

UNIVERSITY OF OXFORD

DOCTORAL THESIS

**Quantum electrodynamics of
semiconducting nanomaterials in optical
microcavities**

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Abstract

Quantum electrodynamics of semiconducting nanomaterials in optical microcavities

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Semiconducting nanocrystals in open-access microcavities are promising systems in which enhanced light-matter interactions lead to quantum effects such as the modulation of the spontaneous emission process and exciton-polariton formation. In this thesis I present improvements of the open cavity platform which serves to confine the electromagnetic field with mode volumes down to the λ^3 regime and demonstrate results in both the weak and strong coupling regimes of cavity quantum electrodynamics with a range of different low-dimensional materials. I report cavity fabrication details allowing a peak finesse of 5×10^4 and advanced photonic structures such as coupled cavities in the open cavity geometry.

By incorporating two-dimensional materials and nanoplatelets in the cavity I demonstrate the strong coupling regime of light-matter interaction with the formation of exciton-polaritons, quasi-particles composed of both photon and exciton, at room temperature. In the perturbative weak coupling regime I show pronounced modulation of the single-photon emission from CdSe/ZnS quantum dots and the two-dimensional material WSe₂ and demonstrate Purcell enhancement of the spontaneous emission rate by factors of 2 at room temperature and 8 at low temperature. The findings presented in this thesis pave the way to establish open microcavities as a platform for a wide range of applications in nanophotonics and quantum information technologies.

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“Science is a way of thinking much more than it is a body of knowledge.”

Carl Sagan

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List of Abbreviations

AFM	A tomic F orce M icroscopy
CVD	C hemical V apour D eposition
CQED	C avity Q uantum E lectrodynamics
CW	C ontinuous W ave
DBR	D istributed B ragg R eflector
FDTD	F inite D ifference T ime D omain
FIB	F ocused I on B eam
FWHM	F ull W idth H alf M aximum
HBT	H anbury, B rown and T wiss interferometry
HWHM	H alf W idth H alf M aximum
LT	L ow T emperature
NA	N umerical A perture
NPL	N ano P latelet
PL	P hotoluminescence
RoC	R adius of C urvature
SEM	S canning E lectron M icroscopy
SPAD	S ingle P hoton A valanche D etector
SPE	S ingle P hoton E mitter
TEM	T ransmission E lectron M icroscopy
TEM_{m,n}^q	T ransverse E lectro- M agnetic (<i>q, m, n</i> are the mode numbers)
TRPL	T ime R esolved P hotoluminescence
TMDC	T ransition M etal D ichalcogenide
WLI	W hite L ight I nterferometer
XPB	X P olariton B ranch, where X can be U pper, M iddle or L ower

Physical Constants

Boltzmann constant	$k_B = 1.380\,648\,52 \times 10^{-23} \text{ J K}^{-1}$
Electron charge	$e = 1.602\,176\,620\,8 \times 10^{-19} \text{ C}$
Planck's constant	$h = 6.626\,070\,040 \times 10^{-34} \text{ J s}$
Reduced Planck's constant	$\hbar = 1.054\,571\,800 \times 10^{-34} \text{ J s}$
Vacuum permittivity	$\varepsilon_0 = 8.854\,187\,817 \times 10^{-12} \text{ A s V}^{-1} \text{ m}^{-1}$
Vacuum permeability	$\mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2$
Speed of Light	$c = 2.997\,924\,58 \times 10^8 \text{ m s}^{-1} \text{ (exact)}$
Conversion factor between wavelength and energy	$hc = 1239.84 \text{ eV nm}$

List of Symbols

Symbol	Name	Unit
$\mathcal{F}$	Finesse	1
F_P	Purcell factor	1
g	Coupling parameter	Hz
V	Mode volume	m ³
q, m, n	Longitudinal and transverse mode numbers	1
Q	Quality-Factor	1
w_0	Gaussian beam waist	m
z_R	Rayleigh length	m
γ	Decay rate	Hz
δ	Detuning	Hz
$\Delta\nu_{\text{FSR}}$	Free spectral range	Hz
η	Efficiency (collection or quantum)	1
λ	Wavelength	m
μ	Transition dipole moment	C m
ν	Frequency	Hz
ξ	Dipole alignment factor	1
θ_d	Beam divergence	rad
τ	Cavity or excited state lifetime	s
φ	Phase angle	rad
ω	angular frequency	rad
Ω_{Rabi}	Rabi splitting	Hz

For Guido, Ulla, Katharina & Valerian ...

1 Introduction

1.1 The technological landscape

Controlling individual quantum states is difficult. While photonic and semiconductor based devices are essential components of modern information infrastructure which have allowed for long-haul fibre based communication with optical repeaters, advanced metrology and powerful supercomputers, a scalable solution for the building blocks of quantum networks requires a new approach. The aim of such a network is to further technological capabilities beyond binary systems to harness quantum superposition states, which could allow for paradigm shifting advances in the prediction of complex systems by quantum simulations [1–4], novel cryptographic methods [5] with the potential to break existing protocols [6], enhanced sensors [7] and metrology [8]. Evidently the future technological landscape is shaped by current research and it is worth noting the high level of attention and financial support for photonic and emerging quantum technologies, on both european and UK national level [9–11].

The understanding of quantum mechanics has shaped most of what we identify as technology around us and has enabled engineering on atomic length scales - even so the intrinsic quantum nature of particles remains elusive and the challenge to work with and manipulate qubits in technological applications appears, at times, quite daunting. Meanwhile the number of tools and the level of understanding in the scientific community grows and the possible paths to achieve the necessary level of control over isolated quantum systems is converging - from ionic traps with single atoms, to point defects in bulk materials to nanocrystals.

This project is situated in the field of condensed matter physics, where excitonic states in semiconducting nanocrystals such as quantum dots and two-dimensional materials are utilised as quantum states. In this thesis a nanophotonic approach is employed, that strives to enhance the coupling between an electric field and excitonic states with optical microcavities that provide small electric field mode volumes of λ^3 order. Thus a vital part of this project is the production and improvement of open-access microcavities with dimensions on the order of a micrometre, fabricated with Focused Ion Beam milling in order to achieve nanometric precision of the cavity shape. A second focus lies on the materials hosting the excitonic states: here a diverse range of colloidal nanoparticles such as quantum dots and nanoplatelets are utilised and the recently emerged atomically flat two-dimensional transition metal dichalcogenides are investigated. All of these systems are semiconducting nanomaterials with promising applicability in metrology, quantum information processing,

new forms of lasers, LEDs and single photon sources.

1.2 The fundamental science

Alongside the technological motives for this thesis outlined above, reasons to pursue experiments focusing more on the understanding of the fundamental science emerged over the course of the project.

This shift in interest was caused while reproducing the recently reported strongly coupled exciton-polariton states, mixed states of both excitonic and photonic nature, in a microcavity with a two-dimensional material. Both the phenomenon and the material have recently received increased attention. While polariton states have been observed in different materials before, the combination of ambient temperature operation and an atomically-flat host material renders the system unique. The exciton-polariton states formed in the system show atypically large Rabi splittings, associated with the strong interaction of photonic mode and exciton state. Exciton-polariton states can be used to explore states of matter akin to Bose-Einstein condensates [12] and to create hybrid states with different exciton species [13], enabling modulation of the energy levels and new energy transfer pathways [14]. Adding to that, there are ongoing studies to increase the understanding of the nature of the collectively coupled polariton states [15–18] and there remain conceptual difficulties with the role of single oscillators within the ensemble of coherently coupled photon-exciton states.

1.3 Thesis outline

This thesis is grouped into eight chapters, of which the first three have an introductory character. Chapter 5 - 7 contain original research with both published and unpublished work:

Chapter 2: Literature review

This thesis builds upon the diverse results published by the scientific community over the last decades. The bulk of the work stems from the last two decades, where optical microcavities have been used increasingly to modulate the properties of single emitters. This chapter presents the relevant literature in historic order and grouped into the three main areas of this thesis: excitonic transitions in nanomaterials, photonic environments engineered by microcavities and quantum optical effects of excitons coupled to single cavity modes.

Chapter 3: Theoretical foundations

This chapter contains the derivation of the key concepts and expressions for the description of the experimental data in later chapters. Care is taken to present the relevant topics for this thesis in a comprehensive way and to refer

to the extensive literature where the scope of the thesis poses limits. Note that many derivations can be found in the physical compendium at the end of the thesis.

Chapter 4: Experiment design

On the basis of the last two chapters it is instructive to explore the experimental setup and equipment that were used to collect the data. Additionally details of the fabrication of FIB-milled microcavities are given and the different steps of the sample preparation are presented that later chapters will reference to.

Chapter 5: Advances in open microcavities

After presenting both the theoretical and experimental background, the first experimental chapter presents improvements in both shape and confinement quality of the FIB-milled microcavity. With the concepts put forward in this chapter the reader has a thorough understanding of the cavity mode structure and figures of merit, necessary for the appreciation of following chapters.

Chapter 6: Planar cavity strong coupling

In the second experimental chapter, collective polariton states obtained with planar microcavities at room temperature are presented. To give a comprehensive picture, three recently published studies about exciton-polariton states in two-dimensional WS_2 and colloidal NPLs are put forward. All of the presented polariton states are of a collective nature, where the number of oscillators coupled to a cavity mode increases the coupling energy.

Chapter 7: Single photon sources in open microcavities

In the penultimate chapter FIB milled cavities are used to enhanced single photon emission from single quantum dots at room temperature and single defects in the two-dimensional material WSe_2 at low temperature. Sizeable Purcell factors are reported for both materials, which represent a clear indication for the suitability of FIB milled open cavities to produce enhanced single photon sources.

Chapter 8: Closing perspective

In the last chapter the findings of the presented data are summarised in the context of nanophotonic applications and future research directions.

2 Literature review

The following chapter introduces the topic of cavity quantum electrodynamics (CQED) with the focus on excitons in nanocrystals as interacting system. The exposition will be mostly historical, with a focus on the most relevant publications for this thesis.

In the first section I will briefly introduce the matter part, that is low dimensional nanocrystals such as quantum dots, nanoplatelets and two-dimensional materials with strong excitonic signatures. The next section combines electronic and photonic states by presenting the main concepts of cavity coupling and the implementation of matter in different cavity structures. To give a comprehensive overview, I will present the key figures of merit of common cavity systems together with results in the field over the last 15 years ranging from polariton formation to single photon sources. The third and last section of this introductory review focuses on the open cavity environment which has particular relevance for this thesis as all subsequent experimental results are obtained in this system. In this geometry I will present FIB-milling as a fabrication method to create the topography of concave cavity features with nanometric precision and show that coupled cavity structures give rise to advanced photonic systems.

2.1 From quantum dots to nanoplatelets and two-dimensional materials

For a bulk semiconductor the bandgap energy is one of the most important parameters as it gives the energy between conduction and valence band. In the absence of interband defects only photons exceeding that energy can be absorbed and promote electrons across the band edge. This situation changes when the dimensions of the same material are reduced to nano-scales of only a few thousand atoms, where quantum confinement leads to a quantisation and increase in energy of available states. Here the Bloch wave function of the bulk crystal is modulated by an envelope function given by the boundaries of the material and the translational symmetry of the crystal lattice is broken.

The field of low dimensional semiconductor science grew rapidly in the 1980s with the advent of epitaxial techniques for growing quantum wells, now found in lasers for everyday use. Further reductions in dimensionality to make quantum wires and dots followed and other growth techniques in solution [19] and with catalyst particles [20] emerged that superseded the epitaxial method.

For certain nanocrystals such as zero-dimensional QDs where the material is bounded in all three dimensions, atom like exciton states can be observed, offering well defined energetic transitions with low dephasing rates and strong dipole moments, rendering these ‘artificial atoms’ to be one of the candidates for the realisation of quantum information processing. It is this size-dependent modulation of absorbing and emitting states that renders nanocrystals interesting for many applications like QD-LEDs [21–23], lasers [24], biomedicine [25, 26] and solar cells [27, 28].

Historically zero-dimensional nanoparticles were synthesised first (seminal papers by Ekimov et al. around 1985 [29]), with one-dimensional nanowires and nanotubes following in the 1990s [30, 31] and the first realisation of a two-dimensional material, graphene in 2004 by Novoselov [32].¹ In the last decade this rich field has been extended by two-dimensional monolayer Transition Metal Dichalcogenides (TMDCs) [33] and quasi two-dimensional nanoplatelets [34], each exhibiting pronounced excitonic effects giving rise to interesting optical properties. The quantum size effect in semiconducting crystals was first demonstrated by Ekimov and coworkers in I-VII and II-VI compounds embedded in a glassy dielectric matrix in the mid 1980s [29]. Later work by Efros et al. developed the theory of the bound exciton, biexciton and trion states in such microcrystallites [35]. A good review over the early progresses with semiconducting quantum dots has been written by Alivisatos in 1996 [36]. Quantum dots can be grown in solution, one then speaks of colloidal particles. The other growth method, commonly encountered in condensed matter systems is the epitaxial growth, starting with a solid substrate and a crystal seed to chemically deposit more and more layers of the active material. It is then straightforward to incorporate the grown quantum dots in monolithic structures, such as waveguides or electric junctions.

2.1.1 Nanoplatelets

The interaction strength between an electric field and an excitonic state depends, in a first approximation, on the dipole transition moment between ground and excited state. While spherical, small QDs offer clean quantisation of excitonic states and relatively low transition dipole moments, more elongated structures with larger degrees of asymmetry can be used to cater for specific applications, yielding more directional, partly polarised emission patterns, multiexcitonic states and larger transition dipole moments. Recently a new class of 2D structures coined nanoplatelets (NPLs) has been observed, which is interesting in this regard. The platelets, first reported by Ithurria et al. in 2008 [34], promise to offer strong excitonic interaction with light due to a large coherence area of the exciton wavefunction in the plane of the platelet, an effect named giant oscillator strength.

¹Semiconducting quantum wells similarly confine charge carriers to two dimensions and have been used in condensed matter physics since the 1980s.

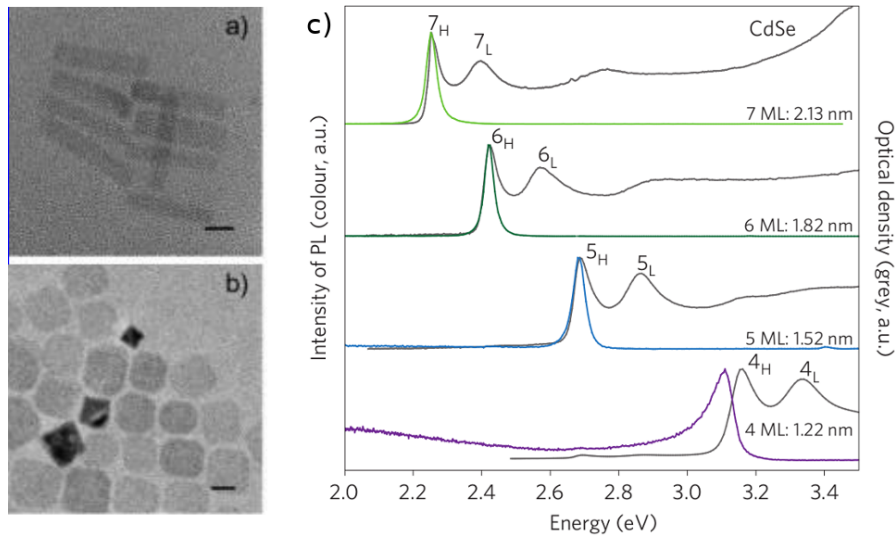


FIGURE 2.1: **Colloidal CdSe nanoplatelets: TEM images and optical properties.** a) TEM images of CdSe colloidal platelet shaped nanocrystals. b) Same synthesis as in a) with a different precursor injection, demonstrating the impact of the chemical environment on the platelet growth. c) Absorption and emission spectra of CdSe nanoplatelets. The two strongest transitions, light and heavy hole in the effective mass approach, with a platelet thickness of M monolayers denoted M_L and M_H respectively are shown for four different species of platelets with thicknesses ranging from 4 to 7 monolayers. (a, b reproduced from [34], c from [37])

Ithurria et al. report CdSe structures with dimensions of 6 to 40 nm in the plane and about 2.2 nm in height which were visible under TEM as demonstrated in Fig. 2.1a,b. Systematic control of the ratio of the substances, the reaction times and the temperatures used made it possible to vary the shape and aspect ratio of the platelets. For this first batch of NPLs a quantum yield of 30% was reported, but enhanced to about 50% in a publication in 2011 [37]. Here a thorough study of different platelet types (CdSe, CdS and CdTe) is presented and the dependence of the spectral absorption and emission energy on the platelet thickness is demonstrated.

As is apparent from Fig. 2.1c the breaking of translational symmetry occurs in the out-of-plane dimension² and so the energy of the transitions can be lowered by allowing more layers to grow in the vertical direction. The quantitative analytical understanding is obtained by adaptation of the Pidgeon-Brown model [38] for eight bands and is presented in more details in [37]. In general both the heavy and light hole transitions lead to excitonic peaks in the absorption spectra (labelled with the subscript H and L in Fig. 2.1c). PL is only observed from the lowest energy transition with a negligible Stokes shift, indicating a fast relaxation mechanism of excited electrons and excitons.

²Note that the in-plane extensions of the platelets exceed the exciton Bohr radius $a_B = 5.4$ nm of bulk CdSe.

Due to the elongated shape of NPLs an increase in dipole moment of the ground state exciton is anticipated, which renders the material potentially very useful for CQED coupling purposes. Recently evidence for a giant oscillator strength in CdSe NPLs was brought forward by Naeem et al., reporting fast excitonic lifetimes of about 1 ps obtained by measuring the dephasing rates by three-beam four-wave-mixing [39]. Further studies on the emission characteristics of single NPLs found blinking behaviour similar to the one known from single QDs, with a power law for the cumulative distribution of the OFF state describing intermittent emission [40]. The OFF state is attributed to fast Auger processes involving free charges around the emitter, thought to be responsible for spectral diffusion as well. At low temperatures the blinking is suppressed and a dramatic increase in intensity and decrease in lifetime is verified. Furthermore a reversible photo degradation and a decrease in emission intensity under vacuum was observed, tentatively connected to the influence of water and oxygen on the trapping surface states.

I keep the exposition very brief at this point but note that Chapter 3 introduces the terminology used in this chapter in more details. The reader may find more information about synthesis and applications of QDs in the literature by Klimov [41] and Rogach [42]. In particular Hines [43] and Boles [44] give good reviews on sample preparation and the role of surface passivation.

2.1.2 Quasi-infinite two-dimensionality

While the previous section explored few monolayer thick structures with transverse dimensions of tens of nanometers, the recent advent of monolayer two-dimensional materials with macroscopic (exceeding $100\text{ }\mu\text{m}^2$) extensions took the principle of quantum confinement in two-dimensions to a new level which has immense influence on current technology. Materials such as graphite and MoS_2 were long known for their robust sheet-like structure with weak interlayer bonding, rendering them useful as dry lubricants. Only recently the interesting properties and the fabrication of the monolayer itself has become the focus of research groups world wide [45].

The first protagonist of this new class of materials was graphene - the noun being derived from graphite - describing atomically flat layers of hexagonally distributed carbon atoms first demonstrated experimentally in 2004 [32]. Graphene has a semimetallic electron configuration without a bandgap, which makes it interact strongly with photons over a wide energy range. Over the following years more and more materials, which were long known in bulk form, were prepared as monolayers and showed unexpected properties. The class of transition metal dichalcogenides (TMDCs) for example, where one transition metal (eg. W or Mo) is paired with two chalcogen atoms (eg. S or Se), exhibits a direct bandgap transition only in monolayer form. A single TMDC layer consists of triangular arrays of the transition-metal sandwiched between two layers of triagonally arranged chalcogen atoms, giving a hexagonal lattice. In the bulk crystal such layers are bound together by weak

van-der-Waals forces and the band structure is that of an indirect semiconductor. As the number of layers is decreased, the material develops a direct transition at the K-point of the Brillouin zone with a bandgap in the range of 1-2 eV.

Owing to the atomically flat structure, the bandgap in 2D TMDCs is additionally strain tunable, as shown experimentally by He et al. [46], allowing the integration in flexible electronics. A good summary of the optical properties of the transition from multilayer to monolayer of the TMDCs relevant to this work (WS_2 and WSe_2) is given by Zhao et al. [47]. Both photoluminescence and absorbance spectra show a systematic transition from monolayer to bulk, where the exciton peaks shift to higher energies for lower layer numbers as a result of increasing confinement. In general the bulk behaviour is restored for a layer number above ten. Even though the thickness of the material is much smaller than the wavelength (roughly 0.1% of the lowest exciton state wavelength) one monolayer of WS_2 (WSe_2) absorbs 18% (6%) of photons at the lowest exciton state wavelength [48].³

The first reports of single layered TMDCs presented the scotch-tape method as the means for monolayer fabrication.⁴ Recently it has become possible to grow atomically thin single-crystal domains of WS_2 by chemical vapour deposition (CVD) which naturally comprises a vital step towards technological applications [51]. In the experimental section of this thesis I will show results from both mechanically exfoliated WSe_2 and CVD grown WS_2 .

Single photon emission from two-dimensional TMDCs

Single photon emission has been observed in a range of systems, including single atoms, quantum dots and localised excitons in a multitude of materials.⁵ In 2015 however the first report of quantum light emission from two-dimensional materials was published (interestingly three groups published very similar data in the same volume of Nature Nanotechnology, which demonstrates the active development of the field) [54–57].

In the reports, the transition metal dichalcogenide WSe_2 was found to contain single photon emitters (SPE) with weakly bound excitons, stable at cryogenic temperatures below 30 K, emitting quantum light with impressive brightness and stability. As the monolayer was cooled down, sharp peaks with linewidths around 120 μeV appeared upon non-resonant optical excitation. Fig. 2.2 shows the autocorrelation data for one single quantum emitter excited with a continuous source (Fig. 2.2a) and a pulsed source (Fig. 2.2b). Both datasets reveal single photon emission, although the interpretation of the plots remains somewhat inconclusive as the presented correlation counts were not normalised. The values of $g^2(0)$ are given in the figure caption however.

³In comparison graphene absorbs roughly 2.3% of the visible spectrum [49].

⁴For a review on the mechanical fabrication of monolayer TMDCs see [50], I describe the process in more detail in Chapter 4.

⁵The books by Haroche [52] or Meystre and Sargent [53] allow comprehensive overviews.

