled to maintain the same integral area, corresponding to the same Debye-Waller factor. Inset: The same plot with a log scale to show the peak intensity difference between the measured and modelled spectra.

To maximise $\mathcal{I}$ for the photons emitted by DBT emitted photons the ratio of coherent to total emission collected needs to be maximised. Dephasing can be reduced by cooling below 3 K, according to measurements in the previous section. It is straightforward to remove light on the vibrational sidebands using a short-pass or band-pass filter. This effectively sets α_{FC} to zero in Eq. 4.17, though of course it also reduces the efficiency η . It is not so simple to remove the photons emitted on the phonon sideband, which according to Fig. 3.19 makes up 28 % of the $\Delta v = 0$ emission at temperatures low enough to reach lifetime-limited fluorescence. This is because the broad phonon sideband overlaps with the narrow ZPL, as shown in Fig. 3.16 or Fig. 4.8. Given the inhomogeneous spread in ZPL frequencies the filter will also need to be tuneable.

Given the limited change in the Debye-Waller factor and spectra between 4.7 K to 10 K, shown in Fig. 3.19 and Fig. 3.16 respectively, there is also expected to be minimal change when DBT is cooled to below 3 K. As such, the 4.7 K spectrum is used as the basis for a model to predict the effect of filtering. This can then be convolved with a filter function to determine the modified Debye-Waller factor, and associated indistinguishability [24]. The broadening of the ZPL by the

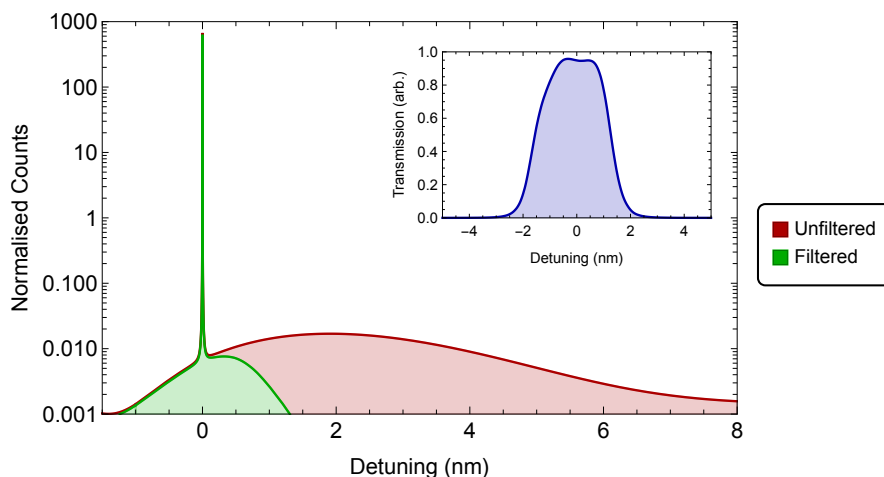


Figure 4.9. – A plot showing the unfiltered (red) and filtered (green) spectra after convolution with the filter response function of our 785.0 ± 1.5 nm bandpass filter. The central frequency of the filter can be shifted to match that of the molecule by tilting the filter. The arrangement shown, with most of the sideband cut off, has the proportion of collected emission from the ZPL of 94 %, and a corresponding $\mathcal{I} = 88$ %. Inset: Response function of the filter.

spectrometer prevents it being directly used. Instead, a 40 MHz Lorentzian is used for the ZPL and the sideband is modelled with a Poisson distribution. These are fitted so the integrals are equivalent to the measured spectrum, with the same Debye-Waller factor. Figure 4.8 compares the spectrum with the model for convolution with filter functions.

A 785 ± 3 nm bandpass filter (Semrock, MaxLine) is regularly used in collection when using blue-detuned excitation. Figure 4.9 shows the calculated spectrum after filtering. The transmission spectrum was measured by scanning the laser across the filter and measuring transmitted power. The exact wavelength range of the filter can be blue-shifted through tilting to optimise the spectral overlap of a molecule and the filter. This increases the proportion of collected light from the ZPL transition from 72 % to 94 %, and the indistinguishability $\mathcal{I}$ from 52 % to 88 %, assuming no excess dephasing or other effects. Even with this relatively simple filtering a high indistinguishability is achievable.

There is also the possibility of using a more narrowband bandpass filter. A holographic 785.00 ± 0.15 nm reflection filter was purchased for this purpose. Figure 4.10 shows the modification of the spectrum when the ZPL is aligned with the filter passband. The transmission spectrum was measured by scanning the laser across the filter and measuring reflected power. This enables a huge increase in the proportion of ZPL emission collected up to 99.7 %, and a

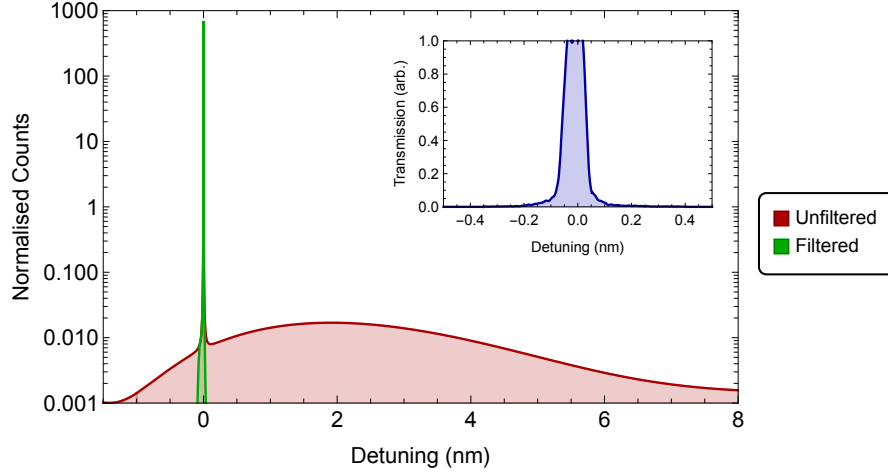


Figure 4.10. – A plot showing the unfiltered (red) and filtered (green) spectra after convolution with the filter response function of a 785.00 ± 0.15 nm bandpass filter. The central frequency of the filter can be shifted by tilting the filter to match that of the molecule. The arrangement shown, with nearly all of the sideband removed, has the proportion of collected emission from the ZPL of 99.7 %, and a corresponding $\mathcal{I} = 99.3$ %. Inset: Response function of the filter.

corresponding $\mathcal{I} = 99.3$ %. As the angle of this filter to the collection beam directly effects both the passband and angle of reflection, the filter is set up separately from the main microscope. The collection is fibre-coupled to the filter, filtered in free space, and fibre-coupled again to be sent to the interferometer. This causes a greater loss in efficiency than just the usual transmission loss due to filtering thanks to loss on a greater number of optical components.

4.3. Measurements

In order to test the interferometer setup and the equivalence between cw and pulsed excitation, HOM measurements were performed with a sample in the Montana cryostat using the microscope shown in Fig. 2.8. Although this is limited to ~ 4.7 K, the ability to keep samples cold without a constant supply of liquid helium makes it ideal for optimising the experimental setup, in particular the interferometer. A nanocrystal growth was performed with approximately 20 times the concentration of DBT used in the previous temperature dependence experiments and filtered through a 1200 nm syringe filter. A higher concentration growth was used to speed up finding a molecule with relatively high collection efficiency. The filtrate was deposited on a Au back reflector sample to enhance collection efficiency and coated with a 200 nm protective PVA layer.

4.3.1. Molecule characterisation

As in previous experiments the terascan functionality of the laser was used to find a molecule. A molecule was identified with a ZPL at 784.4 nm and a vibrational transition at 766.6 nm. Figure 4.11(a) shows the saturation data for resonant and blue detuned pumping, with count rate data taken from linescans and confocal images respectively. Single mode fibre collection and the reflection filter shown in Fig. 4.10 were used to select just the ZPL emission for the blue-detuned pumping case, hence the low count rate relative to the multi-mode fibre and 800 nm LP filtering used for the resonant pumping.

Power broadening data from linescans performed at increasing powers are shown in Fig. 4.11(b), giving a zero-power linewidth of 70 ± 8 MHz, and therefore $\Gamma_2/(2\pi) = 35 \pm 4$ MHz. A blue-pumping $g^{(2)}(\tau)$ measurement is shown in Fig. 4.11(c). A visibility of $0.98^{+0.02}_{-0.03}$ is found, which when accounting for detector timing jitter gives $\mathcal{V} = 1.00^{+0}_{-0.03}$ indicating emission from a single emitter is being collected. Knowing that $S = 0.62$, the shape of the $g^{(2)}(\tau)$ dip gives $\Gamma_1/(2\pi) = 40 \pm 2$ MHz. A TCPSC experiment using pulsed pumping finds $\Gamma_1/(2\pi) = 39 \pm 3$ MHz, in agreement. Combining these results, $\Gamma_1/2\Gamma_2 \approx 58\%$, typical for this temperature.

Figure 4.11(d) shows the fluorescence spectrum recorded from this location without using the narrowband filtering. There are three ZPLs visible around 785 nm, indicating at least three molecules are being excited at this pump wavelength (766.6 nm). The high visibility of the $g^{(2)}(\tau)$ measurement highlights the effectiveness of this filtering for spectrally isolating a single molecule in a highly-doped sample. The inset in Fig. 4.11(d) is the spectrum after filtering and single mode collection, also showing the removal of emission from other molecules.

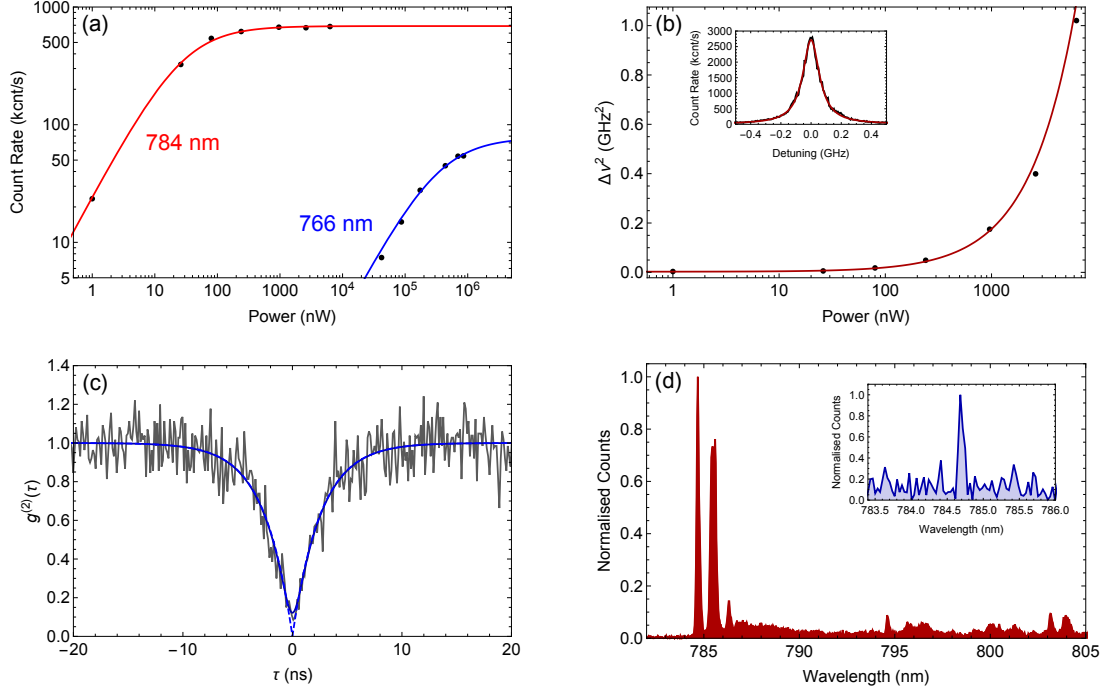


Figure 4.11. – (a) Count rates for resonant (784 nm, points with red curve) and blue-detuned (766 nm, points with blue curve) pumping for different pump powers. Resonant data is taken from fitted linescans (see (b)) and blue-detuned data is from spatial fluorescence scans. Fitted lines are of the form $R = R_{\infty} \frac{S}{1+S}$, giving $R_{\infty} = 689 \pm 7 \text{ kcnt s}^{-1}$ and $R_{\infty} = 77 \pm 3 \text{ kcnt s}^{-1}$ for the resonant and blue-detuned cases respectively. (b) Data points show linewidth as a function of pump power taken from fitting Lorentzians to linescans. Fitted line is of the form give in Eq. 1.11. Inset: Example of detected fluorescence as a function of excitation wavelength showing the Lorentzian shape of a molecule resonance exciting with $P = 80 \pm 1 \text{ nW}$. (c) The black line shows data from the second-order correlation function measurement exciting with $P = 96 \pm 1 \text{ } \mu\text{W}$, showing a characteristic photon anti-bunching dip. Blue line is an exponential decay convolved with the 420 ps detector response function. The dashed line is the deconvolution, showing the visibility of $\mathcal{V} = 1.00^{+0.00}_{-0.03}$. (d) Fluorescence spectrum of the molecule(s). See text for discussion. Counts are normalised to the height of the ZPL of interest. Inset: Spectrum after filtering just the relevant ZPL.

4.3.2. Interference measurements

The emission was then sent to the HOM interferometer. After optimisation of collection around 45 kcnt s^{-1} per detector could be achieved. This is sufficiently high that dark counts are not a meaningful contribution and the integration time of the measurement is not long enough for large polarisation drifts to occur. The polarisation drift was initially significant even over short times, but securing the interferometer to the table and performing measurements when the lab was empty improved this. Monitoring the maximised output of a PBS on one output of the interferometer we find a 2 % to 3 % reduction in counts over half an hour, approximately the length of time of a single $g_{\perp/\parallel}^{(2)}(\tau)$ measurement. As $\mathcal{I}$ is based on the difference between the parallel and perpendicular measurements the polarisation drift on both contributes. This gives an approximately 4 % reduction in $\mathcal{M}$, and therefore in $\mathcal{I}$.