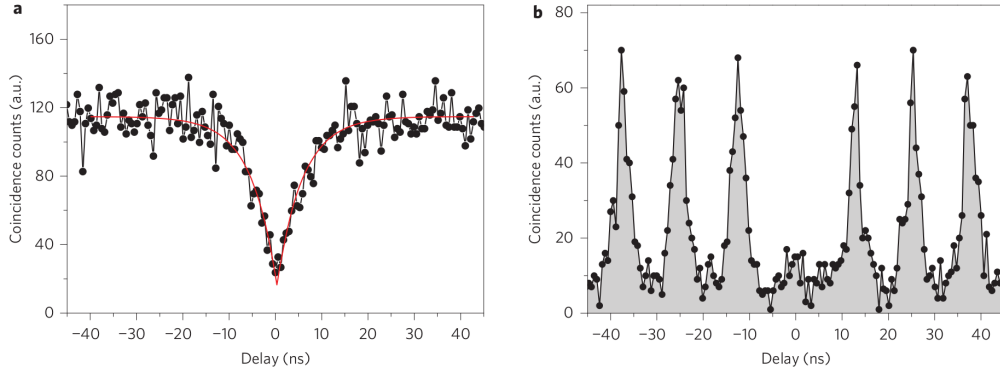


FIGURE 2.2: **Observation of photon antibunching from a localised emitter in monolayer WSe₂.** a) Second-order correlation measurement of the PL under a 6.8 μW CW laser excitation at 637 nm. The red line is a fit to the data, from which the authors extract $g^2(0) = 0.14 \pm 0.04$. b) Intensity correlation measurement under 9.5 μW (average) pulsed excitation at 696.3 nm with a repetition rate of 82 MHz, and a pulse width of ≈ 3 ps, which revealed $g^2(0) = 0.21 \pm 0.06$. (reproduced from [57])

In particular the material was shown to host remarkably bright localised defects, with groups reporting countrates of several MHz [55, 58]. Tonndorf et al. present PLE data and resolve the Rydberg peaks associated with excited states of the localised exciton [56]. They report confinement energies between 40 and 200 meV, at odds with the experimental fact that the emitter is only found for cryogenic temperatures below 30 K.

In addition it is shown that the substrate has strong influence on the lifetime of the defect, in particular that an insulating hBN layer between SiO₂/Si substrate and WSe₂ increases the lifetime from ≈ 1 ns to ≈ 7 ns. In later studies several distinct defect types with and without fine structure splitting were documented [58] and it was shown that single defects can be created by depositing the WSe₂ monolayer on nanorods [59] and that the emitter exhibits strain tunability [60]. The current understanding is thus that the substrate or local inhomogeneities in the host matrix give rise to shallow potential wells which can trap an otherwise delocalised direct gap exciton.

2.2 Cavity quantum electrodynamics with semiconductor nanocrystals

The central theme of this project is the description of a cavity system which can be used to couple matter and light to thereby enhance the control over absorption and emission characteristics. Historically, the field of cavity quantum electrodynamics found its beginning with a paper by Edward Purcell presented in 1946 at a Spring Meeting of the American Physical Society [61], in which he described an increase in the spontaneous emission rate for radio frequency transitions in nuclear magnetic resonance when placing the system in a resonator. The implications of this effect,

that internal recombination processes of atoms or other excited systems are connected to the availability of external states, gave impetus to the field of light-matter interactions in confined spaces (CQED) and led to remarkable comprehensions and technological advances [62]. Instead of treating atoms and their transition in the two-level approximation the focus will be on the analogous exciton state, as it will be at the center of this thesis. For all intent and purposes the two systems can be interchanged at the theory level. The coupling strength g (in units of frequency) between an excitonic system and a cavity mode is proportional to the transition dipole moment μ of the excitonic transition and the electric field in the cavity. I will later show that the latter depends inversely on the square root of the cavity mode volume V , implying that small cavity mode volumes will result in a strong electric field and thus a strong coupling between matter and light.

Comparing the coupling strength g to the decay rate of the cavity $\kappa = \frac{1}{\tau_{\text{cav}}}$ and the emitter $\gamma = \frac{1}{\tau_{\text{em}}}$ one can identify two different scenarios: the weak coupling regime where $g < \kappa, \gamma$ and dissipative effects prevail and the strong coupling regime where $g > \kappa, \gamma$ and hybrid cavity-exciton states are created. I will formally develop the theoretical foundations for the coupling of cavity modes to electronic states in Chapter 3.

The following section provides an overview of nanocrystals coupled to modes of confining photonic structures, experimental results that were reported over the last two decades, which is the timeframe for strong interest in these systems.

2.2.1 All solid-state cavity coupling

1998: The first weakly coupled exciton-cavity system is reported by Gérard and coworkers [63]. The system is composed of InAs quantum boxes placed in the core of small-volume and high-finesse GaAs/AlAs pillar microresonators. Other groups later embed similar InAs QDs in a microdisk, allowing a coupling between the whispering gallery modes (WGM) of the cavity and the exciton state in the quantum dots [64]. For these and similar systems using micropillars Purcell enhancements of the spontaneous emission rate between factors of 2 and 6 have been reported [65, 66].

2004: Reithmaier et al demonstrate for the first time a strongly coupled exciton-cavity system consisting of a single quantum dot and a micropillar cavity [67]. In order to maximise g the group grew large asymmetric $\text{In}_{0.3}\text{Ga}_{0.7}\text{As}$ dots with typical lengths of 100 nm and widths of about of 30 nm and created micropillars with circular cross-sections of few micrometers around the dots.

The measured linewidths at 4 K were 0.2 meV for the cavity mode and 0.1 meV for the exciton peak. For a demonstration of strong coupling conditions the energies of both cavity and exciton had to be brought to a crossing, at which point the two coupled states exhibit two different energies and thus a split spectrum, indicative of an energy exchange between the two systems. At that point the states can be regarded superpositions of equal photonic and excitonic nature. To facilitate the

energy tuning, the group used the fact that the temperature dependence of the exciton is bandgap dependent and has a stronger temperature gradient than the cavity mode. By increasing the temperature from 4 K to 30 K they were able to shift the exciton energy by about 1 meV which resulted in the desired anticrossing behaviour.

Fig. 2.3 (a) shows the spectral data of the avoided level crossing. At about 22 K, right at the anti-crossing point, an equal proportion of both exciton and cavity state is observed, forming the new polariton state. Far away from the crossing point both states resume their bare identity. Comparing this to the weakly coupled data obtained with a different, non-interacting QD in Fig. 2.3 (b), it is evident that in the latter case no strongly bound states form - instead the spectrum exhibits a single peak even for resonant tuning of both systems. The observed Rabi splitting in the strongly coupled case was $\hbar\Omega_{\text{Rabi}} = 140 \mu\text{eV}$.

While the authors give a very low probability ($\approx 10^{-3}$) for multiple dots participating in the coupling an open question is whether the rather large quantum dot allows multiple s-state excitons at the same time. The authors have not presented data to assert single photon emission, which would rule out this hypothesis.

The experiment can be regarded as the first demonstration of the capabilities of semiconducting quantum dots and their expected role in SPS and quantum memory applications.⁶ However, the analysis of the micropillar concept shows clear limitations, allowing no spatial tunability of the emitter, limited spectral tunability and low reproduction success rates due to the stochastic nature of the QD position and pillar deposition.

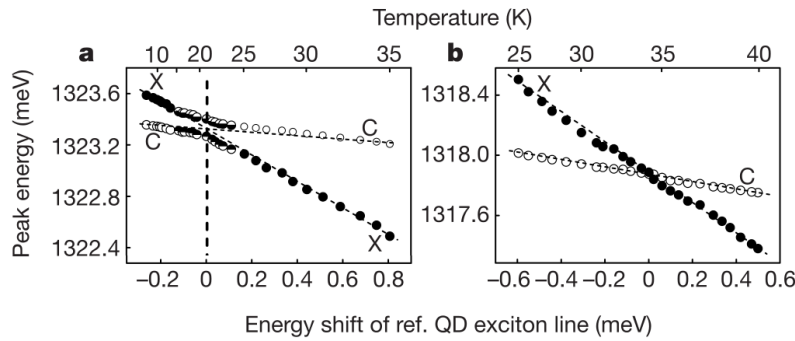


FIGURE 2.3: PL peak energies of the QD cavity system. Dependence on the temperature-generated energy shift of a reference QD for strong (a) and weak (b) coupling. The reference QD-related peak is located about 5 meV above the cavity mode and does not interact with the cavity (bottom scale). At the top is the temperature axis (nonlinear). All data have been obtained by fits of lorentzian lineshapes to the experimental spectra. a) Data for a single dot-cavity system in strong coupling. C (open dots), cavity-mode data; X (filled dots), QD exciton data; partly filled dots, data on or near resonance, where the strong coupling results in coupled modes. b) Experimental results for a dot-cavity system in the weak coupling regime. (reproduced from [67])

⁶Here one needs strong nonlinearities on the single particle level.

2004: A different approach for polariton formation is used by Yoshie et al. [68], where the group succeeded in strongly coupling a single QD embedded in a spacer region to a microcavity in form of a photonic crystal cavity (PCC). This cavity design exhibits very high Q-factors of about 13,300 and low computed modevolumes of $V = 0.07 \mu\text{m}^3$. The sample was grown on a GaAs substrate by molecular beam epitaxy and a single layer of InAs quantum dots was put in the center of the slab. Yoshie et al. performed the same temperature scanning experiment as Reithmaier et al. [67] and found similar results of Rabi splittings of about $\hbar\Omega_{\text{Rabi}} = 170 \mu\text{eV}$. Similar to the work by Reithmaier et al. the single emitter nature was not verified experimentally.⁷

Weakly coupled systems composed of a similar photonic crystal structure around an epitaxially grown InAs QD yielded Purcell enhancements of 10 [69], mostly attributed to the very low modevolumes achieved. The downside of the PCC approach is the divergent beam profile of the cavity mode, making the use of high NA lenses and very small working distances necessary. By altering the diameter of the closest on-axis holes the collection efficiency can be improved, but still lags behind alternative cavity structures.

2006: Two years later Le Thomas et al. [70] demonstrate the strong coupling regime for CdSe nanorods coupled to the evanescent field of a polymer microsphere photon mode. Despite their large mode volumes such spheres offer strong coupling capabilities if one achieves a lifting of degenerate angular momentum states via slight sphere deformation. The group used the natural jitter of the exciton state energy which jumped naturally up to $700 \mu\text{eV}$ at $T = 4 \text{ K}$. The thereby acquired spectra of randomly coupled exciton-cavity systems had to be sorted and analysed post-experimentally to convincingly document the anti-crossing with a Rabi splitting of $\hbar\Omega_{\text{Rabi}} = 40 \mu\text{eV}$. This cavity design offers limited adaptability and technological perspective and suffers from low collection efficiencies, as no directional preference and out-coupling pathway is defined.

2.2.2 Tunable microcavities

As illustrated most early nanocrystalline cavity coupling system were solid state systems with limited tunability. Only in recent years the optimisation of fabrication and experimental design has taken place such that more adaptive and flexible systems are being used increasingly.

2007: Trupke et al. employ an open fiber tip cavity to detect single Rb atoms cooled down with optical molasses [71]. To allow scalability, concave features are fabricated on a silicon wafer by wet-etching isotropically through circular apertures

⁷In fact the authors admit that “the linear spectroscopy that we report here has not proved ... that our dot/nanocavity system will exhibit truly quantum effects”. Such semiclassical, multiparticle strongly coupled systems have been described in the literature and I will discuss a similar system in the following section 2.2.3 and differentiate the semiclassical from the quantum model in Chap. 3.

in a lithographic mask [72]. As the system contained falling atoms instead of excitons, the results are not directly comparable to the work presented in this thesis, but are worth noting because of the open cavity design.

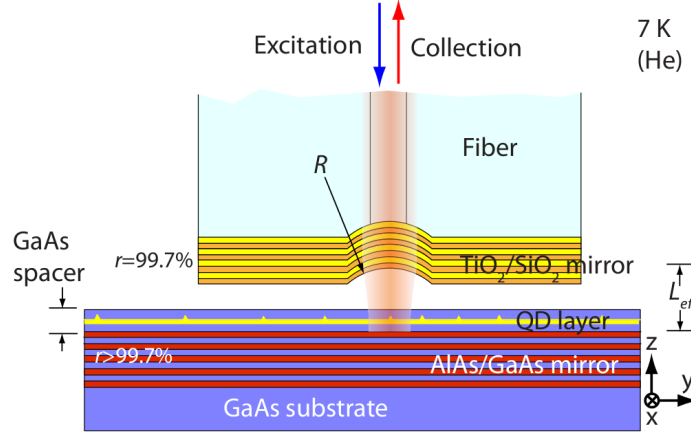


FIGURE 2.4: **Schematic of a fibre based open microcavity.** The nonresonant excitation and collection light is funnelled through a single-mode fibre, whose facet is machined to have a small concave recession. (from [73])

2009: Müller et al. reach weak coupling conditions with a fibre cavity system fabricated with a transfer coating method [73]. Convex microlens arrays etched into fused silica were used as a source template, which after coating could be aligned and attached to a single mode fibre [74]. This procedure gives effective radii of curvature of about $R = 40 \mu\text{m}$ and collection efficiencies of up to 10% regarding emission of a single QD. The QDs were grown as a dilute ensemble of strain-induced InAs spots as shown in Fig. 2.4. Free tunability of the system is attained by positioning the sample with a 3D-piezo stack relative to the cavity on the fibre end.

Experimentally the group showed weak Purcell enhancements, but generally the work can be regarded as a proof of concept demonstration, offering an approach with the key advantage to previous all solid-state systems of full tunability and high DBR quality promising strong coupling conditions even for comparably large mode-volumes.

2011: Barbour et al. demonstrate the spectral engineering capabilities of a single QD in a fully tunable fibre cavity [75]. The group used moderately large cavities with radii of curvature of $R \approx 100 \mu\text{m}$ created by a CO_2 laser ablation method made reflective by a 10 layer DBR stack consisting of alternating layers of TiO_2 and SiO_2 . Single InGaAs quantum dots were then epitaxially grown on top of the planar mirror side DBR.

Fig. 2.5 shows time resolved photoluminescence (TRPL) measurements and the evolution of the radiative lifetime while detuning the quantum dot both spectrally and spatially with respect to the cavity mode. The reported Q -values are in the range of 4500 and Purcell enhancements of up to $F_P = 1.6$ were measured - results,

which do not seem very impressive but can be taken as a first demonstration of the fully tunable open-access microcavity coupled to semiconducting nanocrystals. I will present a very similar study in Chapter 7 of this thesis and contrast the results presented here with the experimental data.

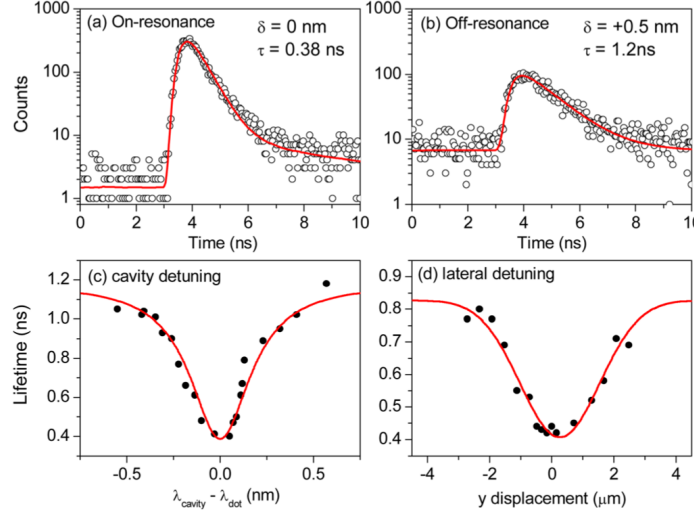


FIGURE 2.5: **Lifetimes for a quantum dot in a tunable open-access micro-cavity at 4 K.** The PL was excited with 50 ps pulses from an 830 nm laser. Decay curves were recorded with timing resolution 500 ps using a silicon avalanche photodetector and time-correlated single photon counting modules. a) Decay curve at the spatial and spectral resonance; b) decay curve at the spatial resonance but spectrally detuned by wavelength 0.5 nm. The curves are the result of a fit taking into account the response of the detector. c) Lifetime at the spatial resonance as a function of spectral (wavelength) detuning with a Lorentzian fit with FWHM 0.25 nm. d) Lifetime at the spectral resonance as a function of spatial detuning with a Gaussian fit with FWHM 2.5 μm . (reproduced from [75])

2012: The latest results from the Photonic Nanomaterials Group's weak coupling work on nanocrystals in FIB milled cavities by Di et al. are published [76]. The cavity system consists of a structured mirror with an array of FIB milled hemispherical cavities with radii of curvature $R = 25 \mu\text{m}$ or $7 \mu\text{m}$ opposite of a movable planar mirror, each mirror having a DBR of 10 pairs of $\text{SiO}_2/\text{ZrO}_2$ with reflectivities around $R = 99.4\%$. A dense solution of CdSe/ZnS quantum dots in octadecene is introduced into the system, allowing coupling of multiple QDs at the same time to optical cavity modes.

The focus of the work lay in demonstrating Purcell enhanced spontaneous decay rates in a new cavity environment, which had recently been developed. Fig. 2.6 shows an exemplary lifetime measurement in free space and inside the cavity (a) and a summary of acquired lifetimes for different mode volumes. The solid line corresponds to predictions made with the expression for the Purcell effect (derived in Chapter 3), showing the inverse relation of the Purcell factor to the mode volume.

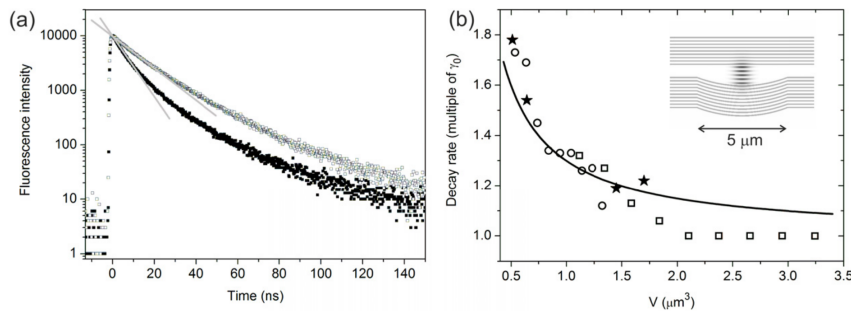


FIGURE 2.6: **Lifetime measurements of ensemble of quantum dots.** a) Lifetime measurements of ensemble of quantum dots in free space (open shapes) and inside the smallest cavity (solid shapes). Lifetimes were obtained by fitting the first 20 ns of the signal, to avoid slow decay components. b) Summary of measured lifetimes over calculated mode volume (stars for FDTD simulation results, circles for $\beta = 7 \mu\text{m}$ and squares for $\beta = 25 \mu\text{m}$). The solid line corresponds to the theoretical prediction. (from [76])

It is striking to see the direct dependence of the Purcell enhancements on the mode volume, giving room to in-situ control the emission characteristics of single emitters in the future.

2013: Besga and coworkers report high quality polariton formation in a fully tunable fibre cavity setup with excitonic states in quantum wells [77]. This work is included in this review to give a comparative perspective about strongly coupled systems with other excitonic states. Their fibre end mirrors displayed radii of curvature of $R \approx 75 \mu\text{m}$, which were covered with a DBR mirror allowing modes with Q factors of above 100,000 when opposite of a sample with an equal DBR surface. The sample itself consisted of an AlAs/GaAs semiconductor DBR with an active InGaAs quantum well layer on top.

By moving the planar sample vertically the length of the cavity could be tuned freely allowing photoluminescence experiments with variable optical states around the emitter. A laser with $\lambda = 780 \text{ nm}$ was used to drive the excitonic transition of the quantum well. The avoided level crossing could then be demonstrated by recording the PL of the system for different cavity lengths. Dufferwiel published a similar study with FIB-milled cavities in **2014**. To offer a perspective on a slightly different system, I present two reports demonstrating Purcell enhanced spontaneous emission from a single nitrogen vacancy (NV^-) center in nanodiamonds.

2015: Johnson et al. document an enhancement of the zero phonon line by a factor of 6.25 by a cavity with $R = 7.6 \mu\text{m}$ and an overall Purcell enhancement of the radiative lifetime of 1.4 is reported [78]. The low Purcell factor is attributed to the small Debye-Waller factor, which quantifies the amount of emission in the zero phonon line compared to the side band, which is typical for NV^- emission.

2016: Recently Kaupp et al. have shown similar results from a NV center in a nanodiamond embedded in a CO_2 ablated fiber-tip cavities ($R = 90 \mu\text{m}$) [79]. Here a slightly different approach was taken in that instead of filtering out the zero-phonon line with a high Q cavity mode, a low Q cavity with metallic mirrors and a smaller

mode volume ($\approx \lambda^3$) was used to achieve a Purcell enhancement of 2.

Tab. 2.1 gives a summary of key values of the presented papers in this section. Note the variation in cavity systems and that most of the values were obtained at liquid He temperatures. The results obtained for all solid state systems constitute a standard, with which the tunable open-access design is gauged.⁸

Emitter	Cavity	Q-Factor	$V_{mode} / \mu m^3$	$\hbar\Omega_R / meV$	F_P	T / K	Reference
ep. InAs QDs	Microdisk	6,500	-	-	6	4	[64]
ep. InAs QD	Micropillar	1,270	-	-	5	3-10	[66]
ep. In _{0.3} Ga _{0.7} As QD	Micropillar	8,800	0.3	0.140	-	4 - 30	[67]
ep. InAs QD	Photonic crystal	13,300	0.07	0.170	-	13 - 29	[68]
CdSe Nanorod	Microsphere	100,000	8	0.04	-	4	[70]
ep. InAs QD	tun. transf. coated Fiber	23,000	44	-	weak	4	[73]
ep. InGaAs QD	tun. CO ₂ abl. Fiber	5,000	26*	-	1.6	4	[75]
ep. InAs QD	Photonic Crystal	10,000	0.02	-	10	10- 30	[69]
coll. CdSe QDs	FIB milled silica	10,000*	0.5	-	1.7	300	[76]
ep. InGaAs QW	tun. CO ₂ abl. Fiber	100,000	58*	3.4	-	4	[77]
ep. InGaAs QW	FIB milled silica	35,000	5*	5.5	-	4	[80]
NV ⁻ in ND	tun. FIB milled silica	3000	1.24	-	1.4	300	[78]
NV ⁻ in ND	tun. CO ₂ abl. silver	50	0.33	-	2	300	[79]

TABLE 2.1: **A summary of the key values for the cavity QED coupling results presented in this section.** Q-Values are referring to the cavity length used to obtain the data. Values marked with (*) had to be inferred indirectly.

In summary, the expectations one has for the FIB milled fully tunable design are thus:

- Highly directional, low divergence out-coupling beams to increase the collection efficiency.
- In-situ spectral tunability of the cavity mode.
- The ability to use a ‘sensor’ cavity to analyse multiple emitters by moving the mirror with the deposited emitter relative to the other.
- Low modevolumes facilitated by the small radii of curvature, allowing a large electric field per photon.

In this way it is possible to deterministically align the cavity mode spatially and spectrally relative to a wide range of emitters and to reach a high level of control over both the density of optical states accessible for the emitter and the strength of light-matter coupling.