In order to test the relationship identified in Eq. 4.16, cw-pumped $g_{\parallel/\perp}^{(2)}(\tau)$ measurements are performed at various saturation parameters. It is assumed in Eq. 4.16 that both measurements have the same S . To ensure there is not drift between measurements the S parameter for each measurement is determined by fitting the $n = \pm 1$ antibunching features. These have exponential decays given by $e^{-\Gamma_1(1+S)|\tau \pm \Delta\tau|}$, allowing precise measurement of S if Γ_1 is known.

Figure 4.12(a) and (b) show the $g_{\parallel}^{(2)}(\tau)$ and $g_{\perp}^{(2)}(\tau)$ measurements taken at $S = 1.3 \pm 0.1$. These are overlaid with Eq. 4.18 convolved with the 430 ps detector response function. The first beamsplitter ratio is set to $t_0/r_0 = \sqrt{0.5}$ from characterisation measurements. A global prefit of the side peaks for both the parallel and perpendicular measurements gives the S , r_1/t_1 and $\Delta\tau$ values using the measured $\Gamma_1/(2\pi) = 40 \pm 2 \text{ MHz}$ and $\mathcal{V} = 1$ values. Values of $\mathcal{M}_{\parallel} = 0.98$ and $\mathcal{M}_{\perp} = 0.04$ are used for the parallel and perpendicular measurements respectively. The $\mathcal{M}_{\parallel} = 0.98$ value is based on the expected α after filtering and polarisation drift. The $\mathcal{M}_{\perp} = 0.04$ value is based on the typical polarisation drift over the timescale of a measurement. With the $g_{\parallel}^{(2)}(\tau)$ measurement a fibre PBS can be used before one of the APDs to monitor the polarisation drift, and correct or restart the measurement if this becomes significant. With a $g_{\perp}^{(2)}(\tau)$ measurement this is no longer possible as the two arms needs orthogonal polarisations, so there is a greater polarisation drift during that measurement. This same process is repeated for measurement at $S = 4.4 \pm 0.2$, shown in Fig. 4.12(c) and (d).

For these two values of S Eq. 4.16 was used to determine the two values of $\tilde{\mathcal{I}}(S)$. These were then extrapolated to $S = 0$ to give $\mathcal{I}$. This can either be performed using the data (black points) or Eq. 4.18 (green points) for the measured experimental parameters. Figure 4.13 shows

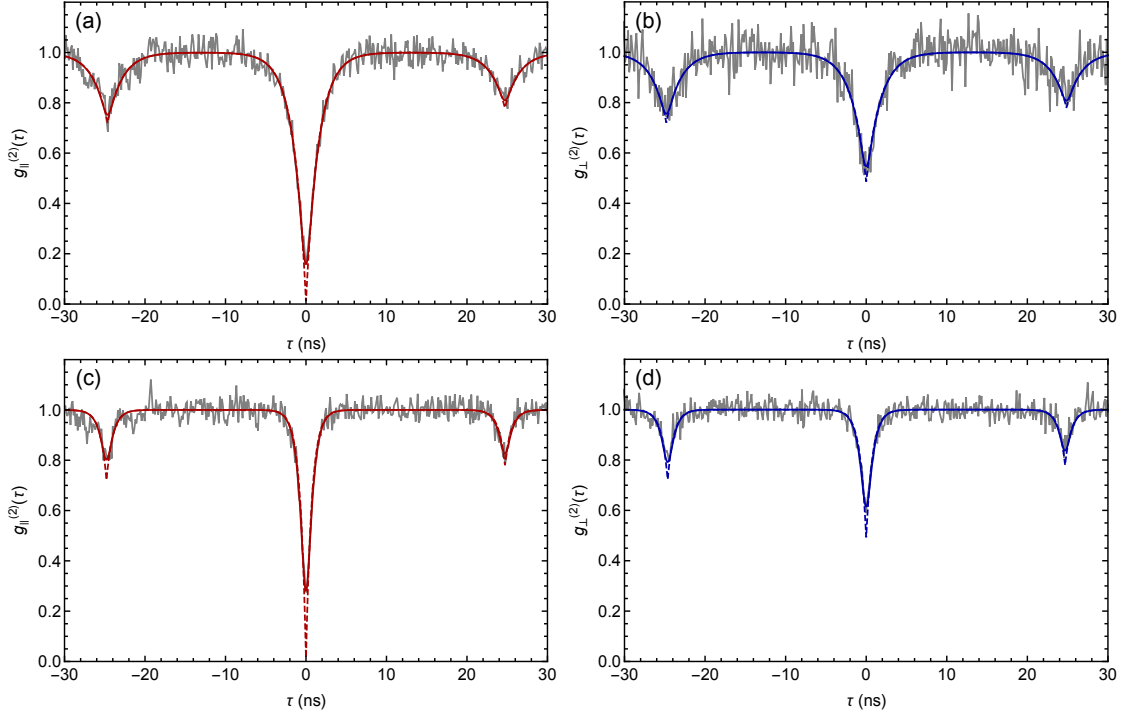


Figure 4.12. – (a) A cw excitation $g_{\parallel}^{(2)}(\tau)$ measurement showing two-photon interference taken at $S = 1.3 \pm 0.1$. Data points are shown with the black line. Overlaid is Eq. 4.18 (dashed red line), and this convolved with the detector response function (solid red line). Parameters are from independent measurements performed on the molecule. (b) A cw excitation $g_{\perp}^{(2)}(\tau)$ measurement on the same DBT molecule. Anti-bunching is visible, however there is limited two-photon interference. As in (a), Eq. 4.18 (dashed blue line) and the convolved form (solid blue line) are overlaid. (c) and (d) are the same for $S = 4.4 \pm 0.2$.

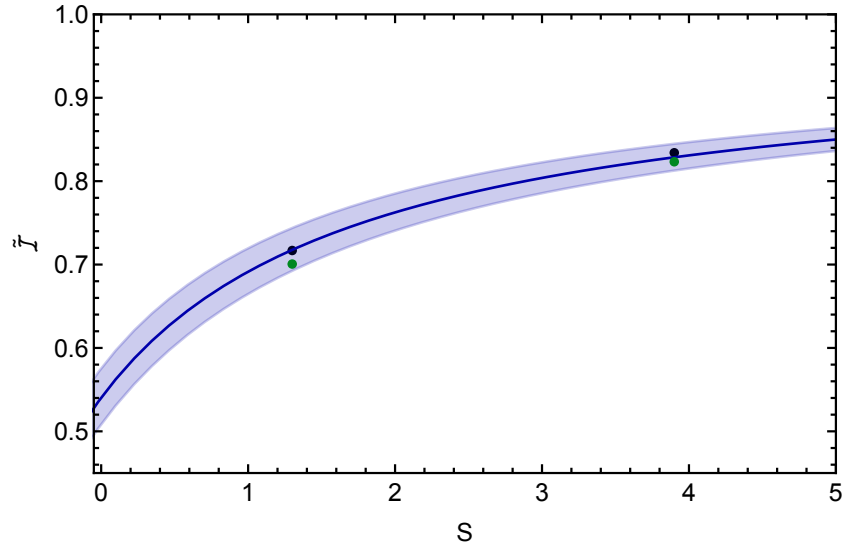


Figure 4.13. – Measurement of $\mathcal{I}$. Points: values of $\tilde{\mathcal{I}}(S)$ derived using Eq. 4.16 from the integrals of the measured $1 - g_{\perp/\parallel}^{(2)}(\tau)$. The normalised experimental data (black) and Eq. 4.18 (green) integrals are shown. Blue line: extrapolation to $S = 0$ using Eq. 4.20, giving a non-dephasing indistinguishability of $\mathcal{M} = 0.96 \pm 0.01$. Shaded region is from the uncertainty in Γ_1 and Γ_2 .

these two methods for the two pairs of measurements. The extrapolation was performed using a modification of Eq. 4.16:

$$\tilde{\mathcal{I}}(S) = \mathcal{M} \frac{\Gamma_1(1+S)}{\Gamma_1(1+S) + 2\Gamma_2^*}, \quad (4.20)$$

with $\mathcal{M}$ as the free parameter. A value of $\mathcal{M} = 0.96 \pm 0.01$ is found, which is slightly below the expected value from α_{FC} and α_{DW} after filtering. The difference is probably due to a small polarisation drift. The shaded blue region is from the uncertainty in Γ_1 and Γ_2 . Taking the value at $S = 0$ we find $\mathcal{I} = 0.53 \pm 0.01$. This was then verified using pulsed excitation.

The pulsed laser was tuned to 766 ± 5 nm and used to excite the molecule. The count rate here dropped to the region of 10 kcnts^{-1} per detector, which is much closer to the dark counts and background level of the detectors. For that reason, the background was subtracted based on fitting the exponentials at τ values far from 0. The long integration time required also required regular polarisation re-optimisation. Figure 4.14(a) and (b) show the $g_{\parallel}^{(2)}(\tau)$ and $g_{\perp}^{(2)}(\tau)$ measurements taken using 4.5 mW average pulse power at 766 ± 5 nm. The data is fitted with Eq. 4.19 convolved with the detector response function. Although there is a slight timing mismatch between the pulse repetition rate, it is small enough relative to the detector jitter that this equation can be used.

As with the cw case, Γ_1 , Γ_2 , r_1/t_1 , r_0/t_0 and $\mathcal{V}$ values are taken from previous measurements. For the $g_{\parallel}^{(2)}(\tau)$ measurement a $\mathcal{M}_{\parallel} = 0.86$ is found. This comes from three factors: the 0.98 expected from α_{FC} and α_{DW} after filtering, a further $e^{-\Gamma_1 \Delta t} = 0.91 \pm 0.02$ coming from the 0.19 ns timing error, and a final 0.97, presumably due to polarisation error. A value similar to the cw case of $\mathcal{M}_{\perp} = 0.04$ is found due to polarisation drift.

Equation 4.9 shows how to find $\mathcal{I}$ by integrating the $n = 0$ peak. However this peak is overlapped by the wings of the $n = \pm 1$ peaks because the time between pulses is not long enough compared with the decay time of the molecule. One solution to this was to fit the outer peaks using Eq. 4.19, then subtract the contribution of their wings near the centre before using Eq. 4.9. This approach gave $\mathcal{I} = 0.47$. As an alternative, Eq. 4.19 was used to model the whole spectrum and hence to determine the $n = 0$ peak. In this case the use of Eq. 4.9 gave $\mathcal{I} = 0.49$. The average of these two, divided by 0.91 ± 0.02 to account for the timing error, gave $\mathcal{I} = 0.53 \pm 0.03$. This matches the value of $\tilde{\mathcal{I}}(S = 0) = \mathcal{I} = 0.53 \pm 0.01$ found using cw excitation.

This experiment has demonstrated and studied interference between separate photons emitted from a DBT molecule. We have also developed a new method of analysing the $g^{(2)}(\tau)$ spectra to deduce full photon wavepacket indistinguishability from cw excitation. We are currently working with theory collaborators on deriving Eq. 4.13 from the definitions of the correlation functions

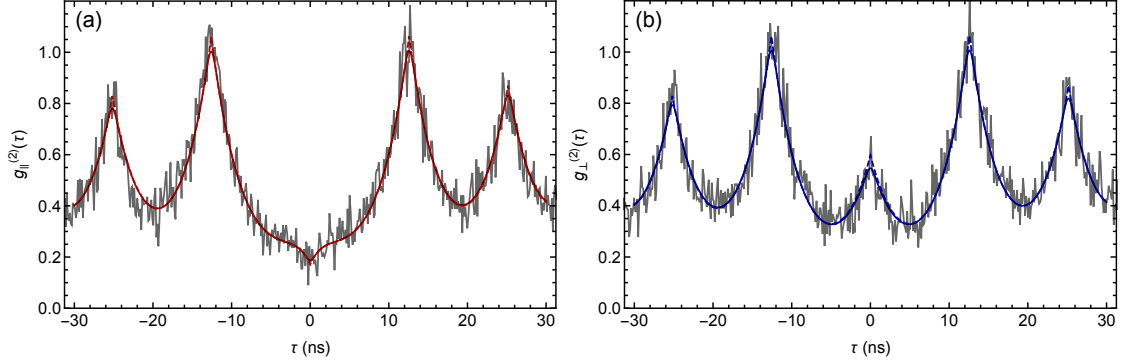


Figure 4.14. – (a) A pulsed excitation $g_{\parallel}^{(2)}(\tau)$ measurement showing two-photon interference. Data points are shown with the black line. Overlaid is Eq. 4.19 (dashed red line), and this convolved with the detector response function (solid red line). Parameters are from independent measurements performed on the molecule. The reduction in the peaks at ± 25 ns is due to the delay fibre length corresponding to approximately two laser repetitions. (b) A pulsed excitation $g_{\perp}^{(2)}(\tau)$ measurement on the same DBT molecule. Anti-bunching is visible, however there is negligible interference. As in (a), Eq. 4.19 (dashed blue line) and the convolved form (solid blue line) are overlaid.

to formalise this method and are hoping to submit this soon¹.

Future experiments will attempt to cool the molecules to a point where $\Gamma_2 \rightarrow \Gamma_1/2$, allowing an indistinguishability approaching unity to be measured [23]. The interferometer will also be spliced to remove the timing mismatch and allow more direct comparison between the cw and pulsed cases [113]. A slower repetition pulsed laser will also be investigated, either through a new laser or some form of pulse-picking on the current one, to avoid the overlap of peaks in the coincidence spectra. A higher collection efficiency would reduce integration time, making polarisations drift less significant, and methods of achieving this will be discussed in the following chapter. Purcell enhancement of the ZPL decay would increase the efficiency of the photon source, as fewer photons would need to be filtered out.

¹We have now submitted this work.

5. Emission enhancement

The dipolar emission pattern of a DBT molecule in bulk Ac has a poor overlap with a single mode optical fibre [116]. There are two main approaches to increasing the photon collection efficiency from an emitter. The collection efficiency can be improved with the help of lenses or mirrors. For example, a solid immersion lens placed above the emitter can reduce the angular spread of the emission pattern to improve the coupling into low numerical aperture optics [116]. This will likely be necessary to achieve sufficiently high collection in the bath cryostat for a lifetime-limited HOM interference measurement. There is also the possibility of using a gold mirrored substrate to redirect emission upwards, which has already been used for the experiments in Section 3.2 and 3.3. This redirection can either be in the form of reflection of emitted photons or the alteration of the emission pattern of the emitter itself. The use of a back-reflector and nanocrystals has already increased count rates to $> 1 \text{ Mcnts}^{-1}$, compared to the 150 kcnts^{-1} typical for a cosublimated Ac crystal on glass.

One can also use nanophotonic devices to modify the environment seen by the emitter and directly affect the emission pattern of the light. Careful design of the structure and its mode(s) can also allow enhancement of the decay, resulting in a shorter emitter lifetime [31]. This chapter will begin by outlining the theory behind enhancing emission, first by looking at Fermi's golden rule for a solitary two-level system and then for an emitter near a waveguide. Results from using a melt-growth technique to couple DBT to a Si_3N_4 waveguide will be shown, which are also published in Ref. [66]

Fermi's golden rule will then be revisited to explain the effects of nanophotonic cavities, in particular circular Bragg grating cavities, on the emission of an emitter within a cavity. This will be followed by a section covering testing the compatibility of Ac nanocrystals with the necessary fabrication steps for polymer bullseye structures. Preliminary data from nanocapsules covered in TiO_2 will follow, which provide a possible method that would allow for deterministic fabrication of structures, circular Bragg cavities or waveguides, in high refractive index material around chosen DBT molecules. Finally, the chapter, and thesis, will finish with a discussion of future

experiments and areas of interest.

5.1. Fermi's golden rule

To simplify notation the following sections will use Γ to refer to a population decay rate, dropping the subscript 1 from Γ_1 . Fermi's golden rule [26, 70, 31] gives the decay rate of a two-level system as

$$\Gamma = \frac{2\pi}{\hbar^2} |\mathcal{M}_{10}|^2 \rho(\omega), \quad (5.1)$$

where $\mathcal{M}_{10} = \langle 0|\mathcal{H}|1\rangle$ is the matrix element of the transition from $|1\rangle$ to $|0\rangle$ for the transition-inducing Hamiltonian $\mathcal{H}$. $\rho(\omega)$ is the density of final states per unit angular frequency. The frequency of the transition is ω . The interaction Hamiltonian, $\mathcal{H} = -\mathbf{d} \cdot \mathbf{E}$, is the interaction of the molecular transition dipole $\mathbf{d}$ with the electric field $\mathbf{E}$. The matrix element can then be expressed as $\mathcal{M}_{10} = -d_{10}E$ where $d_{10} = \langle 0|d|1\rangle$, with d as the component of $\mathbf{d}$ aligned with $\mathbf{E}$, and E is the absolute value of $\mathbf{E}$. With no external electric field, such as a laser, the vacuum electric field energy in one mode gives E :

$$E = \sqrt{\frac{\hbar\omega}{2\epsilon_0 V}}, \quad (5.2)$$

where V is the volume of a region containing the emitter. Averaging over all orientations of vacuum field gives

$$|\mathcal{M}_{10}|^2 = \frac{1}{3} d_{10}^2 E^2 = \frac{d_{10}^2 \hbar \omega}{6\epsilon_0 V}. \quad (5.3)$$

The vacuum density of states in the limit of large V is [27]

$$\rho(\omega) = \frac{\omega^2 V}{\pi^2 c^3}. \quad (5.4)$$

Substituting Eq. 5.3 and Eq. 5.4 into Eq. 5.1 gives the well-known result for the spontaneous emission rate of a two-level system in a vacuum

$$\Gamma_{\text{vacuum}} = \frac{d_{10}^2 \omega^3}{3\pi \hbar \epsilon_0 c^3}. \quad (5.5)$$

When the dipole is in a homogeneous material of refractive index n , the decay rate is modified to become [117]

$$\Gamma_{\text{hom}} = n \frac{d_{10}^2 \omega^3}{3\pi \hbar \epsilon_0 c^3} \left(\frac{n^2 + 2}{3} \right)^2. \quad (5.6)$$

The DBT molecule has several decay branches $S_{1,0} \rightarrow S_{0,n}$. These can be accounted for using the more general $\mathcal{M}_{(1,0),(0,n)} = \langle S_{1,0} | \vec{d} | S_{0,n} \rangle$ in Eq. 5.1 for each individual decay rates $\Gamma(\omega)_{(1,0),(0,n)}$. These are summed to find the total population decay rate Γ .

Fermi's golden rule suggests the different approaches that allow for Γ to be modified. Confinement of light, such as in a waveguide or cavity, results in a smaller mode volume and a higher electric field $\mathbf{E}$, see Eq. 5.2, which increases coupling strength to an appropriately placed emitter [85, 118]. Moreover, this modifies the density of states $\rho(\omega)$ and can increase it far above the free-space density. This chapter will outline how waveguides and circular Bragg cavities can achieve this, after a brief discussion on how to experimentally quantify the effectiveness of a nanophotonic structure.

β factor and Purcell enhancement

When the emitter is an inhomogeneous medium, whether this is just near a material boundary or coupled to a nanophotonic structure, ρ and $\mathcal{M}$ will likely be modified. Designing nanophotonic structures to have a specific effect will be discussed later in this section, however there are two general properties that are useful when considering the effectiveness of this modification; the amount of emission coupled to the nanophotonic structure and the change in radiative decay rate.

The first can be described as the ratio of the emission into the mode of the interest, the mode guided by the structure, Γ_{guided} , to the total emission rate Γ . This is called the coupling or the β factor and can be expressed as

$$\beta = \frac{\Gamma_{\text{guided}}}{\Gamma_{\text{guided}} + \Gamma_{\text{unguided}}} = \frac{\Gamma_{\text{guided}}}{\Gamma} \quad (5.7)$$

where Γ_{unguided} is the decay rate into all other modes. Figure 5.1 shows a diagram of this. The coupling β is either equal or more typically proportional to the overall collection efficiency η_{col} , depending if the point of measurement is within the structure or the emission is coupled out respectively. Depending on how broadband the device coupling is there is the possibility of different β values for different transition frequencies. These could be considered in different ways depending on the intended use. A combination of the Franck-Condon factor and the coupling to the structure, $\alpha_{\text{FC}}\beta$ [66] gives the number of ZPL photons captured by the structure, a useful quantity for quantum information purposes. This could be further expanded by considering parameters in Eq. 4.17, such as α_{DW} and the broadening $\Gamma_1/2\Gamma_2$. Alternatively, a Franck-Condon factor weighted-average of the β factors for each transition could be considered when the frequency of the emission is not important.

The modification to the decay rate caused by the structure is called the Purcell factor F_p . This takes into account the radiative emission enhancement (or reduction for $F_p < 1$) caused by the

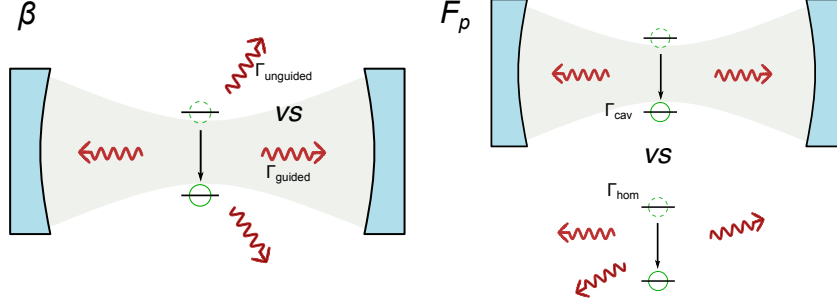


Figure 5.1. – Schematic representations of the coupling, or the β factor, and the Purcell factor F_p of a two-level system coupled to a nanophotonic structure. A cavity, with cavity mode shown in gray and mirrors in blue, is shown here but this is applicable to waveguides or any other nanophotonic structure. For the β factor (left) the total emission rate Γ is just a sum of Γ_{guided} and Γ_{unguided} . The Purcell enhancement (right) is found by comparing the decay rate in the nanophotonic structure Γ_{cav} (top image) to the decay rate in a homogeneous medium of the same refractive index Γ_{hom} (bottom).

structure. There is some variation in the exact definition used in literature here; one definition is

$$F_p = \frac{\Gamma_{\text{cav}}}{\Gamma_{\text{hom}}}, \quad (5.8)$$

where Γ_{cav} is the decay rate of the emitter into the nanophotonic structure guided mode(s), and Γ_{hom} is the decay rate of the emitter in a homogeneous medium, as in Eq. 5.6 [27]. This is shown in Fig. 5.1. There are other definitions where Γ_{cav} is replaced by Γ'_{cav} which is the total decay rate of the emitter in the cavity [31], not just into the cavity mode(s). Alternatively, it can be defined as [22]

$$F_p = \frac{\Gamma'_{\text{cav}}}{\Gamma_{\text{hom}}} - 1. \quad (5.9)$$

However, in the case of the cavity causing no reduction in emission

$$\Gamma'_{\text{cav}} = \Gamma_{\text{cav}} + \Gamma_{\text{hom}} \quad (5.10)$$

and this is equivalent to Eq. 5.8. It is worth noting that experimentally Γ'_{cav} is the value that would be measured when a TCSPC or $g^{(2)}(\tau)$ experiment is performed, making Eq. 5.9 a useful definition. Defining F_p is further confused by emitters with multiple decay pathways, as the stated Purcell factor can be describing the enhancement in total or in relation to the decay rate of the enhanced transition [22]. This is equivalent to replacing Γ_{hom} with $\alpha_{\text{FC}}\Gamma_{\text{hom}}$. This spread in definitions makes comparing F_p in the literature difficult, and one must check what exactly is being calculated.

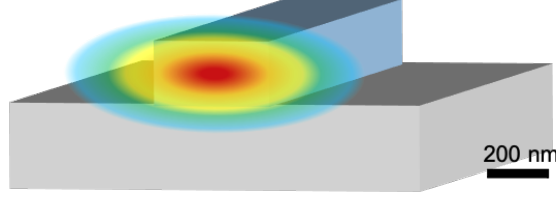


Figure 5.2. – Sketch of a waveguide (blue) on a substrate (grey). The coloured plane represents the electric field intensity of the guided mode, with red being the most intense and blue the least. The field is strongest within the waveguide, however it does extend past the waveguide; evanescent coupling takes advantage of this to couple emission into the waveguide.

5.1.1. Waveguides

Waveguides use a guide of higher refractive index material to confine and guide light. Figure 5.2 shows a sketch of a waveguide and the electric field intensity for the confined, guided mode. For an emitter coupled to a waveguide, the β factor can be expressed as $\Gamma_{\text{wg}}/\Gamma$, where Γ_{wg} is the emission rate into the waveguide mode(s) [119] which can be calculated using Eq. 5.1. For a nanophotonic waveguide the cross-sectional area will be small enough to (by design) only support a single mode and the density of states $\rho(\omega)$ can be found by counting modes in the waveguide [120]:

$$\rho(\omega) = \frac{L}{2\pi\nu_g(\omega)} \quad (5.11)$$

where $\nu_g(\omega)$ is group velocity and L is the length of the waveguide. The coupling to this mode for an emitter at position $\mathbf{r}_0$ is

$$|\mathcal{M}_{\text{wg}}|^2 = |d_{\text{wg}}E(\mathbf{r})|^2 = \frac{d_{\text{wg}}^2\omega}{2\hbar\epsilon_0 n^2 L A_{\text{eff}}(\mathbf{r}_0)} \quad (5.12)$$

where $d_{\text{wg}} = d \cos \theta$ is the projection of the emitter dipole onto the electric field direction of the mode and $A_{\text{eff}}(\mathbf{r}_0)$ is the effective mode area for coupling to the molecule. This is defined as [70]

$$A_{\text{eff}}(\mathbf{r}_0) = \frac{\int \int \epsilon(\mathbf{r}) |\mathbf{E}(\mathbf{r})|^2 dA}{\epsilon(\mathbf{r}_0) |\mathbf{E}(\mathbf{r}_0)|^2} \quad (5.13)$$

where ϵ is the relative permittivity and $\mathbf{r}$ is position in the transverse plane containing the dipole, and $\mathbf{r}_0$ is the position of the dipole. The effective mode area quantifies the strength of the electric field at the emitter. This allows the radiative decay rate into the waveguide to be found;

$$\Gamma_{\text{wg}} = \frac{d_{\text{wg}}^2\omega}{2\hbar n^2 \epsilon_0 A_{\text{eff}}(\mathbf{r}_0) \nu_{\text{vg}}(\omega)} \left(\frac{n^2 + 2}{3} \right)^2. \quad (5.14)$$

The additional $\left(\frac{n^2+2}{3}\right)^2$ term is introduced by local field correction in a dielectric medium [70, 117]. This results in a β factor of

$$\beta = \frac{\Gamma_{\text{wg}}}{\Gamma_{\text{tot}}} = \frac{3}{8\pi} \left(\frac{d_{\text{wg}}}{d}\right)^2 \frac{(\lambda/n)^2}{A_{\text{eff}}(\mathbf{r}_0)} \frac{c/n}{\nu_g}. \quad (5.15)$$

Anthracene is birefringent and the refractive index used would need to account for the relative alignment of the waveguide mode and the crystal axis of the Ac crystal.

Inspection of this equation allows us to see how best to design an optimised waveguide to maximise the coupling β , and therefore collection efficiency η_{col} . It is worth noting that this is the total decay rate of the emitter, and for finding the coupling of coherent ZPL photons would require the Debye-Waller and Franck-Condon factors to also be considered. For the type of waveguides considered here, namely those without any cavities, there is not expected to be a significant Purcell factor [70, 66]. The emission into the waveguide arises almost entirely from improved mode overlap.