⁸Albeit the apparent advantage of the older solid state approach to produce examples of strongly coupled systems, it must be pointed out that most approaches suffer from low collection efficiencies (microdisks, microspheres and photonic crystals) and limited scalability due to low reproducibility linked to the stochastic nature of the nanocrystal position within the electric field.

2.2.3 Exciton-polaritons with two-dimensional TMDCs

While single particle strong coupling depends strongly on the photon number,⁹ an analogous effect without the associated single exciton nonlinearities can be observed classically for media that interact strongly with light and was shown first by Weisbuch et al. in 1992 for semiconducting quantum wells [81]. A couple of years later Lidzey et al. demonstrated the occurrence of exciton-polaritons in organic materials at room temperature [82]. The coupling strength g in these N -particle systems scales with $\sqrt{N}$, and thus a dense material of interacting oscillator sites can reach the strong coupling limit.

In 2015 Liu et al. embedded a CVD-grown MoS₂ monolayer within a monolithic DBR structure composed of alternating SiO₂/Si₃N₄ layers [83]. The data presented in Ref. [83] is of particular relevance as two chapters of this thesis will present similar data of room temperature polaritons in WS₂, which have been published recently. Fig. 2.7 shows the reflectivity of the device for angles of incidence between 7.5° and 30° for TM polarised light. As the angle is changed the energy of the cavity mode is shifted across the exciton energy at 1.875 eV.

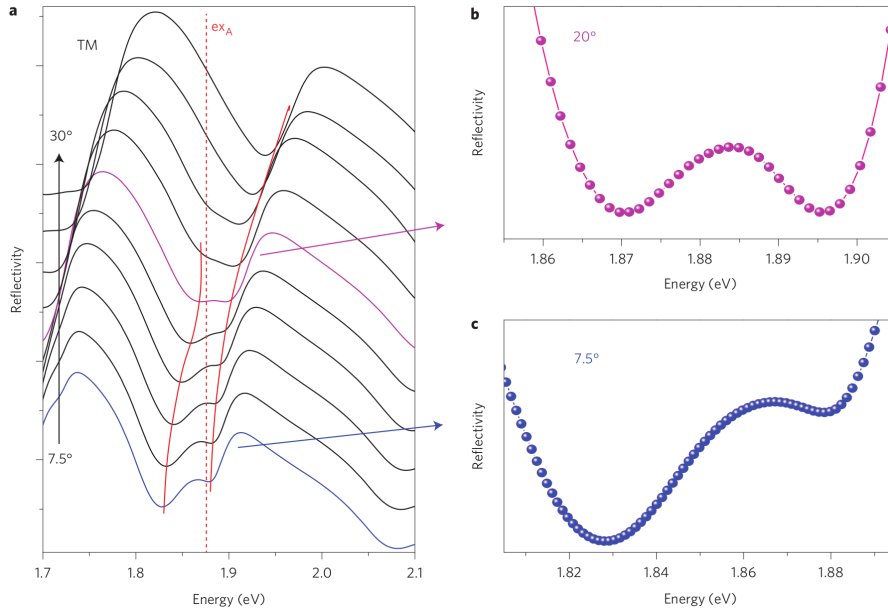


FIGURE 2.7: **Angle-resolved reflectivity spectra of a microcavity containing monolayer MoS₂.** a) Angle-resolved reflectivity spectra for TM polarization from 7.5° to 30°. The vertical red dashed line represents the MoS₂ A exciton energy. Red curves trace the dispersion of microcavity polariton modes. b,c) Expanded views of reflectivity spectral features at 20° (b) and 7.5° (c). Both spectra show two well-defined polariton states at both sides of the ex A energy. (taken as read from [83])

⁹The mathematics of dressed states of the Jaynes-Cummings ladder are laid out in Section. B.10 of the physical compendium.

The authors report a Rabi splitting of $\hbar\Omega_{\text{Rabi}} = 46 \pm 3 \text{ meV}$ and state that the strong coupling condition is fulfilled. In fact the strong coupling condition is fulfilled when the dip between the split exciton-polariton states can be fully resolved, that is when the width of the individual peaks is less than the splitting. This is not the case for the data presented here. The authors ‘visually increase’ the size of the dip by zooming in to the respective peak, ie. by neglecting data to the sides of the cavity modes. Instead of such a weak visual analysis a proper background subtracted spectrum would reveal that the individual modes are broader than the splitting. The data presented by Liu et al. thus documents only the onset of polariton-formation with TMDCs. I will contrast the presented results with experimental data obtained from an open cavity approach and discuss the differences in Chapter 6.

2.3 Focused-Ion-Beam milled microcavities

As presented in the last section, cavities relying on DBR mirrors are in use for a few decades and well understood. In terms of concave feature fabrication however, different approaches such as coating-transfer [74], trapped gas bubbles in glas [84], wet-etching through circular masks [72] and CO₂-ablation [75, 85] have been used and shown different degrees of suitability for low modevolume applications. In 2010 Dolan et al. [86] demonstrated a new cavity fabrication method using a Focused Ion Beam (FIB) [87] to mill concave cavities into a silica substrate.

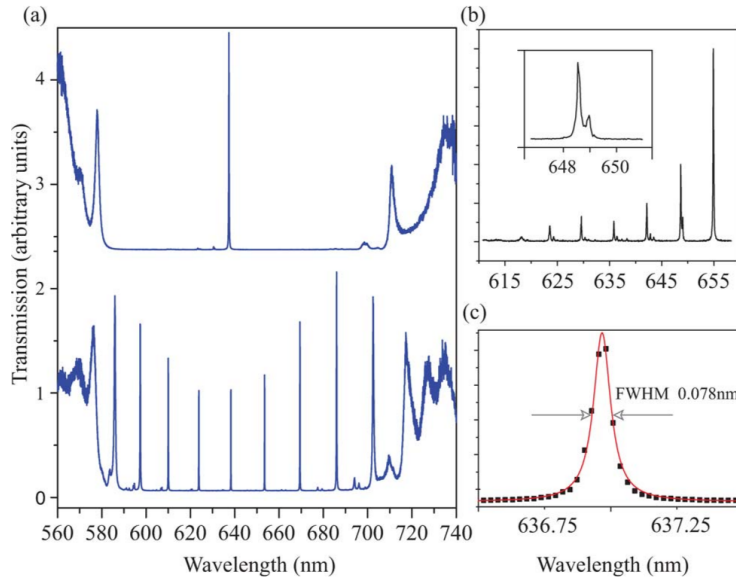


FIGURE 2.8: **Mode characteristics of FIB milled cavities.** White-light transmission spectra: a) A cavity with $R = 25 \mu\text{m}$ at $L = 3.0 \mu\text{m}$ and $L = 12.3 \mu\text{m}$. b) Hermite-Gauss modes from a single longitudinal mode with (1,0) (0,1) splitting (inset). c) A high-Q longitudinal resonance (scatter) with Lorentzian curve fit (solid curve) (reproduced from [86])

For this proof-of-concept work the group used hemispherical microcavities with radii of curvature of 7 and 25 μm allowing mode volumes of $2.2 \mu\text{m}^3$ with coating-limited finesses around 450 and Q -factors over 10^4 . Fig. 2.8 shows white light transmission spectra of a selected cavity with a big radius of curvature of $R = 25 \mu\text{m}$. The visible transmission peaks in (a) are longitudinal modes which obey $L = q \frac{\lambda}{2}$, q being a natural number, the longitudinal mode index.¹⁰ The transmission peaks in (b) are of a different nature; only the rightmost mode at a wavelength of 655 nm is a longitudinal $m = n = 0$ mode. Here m and n are the integer transverse excitation quantum numbers, which count the number of nodes of the electric field in the transverse plane. The peaks to the left of this $m + n = 0$ peak correspond in this notation to the higher excited $m + n = 1, m + n = 2, \dots$ modes.¹¹ For an azimuthally symmetric cavity those modes would be $m + n + 1$ -degenerate, here a lift of this degeneracy can be observed, which is due to a small ellipticity of the cavity shape. The high quality factors of over 10^4 were achieved even with comparably low reflectivity mirrors consisting only of 10 $\frac{\lambda}{4}$ -layers of alternating $\text{SiO}_2/\text{ZrO}_2$. Thus the reported cavities have photon leakage rates of $\kappa > 10^{11}$ Hz and theoretical values for F_P approach 20. In a second publication by Trichet [88], the fabrication method was shown to allow nanometric control over the feature shape with a measured surface roughness of $\sigma = 0.7 \text{ nm}$ which translates into a maximal reflectivity of $R = 0.9998$, corresponding to a finesse of up to 15,000.

Some of the data presented in this thesis were obtained with similar cavities, fabricated with the same FIB and can be regarded as direct successors of this work, striving to improve cavity characteristics such as mode structure and quality factor where possible.

2.4 From single cavities to photonic molecules

As part of the open cavity improvement, Chapter 5 of this thesis presents coupled open cavities. While the results can be appreciated without historic context, a brief exposition of similar works with different cavity systems is relevant at this point.

Due to the outlined ability of a cavity to confine light in discrete photon states optical microcavities have been coined ‘photonic atoms’. A natural progression was to extend the picture from single structures to arrays and chains of optical cavities to create ‘photonic molecules’ (PM). These molecules can be used to create optical supermodes with variable degrees of coupling between specific modes, which could in principle be used to facilitate the adaptable ‘wiring’ between the qubits of a quantum processing network. One of the easiest topologies is a coupled-resonator optical waveguide (CROW), which has been studied in depth over the last decade [89, 90].

¹⁰The spectral distance between longitudinal modes is the free spectral range, which decreases with increasing cavity length (top and bottom in Fig. 2.8a).

¹¹I will give a more comprehensive picture of the states in the next chapter.

Such a design would additionally allow micrometer sized applications for high-sensitivity refractive index [91], stress [92] and rotation measurements [93]. Another strong motivation for current coupled cavity research lies in utilising the unconventional photon blockade with a weakly non-linear medium for two coupled modes for single photon creation [94].

Fig. 2.9 shows different structures to enable a coupling between adjacent cavity modes. While all designs utilise interfacing via evanescent field coupling the variety in shape and possible topologies is visible. A single diatomic PM emanates all the basic physical properties that will be used in bigger networks and so a thorough understanding is valuable. The similarity between diatomic chemical and photonic molecules consists in the hybridised nature of orbital and photonic states respectively, giving rise to in-phase bonding and out-of-phase anti-bonding super modes [95].

In 2011, Vasconcellos et al. studied coupled micropillars with a range of interpillar distances and diameters. Based on the data they tracked the mode evolution as a function of the distance and found polarisation splittings of order of tens of μeV s for highly elliptical configurations [96]. More studies of coupled cavities as a tool to control the coupling to single QDs [97] and create long distance coupled states between two cavities with the help of a wave guide [98] have been published recently.

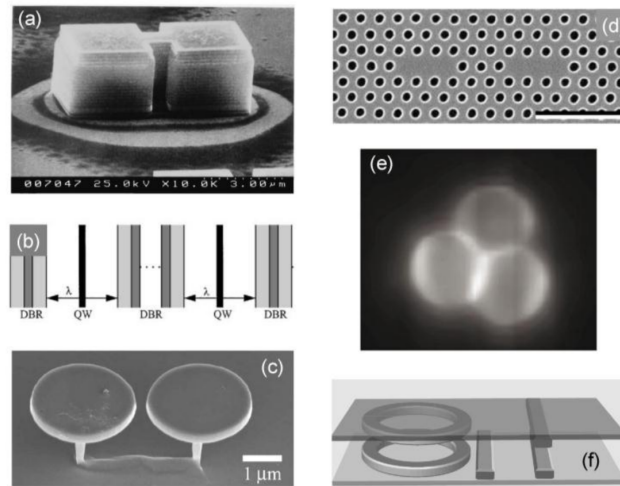


FIGURE 2.9: **Realisations of photonic molecules:** a) square-shape photonic dots coupled via a semiconductor bridge, b) planar Fabry-Pérot cavities coupled through a partially-transparent Bragg mirror, c) whispering-gallery mode microdisks side-coupled via an airgap, d) closely located defects in a photonic crystal membrane, e) triangular photonic molecule composed of touching microspheres, f) vertically coupled microrings. (reproduced from review article [99])

3 Theoretical foundations

The central equation for this thesis is the expression for the coupling energy $\hbar g$ between a cavity mode with volume V and an electronic state with a transition dipole moment μ :

$$\hbar g = \frac{1}{3} \mu \left(\frac{\hbar \omega}{2 \varepsilon_0 V} \right)^{\frac{1}{2}} \quad (3.1)$$

As will be seen later, the factor $\frac{1}{3}$ originates in the orientation of the dipole relative to the electric field, μ contains information about the wavefunction of the electronic states and the factor $E_\omega = \left(\frac{\hbar \omega}{2 \varepsilon_0 V} \right)^{\frac{1}{2}}$ quantifies the vacuum electric field per photon. The first part of this chapter focuses on μ by describing excitonic transitions in nanocrystals. In the second part light fields in confined spaces will be introduced and an expression for the mode volume V together with E_ω is derived. With these foundations the implications of Eq. 3.1 can be explored to describe the coupling of light and matter, here summarised in the exchange rate g , in the third and last part of this chapter.

3.1 Semiconductor nanocrystals

The theoretical description of nanocrystals, in particular quantum dots, has been developed over the last decades and several commonly used models describe the electronic properties in good detail. Here a very brief introduction into the nature of the transitions that lay at the center of this thesis is given. The reader is referred to the extensive literature on the subject at the end of each section.

3.1.1 Energy bands and solid state transitions

A semiconductor in bulk form is classified by its band structure, which emerges from the hybridisation of atomic orbitals of the underlying crystal. In particular the energy and momentum difference between valence band maximum and conduction band minimum, that is the band gap energy and the direct or indirect nature of the transition are the main parameters for the description. Interband transitions lead to a finite absorption cross section for photons with an energy exceeding the band gap.

The key observation that distinguishes nanocrystals from the bulk material, is that as the size of the crystal is reduced the energy of its lowest energy state increases, that is the photoluminescence color shifts to the blue. This phenomenon is straightforwardly understood by the ‘particle in a box’ model, where the energy of

the n -th excited state is given as $E(n) = \frac{\hbar^2 \pi^2 n^2}{2md^2}$, where d is the side length of the box and m is the mass of the particle. Klimov gives a comprehensive introduction to the different theoretical approaches to obtain the energy structure and electron-hole wavefunctions in nanocrystals, starting from a ‘particle-in-a-sphere’ model with a constant potential over the implementation of a band structure within the effective mass approximation [41]. This approximation emerges from the parabolic shape of band maxima, whose curvature can be quantified by the inverse of the effective electron or hole mass.¹ More advanced models exist and frequently involve expanding the parabolic shape of the bands in orders of k and applying nondegenerate perturbation theory to account for effects like spin-orbit coupling between the bands ($\mathbf{k} \cdot \mathbf{p}$ method and Luttinger Hamiltonian) [41].

Fig. 3.1A presents a schematic of the band structure for metal and semiconductor in bulk, nanocrystal and atomic shape. The area below the Fermi energy is shaded and denotes band regions with occupied electron states. The band occupation interestingly explains why semiconductor nanocrystals show a stronger size effect than metals: For a semiconductor the lowest and highest energy states in conduction and valence band contribute to the optical spectrum, which is thus sensitive to a change of the states energy.² For a metal the edge states do not contribute to transitions and thus variations in size have little effect on the optical properties.

3.1.2 Density of electronic states in different dimensions

Panel B in Fig. 3.1 shows the density of electronic states within one band. As the dimensionality of the idealised matter block is reduced the shape of the density evolves from inversely parabolic to fully quantised.³ The spacing of the quantised states results from the size in the reduced dimension. The occupation of each band is then given as the product of the electronic states and the Fermi distribution for the specific temperature.

¹Free electrons have a parabolic relation between energy and wavevector $E = (\hbar^2/2m)k^2$ and one can regard the reciprocal mass $1/m$ as the curvature of the energy-wavenumber dispersion. In a semiconductor, the band maxima and minima can be approximated as parabolas with effective masses m^* , a concept which will be encountered frequently in later chapters in the form of heavy and light hole transitions. Reduced effective masses of $m^* \approx 0.05m_e$ are typical for most semiconductors.

²A sizeable change in energy structure for atom numbers of order 10^4 is seen for semiconductors compared to 10^2 for metals.

³The analytical form of the density of states is derived in Section B.8 of the physical compendium.

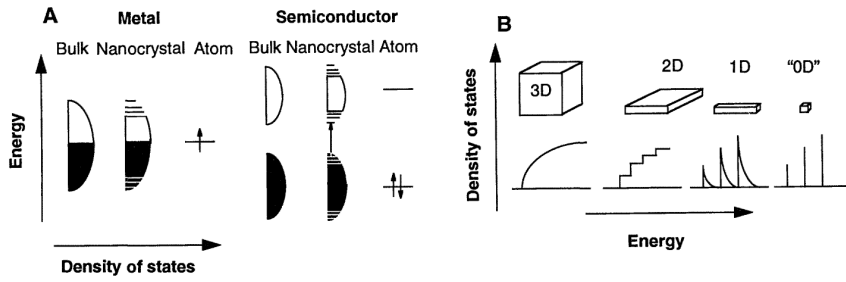


FIGURE 3.1: **Density of states in low dimensional materials.** A) Schematic illustration of the density of states in metal and semiconductor clusters. B) Density of states in one band of a semiconductor in which an ideal semiconductor is presented as a function of its dimensionality. (from [36])

3.1.3 Excitons and transition dipole moments

Within the simple band picture presented above the lowest allowed transition has the energy of the band gap as long as the dimensions of the crystal are large enough. In many systems this is not the case however and bound states within the band gap are visible upon spectroscopy. Later chapters will almost exclusively treat such bound states, which are called excitons and consist of bound electron-hole pairs with a binding energy of E_b . Typically one differentiates excitons depending on the magnitude of E_b relative to the confining potential U :

In the weak confinement case $E_b \gg U$ and thus the wavefunction of the electron-hole pair decomposes into a center-of-mass and relative motion. Here the exciton state has hydrogen-like hole and electron wavefunctions Ψ_h and Ψ_e with energy levels $E_{\text{exc}}(n) = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a_0n^2}$ and is thus sufficiently well known that a detailed treatment is omitted at this point.

In the strong confinement case, $E_b \ll U$ and the confining potential cannot be treated as a perturbation. In fact the Coulomb interaction now acts perturbatively on the states dominated by U . The electron-hole state wavefunction thus results from the shape of the confining potential - typically this is the case for colloidal quantum dots and nanoplatelets. In first approximation, the groundstate $|\Psi_h, \Psi_e\rangle$ of the electron-hole pair is simply given by the product of electron and hole single-particle states of lowest energy in the structure.⁴

One further distinction can be made on the basis of the exciton Bohr radius a_0 relative to the lattice constant a of the hosting semiconductor:

- Frenkel-excitons ($a_0 < a$): The exciton Bohr radius is smaller than the lattice constant and the exciton is bound to specific lattice sites. It is commonly found in molecular solids and organic dyes and has a relatively low mobility.

⁴The weak and the strong confinement case can be equally defined by the size of the exciton Bohr radius a_0 relative to the confinement length d : For $a_0 \ll d$ the exciton is weakly confined and the dynamics of the electron hole-pair is dominated by the Coulomb attraction. For the opposite case $a_0 \gg d$ strong confined exciton states emerge and confinement effects dominate.

- Wannier-Mott excitons ($a_0 > a$): The exciton wavefunction spans multiple lattice sites and the exciton moves within the crystal. It is prevalent in crystalline semiconductors and has a relatively large mobility.

An important parameter to estimate the strength of an optical transition is the transition dipole moment. It is defined as

$$\mu = \langle \Psi_{\text{final}} | e\mathbf{r} | \Psi_{\text{initial}} \rangle = \langle \Psi_{\text{h}}, \Psi_{\text{e}} | e\mathbf{r} | \Psi_{\text{e, valence}}, \Psi_{\text{h, conduction}} \rangle \quad (3.2)$$

Here $|\Psi_{\text{e, valence}}, \Psi_{\text{h, conduction}}\rangle$ is the product state of free valence band electron and conduction band hole wavefunction and $\mathbf{r}$ is the position operator. A large transition dipole moment thus implies a large overlap between the free and bound particle wavefunctions⁵ and can be estimated experimentally. In Section 3.4.4 a relation for the interaction strength of cavity photons with excitons is derived, which involves the transition dipole moment.

Another phenomenon relevant for this thesis is the occurrence of other electron-hole complexes, such as the biexciton (two bound electron-hole pairs with opposite spin orientation) and charged excitons, also called trions, where an additional electron or hole is bound to an exciton. In general the binding energy of such multi-particle states is positive thus lowering its energy.⁶

For the purpose of strongly coupled exciton-photon systems, the energy splitting between multi-particle and single exciton states is of major importance, as it must exceed the coupling energy between cavity mode and exciton to allow hybridisation with single exciton particle properties in the resulting polariton state.

3.1.4 Excited state lifetime and linewidth

An exciton (or multi-particle state from above) will dissociate after a typical time that is called the exciton lifetime or the excited state lifetime. In particular the lifetime τ is given as the inverse of the sum of the decay rates γ_i of a given state: $\tau = (\sum_i \gamma_i)^{-1}$, where the integer i enumerates the decay channels. One decay channel, which is of fundamental importance for this work is the radiative decay channel, in which a photon is emitted during relaxation. If γ_{rad} is the associated decay rate the quantum efficiency of the state may be defined as $\eta = \frac{\gamma_{\text{rad}}}{\gamma_{\text{rad}} + \gamma_{\text{non-rad}}}$. Here $\gamma_{\text{non-rad}}$ is a collective channel for all non-radiative dissipation processes.

For homogeneous transitions, the photoluminescence lineshape will be a Lorentzian with a FWHM of $\Gamma = \frac{2\pi}{\tau}$, which is a direct result of the energy-time uncertainty, referred to as the natural broadening. Many times the lineshape will show additional

⁵In fact the overlap integral takes the position operator into account, which has an odd parity. Since the integral over an odd (even) function with symmetric limits returns a zero (non-zero) value, selection rules emerge which allow transitions depending on the parity of initial and final state.

⁶The magnitude of the biexciton binding energy primarily depends on the Coulomb interaction (or confinement potential in the strong confinement case) and on the correlation between the two excitons, that is the exchange interaction, which can even result in negative values ('biexciton anti-binding').

broadening from inhomogeneous sources, of which most have local nature such as lattice phonons or additional charge carriers in the vicinity of the emitter. Most of the above concepts will be revisited in the next sections in the framework of optical cavities, where a similar nomenclature is used and which is the focus of this thesis.

For a more in-depth exposition of the theoretical treatment of nanocrystals I refer the reader to the books by Klimov [41] and Efros [100]. For the underlying semiconductor band theory the books by Kittel [101] and Singleton [102] give comprehensive introductions.

3.2 Electric fields

The following section provides a brief introduction to photon statistics and Gaussian beams in free space. A short introduction to Maxwell's equation is given in Section B.1 of the physical compendium. Relevant topics are presented comprehensively - for a more extensive derivation that exceed the scope of this thesis the inclined reader is referred to the text books by Loudon [103], Jackson [104] and Cohen-Tannoudji [105].

3.2.1 Photon statistics

Realistic electromagnetic fields are composed of multiple frequency components with varying phase relationships and amplitudes. The characterisation of such light fields is best done by statistical measures, such as correlation functions between two beams or the autocorrelation of a beam itself. A commonly encountered statistical instrument is the second-order autocorrelation function $g^{(2)}(\tau)$ which is defined as

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2} = \frac{\langle E^*(t)E^*(t+\tau)E(t+\tau)E(t) \rangle}{\langle E^*(t)E(t) \rangle^2} \quad (3.3)$$

Here the brackets denote the average values of the arguments⁷. For classical light fields one can show with Cauchy's inequality that

$$g^{(2)}(0) \geq 1 \quad \& \quad g^{(2)}(\tau) \leq g^{(2)}(0) \quad (3.4)$$

Here I have only used that $I(t)$ is a real, non-negative quantity. In case of quantum light fields, where the fields are written as sums of creation and annihilation operators for single modes, this scenario changes and one can obtain

$$g^{(2)}(0) \geq 1 - \frac{1}{\langle n \rangle} \quad (3.5)$$

⁷For ergodic systems time averages and statistical averages are equivalent.

Here n is the occupation number of the single mode for $\langle n \rangle \geq 1$. For a pure number state $\langle n \rangle = n$ and $g^{(2)}(0)$ decreases rapidly for low occupation numbers - in particular a value $g^{(2)}(0) < \frac{1}{2}$ can only be obtained for a single photon state.

In general one compares the width of the photon number distribution of a light field with a Poisson distribution⁸ which has a variance of $(\Delta n^2) = \langle n^2 \rangle - \langle n \rangle^2 = \langle n \rangle$ and thus $g^{(2)}(0) = 1$. For quantum light fields with $g^{(2)}(0) < 1$ one then speaks of sub-Poissonian or anti-bunched light and for $g^{(2)}(0) > 1$ the field is said to have super-Poissonian or bunched characteristics.

3.2.2 Gaussian beams

Maxwell's equations⁹ can be used to derive an equation that describes electromagnetic waves. For monochromatic fields the Helmholtz equation Eq. B.5 directly follows and is a very general description of the spatial electric field distribution and is solved by spherical and plane waves alike. Inspired by the existence of collimated beams in experiments, it is constructive to investigate field distributions centered around a propagation axis for which the z axis ($\mathbf{k} \parallel \hat{\mathbf{z}}$) is a common arbitrary choice. To find a mathematical expression for such beams is essential for this thesis, as modes of cavities with concave mirrors are most easily described by them.

Demanding a product state of the form $E(x, y, z) = E_0 \chi(x, z) \Psi(y, z) \exp(ikz)$ and a slowly varying envelope in this direction (i.e. $kE \ll \frac{\partial E}{\partial z}$), the paraxially approximated Helmholtz equation can be written as:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + 2ik \frac{\partial}{\partial z} \right) E(\mathbf{r}) = 0 \quad (3.6)$$

Finding solutions to Eq. 3.6 is now an algebraic exercise without further physical insights presented in many text books (eg. [106]). The choice of coordinate system governs the symmetries of the solutions and should be adapted to the experimental situation. In cartesian coordinates one obtains Hermite-Gauss beams with the explicit form:

$$E_{n,m}(x, y, z) = \frac{E_0}{w(z)} N_{n,m} \mathcal{H}_m \left(\frac{\sqrt{2}x}{w(z)} \right) \mathcal{H}_n \left(\frac{\sqrt{2}y}{w(z)} \right) \exp \left(-\frac{x^2 + y^2}{w(z)^2} \right) \exp(i\phi_{n,m}(x, y, z)) \quad (3.7)$$

with a normalisation factor $N_{n,m} = (2^{n+m-1} n! m! \pi)^{-\frac{1}{2}}$, a phase factor

$$\phi_{n,m}(x, y, z) = \frac{k(x^2 + y^2)}{2R(z)} - (n + m + 1) \arctan\left(\frac{z}{z_R}\right) + kz$$

⁸Eq. A.3 in the mathematical compendium.

⁹Eq. B.1 in the physical compendium.

and the Hermite polynomials $\mathcal{H}_m(x)$. The z -dependent functions $w(z)$ and $R(z)$ are the beam waist and radius of curvature of the beam front with the analytical form

$$w(z) = w_0 \sqrt{1 + (z/z_R)^2} \quad \& \quad R(z) = z(1 + (z_R/z)^2)$$

The Hermite polynomials $\mathcal{H}_m(x)$, named after the french mathematician Charles Hermite, arise as solutions of a differential equation directly obtained from Eq. 3.6 and are well known in the physical literature.¹⁰ They, together with the Gaussian factor $\exp(-\frac{x^2+y^2}{w(z)})$ give the beams their name and have interesting mathematical properties which will be explored in Section B.5. Here it suffices to point out that m and n are the transverse excitation numbers, which respectively count the number of nodes in the x - and y direction. For most applications in physics the ground mode with $m = n = 0$, which is often denoted as the $\text{TEM}_{0,0}$ mode (Transverse Electro-Magnetic), is the most important state of a Gaussian beam for technological applications.

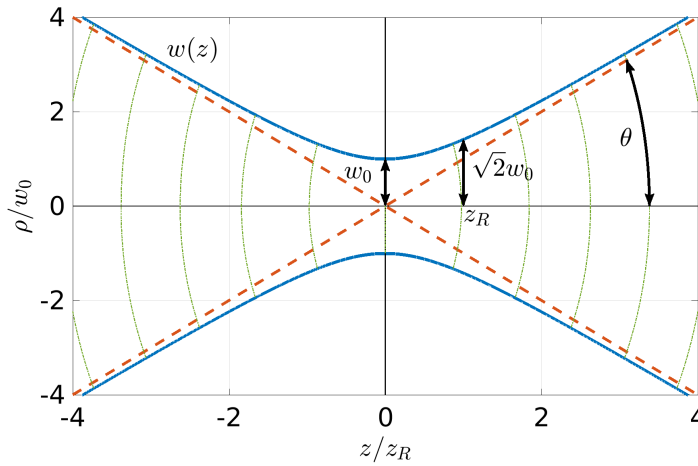


FIGURE 3.2: **Parameters of a Gaussian beam.** The beam waist $w(z)$ is shown with the blue continuous line and has a minimum at $z = 0$ where $w(0) = w_0$. The beam is fully characterised by the two quantities w_0 and the Rayleigh length z_R and has a divergence $\theta = w_0/z_R$ (sketched by the red-dashed line). The green continuous lines show the radius of curvature of the wavefront.

Since Gaussian beams are omnipresent in modern optics and are of particular importance for the work presented in this thesis, it is worth exploring the analytical form given in Eq. 3.7 further together with the diagram presented in Fig. 3.2:

The first exponential term gives the beam its Gaussian profile in the transverse plane, which has a width of $2w(z)$. The smallest beam waist w_0 is reached at the focal point of the beam. It is directly connected to the Rayleigh length $z_R = \pi w_0^2/\lambda$ at whose longitudinal position the beam waist is $2\sqrt{2}w_0$ and the central intensity of

¹⁰As an example, they appear as part of the wavefunctions of the quantum mechanical harmonical oscillator.

the beam has dropped to half of its focal intensity. Note that the longitudinal intensity profile has a Lorentzian lineshape ($\propto 1/w(z)^2$) and the relationship between increasing waist and decreasing intensity ensures energy conservation.¹¹

Another interesting quantity is the divergence θ_d of the beam, which is obtained by evaluating $\theta_d = \lim_{z \rightarrow \infty} \arctan(\frac{w(z)}{z}) = \arctan(\frac{\lambda}{\pi w_0}) \approx \frac{\lambda}{\pi w_0}$, where the approximation is valid for $w_0 > \lambda$ (red dashed lines in Fig. 3.2). It importantly reveals the inverse relationship between the beam waist and the divergence of the beam. The thin green dashed-dotted lines in Fig. 3.2 show the wavefronts of the beam, defined as the surfaces with constant phase $\phi_{n,m}(x, y, z) = 2\pi q$, plotted here for multiple longitudinal mode indices q . Note that the radius of curvature $R(z) = z(1 + (z_R/z)^2)$ goes to infinity for $z \rightarrow 0$ and $z \rightarrow \infty$, which corresponds to plane waves in the longitudinal direction. The minimal radius of curvature is attained at z_R where one finds $R(z_R) = 2z_R$. The last term in the expression for $\phi_{n,m}(x, y, z)$ is called the Gouy-phase $\zeta(z) = \arctan(z/z_R)$ and causes an accumulated extra phase of π when crossing through the mode waist.¹²

Solving Eq. 3.6 in cylindrical coordinates $\{x, y\} \rightarrow \{\rho, \phi\}$ one finds an equivalent set of beams with cylindrical symmetry, the Laguerre-Gauss modes with the radial and azimuthal index p and l . Formally one can show that each Hermite-Gauss mode can be expressed as a sum of Laguerre-Gauss modes and vice versa [108]. Fig. 3.3 shows the transverse intensity distribution $I(x, y, 0) = E(x, y, 0)E^*(x, y, 0)$ for the first nine Hermite- and Laguerre-Gaussian modes. Both sets of modes form an orthonormal basis set in the transverse plane, a fact that I will use in Section 3.3.6 for the approximation of modes for resonators with arbitrary mirror shape.

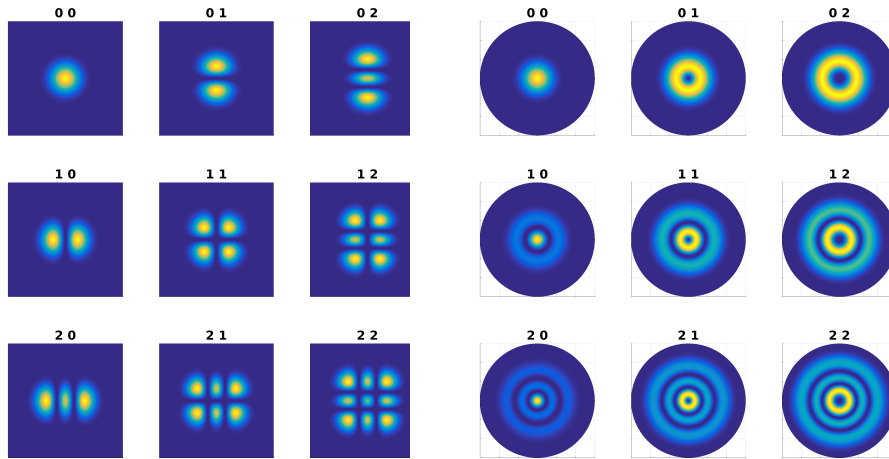


FIGURE 3.3: **Transverse intensity distribution for the first nine base states for Hermite- and Laguerre-Gauß modes.** The numbers above each plot give the respective mode numbers (m, n) for the Hermite-Gauss modes and (p, l) for the Laguerre-Gauss modes.

¹¹This is easily proven by calculating the energy flux $P(z) = \frac{1}{2}c\epsilon_0 \int_A dA E(x, y, z)E^*(x, y, z)$ along the longitudinal axis, which is constant. Here A is the area of the transverse plane.

¹²Its physical origin lies in the transverse spatial confinement, discussed by Feng et al. [107].

3.3 Confined fields

The previous section treated electromagnetic waves in free space. While the derivation of the Gaussian beam and in particular the paraxial approximation implied a directionality of the beam, no dielectric boundaries were introduced which could lead to interference effects and stable electromagnetic modes. In this section the notion of an optical resonator is established - starting from a simple one-dimensional picture, stability conditions for cavity modes are derived and a modemixing formalism is presented that can be used to predict the modes of mirrors with arbitrary shape.

3.3.1 Transfer-Matrix-Method in one dimension

Maxwell's equation in a spatially homogeneous medium with refractive index n can be combined to give the well known wave equation for the electric field.¹³ After writing down a general solution for the electric field and defining a vector with the amplitudes of electric and magnetic field it is constructive to define a transfer matrix $\mathcal{T}_L$ that enforces the propagation through a layer with refractive index n and thickness L . This matrix can be applied to a resonator as depicted in Fig. 3.4 and by demanding a mode that satisfies the amplitudes given above the arrows in the plot one finds:¹⁴

$$r_1 r_2 e^{i2kL} = 1 \quad (3.8)$$

For ideal dielectric mirrors one would have $r_1 = r_2 = 1$ and thus the well known Fabry-Pérot resonance condition $kL = \pi q$ emerges, q being a natural number that is called the longitudinal mode index.

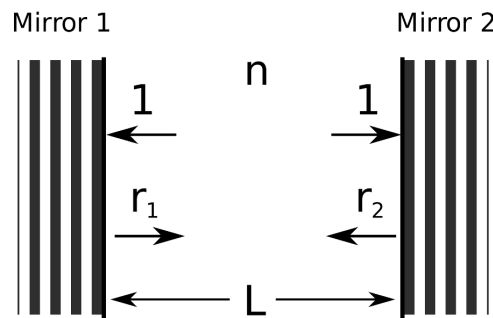


FIGURE 3.4: **Schematic of a one-dimensional resonator.** The cavity is composed of two planar mirrors with reflectivity $R_1 = |r_1|^2$ and $R_2 = |r_2|^2$ and separation L . The amplitudes of forward and backward travelling wave are given above the arrows.

Realistic mirrors have a reflectivity smaller than unity and thus $|r_i| < 1$. A typical choice for the amplitude reflection coefficient for a distributed Bragg reflector r_{DBR}

¹³Eq. B.4 in the physical compendium.

¹⁴The exact derivation is given in the physical compendium in Eq. B.5 and following.

or metallic mirror r_{Met} would be [109]:

$$r_{\text{DBR}} = \sqrt{R} e^{i(k - k_{\text{DBR}}) \frac{L_{\text{DBR}}}{n}} \quad \& \quad r_{\text{Met}} = \frac{n - n_m}{n + n_m} \quad (3.9)$$

Here R is the mirror reflectivity, $L_{\text{DBR}} = \frac{n_a n_b \lambda_{\text{DBR}}}{2(n_b - n_a)}$ is the effective length of the DBR consisting of stacks with refractive indices n_a and n_b with λ_{DBR} the central wavelength, $k_{\text{DBR}} = \frac{2\pi}{\lambda_{\text{DBR}}}$ and n_m the complex refractive index of the metal.

3.3.2 Cavity metrics

For the purpose of introducing the main characteristics of an optical cavity I set $|r_i|^2 = R_i < 1$. For this choice Eq. 3.8 has no solutions for $kL \in \mathbb{R}$. Instead one finds that k must be complex with

$$k = \frac{\pi q}{L} - i \frac{\ln(\sqrt{R_1 R_2})}{2L} := k_{\text{cav}} + i \frac{\kappa}{c} \quad (3.10)$$

This equation directly follows from the definition of the complex exponential function which is 2π periodic. κ can be understood as the decay rate of photons from the cavity (the factor of c enters from the relation $kc = \omega$). To understand the temporal implications of finite losses in the cavity, it is instructive to work out the number of photon round trips n_{rt} after which the field intensity (ie. the number of photons) in the cavity has decayed to $1/e$ of its initial value. The round trip time is given by $t_{\text{rt}} = \frac{2L}{c}$ and from the imaginary part of k one obtains (the real parts cancel in the exponent):

$$\frac{|\exp(iLn_{\text{rt}}k)|^2}{|\exp(0)|^2} \stackrel{!}{=} \frac{1}{e} \quad \Rightarrow \quad n_{\text{rt}} = \frac{-1}{\ln(\sqrt{R_1 R_2})} \quad (3.11)$$

The photon lifetime, ie. the time that it takes before a fraction $1 - 1/e \approx 63\%$ of an initial number of photons in the cavity have disappeared from the mode without further external irradiant power, is now given as

$$\tau_{\text{cav}} = n_{\text{rt}} t_{\text{rt}} = \frac{-2L}{c \ln(\sqrt{R_1 R_2})} = \frac{1}{\kappa} \quad (3.12)$$

Each resonant mode in the resonator is characterised by its longitudinal mode index q . The frequency or wavelength difference between two adjacent modes with $\Delta q = 1$ is called the free spectral range (FSR) and given by evaluating the resonance condition $kL = \pi q$ with $k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{c}$ for two successive longitudinal modes:

$$\Delta\nu_{\text{FSR}} = \frac{c}{2L} \quad \& \quad \Delta\lambda_{\text{FSR}} = \frac{\lambda_1 \lambda_2}{2L} \stackrel{L \gg \lambda}{\approx} \frac{\lambda^2}{2L} \quad (3.13)$$

Additionally, it is useful to define the finesse $\mathcal{F}$ of the resonator, a figure of merit which is given as 2π times the number of photon roundtrips:

$$\mathcal{F} := 2\pi n_{\text{rt}} = \frac{2\pi}{-\ln(\sqrt{R_1 R_2})} = \frac{\Delta\nu_{\text{FSR}}}{\delta\nu} = \frac{\Delta\lambda_{\text{FSR}}}{\delta\lambda} \quad (3.14)$$

One often approximates the logarithm in the above relations with the first term of its Taylor expansion $\ln(\sqrt{R_1 R_2}) \approx \sqrt{R_1 R_2} - 1$ for highly reflective mirrors, which in particular results in $\mathcal{F} \approx \frac{2\pi}{1 - \sqrt{R_1 R_2}}$. The finesse is related to the free spectral range of the cavity at any given length by the linewidth of the resonance peak $\delta\nu = \frac{\kappa}{2\pi}$ in frequency or $\delta\lambda = \frac{\lambda^2 \kappa}{2\pi c}$ in wavelength.¹⁵ Finally I introduce another figure of merit similar to the finesse $\mathcal{F}$, namely the quality factor of a cavity mode which is defined as the ratio between the mode frequency and its linewidth:

$$\mathcal{Q} := \frac{\nu}{\delta\nu} = \frac{\lambda}{\delta\lambda} = q\mathcal{F} \quad (3.15)$$

It reaches high values for low loss cavities and can be understood more intuitively as the number of optical cycles the light field undergoes before its intensity decays to $1/e$ of its original value.

3.3.3 Cavity lineshape

In the preceding section I have established the photon decay time from the imaginary part of the wavenumber appearing for finite roundtrip losses and have defined a resonance mode linewidth $\delta\nu = \frac{\kappa}{2\pi}$. At this point it is instructive to derive the spectral shape of the cavity modes. To this end one analyses the electric field transmitted by a resonator as shown in Fig. 3.4. For the intensity ratio between incoming and outgoing fields the Airy distribution is readily found:¹⁶

$$A_{\text{out}}(\phi) = \frac{I_{\text{out}}}{I_{\text{in}}} = \frac{|E_{\text{out}}|^2}{|E_{\text{in}}|^2} = \frac{(1 - R_1)(1 - R_2)}{(1 - \sqrt{R_1 R_2})^2 + 4\sqrt{R_1 R_2} \sin^2 \phi} \quad (3.16)$$

Fig. 3.5 shows plots of Eq. 3.16 for equal mirror reflectivities ($R_1 = R_2 = R$). One finds the FWHM linewidth in units of frequency as:

$$\delta\nu_{\text{Airy}} = \frac{c}{\pi L} \arcsin \left(\frac{(1 - \sqrt{R_1 R_2})}{2\sqrt{R_1 R_2}} \right) \quad (3.17)$$

which converges to the linewidth given above for highly reflective mirrors. In this case the sine in Eq. 3.16 can be expanded close to resonance and one finds a Lorentzian

¹⁵We see from these relations that the natural unit for the free spectral range and linewidth is the frequency or wavenumber, as it is linearly related to the energy and does not depend on the absolute position, which the wavelength does. Experimentally the wavelength is directly accessible however and thus one commonly quotes the parameters in units of wavelength.

¹⁶The expression is derived in Section B.4 of the physical compendium.

lineshape:¹⁷

$$I(\nu) = \frac{1}{\pi} \frac{\delta\nu/2}{(\delta\nu/2)^2 + (\nu - \nu_q)^2} \quad (3.18)$$

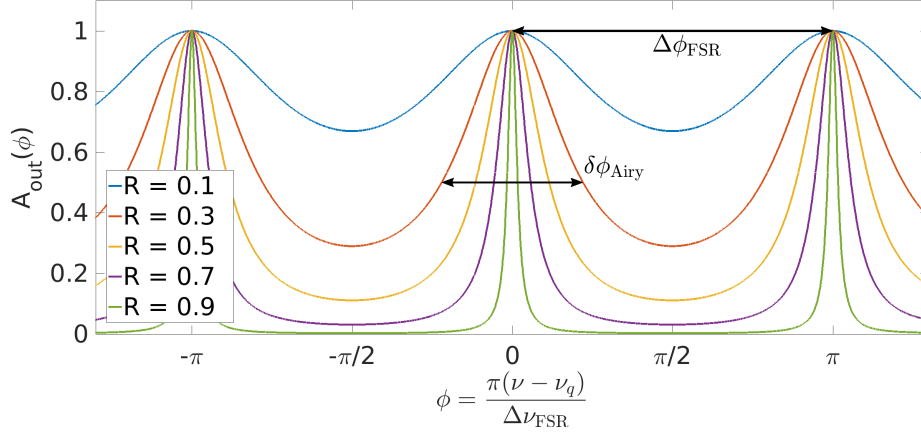


FIGURE 3.5: **Transmission of a one-dimensional resonator.** Ratio of transmitted to incident intensity of a Fabry-Pérot resonator for $R_1 = R_2 = R$. ϕ is the phase that light propagating across the cavity with length L acquires:

$$\phi = \frac{2\pi(\nu - \nu_q)L}{c} = \frac{\pi(\nu - \nu_q)}{\Delta\nu_{\text{FSR}}} = \frac{2\pi L(\lambda_q - \lambda)}{\lambda^2}.$$

3.3.4 Rough surfaces

As we have seen in the previous section, photons will escape the confinement of mirrors with reflectivity $R < 1$ by transmission through the mirror. A different origin for the finite photon lifetime in resonators is the surface roughness of the mirrors, which leads to scattering losses of the reflected beam. For the purpose of this discussion it is helpful to differentiate the total reflectance R_t into specular reflectance R_s (which obeys the law of reflection) and the diffuse or scattered reflectance R_d , so $R_d + R_s = R_t$. R_t is defined as usual as the ratio of reflected power divided by the incident radiant power. By solving the diffraction integral of a beam with incident angle θ_i off a surface with a statistical distribution of surface heights characterised by a Gaussian distribution with standard deviation σ one obtains [110]:

$$\delta_s = \frac{R_d}{R_t} = 1 - \frac{R_s}{R_t} = 1 - \exp \left[-(4\pi \cos(\theta_i) \sigma / \lambda)^2 \right] \approx (4\pi \sigma / \lambda)^2 \quad (3.19)$$

The approximation in the last step is valid if $\sigma \ll \lambda$ for normal incidence ($\theta_i = 0$). From the derivation it is evident that the above expression is only valid for normally distributed surface heights and that in general more statistical figures of the surface roughness are needed. The relevant spatial frequencies of a surface depend on the incident angle and wavelength - for normal incidence all spatial frequencies larger

¹⁷The Lorentzian lineshape is always associated with homogeneous processes, where a single dissipative channel is active. An open cavity influenced by vibrations faster than the timing resolution of the detectors will exhibit inhomogeneously broadened peaks with a Gaussian lineshape.

than $1/\lambda$ do not contribute to the scattered signal. Instead they produce evanescent fields that do not result in radiant power being scattered from the specular beam. As this section can only give a very brief overview over the basic properties of rough surfaces the inclined reader is referred to [110, 111] for a more thorough description.