The dipole of DBT has a fixed orientation relative to the Ac crystal orientation [65], so methods of controlling the alignment of the Ac crystallographic axis if using *in situ* growth methods could be used to maximise d_{wg} . With nanocrystals or nanocapsules there is no obvious way to control this. Either way, the current method is to simply fabricate many devices and rely on random orientation to give some DBT molecules with suitable dipole orientation.

The group velocity ν_g should be minimised by operating close to the band edge of the waveguide. The effective mode area $A_{\text{eff}}(\mathbf{r}_0)$ should be minimised by placing the emitter as close to the waveguide as possible. There is a trade-off here between minimising the distance between the emitter and the waveguide and ensuring the emitter is far enough from the Ac edge to show stable, coherent emission. This is evident when comparing the coupling efficiencies to room temperature waveguides, where $\beta = 21 \pm 1\%$ [121] and $\beta = 12 \pm 2\%$ [97], with coupling to cryogenic waveguides, where $\beta = 3.5\%$ [86] and $\beta = 9 \pm 2\%$ [66]. The experiments at room temperature use molecules closer to the surface because the instability from surface effects or defects is masked by the high thermal dephasing.

All of these utilise evanescent coupling or an interrupted waveguide to couple DBT to the waveguide mode. A higher A_{eff} can be achieved by placing an emitter within the waveguide at the maximum of the mode, however there is no way currently of integrating the organic Ac host matrix with the semiconductor waveguide material, as is commonly done with quantum dots [31]. Preliminary results on embedding PMMA nanocapsules within a TiO_2 layer, which would be an initial step towards fabricating waveguide containing DBT will be presented later in the

chapter [69]. The waveguide dimensions also come into $A_{\text{eff}}(\mathbf{r}_0)$. The waveguide should be small to reduce the cross-sectional area, but not so small that the guided mode spreads far outside of the waveguide.

The experiment presented later in this section used channels to confine the melt-growth to a narrow interaction zone in the centre of the waveguide [66]. There are also some preliminary results using nanocapsules in a TiO_2 layer to allow fabrication of devices around DBT molecules [69].

5.2. Dibenzoterrylene coupled to gap waveguides

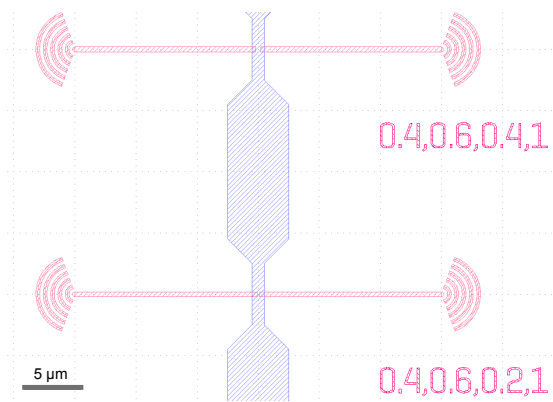


Figure 5.3. – Cropped schematic of the waveguide chip, showing two waveguide structures (red) and the channel (blue) joining them. The numbers are labels for various parameters; waveguide width, grating period, gap width and channel width. Gap width refers to the distance in between the waveguide sections where a gap is present, and channel width refers to the distance between the sides of the Ac channel at the waveguide position.

This section discusses the coupling of DBT to Si_3N_4 waveguides with a gap in the centre. These were designed by Sebastien Boissier and produced by our ORQUID partners in Münster. This design uses a gap in the middle where molecules are located, to see if this can achieve a higher β than evanescent coupling [70].

A schematic of the waveguide design is shown in Fig. 5.3. The chip consisted of five columns, each with 48 devices. Each column shared a common channel running down the chip, to allow filling with DBT/Ac. The waveguides are 400 nm wide (vertical on the image) and 200 nm deep (into the page on the image). A number of parameters were varied across the structures; the channel width, the input/output grating period which affects optimum coupling wavelength, the

gap width and the channel width which affect both the coupling β and photostability. The wide sections of the Ac channel in between the waveguides are there to increase the likelihood of filling the entire length of the channel. The channel is made 1 μm deep for the same purpose.

The use of these waveguides to develop a ‘black-box’ theoretical model is detailed in Ref. [66] and details of the design and fabrication are available in Ref. [75]. I was responsible for the experimental characterisation and measurement of DBT coupling to the waveguide, and therefore this section will focus on the experimental details and on the limitations of this approach. Potential solutions and improvements will then be discussed.

5.2.1. Characterisation and DBT inclusion

Before DBT/Ac was introduced to the waveguide, losses were characterised in the confocal microscope set-up shown in Fig. 5.4. This is the same confocal microscope, with the addition of two grating coupling arms seen on the bottom of the diagram. These allow light to be coupled into/collected from the waveguide through the grating couplers independently of one another and of the main confocal beam path. The grating couplers direct some (in the region of 10%) of the emission out of the waveguide into free space.

The waveguide chip was placed into the sample mount in the microscope and white light was used to locate the waveguides on the chip. A weak laser beam was then sent through each of the grating coupling arms and the CCD camera was used to position the beam on the output couplers, and then to maximise the emission through the other coupler after transmission through the waveguide. Once both arms were roughly aligned, a power meter or APD on the end of the fibre was then used to maximise signal from the laser beam to optimise coupling. The first waveguides examined had no gap and were used to measure the grating efficiency. When taking into account the 12% transmission efficiency per beam path and 78% objective lens transmission efficiency, a coupling efficiency of roughly 8% per grating was found for the 0.60 nm and 0.65 nm pitch gratings. Waveguides with a gap for including Ac were then measured and were found to introduce a $40 \pm 7\%$ loss.

The melt-growth method discussed in Section 2.2 is used to fill the channels running the length of the waveguide. We have found that Ac at its melting point also begins to sublime quickly, so it is quickly heated to the desired temperature of 210 $^{\circ}\text{C}$ using a combination of thermoelectric Peltier heaters and the hotplate to reduce evaporative loss. Capillary forces then pull the liquid mixture into the channel. A high DBT concentration was used to maximise the likelihood of a molecule in the correct location to couple to the waveguide. Controlled cooling at 5 $^{\circ}\text{C s}^{-1}$ is then

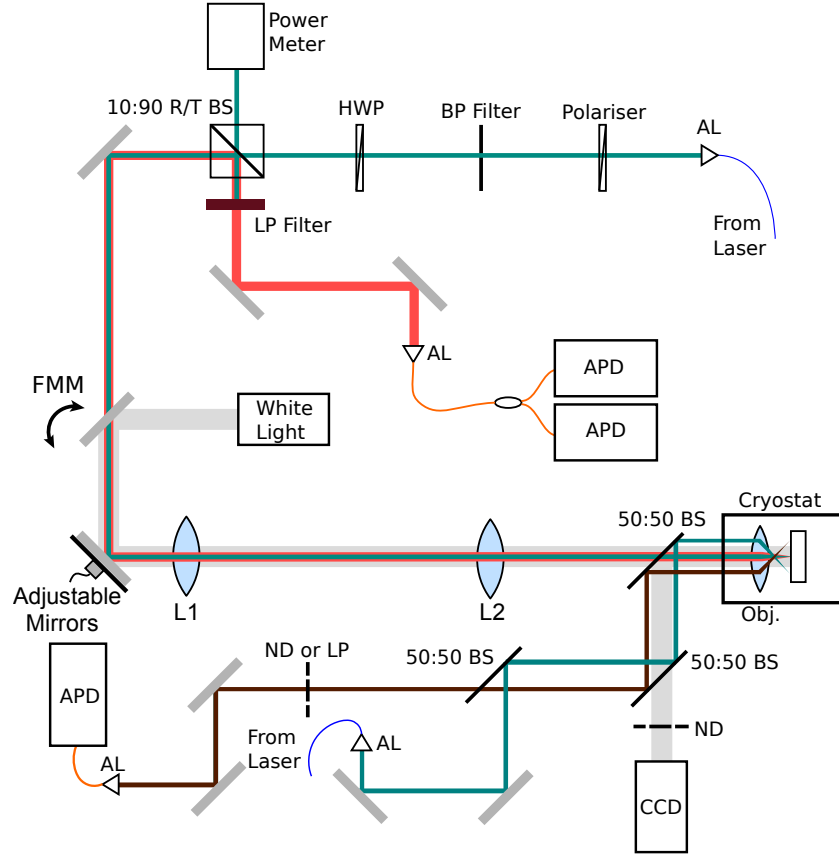


Figure 5.4. – Schematic diagram of the confocal microscope. Teal beam indicates the pump light, red is the fluorescence, brown is fluorescence and transmitted pump light, and grey is the white light used for imaging. PMF: polarisation maintaining fibre; AL: aspheric lens fibre coupler; HWP: half-wave plate; ND: neutral density filter; X:X BS: X reflection and X transmission beam splitter; FMM: flip-mount mirror; L1: first lens; L2: second lens; Obj: microscope objective lens; CCD: charge-coupled device camera; LPF: 800 nm long pass filter; APD: avalanche photodiode. Grey diagonal lines are mirrors. The ND or LP filter in the grating coupling arm allows either transmitted pump light or DBT fluorescence to be measured. The CCD can be used either with an ND filter for viewing laser reflection/scatter, or without for white light imaging.

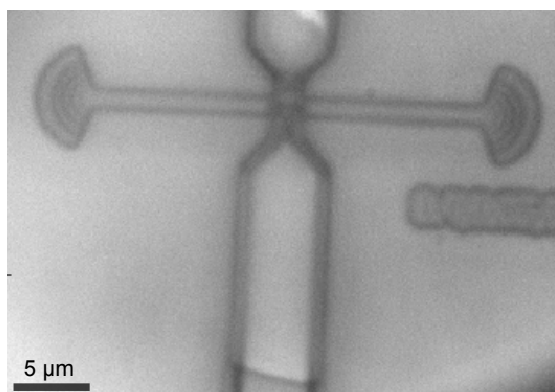


Figure 5.5. – White light image of a filled waveguide. The line at the bottom of the image is a boundary between a filled and empty section of the channel.

used to ideally obtain large crystalline regions of Ac whilst also ensuring good DBT inclusion. If the cooling is too fast the crystal environment will be too disordered for narrow molecules, whilst if the cooling rate is too slow the Ac will be able to crystallise with fewer impurities. As the DBT is effectively an impurity, it will be driven to the edges of the crystal also resulting in instability.

Once the waveguides were cooled the top surface was cleaned with toluene to remove any Ac that solidified outside the channels. The filling was then verified using a microscope, which showed that the number of waveguides with Ac was consistently lower than desired. Figure 5.5 shows a white light image of a waveguide with a filled channel. This might be improved by using a small sealed chamber to increase the Ac partial pressure and lower evaporative loss, however this has not been attempted yet. The partially-filled chip was then placed into a copper sample mount in the cryostat and cooled to 4.7 K.

5.2.2. Measurements

After the cryostat reached the base temperature of 4.7 K white light was used to locate the waveguides with 0.65 nm pitch output coupler period on the sample, as these showed the best coupling to the laser mode. A blue-detuned (approx. 767 nm) confocal microscopy scan was then performed to locate the waveguide gap. Positioned correctly, three waveguides could be seen within one confocal scan viewing area, which could then be checked for molecules with a narrow resonance using a laser scan from 784 nm to 786 nm at 2 GHz s^{-1} . If molecule resonances were seen on the terascan the grating couplers were then used to perform measurements.

The grating arms were used in a second terascan, with the laser light being coupled in through one grating and the transmission output being measured through the other. The confocal collection remained aimed at the centre of the gap. The confocal collection was monitored to detect molecular emission. A significant number of waveguides which initially appeared to have molecules within the waveguide gap did not show any fluorescence when pumping through the output grating. This is most likely due to the gap being empty and the initial laser scan exciting molecules above the gap or on the edge of the laser spot. This was particularly common with the 100 nm and 200 nm gap width waveguides.

When molecular resonances excited through the waveguide were seen through the confocal microscope collection, the laser was scanned across each resonance at a slower speed (typically 200 MHz s^{-1} to 500 MHz s^{-1}). This was using low powered excitation whilst looking for a reduction in the laser light transmitted through the waveguide. A resonant dip in the waveguide transmission is a sign of coupling to a molecule, as discussed in the following section. A guide showing a reduction in transmission was found at 785.2 nm and the optical properties of the molecule were investigated. To maximise the signal-to-noise ratio multiple scans were performed at each power and summed before fitting with Lorentzians of the form in Eq. 1.10. This was then repeated for 11 powers across a range of S values, from 0.002 to 1.8. The maximum count rate was fitted with a saturation curve, as shown in Fig. 5.6(a), giving a saturation power of $P_{\text{sat}} = 28 \pm 2 \mu\text{W}$. The linewidths $\Delta\nu$ as a function of power are shown in Fig. 5.6(b), and upon fitting with Eq. 1.11 give a zero-power linewidth of $135 \pm 2 \text{ MHz}$. This is significantly broader than typical cold DBT molecules presented in this thesis. This is due to a combination of higher temperature due to the lower thermal conduction of complex waveguide structure and proximity of surfaces due to the channel geometry. Linewidth aside, this molecule appeared suitable to investigate for coupling to the waveguide.

Using transmission to measure coupling

The coupling β between the molecule and the waveguide can be inferred from the resonant change in the transmission. For a waveguide that is lossless in the absence of the molecule, the transmission of the laser light is given by [122, 75, 66]

$$T = 1 - \alpha\beta(2 - \alpha\beta) \frac{\Gamma_1/2\Gamma_2}{\Delta^2/\Gamma_2^2 + 1 + S}, \quad (5.16)$$

where T is the transmitted laser power, normalised to the case with no molecule. The Debye Waller and Franck Condon factors are combined to give $\alpha = \alpha_{\text{DW}}\alpha_{\text{FC}}$, and $\Delta = \omega - \omega_0$ is the

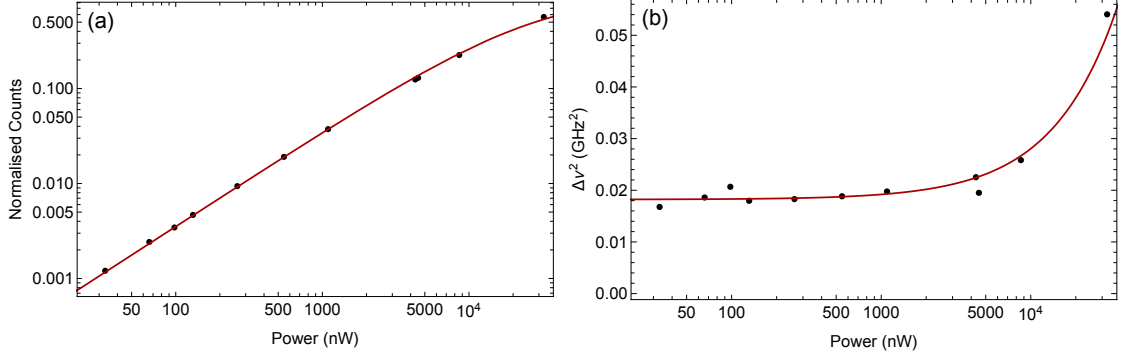


Figure 5.6. – (a) Black data points are maximum count rates for resonant pumping for different pump powers, normalised to R_∞ . The molecule is excited through the waveguide and measured using the confocal collection path. Fitted line is of the form $R = R_\infty \frac{S}{1+S}$. (b) Data points are linewidth as a function of pump power taken from fitting Lorentzians to linescans. Fitted line is of the form give in Eq. 1.11.

detuning of the laser frequency ω from the ZPL transition frequency ω_0 . There are two terms to the modification of the laser transmission. The additive term, with $+\alpha^2\beta^2$ is due to the molecule emitting light into the waveguide, whilst the subtractive term, with $-2\alpha\beta$ is due to interference between the transmitted laser light and light coherently scattered into the output by the molecule dipole. Overall this gives a decrease in counts with changing frequency with a Lorentzian lineshape. The interference is due to a dipole coupled to a waveguide with this geometry scatters light with a π phase shift which can destructively interfere; $\pi/2$ for a driven dipole and $\pi/2$ arises from the waveguide structure [75].

The transmission spectrum becomes more complex when the molecule sits in a gap in the waveguide because there is a propagation phase shift ϕ between the two interfering paths that depends on the size of the gap and the position of the molecule within the gap. As derived in Ref. [66] the normalised transmission of power becomes

$$T = 1 - \frac{\alpha\beta}{|t|} \left(2 \left(\sin \phi + \frac{\Delta}{\Gamma_2} \cos \phi \right) - \frac{\alpha\beta}{|t|} \right) \frac{\Gamma_1/2\Gamma_2}{\Delta^2/\Gamma_2^2 + 1 + S}, \quad (5.17)$$

where $|t|$ is the transmission factor. In the limit of $\phi = \pi/2$ and $t = 1$ this simplifies to give Eq. 5.16. As ϕ varies the asymmetry increases as shown in Fig. 5.7. This behaviour can be seen in Fig. 5.8(a), where fitting Eq. 5.16 to the transmission data results in an incorrect transition frequency. To confirm this was not due to some systematic offset, Fig. 5.8(b) compares molecule fluorescence measured through the confocal collection and output grating; both have the same central frequency.

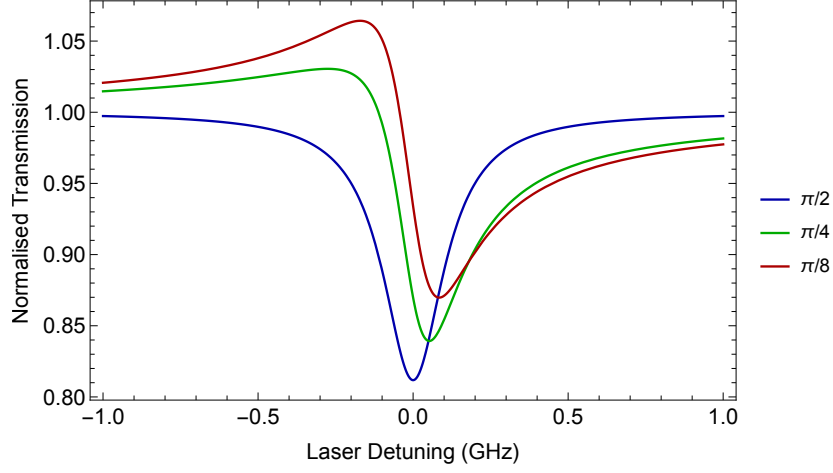


Figure 5.7. – Expected transmission dip reduction using Eq. 5.17 from a DBT molecule coupled to a gap waveguide for different values of ϕ . This is in the lower power limit $S \rightarrow 0$ for a lifetime limited molecule with $\Gamma_1 = 2\pi \times 40$ MHz and $\alpha = 33\%$, typical values for DBT [23]. A transmission coefficient of $t = 1$ is chosen to maximise the visibility and a $\beta = 0.3$

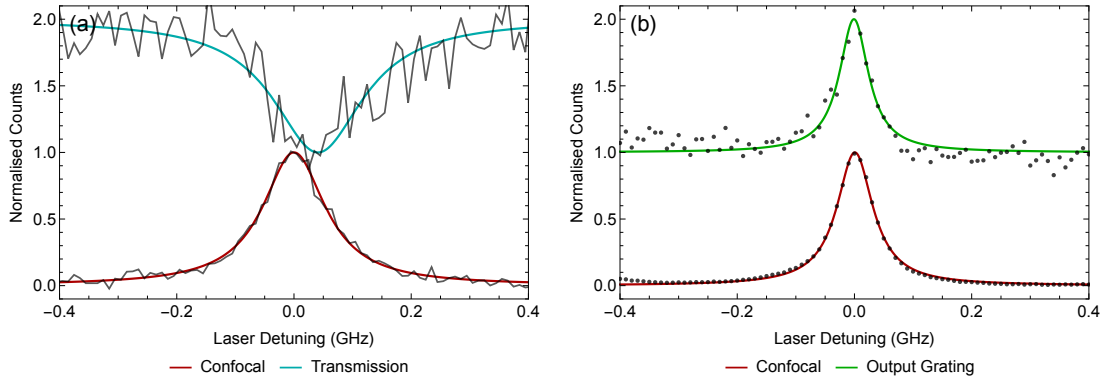


Figure 5.8. – (a) Fluorescence measured through the confocal microscope collection path (data with red curve) and reduction in transmitted laser light (data with teal curve) whilst scanning a laser across a molecule excited through a waveguide at low S . Data is scaled to have a depth/height of 1 to highlight difference in apparent centre of features. Lorentzian lineshapes, using Eq. 1.10 (red) and Eq. 5.16 (teal), are fitted to both sets of data. The two lineshapes have different transition frequencies ω_0 . (b) Fluorescence measured through the confocal microscope collection path (data with red curve) and through the output coupling (data with green curve) whilst scanning a molecule using the confocal microscope excitation. Lorentzian lineshapes are fitted to both, with both having the same transition frequency ω_0 .

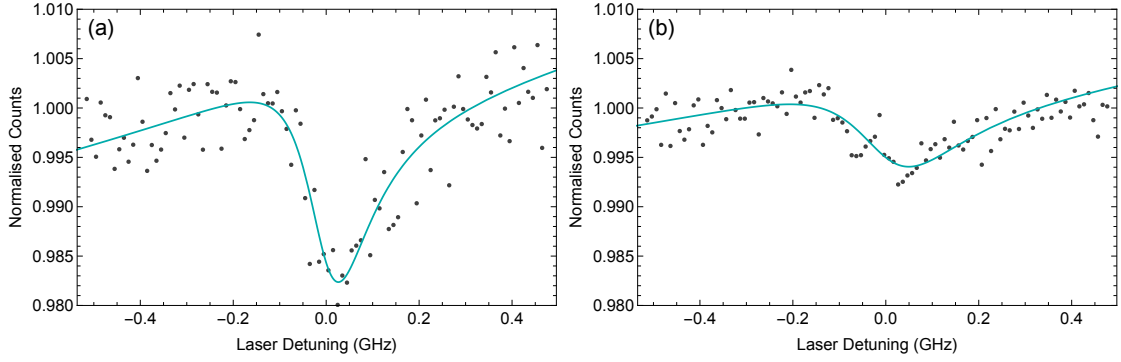


Figure 5.9. – (a) Transmitted laser light as a function of detuning from the molecule frequency ω_0 , showing a reduction in transmission due to coherent scattering, for a low power scan $S = 0.002$. Data is fit with Eq. 5.17 giving a coupling of $\beta = 9 \pm 1\%$ and a phase shift of $\phi = 0.91 \pm 0.07$ rad. (b) The same as (a) for a scan at $S = 1.8$, giving a coupling of $\beta = 9 \pm 3\%$ and a phase shift of $\phi = 0.90 \pm 0.04$ rad.

Using Eq. 5.17 allows β to be determined from transmission measurements on the waveguide. Typical DBT values of $\alpha = 0.33$ [23, 22] and $\Gamma_1/(2\pi) = 35$ MHz were used. The transmission is known from comparing waveguides with and without gaps giving $t = 0.63 \pm 0.06$ [66]. $S = P/P_{\text{sat}}$ values are from the laser power of the scan and the saturation power from the saturation curve shown in Fig. 5.6(a), $P_{\text{sat}} = 28 \pm 2$ μ W. The transition frequency ω_0 is taken from the fluorescence scans. This gives β , Γ_2 and ϕ as the free parameters for fitting. All eleven powers were fitted with Eq. 5.17 combined with a linear background, with the lowest and highest power shown in Fig. 5.9(a) and (b) respectively. At higher laser power the reduction in depth of the feature is due to saturation of the coherent scattering rate. Taking the weighted average of these fits for these parameters gives $\Gamma_2/(2\pi) = 73 \pm 10$ MHz, which is consistent with the 67.5 ± 1.0 MHz found from linewidth scans shown in Fig. 5.6(a). A coupling of $\beta = 9 \pm 1\%$ and a phase shift $\phi = 1.00 \pm 0.06$ rad or $57 \pm 4^\circ$ are found. As discussed in Ref. [66] the measured value of ϕ suggests that the molecule was quite near the edge of the guide and therefore not in the strongest part of the field. At a more central location the coupling would have been stronger. That same discussion argues that the dipole was probably at a considerable angle to the electric field giving further scope for improving β .

5.2.3. Discussion and improvements

The measured coupling of $\beta = 9 \pm 1\%$ compares favourably to other reported values in literature of $\beta = 7\%$ [85] and $\beta = 3.5\%$ [86], showing this gap geometry has some advantage compared to evanescent coupling. There is also room for improvement, not only through better positioning and polarisation, but also through the use of higher refractive index TiO_2 instead of Si_3N_4 and optimisation of the design. The use of channels to position a DBT/Ac melt-growth also shows potential as a deterministic positioning method for use with other photonic devices.

One difficulty of this approach is the filling of the channels with Ac. After four attempts at filling and cooling only one significantly coupled molecule was found. This is not ideal for device production. This could be alleviated somewhat by further optimisation of the filling process. One approach would be to heat the Ac in a sealed container to slow the rate of sublimation and allow capillary action to fill the channels more effectively. It would be useful to find a better channel geometry that would reduce the probability of the molecules sitting near the gap but not being coupled.

However, even with everything optimised the efficiency will always be low in this scheme because $\alpha = 33\%$. This could be addressed by using the Purcell enhancement in a cavity to improve the efficiency. Other work coupling DBT to nanophotonic structures has shown a significant increase in efficiency [86] through the use of a ring resonator cavity. The use of waveguides with periodic refractive index modulation to create mirrors will be touched on at the end of this thesis.

Making the gap small is good for keeping a high transmission T , but not for reaching lifetime-limited emission. The exact cause is not known, but it is likely a combination of crystal defects and impurities near the edge of the Ac. Even with a stable, narrow molecule located within the gap there is still the random distribution of molecule positions and dipole alignments that cause variation in the coupling to the waveguide. Section 5.5 will discuss the possibility of using PMMA nanocapsules [69] embedded in a semiconductor layer that can be patterned with the nanophotonic structure of choice. This promises to provide both a stable environment and controlled alignment of the nanophotonic structure as molecules could be screened prior to insertion into the device.

5.3. Circular Bragg grating cavities

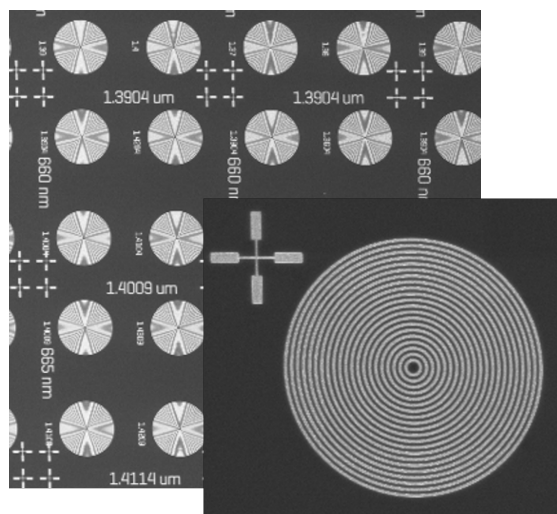


Figure 5.10. – A scanning electron microscope image of an array of circular Bragg grating cavities. Horizontal numbers are the size of the central cavity region and vertical numbers are the pitch, or spacing, of the Bragg grating. Inset: A close up of a single bullseye showing the concentric ring structure clearly. The cross in the top left is an alignment marker with dimensions of $10\text{ }\mu\text{m}$ by $10\text{ }\mu\text{m}$.