3.3.5 Gaussian beam cavity modes

Instead of using the transfer-matrix method that I have used in the previous section for a planar cavity, I employ a more graphically inspired approach to derive the Gaussian beam modes. Taking Fig. 3.6 as a reference one can confirm the three relations:

$$\text{i) } z_2 - z_1 = L \quad \text{ii) } -R_1 = z_1(1 + (z_R/z_1)^2) \quad \text{iii) } R_2 = z_2(1 + (z_R/z_2)^2) \quad (3.20)$$

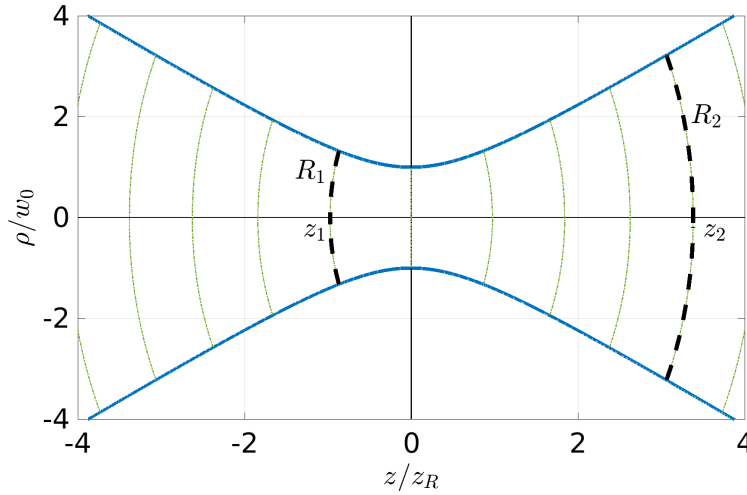


FIGURE 3.6: **Diagram of a Gaussian beam resonator.** Two confining surfaces with radius of curvature R_1, R_2 and longitudinal positions z_1, z_2 respectively match the beam wavefront curvature and lead to cavity modes.

Here I have used the definition for the cavity length and the radii of curvature of the wavefront of the Gaussian beam, which I suppose to match the physical shape of the mirrors positioned at z_1 and z_2 . Note that the radius of the first mirror is negative as it faces rightwards. Solving this system of equations for z_R and w_0 and substituting in the stability parameter $g_i = 1 - \frac{L}{R_i}$ the expressions reproduced in the

physical compendium are found (Eq. B.12). In the plano-concave resonator geometry ($R_1 = \infty, R_2 = R$) these relations simplify substantially:

$$z_R = \sqrt{L(R - L)} \quad w_0 = \sqrt{\frac{\lambda L}{\pi}} \left(\frac{R}{L} - 1 \right)^{\frac{1}{4}} \quad (3.21a)$$

$$z_1 = 0 \quad w_1 = w(z_1) = w_0 \quad (3.21b)$$

$$z_2 = L \quad w_2 = w(z_2) = \sqrt{\frac{\lambda L}{\pi}} \left(\frac{R^2}{LR - L^2} \right)^{\frac{1}{4}} \quad (3.21c)$$

In the plano-concave geometry the beam waist is thus always located at the planar mirror surface. Note that the equations imply a strict stability criterion: Since the mode waist w_0 (or the Rayleigh length z_R) must be a real, positive quantity $w_0 > 0$ ($z_R > 0$) it follows from Eq. 3.21a that $L < R$. In particular one is interested in the resonance condition for a cavity mode with mode numbers q, m , and n . For this purpose it is instructive to analyse the phase $\phi_{n,m}(x, y, z)$ of the Gaussian beam given in Eq. 3.7. A stable cavity mode will acquire an additional phase of πq for half a round trip:

$$\Delta\phi = \phi_{n,m}(0, 0, z_2) - \phi_{n,m}(0, 0, z_1) \stackrel{!}{=} \pi q \quad (3.22)$$

Employing this resonance condition and the trigonometric identities Eq. A.6 and A.7 one obtains:

$$\lambda_{q,m,n} = L \left(q - \frac{m+n+1}{2\pi} \arccos(\pm\sqrt{g_1 g_2}) \right)^{-1} \quad (3.23)$$

According to this equation, states will be $m+n+1$ degenerate¹⁸ and excited states with $m+n > 0$ will be spaced evenly with the transverse mode spacing $\Delta^t \lambda$. In the plano-concave geometry $\Delta^t \lambda$ can be used to obtain the radius of curvature of the concave feature, if the cavity length is known:

$$R = L \left[\sin \left(\frac{2\pi \Delta^t \lambda L}{\lambda_1 \lambda_2} \right) \right]^{-2} \quad (3.24)$$

This equation directly follows from Eq. 3.23 and can be used to evaluate the actual confinement radius in a cavity setup. Another relevant quantity for a cavity mode is its mode volume. For a Gaussian cavity mode it is obtained by integrating the electric field as given in Eq. 3.7 over the volume between the two mirrors. One finds that the mode volume is that of a cylinder with a radius of $w_0/2$ and a length of L :

$$V = \frac{\pi w_0^2 L}{4} = \frac{\lambda L^2}{4} \sqrt{\frac{R}{L} - 1} \quad (3.25)$$

¹⁸Hence the reference to states with the sum $n+m$.

3.3.6 Modemixing formalism

In the modemixing formalism introduced by Kleckner et al.[112] solutions of the field distribution of a cavity environment are found by solving the eigenvalue equation $\mathbb{M}|\Psi_i\rangle = \gamma_i|\Psi_i\rangle$, where $\mathbb{M}$ is the modemixing matrix which describes coupling between modes upon a single round trip within the cavity. The modemixing matrix $\mathbb{M}$ is constructed by calculating

$$\begin{aligned} \mathbb{A}_{s,t} &= \int \int_A dA \quad \psi_s^+(x, y, z) \psi_t^{-*}(x, y, z) \quad e^{-2ik\Delta_a(x,y)} \Big|_{z_a} \\ &\rightarrow \mathbb{M} = e^{-2ikL} \mathbb{A} \times \mathbb{B} \\ \mathbb{B}_{s,t} &= \int \int_B dB \quad \psi_s^-(x, y, z) \psi_t^{+*}(x, y, z) \quad e^{+2ik\Delta_b(x,y)} \Big|_{z_b} \end{aligned} \quad (3.26)$$

Here the integration areas dA and dB are two (quasi-infinite) planes positioned at longitudinal positions z_a and z_b respectively. The functions $\psi^\pm(x, y, z)$ are forward and backward propagating basis states that describe the electric field distribution. A common choice for the $\psi^\pm(x, y, z)$ are the Hermite-Gauss or Laguerre-Gauss modes introduced above. The term $\Delta(x, y)$ appearing in the exponent describes the deviation of the mirror surface from a plane positioned at z_a and z_b respectively. Fig. 3.7a shows a sketch of the cavity configuration used for the formalism in this thesis. For a planar mirror positioned at z_a one would have $\Delta_a(x, y) = 0$ and the matrix element $\mathbb{A}_{s,t}$ depends only on the basis states $\psi^\pm(x, y, z)$. In particular one finds $\mathbb{A}_{s,t} = \delta_{s,t}$ if an orthonormal basis set is used. The red shaded area in Fig. 3.7a shows the deviation of the mirror surface from a plane, which is described by $\Delta_b(x, y)$.

The integral given by Eq. 3.26 quantifies the pairwise overlap of basis states $\psi_s^+(x, y, z)$ and $\psi_t^{-*}(x, y, z)$ with the phase accumulated relative to a given plane due to the shape of the concave mirror $\Delta_b(x, y)$.¹⁹

Fig. 3.7b,c show the transverse intensity profile of a $\text{TEM}_{0,5}$ mode of a FIB-milled concave cavity as obtained by the modemixing formalism and as seen in a typical experiment. Note the difference between the mode structure of the bare Hermite-Gauss modes shown in Fig. 3.3 and the mode mixing result and the striking agreement between experiment and theory. I will use the formalism in Chapter 5 to describe the mode structure of coupled cavities and give more details about the state composition and computational routines employed there.

¹⁹I give more information about symmetry considerations and mode energy estimation within this formalism in Section B.5 of the physical compendium.

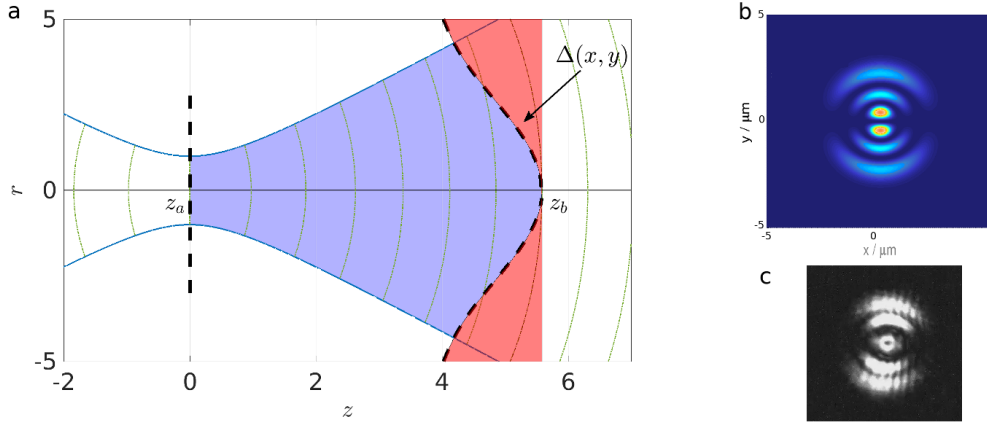


FIGURE 3.7: **Cavity mode description in the mode mixing formalism.**a) Schematics for the mode mixing formalism in this thesis. A planar mirror and a concave mirror with an arbitrary shape specified later are positioned at $z_a = 0$ and $z_b = L$ respectively. The mode waist and wavefront radius of curvature for a Gaussian beam is drawn as in the diagrams before. The blue (red) shaded area gives the mode (mirror surface relative to a plane at z_b defined by $\Delta(x, y)$). b) Transverse intensity profile of $TEM_{0,5}$ mode as obtained by the mode mixing formalism. c) Optical micrograph of a $TEM_{0,5}$ in a FIB milled cavity in a laser transmission experiment.

3.4 Light-matter coupling

After introducing excitonic transitions and confined light fields a good basis is given to develop the main concepts of light-matter interactions employed later in the thesis. I begin with a linear dipole or Lorentz oscillator, an entirely classical picture with which one can derive a description of strongly coupled polariton states.

In the process of the derivation I obtain a criterion for the weak and the strong coupling regime of cavity interactions. Depending on the theoretical framework (quantum vs. classical), this criterion imposes different bounds on the dissipation rates relative to the coupling strength, which will be highly relevant for the experimental results.

The section is closed with a quantum mechanical description of the two coupling regimes: First I contrast the classical polariton dispersion with the quantum version to then show how Fermi's golden rule predicts the strength of the Purcell effect in the weak coupling regime.

As this thesis can only give a brief overview over such foundational topics, I refer the reader to the extensive literature in the field, in particular to the books by Cohen-Tannoudji [105, 113] (for a mathematical overview of the structure of QED), Meystre [53] (for a concise exposition with applied elements) and Haroche [52] (for a detailed historical exposition of our understanding of light-matter coupling).

3.4.1 Linear response theory

In this simple description the atom is modelled as an infinitely heavy positively charged nucleus with a surrounding negative charge cloud (ie. an electron) which is allowed to oscillate about its equilibrium position. The electric susceptibility χ_e of a material characterised by N damped oscillators per unit volume can be deduced as:²⁰

$$\chi_e = \frac{Ne^2}{2\varepsilon_0 m \nu} \frac{1}{(\omega - \nu - i\beta)} = \frac{Ne^2}{2\varepsilon_0 m \nu} \frac{\omega - \nu + i\beta}{(\omega - \nu)^2 + \beta^2} \quad (3.27)$$

The expression relies on the assumption of an ensemble of completely isolated, identical oscillators with Eigenfrequency ω driven by a light field with frequency ν . Fig. 3.8 shows the real and imaginary parts of the electric susceptibility $\chi_e = \varepsilon - 1$ as a function of the frequency difference $\nu - \omega$.

Real and imaginary part of this function describe different effects: $\Re(\chi_e)$ is responsible for refraction, ie. change the phase velocity of waves propagating in the medium, and $\Im(\chi_e)$ describes dissipative effects such as absorption and gain.²¹

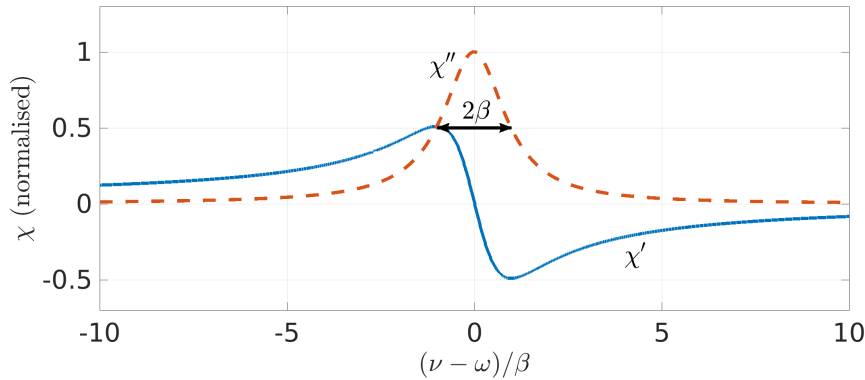


FIGURE 3.8: **Dielectric response in the linear dipole theory.** Electric susceptibility corresponding to a classical damped harmonic oscillator driven by the electric field as given by Eq. 3.27. The real part χ' (blue, continuous line) causes refractive effects, whereas dissipative effects are described by the imaginary part χ'' (red, dashed line)

Note that $\Im(\chi_e)$ has the shape of a Lorentzian with a linewidth of β , a parameter that was introduced in Eq. B.27 as a damping constant. Since I only introduced this parameter phenomenologically, it is worth discussing its physical origin. First of all it is noteworthy that classically the negative charge cloud described by $x(t)$ should collapse onto the positive point charge (the nucleus). The fact that it does not lies at the heart of quantum mechanics and the quantised nature of electronic states. The oscillating electron (or quantum-mechanically arguing, the wavefunction thereof) is however constantly interacting with both its own electric field and, in the quantum theory, with the background of vacuum fluctuations. Classically the damping can

²⁰The expression is derived in Section B.6 of the physical compendium.

²¹Formally this can be seen by replacing the vacuum wavenumber k_0 by the wavenumber in the medium $k = k_0 n = k_0 \sqrt{1 + \chi_e}$ in the solutions of the wave equation.

be conceptualised as a friction of the electron with the field emitted by itself (since an accelerated charge irradiates, as described by the Larmor formula). Quantum mechanically the interpretation is more subtle: Both the vacuum fluctuations and the density of electronic states accessible to the electron contribute to the ‘friction’ captured by the parameter β , leading to finite linewidths and lifetimes of electronic states around us.

3.4.2 Linear response theory within the Transfer-Matrix-Method

The data presented in this section has been published in the peer-reviewed journal Scientific Reports under the title “Room-temperature exciton-polaritons with two-dimensional WS₂” in September 2016 [114].

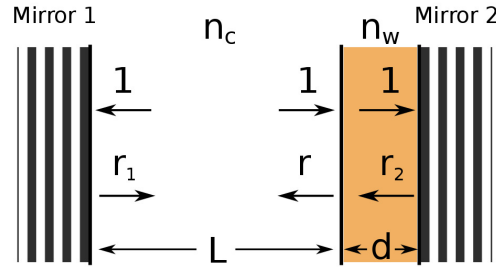


FIGURE 3.9: **A thin dispersive medium inside a planar microcavity.** Schematics of planar cavity with mirror separation $L + d$ and refractive index n_c for the cavity medium and n_w for the thin dispersive medium. The arrows give the amplitudes of forwards and backwards propagating waves as introduced in the text.

In this section I strive to find the resonant modes in a cavity with a thin dispersive layer characterised by its electrical susceptibility of the form given in Eq. 3.27. The thin layer is readily parametrised by its thickness d and the frequency W , which is proportional to the interaction strength and connected to microscopic material parameters by $W = \frac{Ne^2}{2\varepsilon_0 m\nu}$. By employing a transfer matrix approach similar to the one described in Section 3.3.1 with a resonator sketched in Fig. 3.9 one obtains for the wavenumber of the modes:²²

$$k_{1,2} = \frac{1}{2} (k_p + k_x - i(\gamma_p + \gamma_x)) \pm \sqrt{V^2 + \frac{1}{4}(k_p - k_x + i(\gamma_x - \gamma_p))^2} \quad (3.28)$$

Here k_p, k_x and γ_p, γ_x are the wave number and linewidth of the cavity mode and oscillator respectively. An additional parameter that I have introduced is $V^2 = \frac{Wk_d d}{Ln_c^2}$ with k_d the wavenumber in the thin dispersive medium. Commonly one evaluates the system on resonance ($k_p = k_x$) and compares the terms of the radicand. Then $2V < |\gamma_x - \gamma_p|$ marks the weak coupling regime, in which no mode splitting occurs and $2V > |\gamma_x - \gamma_p|$ falls into the strong coupling regime with finite normal mode splitting. Here $k_{1,2}$ are the wavenumbers of the two polariton branches. The

²²I reproduce the derivation in Section B.7 of the physical compendium.

quantity $\hbar\Omega = 2\hbar g = 2\hbar\sqrt{V^2 - \frac{1}{4}(\gamma_x - \gamma_p)^2}$ is called the Rabi splitting and is the energy difference between the two polariton states. Fig. 3.10c shows the dispersion described by Eq. 3.28 for the weak (dashed blue line) and strong coupling regime (blue continuous line) as a function of the detuning $\delta = k_x - k_p$. I will discuss the nature of the coupled system in the following sections, in particular light will be shed on the transition between the two coupling regimes. In Chapter 6 the implications of the linewidth contribution to the Rabi splitting will be explored on the basis of experimental data.

3.4.3 Criteria for different coupling regimes

In the last section I have derived a criterion to distinguish two coupling regimes, the weak coupling regime where the dynamics of the system are governed by exponential decay and the steady-state spectrum displays a single peak²³ and the strong coupling regime, where the energy between the two systems is oscillating and the steady-state spectrum exhibits two split peaks²⁴ (see Fig. 3.10a,b). The steady state spectra and the temporal dynamics of both regimes are connected to each other via Fourier transformations and shall not be explored further at this point. Instead it is instructive to elucidate differences in the coupling criterion inspired by a recent work by Rodriguez [115].

One criterion (I), commonly found in classical formalisms of two coupled, damped oscillators, is that the energy exchange rate should exceed all loss rates. In fact an even more stringent criterion demands that for a strongly coupled system the Rabi splitting should exceed the sum of the linewidths of both constituents.

A different criterion (II), which is the one that has been derived above, demands that the energy exchange rate should be larger than the difference of the loss rates of the two constituents. According to this criterion, two systems with identical loss rates (ie. cavity mode and exciton state with the same linewidth) would be strongly coupled on resonance, regardless of the effective coupling strength.

In this thesis I adopt a position between those two extreme viewpoints and argue that for a strongly coupled system the splitting should be resolvable, that is the splitting should exceed each linewidth individually. For such a system energy will oscillate and photons emitted from a state can be assigned to that state. For systems deep in the strong coupling regime, all three definitions will result in the same conclusion. For the systems described in this thesis however, some results would not fall into the strong coupling definition of criterion I and almost all results (even a non-result from my point of view) would satisfy criterion II.

²³For $2V < |\gamma_x - \gamma_p|$ the radicand in Eq. 3.28 is negative such that the square root term describes a decaying field intensity.

²⁴For $2V > |\gamma_x - \gamma_p|$ the radicand in Eq. 3.28 is positive and two polariton branches form.

3.4.4 Coupling strength

The splitting condition for a coupled cavity - oscillator system has been presented in the previous section, which provides a good starting point to discuss the connection between the classical and quantum mechanical description. In quantum mechanical treatments the interaction between an electronic system characterised by an initial and final state $|i\rangle$ and $|f\rangle$ is given by the dipole interaction Hamiltonian $\mathcal{H}_{int} = e\mathbf{r} \cdot \mathbf{E}$ (the dot product of the position vector $\mathbf{r}$ and the electric field $\mathbf{E}$ times the charge of the electron e). For the matrix element $\mathcal{V}$ one thus finds

$$\mathcal{V} = \langle f | \mathcal{H}_{int} | i \rangle \approx e \langle f | \mathbf{r} | i \rangle \cdot \mathbf{E} = \xi \mu E \quad (3.29)$$

In the approximative step it is assumed, that the electric field varies little over the extent of the states described by $|i\rangle$, $|f\rangle$, ie. that it behaves like a constant and can be pulled out of the integral.²⁵ In the last step the quantity μ is introduced, which is the transition dipole moment $e \langle f | \mathbf{r} | i \rangle \equiv \mu$ established before in Eq. 3.2. To abbreviate, the projection of the two vectors is can be expressed as $\xi = \frac{|\mathbf{r} \cdot \mathbf{E}|}{|\mathbf{r}| |\mathbf{E}|}$. The interaction strength is now commonly written as a frequency g :

$$g = \xi \mu E / \hbar \quad (3.30)$$

The rate of exchange between the two systems is thus a linear function of the transition dipole moment and the electric field. In a cavity with mode volume V and frequency $\nu = \omega/2\pi$ the ‘electric field per photon’ is given as:²⁶

$$E_\omega = \left(\frac{\hbar \omega}{2\epsilon_0 V} \right)^{\frac{1}{2}} \quad (3.31)$$

which results in a coupling energy of

$$\hbar g = \xi \mu \left(\frac{\hbar \omega}{2\epsilon_0 V} \right)^{\frac{1}{2}} \quad (3.32)$$

Eq. 3.32 is the fundamental equation quoted at the beginning of the section which motivates the use of low mode volume cavities for the enhancement of the light-matter interaction. Note that the prefactor ξ can be averaged to $\xi = 1/3$ for random dipole orientations.

²⁵This is justified by the typical exciton Bohr radius, which is for example $a_0 \approx 5.5$ nm in CdSe and therefore much smaller than the wavelength in the visible.

²⁶The derivation of the expression is presented in Section B.4.1 of the physical compendium.

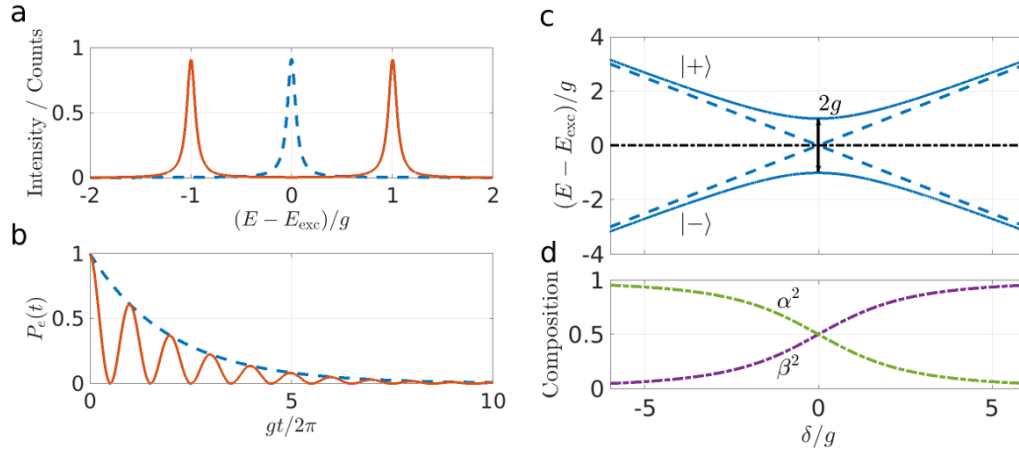


FIGURE 3.10: **Weak and strong coupling regime.** a) Spectrum of a weakly coupled (blue, dashed line) and strongly coupled system (red, continuous line). b) Temporal dynamics of the system: Excited state population for the weakly coupled (blue, dashed line) and strongly coupled regime (red, continuous line). c) Strongly coupled polariton state (blue, continuous line) and bare state energies (blue, dashed line) as a function of the detuning between cavity and exciton $\delta = E_{\text{cav}} - E_{\text{exc}}$. d) Bare state composition of the lower polariton state plotted above, as quantified by α and β in Eq. 3.35. For the upper polariton branch the same graph is true with interchanged α and β . $N = \hbar = 1$ in all plots.

3.4.5 Collective strong coupling: Reversible energy exchange

In Section 3.4.2 I have shown how strongly coupled polariton states emerge in a classical picture. Here this concept is extended by briefly discussing an ensemble of N two-level systems coupled to one cavity mode in a quantum mechanical treatment and showing the similarities in the emerging mathematical description.²⁷ In the rotating wave approximation and under a number of assumptions that will be discussed below the system Hamiltonian can be written as:

$$\mathcal{H} = \hbar\nu a^\dagger a + \sum_i^N \hbar\omega\sigma_{z,i} + \sum_i^N \hbar g(a^\dagger\sigma_{-,i} + a\sigma_{+,i}) \quad (3.33)$$

Here $a^\dagger, a$ are the creation and annihilation operators for a cavity mode and $\sigma_{+,i}, \sigma_{-,i}$ are the raising and lowering operators of the i -th two level system. I have subtracted the zero-point energy from the cavity part of the Hamiltonian. The form of the Hamiltonian implies that the cavity mode couples to each two-level system in exactly the same way. It assumes that the electric field of the mode varies little over the extent of the ensemble of two-level systems and that the orientation of the transition dipole moments of the systems is the same. A further assumption is that the two-level systems are identical, that is $\omega_i = \omega$.

²⁷The Jaynes-Cummings ladder that emerges in a single particle system is presented in Section B.10 of the physical compendium. It is instructive to see that polariton states can be represented as rotations in the two-dimensional space spanned by the bare states. The current section is derived in close analogy to this dressed state picture.

The Hamiltonian describes the coherent dynamics of collectively coupled states. Rearranging the Hamiltonian in matrix form, one obtains an arrowhead matrix. On resonance ($\nu = \omega$) and in the one-quantum basis the eigenvalues of the matrix are

$$E^{\pm} = \hbar\omega \pm \sqrt{N}\hbar g \quad (3.34)$$

The polariton branches are composed of the symmetric and anti-symmetric linear combinations of the collective excited state of the two-level systems

$$|A\rangle = \frac{1}{\sqrt{N}} \sum_i^N \sigma_{+,i} |0\rangle$$

and the singly excited cavity mode $a^{\dagger} |0\rangle$:

$$|\pm\rangle = \frac{1}{\sqrt{2}} (a^{\dagger} |0\rangle \pm |A\rangle)$$

By focusing on the single-quantum subspace of the system, the linear response of the system is analysed. One finds that the Rabi splitting at resonance scales with $\sqrt{N}$, which allows to enter the strong coupling regime by increasing the number of interacting systems, ie. by collectively coupling an ensemble of similar excitons to one cavity mode. The system can now be described in the linear regime, that is by neglecting particle interaction and multiphoton processes, by the stationary Schrödinger equation in matrix form

$$H \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} E_{\text{cav}} & \sqrt{N}\hbar g \\ \sqrt{N}\hbar g & E_{\text{exc}} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (3.35)$$

In the absence of coupling $g = 0$, this Hamiltonian is diagonal and the energy eigenstates of the system are the bare states. With finite coupling $g > 0$ however, the system will have new eigenstates $|\pm\rangle$ which can be expressed as linear superpositions of the bare states. After diagonalisation of Eq. 3.35 one obtains the energy and composition of the new states. Not surprisingly one arrives at the equation of two coupled oscillators

$$(E - E_{\text{cav}})(E - E_{\text{exc}}) = N\hbar^2 g^2 \quad (3.36)$$

which has solutions of the form Eq. 3.28 with $V = \sqrt{N}\hbar g$ as given above.²⁸ The equation describes polariton states characterised by the photonic content α^2 and the exciton content β^2 . Both the energy dispersion as well as those coefficients are plotted in Fig. 3.10. Here the detuning $\delta = E_{\text{cav}} - E_{\text{exc}}$ is introduced: As δ is increased from left to right, an avoided level crossing at $\delta = 0$ is visible in Fig. 3.10c for a finite coupling constant g . In the strongly coupled system, the composition of the lower (upper) polariton state changes from purely photonic (excitonic) to excitonic

²⁸Note the missing damping terms of the form $i\gamma$ in this expression.

(photonic), as shown in Fig. 3.10d.

In this exposition I have neglected any sources for incoherent dynamics, such as dissipation and dephasing-type of interactions. In fact, this section only motivates the scaling of the coupling strength of multiple emitters within a cavity. It is thus outside the scope of this thesis to introduce the interesting mathematical tools, such as master equations with Lindblad terms for different decay channels and non-Markovian dynamics of the polariton states (Ref. [52] Ch. 4 gives a good introduction and the recent publications [16, 17] allow an overview over the current state in this field of research).

3.4.6 Weak coupling: Dissipation prevails

In quantum mechanical treatments one often finds approximate solutions to a given problem by perturbative methods. In the weak coupling regime it is constructive to employ Fermi's Golden rule from this rich toolbox, named after the physicist Enrico Fermi:

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar^2} |\mathcal{V}_{i \rightarrow f}|^2 \mathcal{D}(\omega) \quad (3.37)$$

The expression describes the transition rate $\Gamma_{i \rightarrow f}$ of a quantised system coupled to a continuum of states by virtue of an interaction Hamiltonian $\mathcal{H}_{int}$. I have introduced the matrix element $\mathcal{V}_{i \rightarrow f}$ in Eq. 3.29 and explained how it accounts for the coupling strength between an electronic transition and the electric field. The continuum of final states is described by the density of states $\mathcal{D}(\omega)$, here of photonic nature. As the difference between the two expressions accounts for the Purcell factor, it is instructive to derive $\mathcal{D}(\omega)$ for both free space and a cavity mode. In the first case for free space, the density of optical states reads:²⁹

$$\mathcal{D}_{fs}(k)dk = 2 \left(\frac{\pi}{L} \right)^{-3} \frac{\pi}{2} k^2 dk \stackrel{L=1}{=} \frac{k^2}{\pi^2} dk \quad (3.38)$$

Since $\omega = ck$ one can write $\mathcal{D}_{fs}(\omega)d\omega = \frac{\omega^2}{\pi^2 c^3} d\omega$. One thus finds a quadratically increasing density of optical states in free space, which is a broad function compared to the lineshape of an optical resonator that has been stated before in Eq. 3.5. In fact, assuming the Lorentzian lineshape that was found in the low loss limit in Eq. 3.18, one can write the density of states for an optical cavity

$$\mathcal{D}_{cav}(\omega)d\omega = \frac{1}{\pi} \frac{\delta\omega}{\delta\omega^2 + (\omega - \omega_0)^2} d\omega \quad (3.39)$$

Note that this density of states holds for the three dimensional cavities where both longitudinal and transverse confinement exists.

To employ Fermi's golden rule and to predict the interaction strength in general one needs to calculate the matrix element given in Eq. 3.29. With it one obtains

²⁹The derivation of the expression is largely equivalent to the one for the electronic density of states that is presented in Section B.8 of the physical compendium.

the transition rate as mediated by the electric dipole interaction for the two different densities of optical states 3.38 and 3.39 derived above:

$$\Gamma_{i \rightarrow f}^{\text{fs}}(\omega) = \frac{2\pi}{\hbar^2} \xi^2 \mu_{i \rightarrow f}^2 \frac{\hbar\omega}{2\varepsilon_0} \frac{\omega^2}{\pi^2 c^3} \quad \stackrel{\omega=\omega_0}{=} \frac{\omega_0^3}{3\pi\varepsilon_0 \hbar c^3} \mu_{i \rightarrow f}^2 \quad (3.40)$$

$$\Gamma_{i \rightarrow f}^{\text{cav}}(\omega) = \frac{2\pi}{\hbar^2} \xi^2 \mu_{i \rightarrow f}^2 \frac{\hbar\omega}{2\varepsilon_0 V_{\text{cav}}} \frac{1}{\pi} \frac{\delta\omega}{\delta\omega^2 + (\omega - \omega_0)^2} \quad \stackrel{\omega=\omega_0}{=} \frac{\omega_0}{\hbar\varepsilon_0 V_{\text{cav}} \delta\omega} \xi^2 \mu_{i \rightarrow f}^2 \quad (3.41)$$

Here the dipole alignment factor ξ^2 has been averaged to $1/3$ for the free space case as described before. The ratio of the two transition rates at resonance now defines the Purcell factor:

$$F_P = \frac{\Gamma_{i \rightarrow f}^{\text{cav}}(\omega_0)}{\Gamma_{i \rightarrow f}^{\text{fs}}(\omega_0)} = \frac{3}{4\pi^2} \left(\frac{\lambda}{n} \right)^3 \frac{Q}{V_{\text{cav}}} \quad \& \quad \mathcal{P}_\mu(\mathbf{r}, \omega) = F_P \xi^2 \chi^2 \frac{\delta\omega^2}{\delta\omega^2 + (\omega - \omega_0)^2} \quad (3.42)$$

Here the definition of the Q -factor introduced in Sec. 3.3.2 was used and ω_0 was replaced by the wavelength in the cavity $\omega_0 = 2\pi nc/\lambda$. The second expression $\mathcal{P}_\mu(\mathbf{r}, \omega)$ gives the alignment, spatial and spectrally dependent Purcell enhancement. The dipole-electric field alignment parameter ξ has been defined before, χ is similarly defined to quantify the spatial position within the cavity mode $\chi = \frac{|E(\mathbf{r})|}{|E_{\text{max}}|}$ and the last term describes the spectral detuning.

Frequently one encounters situations where the cavity mode only subtends a small solid angle. Since such a situation allows the coupling to the free space density one introduces the effective Purcell factor, which is defined as

$$F_P^{\text{eff}} = \frac{\Gamma_{i \rightarrow f}^{\text{cav}}(\omega_0) + \Gamma_{i \rightarrow f}^{\text{fs}}(\omega_0)}{\Gamma_{i \rightarrow f}^{\text{fs}}(\omega_0)} = F_P + 1 \quad (3.43)$$

For the interested reader this equation is derived in Section B.9 of the physical compendium.

4 Experimental methods

This chapter introduces the laboratory equipment and measurement routines which are used to record the data presented in the following chapters. I first discuss the experimental techniques and the involved equipment to then explore how both the cavity mirrors and the samples are created. On this basis I will introduce the two main experimental cavity setups, a universal platform developed for room temperature operation and a low temperature setup, mainly developed by Sam Johnson and Laiyi Weng, which provides confocal microscopy capabilities.

4.1 Experimental techniques

4.1.1 Time-resolved photon counting (TRPL)

An important tool in analysing luminescing systems is to record the temporal order of emitted photons. Typically, the system in question is excited by a pulsed light source giving a temporal reference point. In this scheme, the system could be an electronic system like an atom or a quantum dot, or it could be a cavity mode as well. The systems have in common that after the excitation pulse the stored energy is maximal, to then dissipate photons over time. A second mode of operation is the continuous excitation mode, where no temporal reference point is given and the photon stream is detected in a steady state.

To resolve the photon stream, the photon detection has to occur with a temporal resolution better than the decay constant of the system in question. This puts a particular demand on the timing accuracy of trigger and detection pulses. The detectors used for this task are Single Photon Avalanche Diodes (SPAD), which can detect even a single electron-hole pair when created close enough to the active region by impinging photons. The charges are separated and amplified via impact ionisation by a strong electric field created with a large applied reverse voltage across the junction.

After detection of an avalanche event, the device is 'reset' to allow the charges to dissipate. This results in a dead-time of order of 100 ns, implying maximal count rates around 10 MHz for typical Si SPADs. The exact characteristics of SPADs can be adapted to facilitate either better single photon detection efficiencies ($\eta \approx 70\%$ is a typical value) or higher count rates with lower efficiencies. In this thesis I will mostly use Fiber coupled SPADs (Perkin Elmer SPCM-AQRH) with a timing resolution of a few hundred ps. For experiments which demand better timing resolution, a PDM SPAD from Micro Photon Devices is utilised which has a resolution < 50 ps and a

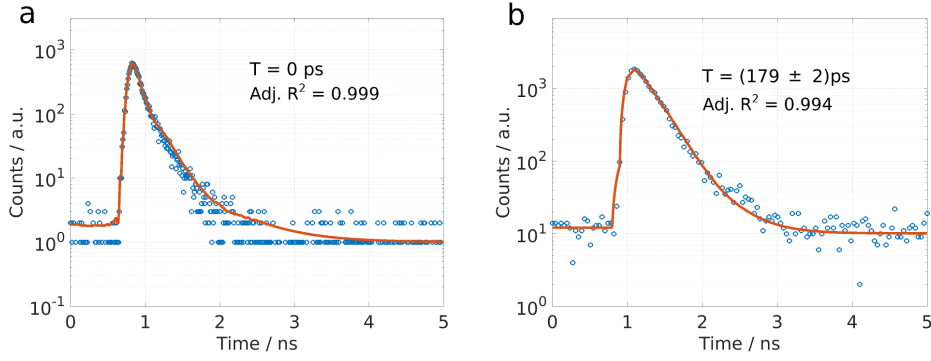


FIGURE 4.1: **Time-Resolved photon counting.** TRPL data recorded with a PDM SPAD for a) illumination by a Fianium WhiteLase pulsed laser and b) signal of cavity populated with the same laser. The red line corresponds to a fit with the function that is used to analyse the photon stream from the cavity. It is a convolution of the instrument response function with a monoexponential decay, whose time constant is measured. It gives 0 ps for the response function itself as expected (a) and a finite decay time if the photon stream is not instrument limited (b).

lower detection efficiency of $\eta = 49\%$ at $\lambda = 550$ nm which drops rapidly for lower and higher wavelengths.

To correlate the individual trigger and detection events an Edinburgh Instruments extension card (TCC900) is used. The above stated reasons for the temporal limits of the detection system make the recording of the instrument response function imperative. Here the pulsed excitation laser is directly detected by the SPAD. Fig. 4.1a shows the response function of the fast SPAD when irradiated by a Fianium WhiteLase system with a nominal pulse width of 6 ps.¹ Any detection event with this system will be described by a convolution of a decaying photon signal (possibly multi-exponential) and the instrument response function. For a monoexponential decay one can thus write down the measured signal $\mathcal{S}_\tau(t)$ as:

$$\mathcal{S}_\tau(t) = (\mathcal{F}_\tau * \mathcal{I})(t) \quad \& \quad \mathcal{F}_\tau(t) = \begin{cases} A \exp(-\frac{t-t_0}{\tau}), & \text{if } t \geq t_0 \\ 0, & \text{otherwise} \end{cases} \quad (4.1)$$

Here $\mathcal{I}(t)$ is the instrument response function and $\mathcal{F}_\tau(t)$ is a monoexponential function with amplitude A decaying with time constant τ from time t_0 onwards. Both of these functions are convoluted to give the measured signal (the convolution is given by Eq. A.4 in the mathematical compendium). Fig. 4.1 shows measured signals (blue markers) and the fit of Eq. 4.1 to the data (red lines) for the instrument response function itself (a) and the signal from a cavity mode (b). The fit returns 0 ps for the instrument response function itself as expected from a null measurement and a significant positive value for τ for the measurement with signal from a decaying system. Note that for systems where the decay constant τ is substantially larger

¹The laser is highly attenuated for this measurement.

than the timing resolution of the SPAD it is sufficient to fit the signal with a pure monoexponential decay and to neglect the response function.

4.1.2 Hanbury-Brown-Twiss interferometry

In order to establish single photon sources it is vital to have measuring routines which quantify the quality of an emitter. Ideally, using a perfect photon detector with no dead time and unit detection efficiency, such a measurement would be straightforward - just measure the flux of photons of your source on timescales faster than the lifetime of the emitter and record the single photons for statistical analysis. In reality this is however not possible due to the limitations inherent to the detectors outlined above and so a little more involved measuring schemes have been developed to attain the ability to characterise the statistics of a photon beam. The most common tool is the second-order intensity correlation function $g^{(2)}(\tau)$ introduced in Section 3.2.1:

$$g^{(2)}(\tau) = \frac{\langle I_1(t)I_2(t+\tau) \rangle}{\langle I_1(t) \rangle \langle I_2(t) \rangle} \quad (4.2)$$

This function describes the correlation of the intensity signal $I(t)$ with itself at later times τ . The subscript 1, 2 identifies the detector used to measure the intensity originating from the same source (see Fig. 4.2). For single photon emission one would expect to find no correlation at $\tau = 0$, since no two photons can be detected at the same time, in other words $g^{(2)}(0) = 0$. Experimentally a setup devised by Hanbury-Brown and Twiss (HBT) shown in Fig. 4.2 serves the purpose of measuring correlations between two signals by splitting an incoming signal by a beam splitter and measuring the signal with two photon detectors D_1 and D_2 . For the HBT measurements in this thesis a 50:50 fiber splitter (Thorlabs FCMM50-50A) is used.

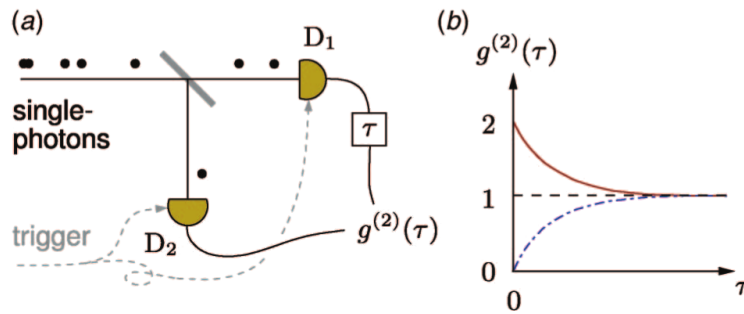


FIGURE 4.2: **Hanbury-Brown and Twiss (HBT) interferometry.** (a) Basic principle of the HBT technique to obtain correlation statistics for single-photon characterisation. The autocorrelation function of the photon stream is measured using two detectors behind a beam splitter with one signal delayed by τ . (b) The correlation function can show signs of either systematic correlations (solid line), random correlations (dashed line), or no correlations (dash-dotted line), where the latter is an indication of non-classical light being measured. (reproduced from [116])

By recording the photon counts on both detectors a histogram of times τ between photon counts on D_1 followed by photon counts on D_2 can be obtained, in effect counting the amount of time between arbitrary start and stop signals given by both detectors. Fig. 4.3 shows a few sample measurements, demonstrating both anti-bunching and bunching characteristics depending on the average number of atoms in the cavity (panel a and b). Panel c shows clear anti-bunching behaviour for a single atom in an ion trap.

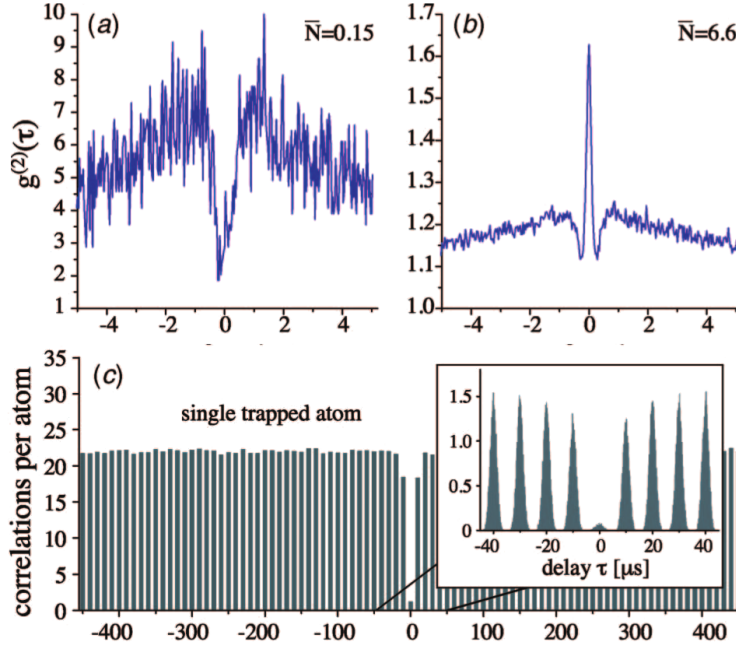


FIGURE 4.3: **Second order autocorrelation function** $g^{(2)}(\tau)$. The function $g^{(2)}(\tau)$ measured using a HBT setup for different types of cavity-based photon emitters. (a) and (b) are recorded for a continuously driven system, with a stream of atoms falling through the cavity. Antibunching is visible for small average atom number $\bar{N}$, and a pronounced thermal bunching peak is found for $\bar{N} \gg 1$. (c) Corresponds to the ideal case, with a single emitter (atom) trapped inside a cavity. Anti-bunching and sub-Poissonian photon statistics are evident, and no envelope function is visible in the correlation function. (reproduced from [116])

Experimentally one obtains a histogram of the times between detection events of both detectors. Depending on the size of the timing bins chosen to build up the histogram such measurements can take a long time - in general Eq. 4.2 implies a quadratic dependence of the time to acquire the same number of correlation counts on the channel countrate. For the data presented in this thesis I use an equation derived with a three level model to fit the experimental data

$$g^{(2)}(\tau) = 1 + p \left(b e^{-|\tau|/\tau_2} - (1 + b) e^{-|\tau|/\tau_1} \right) \quad (4.3)$$

Here p is the probability that the photon was emitted by the single emitter ($p > 0.5$ implies $g^{(2)}(0) < 0.5$), b describes the bunching around the central dip typical to a

three-level system at large pumping powers and τ_1, τ_2 are the associated time scales of the radiative decay and the bunching processes [79, 117]. The detection of photons in this measurement is done with the same SPADs described above for the TRPL measurement.