This section describes work on circular Bragg gratings, or bullseyes, inspired by work on quantum dots using semiconductor circular Bragg gratings [123, 114, 124] and molecular emitters placed within polymer circular Bragg gratings on distributed Bragg reflectors [125]. Resonances of the Bragg gratings surrounding the emitter, located in the centre, modify the density of states of the light field to enhance the decay rate of the emitter. In addition the Bragg reflectors scatter the emission out of the plane [126]. The former effect increases the Purcell factor F_p while the latter increases the collection efficiency η_{col} . Figure 5.10 shows an array of these circular Bragg grating cavities. The inset shows the concentric rings of different materials, and consequently refractive indices, which act as the mirror(s) for the cavity.

This section will focus on the emission enhancement through the Purcell effect [127] for cavities in general, and then discuss the parameters possible for bullseye cavities containing DBT. Fermi's golden rule can be used to calculate the radiative decay rate into the cavity provided the density of states for the light field is approximately constant over the linewidth of the emitter [27]. This will be the case for a bullseye cavity.

For a single cavity resonance the density of states is described by a normalised Lorentzian function

$$\rho_{\text{cav}}(\omega) = \frac{2}{\pi\kappa} \frac{\kappa^2}{4(\omega - \omega_{\text{cav}})^2 + \kappa^2}, \quad (5.18)$$

where κ is the decay rate for power in the cavity and ω_{cav} is the frequency of the resonance. The quality factor of the cavity is $Q = \omega_{\text{cav}}/\kappa$. When the emitter and cavity are resonant and $\omega_{\text{cav}} = \omega$, this can be simplified to

$$\rho_{\text{cav}}(\omega) = \frac{2}{\pi\kappa} = \frac{2Q}{\pi\omega}. \quad (5.19)$$

For the matrix element of the resonant transition Eq. 5.3 can be used, however the $1/3$ term averaging over all possible orientations of the free-space vacuum field is replaced with a ζ^2 term, representing the alignment of the dipole with the cavity. This gives

$$|\mathcal{M}_{10}|^2 = \zeta^2 d_{10}^2 E^2 = \frac{\zeta^2 d_{10}^2 \hbar \omega}{2\epsilon_0 V_{\text{cav}}}, \quad (5.20)$$

for the matrix element¹. The volume term V_{cav} refers to the cavity mode volume. Using Eq. 5.1 the decay rate into the cavity Γ_{cav} is

$$\Gamma_{\text{cav}} = \frac{2Q\zeta^2 d_{10}^2}{\epsilon_0 \hbar V_{\text{cav}}}, \quad (5.21)$$

and the corresponding Purcell factor given by this cavity is

$$F_p = \frac{3}{4\pi^2} \frac{Q}{V_{\text{cav}}/\lambda^3} \zeta^2. \quad (5.22)$$

Note the λ is the wavelength within the cavity, so requires consideration of the refractive index in a solid cavity. This equation gives a useful guide to designing cavities: a high quality factor and a low mode volume will increase enhancement of radiative decay. Enhancing the ZPL decay rate relative to other decay pathways can also increase α . The Purcell factor can also be directly related to the coupling to the structure, or the β factor by [27]

$$\beta \approx \frac{\Gamma_{\text{cav}}}{\Gamma_{\text{cav}} + \Gamma_{\text{hom}}} = \frac{F_p}{1 + F_p} \quad (5.23)$$

with the second equality only holding if there is no reduction or redirection of the emission when compared to the homogeneous case; this would not be correct for the waveguides discussed above [70, 66].

This method of increasing α is dependent on the ZPL transition being resonant with a single cavity mode. The cavity formed by the Bragg reflectors typically has a single broad mode, or a

¹Note that some authors include the electric field in the density of states and not in the matrix element [128, 31].

couple of well-spaced, broad mode(s) [124], meaning that Fermi’s Golden rule and Eq. 5.18 are suitable. For the preliminary devices tested in the lab the cavity linewidth is 2 nm to 4 nm, which means the ZPL and phonon sideband will have their decay rates enhanced but the $S_{1,0} \rightarrow S_{0,n>0}$ vibrational decays will not. A cavity linewidth κ of the same order as the inhomogeneous broadening also simplifies the coupling of DBT to the bullseye cavities. It means that tailoring of the cavity resonance to individual molecules is not necessary as long as the cavity mode is centred at the correct frequency. There is also no need for active tuning of the cavity or molecule resonances required to keep them resonant.

The 2 nm to 4 nm linewidth at 785 nm gives a quality factor of $Q = 200$ to 400. Simulations of this design in the finite-difference time-domain software Lumerical gives a mode volume in the region $V = 0.160 \mu\text{m}^3$, corresponding to a Purcell factor of approximately $F_p = 10$, depending on the exact design, when substituted into Eq. 5.22. Although this is only a modest enhancement, a large F_p is not necessarily desirable. By definition, improving Q would give a narrower cavity linewidth κ , negating the advantages discussed above. Similarly, a smaller cavity mode volume V necessitates more precise positioning of the DBT molecule, which is not particularly easy to achieve.

Recent work [22] coupling DBT to a large volume Fabry-Perot cavity shows a Purcell factor of $F_p = 38 \pm 5$ with a quality factor of $Q = 230,000$. This work shows excellent extinction, around 99 %, of cavity transmission when resonant with the molecule, and phase shifts in the transmitted light of 66° . However the recorded fluorescence count rate from the molecule is also very low, with Fig. 2(d) in Ref. [22] indicating values of 130 cnts s^{-1} , in part due to the poor overlap of the cavity mode with the Gaussian single mode of the fibre. This would obviously not be suitable for many experiments detailed in this thesis. Within the group we are working on a microcavity that is mode-matched to an optical fibre to create a high efficiency photon source [83], however it is a challenge to maintain alignment when cooling to cryogenic temperatures and when subjected to the vibrations of the cryostat.

With this in mind, there are three approaches to coupling DBT to the circular Bragg gratings being investigated in the group. The first is to use polymer-devices patterned using electron beam lithography into a PMMA thin film spin-coated on a deposition of nanocrystals. This is inspired by work on polymer based devices [125]. This should allow deterministic cavity placement around pre-selected nanocrystals, which could be selected either through white-light imaging or cryogenic analysis to screen for optimum properties. The following section will discuss experimental work testing the compatibility of Ac nanocrystals with these various fabrication

methods.

Other approaches in the group use more conventional semiconductor cavities [46], typically with TiO_2 as opposed to Si_3N_4 to take advantage of the higher refractive index. One approach is to coat the cavity with a protective polymer film which can then be etched in the optimum coupling position to give a hole leading to the cavity. Deterministic hole-filling methods can then be used to place nanocrystals within these holes [129, 130]. With this approach the molecule sits above the cavity mode, rather than directly within it. An alternative method is to coat the more robust PMMA nanocapsules in a sputtered semiconductor film, which can then be etched to place the DBT molecule within the cavity mode.

5.4. Nanocrystal and nanocapsule compatibility with circular Bragg gratings

This section will outline experiments to check the compatibility of Ac nanocrystals with various nano-fabrication techniques. This is primarily focused on the patterning of polymer bullseyes although relevant for most nanophotonic devices. With nanophotonic devices favouring the smallest possible Ac nanocrystal to minimise disruption to the modes of the device and also requiring optimisation for a given wavelength, the effect of nanocrystal size on the ZPL transition energy gap will be investigated.

The effect of SEM imaging, and electron beam lithography, on the DBT will also be investigated through the measurement of molecules after exposure to the electron beam of an SEM. Not only is SEM a common technique used in finding alignment markers on a substrate to be fabricated, but electron beam lithography is also an ideal tool for patterning polymer structures. If the DBT is unaffected by exposure to the electron beam this would enable a larger number of techniques to be employed in the fabrication of devices.

The effect of thermal cycling will also be investigated. If molecules maintain their ZPL emission wavelength after thermal cycling this would enable molecules to be investigated at cryogenic temperature and then have optimised nanophotonic structures fabricated around them. This technique, or variations upon it, are commonly used with QDs [131]. It would also allow promising molecules for a HOM interference measurement to be identified and characterised in the closed-cycle Montana cryostat without time pressure, before the time-sensitive ‘open’ bath cryostat is used to reach temperatures low enough for $\Gamma_2 \rightarrow \Gamma_1/2$.

5.4.1. Size dependence of ZPL wavelength

This section will cover an investigation into the effect of Ac nanocrystal size on the inhomogeneous broadening of the DBT molecules within. With photonic structures designed to enhance emission at specific wavelengths whilst being physically compatible with a specific Ac nanocrystal size, the relationship between these two factors is of interest. Other experiments within the group using rubidium (Rb) vapour as a quantum memory for single photons also require photons resonant with Rb transitions, around 780.2 nm [15], so a characterisation of the expected inhomogeneous broadening from different growth methods is also of interest for this.

The histograms in Fig. 2.9(b) and 2.17(b) for ZPL wavelength for nanocrystal and nanocapsule growths show an inhomogeneous broadening of 3 nm to 4 nm around 783 nm. Since taking these

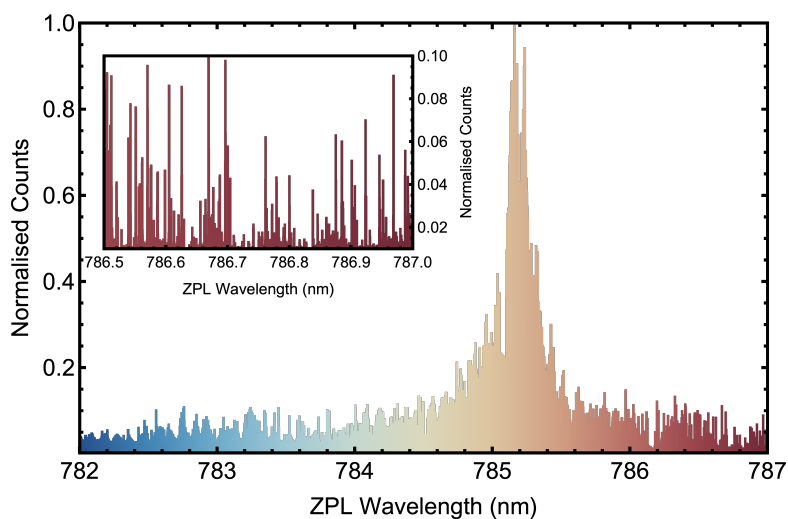


Figure 5.11. – Normalised count rate of red-shifted fluorescence as a function of laser wavelength whilst ‘tera’-scanning the Ti:Sapphire (MSquared SolsTiS) laser on a highly DBT-doped Ac cosublimation growth crystal. Individual molecule resonances are visible as narrow lines. Around 785 nm the high density of molecules makes distinguishing individual molecules difficult. Inset: A zoom in of 786.5 nm to 787 nm to show individual resonances.

data improvements to the laser system enabled rapid automatic scanning across a 6 nm range. A ‘tera’-scan performed on a highly-doped cosublimated crystal, shown in Fig. 5.11, shows a much narrower inhomogeneous broadening centred around 785.5 nm. This caused us to wonder if the frequency of the molecule is significantly affected by the size of the Ac host matrix. With the use of alignment markers on the substrate it became possible to associate positions in the optical microscope images with those in SEM images. This allowed us to measure the inhomogeneous broadening as a function of nanocrystal size.

A 1200 nm syringe-filtered high DBT concentration nanocrystal growth was deposited onto a Au-grid substrate and protected with a layer of PVA, before being cooled to 4.7 K in the cryostat. A high intensity spatial scan was performed to locate nanocrystals. The high concentration (approx. 10 molecules per nanocrystal) growth means all nanocrystals are expected to contain DBT molecules. Excitation laser ‘tera’-scans from 780 nm to 786 nm on all visible points of fluorescence were used to scan nanocrystals whilst measuring red-shifted fluorescence to locate DBT molecules. In total 31 nanocrystals were scanned. In order to facilitate the scanning of a large range (780 nm to 786 nm) on numerous sites, scans were performed at 5 GHz s^{-1} at $1 \mu\text{W}$ measured power, corresponding to an S of between 1 and 10. Lorentzians were fitted to

resonances visible in the scans to determine ZPL wavelength. In order to only record stable ZPLs the fits were filtered based on having an R-squared value greater than 0.9, on the assumption that a blinking molecule would not be well described by a Lorentzian.

The sample was then removed from the cryostat and the grided substrate was used to locate the same nanocrystals in a scanning electron microscope (SEM). This allowed an area, and therefore a diameter, to be associated with each nanocrystal. Image processing functions in Mathematica were used to provide the area for all visible nanocrystals, which were then associated with the above laser scans by their position on the Au grid. In order to calculate a diameter from the area the nanocrystals were taken to be circular. After rejecting unstable molecules or unclear SEM data we were able to relate ZPL frequencies to size for 22 nanocrystals.

Figure 5.12(a) shows the wavelength of stable ZPLs plotted against the diameter of the Ac nanocrystal. This result is entirely consistent with Fig. 2.9(b) and, further, demonstrates that there is no correlation between nanocrystal size and ZPL wavelength distribution. Figure 5.12(b) shows the histogram of all stable ZPL wavelengths with a definite blue-shift in central frequency when compared with Fig. 5.11. This is promising for finding a molecule resonant with Rb at 780.2 nm. The fraction of molecules that are stable, based on the previous R-squared metric, is shown as a function of diameter in Fig. 5.12(c). This also shows no clear correlation, so it seems that the size of the nanocrystal (over this range) does not affect the stability of the molecules either. In conclusion, diameters between 600 nm and 850 nm the size of the nanocrystal has no evident effect on either the inhomogeneous broadening or the photostability of the DBT molecules. It remains unclear why the wavelength is longer and the distribution narrower in the cosublimated crystals, which are $\sim 1 \mu\text{m}$ thick.

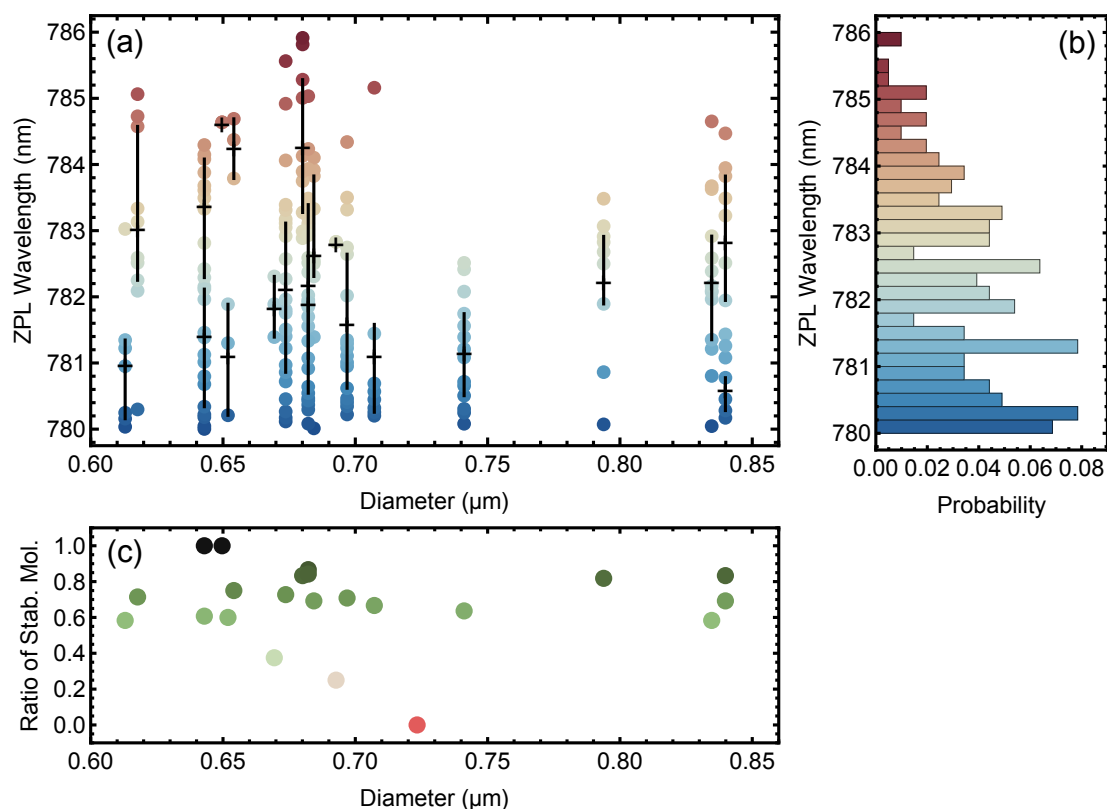


Figure 5.12. – (a) Data points are individual DBT ZPL wavelengths, plotted vs Ac nanocrystal diameter. Black ‘+’ is the mean of the data per nanocrystal, with black bar showing the 25th and 75th percentile (when the number of molecules allows). Diameter is from SEM imaging and assuming circular nanocrystals. ZPL wavelength is determined by fitting Lorentzians to stable molecules within the scan range. Stability was determined by the quality of the Lorentzian fit; a fit with an R-squared value lower than 0.9 was rejected. Molecules are from scans of 22 nanocrystals. (b) Histogram showing likelihood of ZPL being at the given wavelength, from summing measurements on all 278 molecules. (c) Fraction of molecules that are stable as a function of nanocrystal diameter.

5.4.2. SEM compatibility

After imaging the nanocrystals in the SEM to make Fig. 5.12, the sample was placed back in the cryostat to check whether the thermal cycling and exposure to the electron beam had damaged the emitters. No spectrally narrow molecules were found. However, the sample had been exposed to a very high dose of electrons because many SEM images had been taken. A similar sample was prepared and imaged just once in the SEM, prior to cooling in the cryostat. This showed typical narrow emission from the DBT within, a promising start.

Another Ac nanocrystal growth was then prepared and deposited onto a substrate and coated in PVA. Electron beam lithography was used to pattern a grid of bullseyes into the PVA layer. This sample was then cooled and white light imaging was used to find nanocrystals that spatially overlapped with bullseye structures. A nanocrystal was identified and scanned from 780 nm to 784 nm. Figure. 5.13(a) shows the section of this scan containing resonances. A white light image of the location of the nanocrystal is inset. Although the nanocrystal is not located at the centre of the bullseye, and will therefore not have enhanced emission, it has been patterned over making it ideal to test compatibility with the electron beam lithography.

Fluorescence spectra were measured at 36, 68, 120, 481, 1000 and 2000 nW, with Fig. 5.13(b) showing a zoom in on the brightest molecule visible in Fig. 5.13(a). Lorentzians are fitted to these resonances to obtain the linewidth and peak count rate for each molecule at each power. This data was then used to fit power-broadening curves, shown in Fig. 5.13(c), and saturation curves, shown in Fig. 5.13(d) for the 14 stable molecules (out of 18 molecules), as determined by the R-squared parameter. The mean zero-power linewidth found is 90 ± 30 MHz. All these data are typical of DBT within an Ac nanocrystal, indicating that the electron beam exposure used to fabricate the bullseyes is not enough to alter the optical properties of the DBT. There remains the questions of whether thermal cycling damages the DBT.

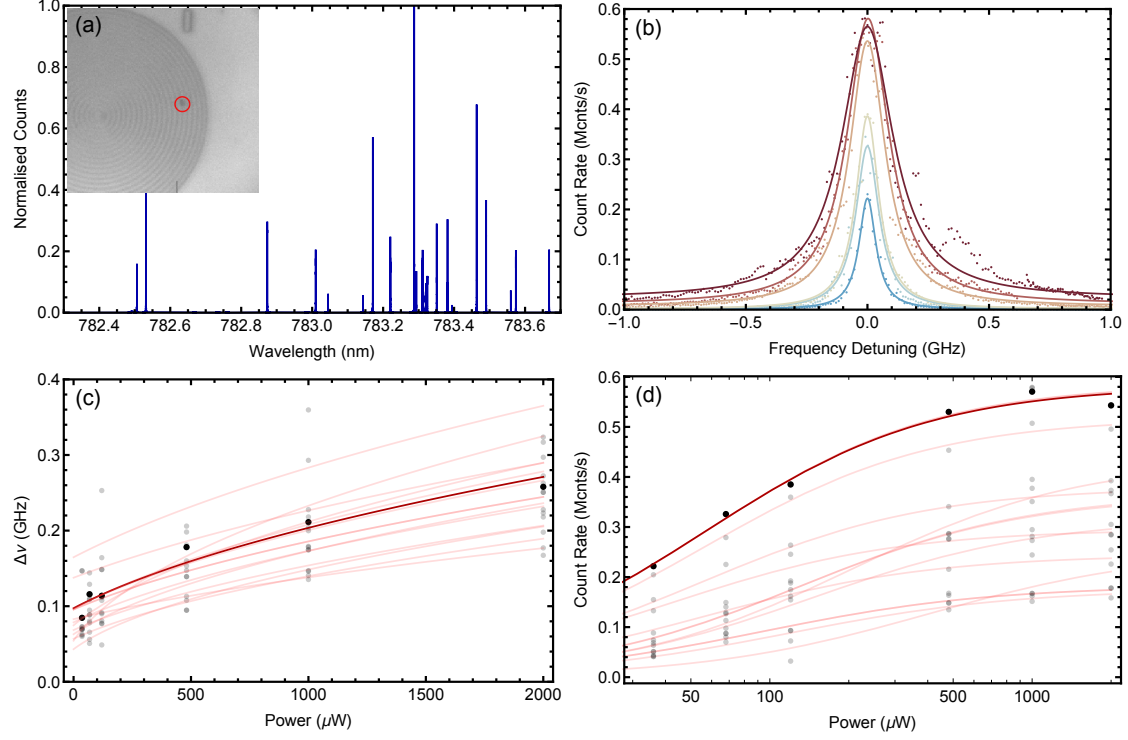


Figure 5.13. – Fluorescence data for a DBT-doped nanocrystal within the patterned area of a polymer bullseye structure. (a) Scan from 782.3 nm to 783.7 nm at a power of 36 nW. Normalised to maximum counts of the brightest molecule. Inset: White light image of the bullseye structure with a red circle around the nanocrystal. (b) Points are count rate data from the brightest molecule as the laser is scanned across it at increasing powers. Lines are Lorentzians fit to the data. (c) Linewidth power-broadening data (black and grey) and fits (red and lighter red lines) on stable molecules (judged by R-squared value). Points are from fitting linescans and lines are fits of the form Eq. 1.11. Mean zero-power linewidth is 90 ± 30 MHz. The darker points and line are from the molecule in (b). (d) Saturation data (black and grey) and fits (red and lighter red) on stable molecules (judged by R-squared value). Points are from fitting linescans and lines are fits of the form Eq. 1.9. The darker points and line are from the molecule in (b).

5.4.3. Thermal cycling

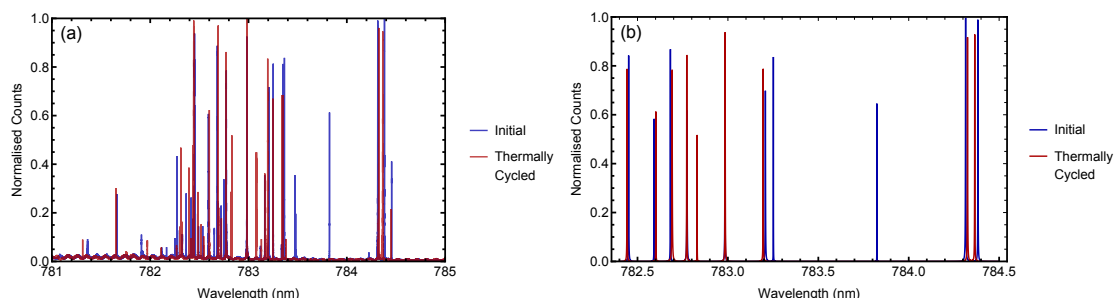


Figure 5.14. – (a) Wavelength scans from 781 nm to 785 nm performed on a DBT containing Ac nanocrystal before (blue) and after (red) thermal cycling. (b) Selected strong, stable (see text) linewidth fits to ZPL transitions showing 80 % of molecules are present after thermal cycling.

To determine the effect of thermal cycling on emission wavelength a 1200 nm syringe-filtered high DBT concentration nanocrystal growth was deposited onto a gold grided substrate and protected with a layer of PVA, before being cooled to 4.7 K in the cryostat. A nanocrystal was identified and scanned from 780 nm to 785 nm with 1500 nW of power to obtain the blue spectrum in Fig. 5.14(a). The cryostat was then heated to room temperature and left overnight before being cooled back to 4.7 K and scanned again to obtain the spectrum in Fig. 5.14(a). There is a clear correspondence in the wavelength of zero-phonon-lines, although some seem to have shifted, appeared or disappeared.

To quantify this further, strong emitters were identified by selecting all features with a normalised height greater than 0.5 and these were fitted with a Lorentzian. The R-squared value of the fit was then used to select 10 stable molecules from the first scan and 9 from the second. Those selected fits, plotted in Fig. 5.14(b), show 8 of the peaks have closely similar wavelengths and comparable strength. This implies these are the same molecules. There is a mean frequency shift of 4 GHz, and no significant change in the linewidth. This is a small sample size, but does suggest a high (80 %) chance that molecules will survive thermal cycling, the first step in deterministically fabricating optimised devices around DBT.

5.5. TiO₂ coating

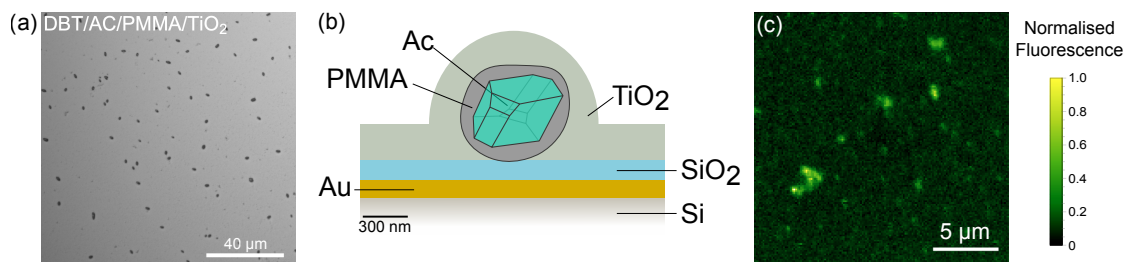


Figure 5.15. – (a) White light image of PMMA nanocapsules sputtered with 300 nm of TiO₂. (b) Schematic of expected structure. (c) Fluorescence image of the sample at room temperature.

For nanophotonic structures it is typically advantageous to use a material with a higher refractive index as that allows greater confinement of the electric field in the guided mode, decreasing A_{eff} in the waveguide case and lowering V_{cav} when considering a cavity. Being able to integrate the DBT within this material would be an even greater advantage, allowing DBT to be placed at the maximum of the electric field inside the structure. If this material were compatible with semiconductor manufacturing techniques it would allow the nanophotonic structure to be built around the molecule [131, 46].

TiO₂ has a refractive index of $n \approx 2.35$ at 785 nm, higher than Si₃N₄ with $n \approx 2$ used for the waveguides discussed previously [66] and PMMA with $n \approx 1.4$ used for the circular Bragg gratings. It is also compatible with widely available fabrication methods and can be deposited using the sputterer in our laboratory. However, the high vacuum and heating associated with the sputtering process would cause uncoated Ac to sublime, while a protective PVA layer would greatly inhibit inclusion of the anthracene in a nanophotonic device. These problems would be solved using the PMMA coated Ac nanocapsules, introduced in Section 2.4. PMMA is already used as a resist in many nanofabrication processes. The small size of the nanocapsules should minimise disruption of the guided mode(s) and they are more physically robust than uncoated nanocrystals. As a proof of principle experiment we used magnetron sputtering (AMOD 520 Resistive and Sputter Deposition System, Angstrom Engineering) to deposit 300 nm of TiO₂ on top of a sample of PMMA nanocapsules on a 160 nm SiO₂ spacer layer above a 150 nm Au reflector on a Si substrate. The deposition takes 5.5 h at elevated temperature in vacuum [69].