4.1.3 Saturation curves

Lets suppose a single photon emitter has a decay rate $\gamma = 1/\tau = \gamma_{\text{rad}} + \gamma_{\text{nrad}}$. For impinging photons with sufficient energy to excite the system from the ground to the excited state (but below the ionisation energy), the absorption probability is proportional to the square of the transition dipole moment from ground to excited state. If the system is already in the excited state, the probability to absorb a photon vanishes, in other words the system becomes transparent. For continuous wave excitation with power p of a single emitter the detected count rate will thus show a saturation behaviour described by

$$C(p) = \frac{I_{\text{sat}}p}{p + P_{\text{sat}}} + Bp \quad (4.4)$$

Here I_{sat} is the saturation count rate, P_{sat} is the saturation excitation power and B is a background term (supposing a background that grows linear with the excitation power, typical for a non-saturable system). Neglecting nonlinear effects such as two-photon absorption, I_{sat} is related to the radiative decay rate of the emitter by $I_{\text{sat}} = \eta_{\text{col}}\eta_{\text{det}}\gamma_{\text{rad}}$, where η_{col} is the collection and η_{det} the detection efficiency of the optical system. In this simplified picture, the saturation power P_{sat} is proportional to the total decay rate $P_{\text{sat}} = c\gamma$, where c is a proportionality constant involving the transition dipole moment and characteristics of the excitation light source.

To obtain excitation dependent data a neutral density (ND) wheel is mounted on a stepper motor such that the excitation laser passes the wheel. The device allows to modulate the excitation light power by four orders of magnitude in a thresholdless manner. Typically the countrate is monitored with a SPAD and averaged over a few seconds at every point. For unstable light sources, such as blinking quantum dots and spectrally shifting nanoplatelets I commonly record the same data multiple times in opposite directions - meaning for rotation directions of the ND wheel which increase as well as for ones that decrease the excitation power. The motivation for this procedure is to prevent bleaching effects common to unstable emitters to affect the result.²

4.1.4 Cavity ringdown

The finesse of a cavity can be obtained by measuring the linewidth $\delta\lambda$ of a cavity mode and relating it to the free spectral range $\Delta\lambda$: $\mathcal{F} = \frac{\Delta\lambda}{\delta\lambda}$. At a wavelength of $\lambda =$

²Single emitters frequently exhibit memory effects caused by the interplay between surrounding dielectric environment and excitation light which may result in temporal or permanent bleaching.

578 nm the spectrometer³ has a resolution of 30 pm, which limits the measureable $\mathcal{Q}$ factor to $\mathcal{Q} \approx 2 \cdot 10^4$ and the Finesse to $\mathcal{F} = \frac{\mathcal{Q}}{q} = 4000$ at the smallest cavity length with longitudinal mode number $q = 5$.⁴ For the $\mathcal{F} > 10^4$ regime one therefore has to resort to other measures. Often times the cavity length is scanned such that a cavity mode traverses a very narrow laser line, which can be used to establish the cavity linewidth. A different method, frequently used for long cavities, is to measure the decay of the photon population of the cavity mode directly in the spirit of the TRPL experiment described before. The round trip time of a cavity with length L is $t_{rt} = \frac{2L}{c}$, which results in femtosecond round trip times for the cavity lengths in which I am interested ($L < 10 \mu\text{m}$). For macroscopic cavity lengths ($L > 1 \text{ cm}$) each round trip after an initial mode population can be observed as a peak in photon counts with a decaying envelope with a time constant $\tau = \frac{1}{\kappa}$ (i.e. a ringdown measurement). Since one cannot resolve femtoseconds by means available in our laboratory, this is not the case for ultra-short cavities and instead only the decaying envelope can be detected. The lifetime of the cavity mode is then given by

$$\tau = \frac{t_{rt}}{2\pi} \mathcal{F} = \frac{L}{\pi c} \mathcal{F} = \frac{\lambda}{2\pi c} \mathcal{Q} \quad (4.5)$$

which gives for the finesse $\mathcal{F} = \pi c \tau / L$.⁵ For $L \approx 10 \mu\text{m}$ and a finesse of $\mathcal{F} \approx 10^4$ one thus expects a cavity lifetime of $\tau \approx 100 \text{ ps}$, which is resolveable with a fast SPAD and a short populating laser pulse as demonstrated in Fig. 4.1. To expedite the characterisation of a cavity a stepper motor is attached to a Thorlabs z-positioner to facilitate scanning of the cavity length and to obtain values for $\mathcal{F}$ as a function of L .

4.1.5 Cavity scanning

An open cavity in the plano-concave geometry ideally allows one to move both mirrors relative to each other. The resonance condition within a cavity is given by $qn\lambda = 2L$ as shown in Chapter 3.⁶ Taking the derivative of this relation we find $dL/d\lambda = qn/2 = L/\lambda$ which implies $dL/L = d\lambda/\lambda$. The magnitude in changes in wavelength of a cavity mode is thus inversely proportional to the cavity length, i.e. for short cavities a small change in cavity length results in a large change in resonant mode position. Short cavities are therefore relatively sensitive to vibrations and therefore a sufficient accuracy in positioning both mirrors is required in order to preserve the optical quality of the cavity. Given such accuracy, a common measurement technique is to scan the cavity length such that several modes cross the energy of the probe system. I will present the experimental setup to achieve this goal in the

³SG 1 as introduced in Section 4.2.3.

⁴For longer cavity lengths the linewidth of the cavity modes decreases and thus is even harder to resolve spectroscopically.

⁵The experimental uncertainty of $\mathcal{F}$ is hence given by $\sigma_{\mathcal{F}} = \mathcal{F} \sqrt{(\sigma_L/L)^2 + (\sigma_{\tau}/\tau)^2}$.

⁶Reminder: q is the longitudinal mode index and n is the refractive index within the cavity.

next section. In a cavity scanning experiment I either systematically vary the cavity length or the transverse position of the planar mirror and further differentiate two modi of operation:

- **Transmission Experiment:** The cavity system is illuminated from the back and the transmitted light is collected with an objective lens at the other side of the cavity (front). The light source covers a large wavelength range compared to a cavity mode. In the data presented in this thesis I use a white lamp (Bentham WLS100 or Thorlabs MWWHF2) or a supercontinuum laser (Fianium White-Lase with SuperChrome filter) for the illumination. The detected spectra are calibrated with the spectrum of the respective light source to avoid systematic deviations caused by a non-flat excitation spectrum.
- **PL Experiment:** The system is excited by a laser through the front objective and PL originating from the sample is collected with the same objective. In this thesis lasers with central wavelengths of $\lambda = 405 \text{ nm}$, 473 nm , 532 nm and 637 nm in both pulsed and cw mode are used (all lasers are 3B classified).

The transmission experiment is a good tool to characterise the cavity system. The linewidth, spacing and individual strength of the modes as the cavity length is changed allow to infer the cavity length, the cavity figures of merit and the absorption spectrum of matter within the cavity. In the weak coupling limit the changes in mode linewidth can be used to deduce the linear susceptibility of the absorbing material, in the strong coupling limit the mode splitting allows to quantify the light-matter coupling strength as outlined in Chapter 3. More information about the radiative properties of the material in the cavity is obtained by the PL cavity scanning experiment. Here the changes in mode population and temporal characteristics of the photon stream allow to deduce the PL lineshape, lifetime and brightness of the sample.

4.2 Experimental setup

In the following section I present two open cavity experiments, one at room temperature and one suitable for operation at 4 K. The majority of experimental results in this thesis is obtained at room temperature and only the last chapter describes the employment of the low temperature setup to harness single photons from monolayer WSe₂.

4.2.1 Substrate preparation

The open microcavity consists of two opposing mirrors. In order to bring the two mirror surfaces close to each other ($L < 1 \mu\text{m}$) it is helpful to reduce the lateral dimensions of one of the mirrors. This is achieved by cutting away material from a

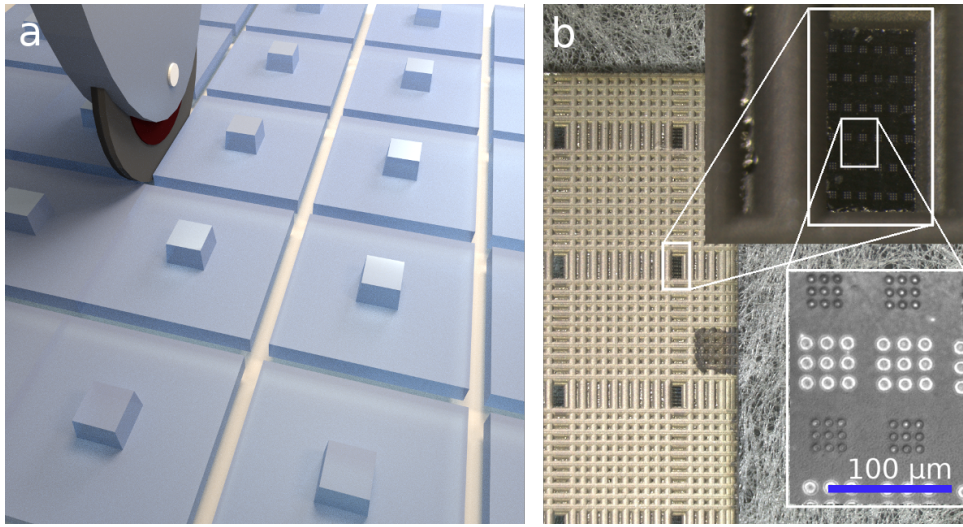


FIGURE 4.4: **Silica substrate fabrication.** a) Artistic impression of substrate fabrication with plinths. A silica dicer is used to remove material from a fused silica substrate such that a central plinth is left standing. The dimensions of the plinths range from 100 to 500 μm with an elevation above the rest of the substrate of 100 μm . In a second step the individual substrates holding the plinths are separated. b) Photograph of silica substrate after FIB milling and coating. The insets show a zoomed view on one plinth with visible concave cavity features.

fused silica substrate with a dicer. Fig. 4.4 gives a graphic impression of the dicing process. The rectangular elevated features that are left standing after this step (which are called plinths in the following) have lateral dimensions between 100 and 500 μm and an elevation above the rest of the substrate of roughly 100 μm . In a second step, the substrates holding the plinths are separated. For experiments with planar mirrors only, the plinths can be made reflective at this point with a metallic or dielectric coating.

For plano-concave microcavities with low mode volumes however a Focused Ion Beam (FIB) is used to mill concave features into the surface of the plinths. Fig. 4.5 schematically shows the workflow involved in the fabrication of the small features. The process is started by writing a list of coordinates and dwell times for the FEI FIB200 into a stream file, which define the desired feature. A tool to facilitate this graphically was developed by Aurélien Trichet in his first year as a postdoctoral researcher in the PNG group. He calibrated the different ion beam currents accessible with the FIB200 to their sputtering rate and beam diameters as inferred from the comparison of targetted and measured shape. The resulting stream file generator allows the conversion of an arbitrary shape into a series of discrete coordinates with associated dwell times for the focused ion beam (within the limits given by beam diameter and angle of incidence of the beam). More information about the FIB milling and the topographic accuracy can be found in the recent paper by Trichet et al. [88] and in Chapter 5, where large and more complex FIB milled features are presented.

The next step is to distribute the features on a silica plinth, first graphically with

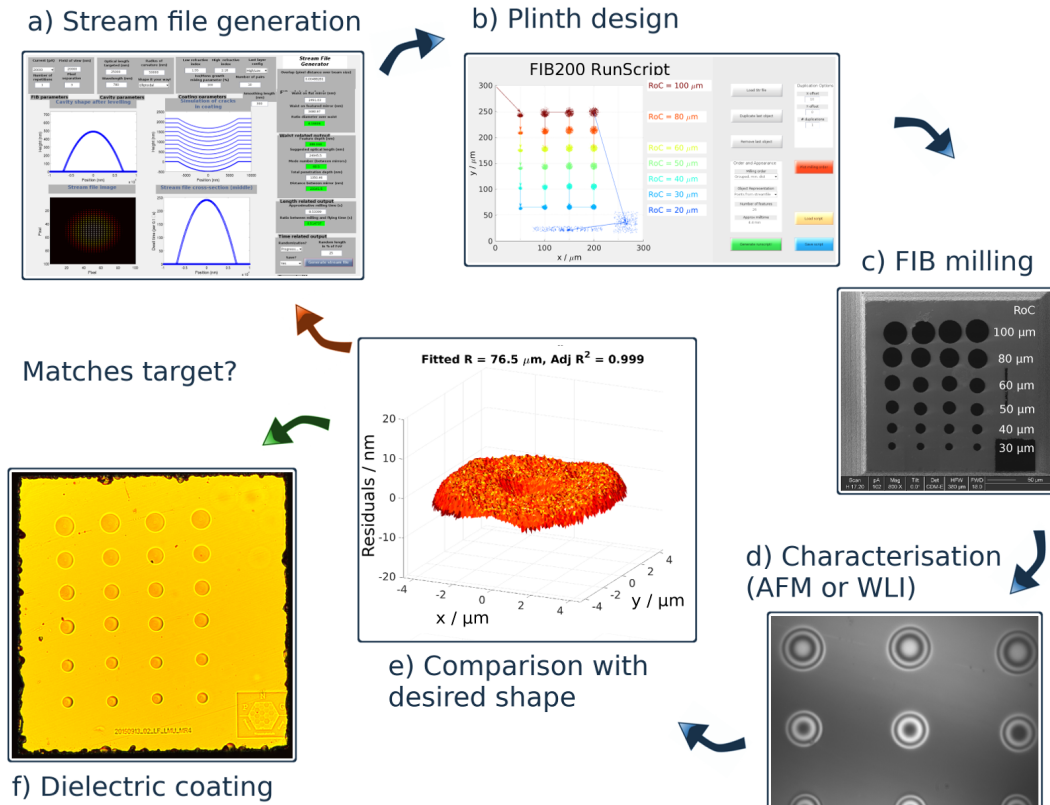


FIGURE 4.5: **Cavity fabrication workflow.** a) A stream file is generated for each concave feature, consisting of a list of coordinates and dwell times for the focused ion beam. The generator was developed by Aurélien Trichet. b) The features are graphically distributed on the plinth and a script for the FIB200 is generated. c) The design is milled into a silica plinth with a FEI FIB200. To make the surface of the silica conductive, a thin layer of gold is sputtered onto it before the milling. d) The gold is removed from the substrate and the milled features are characterised with optical (WLI) or mechanical (AFM) measures. e) The shape is compared to the target and if it matches the target (residuals below a few nanometer), the sample is sent to an external company for coating (f). If the mismatch is above tolerance, the stream file is adapted and the desired shape is obtained by incremental iteration through the fabrication steps.

a self-written generator and then physically with the FIB200 (Fig. 4.5b,c). In order for accurate milling without charging distortions, the surface of the silica plinths has to be made conductive, which is achieved by sputtering a thin layer of gold on top of the sample. Later results indicated that this step deteriorated the surface quality of the substrates, as residues of the gold could not be removed later. Recent efforts have thus consisted of replacing the gold layer by an electron flood gun in a dual beam FIB, allowing distortionless milling without a sputtering step. A subset of the milled features is generally characterised after each milling batch to verify that the targetted shape is obtained. The characterisation is either facilitated by optical means (WLI as shown in Fig. 4.5d) or via AFM measurements. If the measured shape matches the target (ie. the residuals between target and measured shape are below a few nanometers [88] as shown in Fig. 4.5e) the sample is sent to an external company for dielectric coating. A typical dielectric coating consists of 10 to 20 alternating layers of $\text{SiO}_2/\text{Ta}_2\text{O}_5$ or $\text{SiO}_2/\text{TiO}_2$ with macroscopic reflectivities of $R > 99.7\%$ ($R = 99.997\%$ with the best coatings).

4.2.2 Sample preparation

A substantial amount of experimental time involved sample preparation. Here I will only give a very brief overview of how the nanocrystals were introduced into the cavity environment. In particular the work with single quantum dots and nanoplatelets hinges on the creation of a suitable environment. While incremental improvements in emitter durability and brightness were achieved by experimenting with different solvents, encapsulating polymers and deposition techniques, several single emitter experiments were not successful because the materials were not stable enough in the cavity. The length of the following section therefore does not reflect the experimental time devoted to this task.

The mirrors forming the cavity consist of silica substrates with either dielectric or silver coatings as described in the previous section. For a successful cavity coupling experiment the emitter has to be fixed on top of such a multilayer DBR or metallic coating without detrimentally affecting the emitter properties and in a way that the coupling to the electric field is maximal.

Colloidal nanoparticles

Colloidal nanoparticles such as quantum dots and nanoplatelets are grown in solution as referred to in Chap. 2. The materials deployed in this thesis were synthesised by collaborators from other research groups or bought from large suppliers such as Sigma Aldrich. The sample preparation therefore started with the nanoparticles dispersed in solution. To enable single emitter experiments, the density of particles in the solution had to be reduced according to the deposition process. In general a dilution by factors between 10^3 and 10^6 was found to be suitable, depending on the

initial density of the nanoparticles. In the following two deposition methods can be differentiated:

- **drop casting:** Here a single drop from the solution containing the nanoparticles is taken with a micropipette and gently placed on the mirror surface. Depending on the vapour pressure of the solvent the drop evaporates over timeframes between a few seconds (hexane, chloroform, ethanol) and minutes (toluene). The residues form a coffee stain pattern, whose structure and particle density depend on the ligands and polymer components of the solution.
- **spin coating:** A single drop or multiple drops in succession are dropped onto the spinning mirror. The liquid is pulled apart rapidly by centrifugal forces and a flat film remains. Typically the mirror is set to rotate at 3000 rpm and a solution with the polymer PMMA (Poly(methyl methacrylate)) is used to create a thin homogeneous film (≈ 20 nm thick).

Both methods have been employed to obtain single emitter samples. Drop casting is better suited to solutions without a polymer admixture, whereas the spin coating process can be gauged to give a precise film thickness with good flatness. For the CdSe/CdS core shell quantum dots a solution with the solvent chloroform (CHCl_3) with an admixture of 0.5 wt% PMMA and 0.2 wt% of the ligand HDA⁷ was found to give good results when spin coated onto the dielectric mirror.

Single nanoplatelet experiments showed that a slightly larger percentage of PMMA and the addition of oleic acid⁸ added to the stability of single emitters. In particular the hosting polymer is thought to shield the single particles from photoinduced dissociation caused by ligand-loss in low-pressure environments. While improvements with core-shell nanoplatelets were achieved by incrementally changing the ingredients and making the polymer thicker, the resulting experiment could not be finished successfully. The main reasons were the unstable nanoparticles, which showed intense spectral wandering and PL blinking even for small excitation powers and thick (> 50 nm) polymer encapsulations and a flow cryostat setup unsuited for cavity operation. An experiment with single CdSe/ZnS quantum dots showed good results however and will be presented in a later chapter. Furthermore, an ensemble experiment with CdSe core-only nanoplatelets yielded good results and will be presented as well. The sample preparation here foresaw drop casting of the original solution (consisting of toluene with oleic acid acting as a ligand) onto a silver mirror to create an inhomogeneous oleic acid-nanoplatelet film without polymer admixture.

⁷2-[hydroxy(methanoyl)amino]ethanoic acid.

⁸(9Z)-Octadec-9-enoic acid.

WS₂ monolayers

The WS₂ flakes are grown via chemical vapour deposition (CVD) by a partner group in Oxford lead by Jamie Warner. The growth process is described in a recent publication by Rong et al. [51]. After the CVD process the flakes are transferred onto the dielectric mirror stack, which has a low refractive-index terminated configuration to provide an anti-node of the electric field at the mirror surface and thus optimal coupling to the monolayer. The transfer process is facilitated by coating the as-grown WS₂ flakes on SiO₂ with a helper layer of PMMA. After etching away the substrate, the floating PMMA film is transferred manually onto the DBR and baked at 150° for 15 min on a hot plate (in ambient conditions). The remaining PMMA is then dissolved by placing the sample in an acetone bath for 10 min.

To enable electrical control within the cavity, silver electrodes with a width and a spacing of 90 μm are thermally evaporated on top of the DBR before the WS₂ transfer process. The thickness of these electrodes is approximately 50 nm. The WS₂ can then be transferred onto the dielectric mirror stack as described before. The distribution of WS₂ flakes relative to the electrodes is random, with 90% of the flakes overlapping partially with the silver electrodes. The results presented later are obtained from a flake which was not in physical contact with the electrodes, thus ensuring purely electrostatic tuning. The other component of a hybrid organic-inorganic system that I will present later is the organic J-aggregated dye TDBC. After dissolving the dye in a gelatine-water solution, the mixture was spin-coated onto the small silver mirror to give a polymer-dye layer of about 300 nm thickness. The absorbance of the TDBC film can be tuned by varying the concentration of the dye.

WSe₂ monolayers

The WSe₂ monolayer is created via mechanical exfoliation from bulk WSe₂. Here a scotch tape is used to remove large crystallite from the bulk material. The material on the scotch tape is then brought into contact with a PDMS (polydimethylsiloxane) silicone layer and transferred onto the planar DBR in a dry stamping process. The materials adhesivity shows a strong time dependence, which makes it possible to remove the WSe₂ from the scotch tape by a fast motion and to deposit the material on the plain DBR surface by a very slow peeling motion. Most of the material, that was deposited in this way, consisted of several layers of WSe₂. In fact only a few monolayer flakes with extensions over a few micrometers could be obtained in one exfoliation process and were found via optical microscope inspection.