Figure 5.15(a) shows a microscope image of the nanocapsules after coating with TiO₂. The nanocapsules are still visible; they have not been destroyed by the deposition process. Fig-

ure 5.15 shows a schematic of the expected structure. The sample was then placed into the room temperature confocal microscope and excited with 60 μW of 751 nm pulsed laser light. The fluorescence from DBT is visible in the scan shown in Fig 5.15(c). This is a very low amount of power for blue-detuned room temperature excitation as unfortunately the Ti:Sapphire laser was waiting for repair. For reference, 2.6 mW was used for the room temperature scans that identified nanocapsules in Fig 2.14. Cryogenic testing and optimisation of the deposition process are the next steps in integrating DBT into TiO_2 .

6. Summary and outlook

Summary

This thesis has focused on understanding the effects of temperature on and increasing the efficiency of single photon emission from DBT in Ac. The basic theory behind the measurements used for quantifying these effects were outlined in the first chapter, along with a brief look at the performance of major deterministic sources of single photons. This was followed by a chapter discussing various growth methods used in this thesis to prepare the DBT/Ac solid-state matrix. The co-sublimation and melt-growth methods were established in the group by other members, whilst I used literature [68] to replicate reprecipitation growth methods for producing nanocrystals in-house. I developed a novel method of using PMMA to encapsulate Ac [91] to give PMMA nanocapsules, which show stable single photon emission at both room and cryogenic temperatures, and this is presented [69].

The third chapter covered the effects of temperature on DBT excitation and fluorescence. A rate equation based model was developed that can describe the excited state population of a molecular emitter based on the relative strengths of the vibrational transitions [30]. The model successfully explains values measured at room temperature and the dephasing rate Γ_2 , required to recover deterministic excitation. This model is of particular interest when calculating room temperature coupling of DBT, or other molecules, to nanophotonic devices [97].

The effects of cryogenic temperatures on DBT was then investigated. A single, isolated molecule was identified and linescans, spectra and the second-order correlation function $g^2(\tau)$ were measured from 4.7 K to 40 K. The effects of temperature on the dephasing rate Γ_2 , Debye-Waller factor α and the partial Franck-Condon factor were investigated. The spectral data was used by collaborators to develop a theoretical model that could successfully predict the changes in linewidth and the $g^2(\tau)$ with temperature [23]. This data was also used to design the filtering for the next experiment which focused on the indistinguishability $\mathcal{I}$ of photons from DBT.

The basic theory behind the probability of two-photon coalescence at a beamsplitter, indistinguishability $\mathcal{I}$, was outlined. The expected effects of dephasing and timing resolution on the

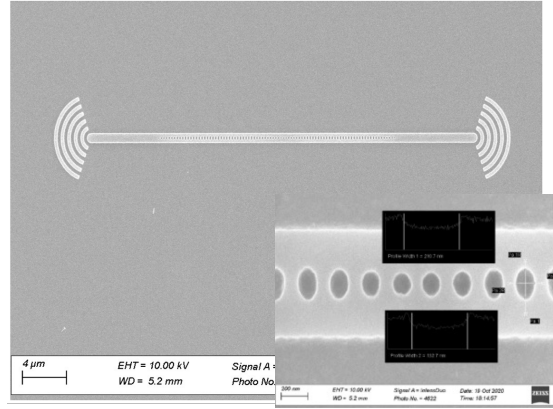


Figure 6.1. – Scanning electron microscope image of a ‘nanobeam’ waveguide cavity using spaced holes to modify the effective refractive index act as reflectors with interference output gratings at each end. Inset: Close up image of the holes in the centre showing the tapering which forms the cavity mode in the centre of the device.

measurement were described. A novel link between cw and pulsed excitation measurements was drawn which allows for full wavepacket $\mathcal{I}$ to be calculated from a cw measurement. The spectral data was then used to decide on a suitable filter to use, balancing ease of use and tunability with sideband rejection. A DBT molecule was then identified and used to perform cw and pulsed measurements. A maximum $\mathcal{I} = 53\%$ was found, primarily limited by thermal dephasing, with good agreement between both the theory and data for the cw and pulsed measurements.

Chapter 4 covered ongoing work to enhance the collection efficiency η_{col} from DBT through the use of nanophotonic structures. Fermi’s golden rule [27] was used to explain the design choices for the structures used. Integration of DBT with waveguides was discussed, where I measured a coupling to the waveguide of 9%, which is the highest reported for coupling single molecules to a cryogenic waveguide structure [66]. Experimental results related to the integration of Ac nanocrystals into circular Bragg gratings were presented, which pave the way for significantly enhancing the collection efficiency of a DBT molecule.

Future Work

The main limitations on the indistinguishability measurements are the excess thermal dephasing and collection efficiency, especially in the pulsed measurements shown in Fig. 4.14. Improving on these through the use of the bath cryostat and a solid-immersion lens is the one of the short term experimental goals. As I finished writing this thesis we submitted our work showing the

relationship between the pulsed and cw excitation measurements.

The other short term experimental goal is the deterministic patterning of a polymer circular Bragg cavity around a suitable Ac nanocrystal, with the aim of measuring a higher η_{col} into a single mode fibre and possibly even Purcell enhancement. We are currently developing our fabrication capabilities in this regard. Waveguides with cavities around the coupling region, often called nanobeam cavities, are also currently being investigated to increase the coupling β to the waveguide mode. Figure 6.1 shows an SEM image of one of these devices. Nanobeam cavity waveguides use two series of tapered holes in the waveguide to act like reflectors, tuned to the DBT resonance. Other work with DBT using coupled to waveguides with ring resonator cavities has shown an increase in coupling from $\beta = 3.5\%$ to 23% when comparing molecules in and outside cavities [86].

A longer term goal is to investigate the embedding of PMMA nanocapsules in semiconductor materials, primarily TiO_2 , more closely. This will allow for the fabrication of structures with a higher refractive index. Cryogenic testing is required to see if the molecules properties are affected and undoubtedly the process needs to be optimised. Hopefully the techniques developed regarding bullseye placement using the nanocrystals in polymer films will be useful in the fabrication here. Deterministic placement using ‘hole-filling’ techniques [129, 130] could also allow for DBT to be coupled to structures with more control. A polymer layer could be patterned above structures and controlled evaporation could then deposit nanocapsules within the resultant holes. Preliminary tests have been performed with nanocrystals, however the inability to polymer coat them afterwards resulted in blinking molecules at room temperature and no narrow molecules at cryogenic temperatures.

After the fabrication of a single photon source with improved collection efficiency, at lifetime-limited temperatures in the new cryostat, there are several planned experiments to use the photons. Repeating the indistinguishability measurements to achieve interference probabilities approaching one would be a straightforward but valuable experiment. It is also possible to place an additional beamsplitter on one output of the interferometer to measure indistinguishability without having to perform two measurements with orthogonal polarisations [64, 132], and this has not yet been experimentally performed with cw excitation. Another short term goal would be to perform pump-probe spectroscopy of rubidium with a single photon probe beam, which would build on previous publications in the group [15]. This would also require tuning of the DBT molecules, ideally through the use of Stark tuning electrodes. This would be the foundation of a longer term goal of storing single photons in a Rb quantum memory.

A. Appendix and Backmatter

A.1. Appendix to Chapter 1

This section covers the derivation of the time dependance of a resonantly excited $g^{(2)}(\tau)$ measurement. This is based on Ref. [71]. In the case of resonant pumping, $\Delta = 0$, substitution of $\rho_{01} = \frac{1}{2}(u - iv)$ into Eq. 1.3 gives

$$\frac{d\rho_{11}}{dt} = -\frac{d\rho_{00}}{dt} = \frac{1}{2}\Omega v - 2\Gamma_1\rho_{11} \quad (\text{A.1})$$

$$\frac{dv}{dt} = \Omega(\rho_{00} - \rho_{11}) - \Gamma_2 v. \quad (\text{A.2})$$

Here, u and v represent the real and imaginary parts of the coherences respectively. Under resonant pumping, $u = 0$ in these equations. To remove the time differentials here a Laplace transform can be used, with $\rho(t) \rightarrow \tilde{\rho}(s)$ and $\frac{d\rho(t)}{dt} \rightarrow s\tilde{\rho}(s) - \rho(0)$, where $\tilde{\rho}(s) = \mathcal{L}\{\rho\}(s)$. Applying this transformation gives

$$s\tilde{\rho}_{11}(s) = 1 - s\tilde{\rho}_{00} = \frac{1}{2}\Omega\tilde{v}(s) - 2\Gamma_1\tilde{\rho}_{11}(s) \quad (\text{A.3})$$

$$\frac{dv}{ds} = \Omega(\rho_{00} - \rho_{11}) - \Gamma_2 v. \quad (\text{A.4})$$

Solving these equations, with $\rho_{11} = 0$, we find

$$\tilde{\rho}_{11}(s) = \frac{\frac{1}{2}\Omega^2}{2s(s^2 + \Gamma_1\Gamma_2 + s(\Gamma_1 + \Gamma_2) + \Omega^2)}. \quad (\text{A.5})$$

This solution now needs to be inverse Laplace transformed to give a solution in terms of t . The inverse Laplace transform can be expressed as

$$\mathcal{L}^{-1}\left\{\sum_i \frac{c_i}{s - s_i}\right\}(t) = \sum_i c_i e^{s_i t}. \quad (\text{A.6})$$

To take advantage of this, Eq. A.5 needs to be rearranged. The denominator of Eq. A.5 is a cubic polynomial, allowing it to be written in the form

$$\tilde{\rho}_{11}(s) = \frac{c_1}{s - s_1} + \frac{c_2}{s - s_2} + \frac{c_3}{s - s_3}. \quad (\text{A.7})$$

Solving the polynomial gives the roots

$$[s_1, s_2, s_3] = \left[0, -\frac{1}{2}(p-q), -\frac{1}{2}(p+q) \right] \quad (\text{A.8})$$

where the substitutions

$$\begin{aligned} p &= \Gamma_1 + \Gamma_2, \\ q &= \sqrt{(\Gamma_1 - \Gamma_2)^2 - 4\Omega^2} \end{aligned} \quad (\text{A.9})$$

are made for legibility. The corresponding c numerators can be found through substitution

$$[c_1, c_2, c_3] = \left[\frac{2\Omega^2}{p^2 - q^2}, -\frac{\Omega^2}{q(p-q)}, \frac{\Omega^2}{q(p+q)} \right]. \quad (\text{A.10})$$

This is now in the correct form for the inverse Laplace transform, giving

$$\rho_{11}(t) = c_1 + c_2 e^{s_2 t} + c_3 e^{s_3 t} \quad (\text{A.11})$$

where $c_1 e^{s_1 t} \rightarrow c_1$ as $s_1 = 0$. At long timescales the exponential terms approach zero, giving

$$\rho_{11}(t \rightarrow \infty) = \frac{1}{2} \frac{\Omega^2}{\Gamma_1 \Gamma_2 + \Omega^2} \quad (\text{A.12})$$

which is equivalent to Eq. 1.5 for the case of zero detuning. Substituting these two cases into Eq. 1.12 gives the equation for a resonantly cw pumped second-order correlation function measurement [71]

$$g^{(2)}(\tau) = 1 - \frac{p+q}{2q} e^{-\frac{1}{2}(p-q)|\tau|} + \frac{p-q}{2q} e^{-\frac{1}{2}(p+q)|\tau|}, \quad (\text{A.13})$$

where

$$\begin{aligned} p &= \Gamma_1 + \Gamma_2, \\ q &= \sqrt{(\Gamma_1 - \Gamma_2)^2 - 4\Omega^2} \\ \Omega &= \sqrt{\Gamma_1 \Gamma_2 S}. \end{aligned} \quad (\text{A.14})$$

A.2. Publications and Talks

Publications

- **Ross C. Schofield**, Chloe Clear, Rowan A. Hoggarth, Kyle D. Major, Dara P. S. McCutcheon, and Alex S. Clark, ‘Photon indistinguishability measurements under pulsed and continuous excitation’, *In submission* (2021)
- Sebastien Boissier, **Ross C. Schofield**, Lin Jin, Anna Ovvyvan, Salahuddin Nur, Frank H. L. Koppens, Costanza Toninelli, Wolfram H.P. Pernice, Kyle D. Major, E. A. Hinds, and Alex S. Clark, ‘Coherent characterisation of a single molecule in a photonic black box’, *Nature Communications* **12**, 706 (2021)
- **Ross C. Schofield**, Dominika P. Bogusz, Rowan A. Hoggarth, Salahuddin Nur, Kyle D. Major, and Alex S. Clark, ‘Polymer-encapsulated organic nanocrystals for single photon emission’, *Opt. Mater. Express* **10**, 1586-1596 (2020)
- Chloe Clear, **Ross C. Schofield**, Kyle D. Major, Jake Iles-Smith, Alex S. Clark, and Dara P. S. McCutcheon, ‘Phonon-Induced Optical Dephasing in Single Organic Molecules’, *Phys. Rev. Lett.* **124**, 153602 (2020)
- **Ross C. Schofield**, Kyle D. Major, Samuele Grandi, Sebastien Boissier, E. A. Hinds, and Alex S. Clark, ‘Efficient excitation of dye molecules for single photon generation’, *J. Phys. Commun.* **2** 115027 (2018)

Talks

- ‘Coupling a Single Molecule to an Interrupted Nanophotonic Waveguide’, CLEO Europe, Remote, 2021
- ‘Dibenzoterrylene as a single photon source’, Quantum Systems Engineering Skills Hub Talks, Imperial College London, 2020
- ‘Nanophotonic Waveguide Coupling to Organic Molecules in Micro-Capillaries’, Single Photon Workshop, Milan, 2019
- ‘Efficient excitation of a single molecule for photon generation’, Photon, Birmingham, 2018

Awards

- Best Talk, Quantum Systems Engineering Skills Hub Talks, Imperial College London, 2020
- Best Poster, Postgraduate Research Symposium, Imperial College London, 2019
- Alan Gibson Poster Prize, Photon, 2018

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