4.2.3 Room temperature setup

Fig. 4.6 shows the schematics of the optical setup for operation at room temperature. The sample or the modular open cavity system can be mounted on a xyz-positioning stage, allowing movement of the modular system relative to the objective lens. To enable a multi-purpose experimental platform, two different excitation paths from the primary light source (for reflection and PL measurements) and secondary light source (for transmission measurements) are possible. The intensity of the light sources can be modulated automatically with a neutral density filter wheel attached to a stepper motor.⁹

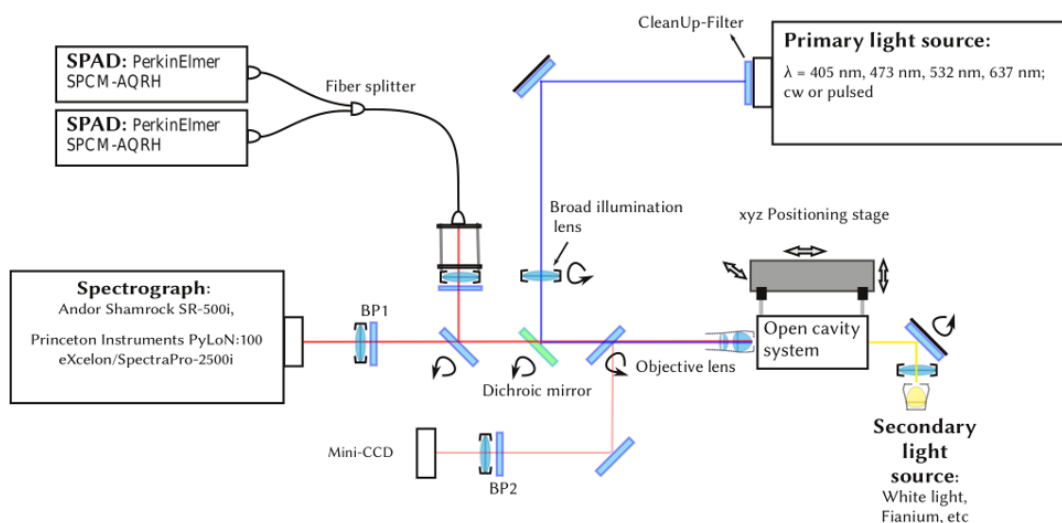


FIGURE 4.6: **Multi purpose optical setup at room temperature.** Schematics of a multi purpose optical setup for room temperature operation. The open cavity system is mounted on a xyz-positioning stage, allowing an adjustable focus and region of interest through movement relative to the fixed objective lens. The setup enables optical excitation with multiple lasers through the objective lens and via transmission by a secondary light source. To analyse the light collected with the objective lens, either a small CCD or a 50 cm spectrograph provides imaging and spectroscopy capabilities. An additional pickup alternatively allows single photon detection with fiber coupled SPADs.

The light from the sample is collected for spectroscopy or imaging either by a small CCD (Pointgrey CM3-U3-13S2C-CS) or by spectrograph SG1 or SG 2.¹⁰ Alternatively the light can be collected by a fiber to analyse it with either one or two SPADs as outlined above.

The heart piece of the setup is the modular open cavity system. Fig. 4.7 presents an exploded view of the components without cage rods or plates. The main stage is movable both by piezo microactuators and manual knobs (Thorlabs MAX311D/M with BPC303 controller).

⁹The stepper motor is driven by a self-programmed Arduino Uno R2 with a stepper motor shield.

¹⁰SG 1: Andor Shamrock 500i with 300 and 1800 lines/mm gratings and a Andor Newton CCD. SG 2: Acton SP-2500i with 300 and 1200 lines/mm gratings and a liquid nitrogen cooled Princeton Instruments PyLoN:100 CCD. Both SGs have a focal length of 500 mm.

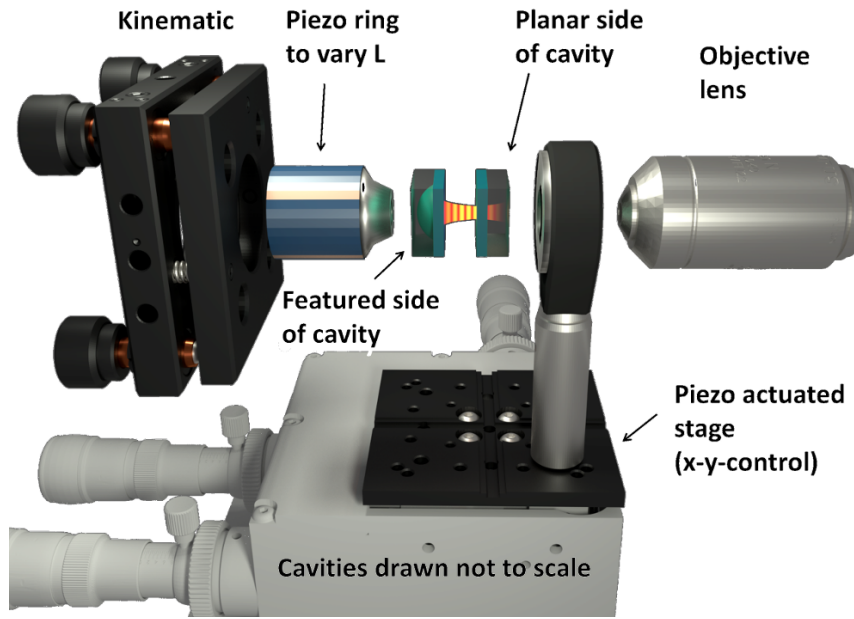


FIGURE 4.7: **Exploded view of room temperature open cavity system.** The kinematic mount is connected to the NanoMax stage at the bottom with cage rods and the piezo ring is recessed into the mount to provide eucentricity to the angular tunability of one side (featured) of the cavity. The other side (planar) is attached to a mount post fixed to the NanoMax stage, providing free movability relative to the first mirror. The whole system can be attached to a xyz-positioning stage in the larger optical setup presented above.

This stage holds the planar part of the cavity, which is fixed on a post on it. The other components of the module (which hold the concave cavity mirror and an aspheric lens to focus the white light from the back onto the chip) are rigidly attached to the base of the stage to minimise vibration between both mirrors.

To successfully align both sides of the cavity, a kinematic mount is utilised which provides angular tunability of the featured mirror. This mount is operated either manually or automatically with detachable DC motors (Thorlabs ZST206). A piezo ring actuator (HPSt 150/14-10/25 from Piezomechanik) is recessed into the mount such that the mirror is attached close to the eucentric point of the mount. It can be used to modulate the cavity length with an applied voltage (applied with a Keithley 2400).

The travel range of the piezo-actuated stage is $20\text{ }\mu\text{m}$ in all three dimensions and the recessed piezo ring provides an additional $10\text{ }\mu\text{m}$ range. For experiments where a larger cavity length range is required, the stage is replaced with a z-positioner connected to a stepper motor.¹¹ This system provides coarse cavity length tuning capabilities with the stepper motor and fine adjustability via the recessed piezo ring.

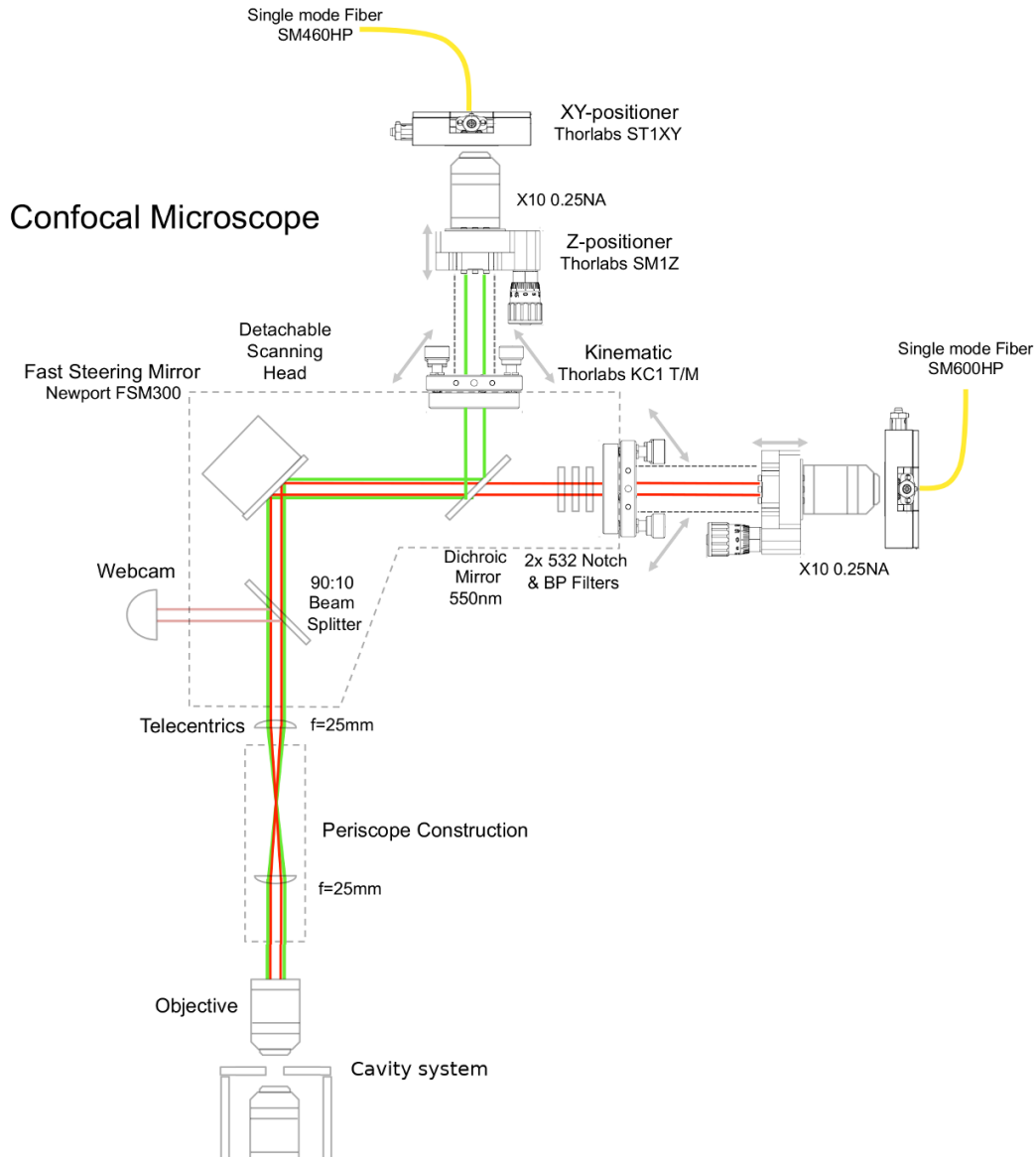


FIGURE 4.8: **Confocal microscope.** Detailed schematics of the confocal microscope with low temperature capability. Both excitation and collection arm can be aligned with kinematic mounts and end with a single mode fiber interface. Excitation light and fluorescence are separated with a dichroic mirror. Together with a fast steering mirror the above components form a detachable scanning head which can be connected to a helium dewar for low temperature experiments. Figure adapted from [118] with courtesy of Dr. Sam Johnson.

4.2.4 Low temperature setup

Low temperature experiments put highest demands on minimisation and durability of the equipment. In the following section I will present a modular confocal microscope setup which can be attached to a bath cryostat consisting of an evacuated hollow tube immersed in liquid helium at 4 K. The system was developed in the PNG group in Oxford over the last years and provides a versatile platform for single emitter spectroscopy.

Fig. 4.8 shows the optical setup of the confocal microscope. The excitation light from a green laser ($\lambda = 532$ nm, both pulsed and cw mode) is modulated and coupled into a single mode fiber on an optical table close to the setup. The fiber is attached to the excitation arm of the scanning head (green rays in Fig. 4.8). From there it is guided to the sample by reflection off a dichroic mirror and a fast steering mirror.

The objective lens is situated in a $4f$ configuration from the steering mirror, mediated by opposing telecentric lenses (with $f = 250$ mm). To separate the fluorescence from the excitation light, a dichroic mirror is placed into the beam path before it enters a collection arm with a range of adaptable filters in front of it. It is coupled into a single mode fiber to be analysed by the SGs or SPADs presented in the section before. The main piece of equipment in the setup is the fast steering mirror (Newport FSM-320) which allows to raster the beam across an area of the sample. For this purpose a Labview Program was developed in the PNG group which provides a user friendly graphical interface, which has been extended on a regular basis by tools such as peak finding algorithms and emitter characterisation routines.

The setup is modular in the sense that the scan head can be placed over a periscope construction for room temperature measurements. The main purpose of the module is however to attach it to the top of a liquid helium dewar (see Fig. 4.9b). Here it interfaces with a vacuum tube which contains the telecentric lenses and the open cavity system. Fig. 4.9 presents the schematics of the tube inside a dewar with two additional interfaces for the vacuum pump and the electric wires leading to the microactuators of the open cavity system.

To allow an efficient communication of the cavity setup, Fig. 4.9c presents an exploded view of the cavity system: Starting from the top it consists of an objective lens (Attocube LT-ASWDO x50, NA 0.82) which is rigidly integrated in the vacuum tube. Below it there is a small cylindrical container (in the actual experiment consisting of cage rods) which holds the planar mirror on top of a small aperture. It rests on a 3-axis piezo stack (Attocube [ANPx101,ANPx100,ANPz100]), which enable to move the whole cavity relative to the optical system. The opposite side of the cavity with the featured mirror is positioned on a 5-axis piezo stack (Attocube

¹¹This motor is driven by the same Arduino Uno R2 with stepper motor shield already used for the ND wheel.

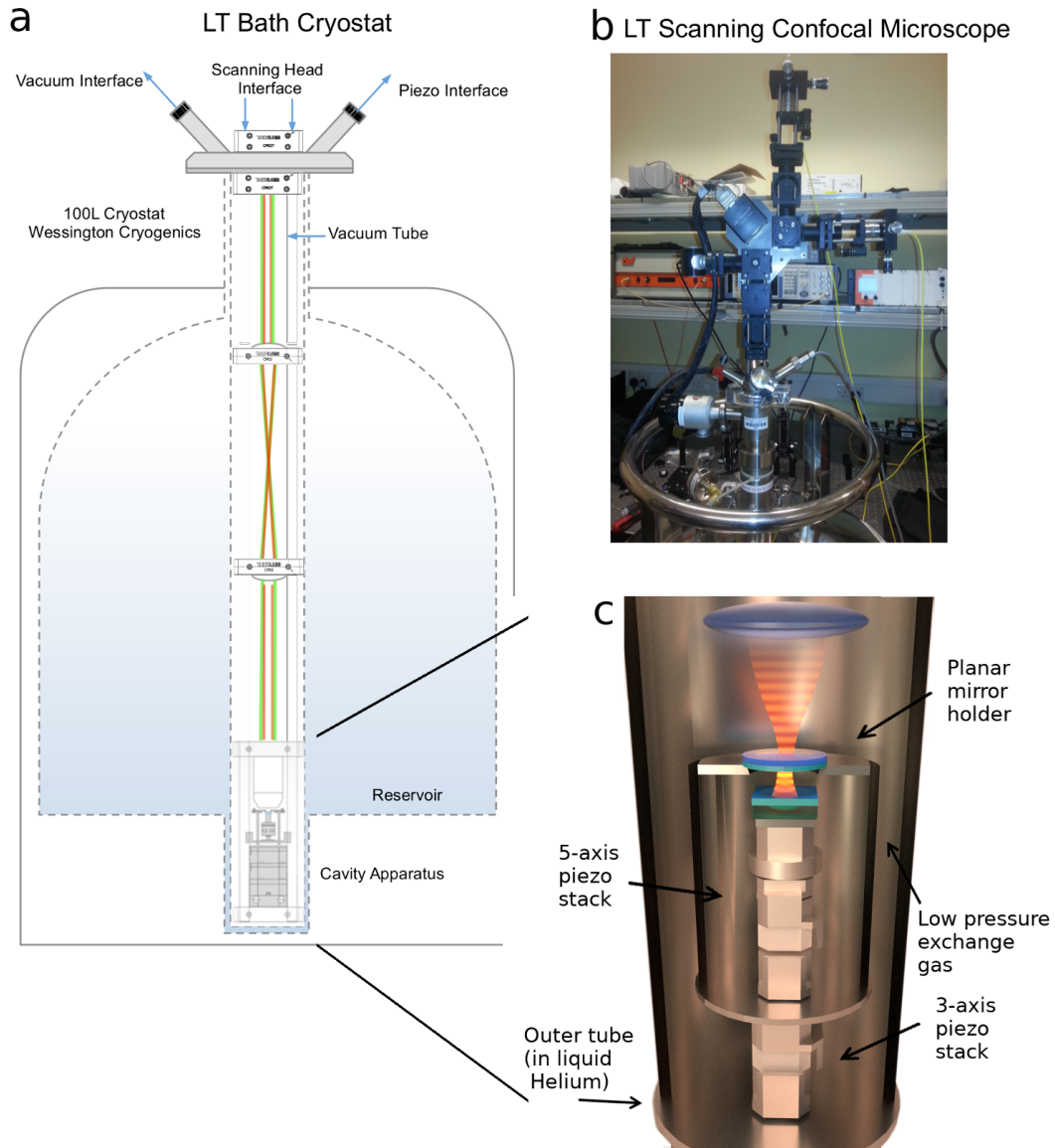


FIGURE 4.9: **Low temperature open cavity system.** a) Schematics of a bath cryostat composed of an evacuated tube immersed in liquid helium. b) Photograph of detachable scanning head mounted on top of the liquid helium dewar. c) Exploded view on the open cavity situated at the bottom of the evacuated tube. The inner cylinder (and with it the cavity) is movable relative to the fixed objective lens and the cavity can be aligned with the innermost 5-axis piezo stack. Panel a, b adapted from [118] with courtesy of Dr. Sam Johnson.

[ANPx51,ANPx51,ANPz51,ANR51,ANGt50]) within the container, where three actuators provide three-dimensional linear motion, one rotates about its axis and the last one provides a tilting capability. With these degrees of freedom it is possible to firstly position particular parts of the planar mirror in the focal region of the objective lens and secondly to align an open cavity around them. The piezo actuators are controlled by benchtop modules (Attocube ANC300 with 3xANM150, ANC300 with 6xANM300), allowing both stepwise and continuous scans. While the stepping motion could be automated by interfacing with the Attocube drivers, the continuous sweep in one dimension (here to modulate the cavity length) was achieved by using an external voltage source (Keithley SourceMeter 2400).

4.2.5 Open cavity alignment

The cavity is aligned by minimising the fringes visible in a white light transmission experiment. For this the mirror separation is reduced below $L \approx 10 \mu\text{m}$ and the cavity image is detected with the small CCD or webcam. It is helpful to use a bandpass filter with a width of a few nm and a central wavelength below or above the stop band edges of the cavity mirrors. The angular mismatch between the planar parts of the two mirrors will cause a fringe pattern, resulting from the differing path lengths in the cavity resonance condition. One can count the number of fringes across a given lateral distance and incrementally improve the mirror parallelity by minimising this number. For the minimal number of fringes (typically ≤ 1 across the lateral extension of the plinth), the remaining angle between the two mirrors is estimated to be smaller than $200 \mu\text{rad}$.

Having a parallel cavity, the cavity length can be measured from the free spectral range in a transmission experiment. If the cavity mode is required over a specific patch of the planar mirror, an incremental procedure consisting of a transverse motion of the planar mirror followed by a correcting transverse move of the featured mirror is a good strategy. Depending on the detection channel, a cavity mode can be tracked either spectroscopically (with the spectrograph) or by the change in brightness (with a SPAD) when mirrors are moved. A locking mechanism which automatically scans the cavity length by a small distance and follows the peak mode brightness was developed to facilitate this task. Here the cavity length is set to the position where the photon count rate from a narrow emitter is maximal.

In the room temperature experiments the optical system is aligned with a specific concave cavity feature and only the planar mirror is moved relative to this fixed axis. This approach enables cavity-enhanced imaging: Here a certain area of the planar mirror is systematically scanned across the cavity mode and the cavity signal is detected. From the observed mode structure much information about the surface of the planar mirror and emitters thereon can be obtained, as will be outlined in the following chapters.

5 Advances in open microcavities

Before using an open cavity in coupling experiments, this chapter presents recent improvements with bare FIB milled microcavities. While the advances in cavity fabrication are of particular interest for the experienced audience, another aim of this chapter is to familiarise the novice reader with the mode structure and capabilities of the length and angle tunable open cavity setup.

In the first part of this chapter, results from a surface optimisation technique utilising CO₂ laser ablation after FIB milling are presented. The data were acquired within the scope of a side project with a research group at the LMU in München, Germany. For this purpose concave features with varying size and radius of curvature were milled with the FIB as lined out in the previous section and then post-processed with a CO₂ laser in München. After publications by Dolan [86] and Trichet [88], the FIB milling process was shown to produce surface topographies of arbitrary smooth shapes with nanometric precision and a surface roughness of approximately $\sigma_{\text{Trichet}} = 0.8 \text{ nm}$. As a result of the combination of the two fabrication methods, here I show smaller surface roughness values of $\sigma = 0.3 \text{ nm}$ allowing a maximal finesse of $\mathcal{F} = 5 \times 10^4$.

In the second part of this chapter it is demonstrated that the FIB milling process can be used to produce advanced concave shapes with coupled modes and varying degree of hybridisation. I explore the parameter space of the inter-cavity separation and compare the experimental findings with a theoretical description obtained within the modemixing formalism.

5.1 Surface optimisation of FIB-milled microcavities via CO₂-laser ablation

The key idea presented in this section is to combine two different methods used extensively over the past decade to fabricate concave features in silica. The two methods are the FIB-milling presented before [86], which has been shown to produce small features ($\varnothing < 10 \mu\text{m}$) with nanometric topographic control [88], and CO₂-laser ablation, which lacks the precise control over the shape but produces very smooth surfaces over a large range of feature sizes ($\varnothing > 5 \mu\text{m}$) [85, 119, 120]. Ideally the combination of both techniques should improve the control over the shape, both on a macroscopic topographic and at a local surface roughness level, thus allowing a large range of radii of curvature for the concave feature and smooth surfaces, leading to versatile high finesse open-access cavities.

5.1.1 CO₂-laser and characterisation setup at the LMU

The CO₂-laser ablation setup in David Hunger's research group at the LMU has been developed over the last years and combines the ability to fabricate and characterise substrates in-situ. It comprises three different work stages at which a sample can be positioned via a motorised control rail. These stages are the CO₂-Laser, a White Light Interferometer (WLI) with a x50 objective and an optical Searcher with a lower magnification lens in place. By using relative coordinates between those three stages, the sample can be located, analysed and worked at in direct succession, which creates an efficient work-flow facilitated by a LabView program. The CO₂-laser operates in pulsed mode and the output is controlled by an Acusto-Optical Modulator (AOM). The wavelength of the laser is 10.6 μm and a maximal power of $P_{\text{max}} \approx 600 \text{ mW}$ can be delivered per pulse.

5.1.2 Characterisation of concave features

A first goal of this project was to explore large feature sizes and radii of curvature that exceed the parameters of $2 \mu\text{m} < \varnothing < 8 \mu\text{m}$ and $2 \mu\text{m} < \text{RoC} < 25 \mu\text{m}$ typically fabricated with FIB milling. For larger features a series of problems were expected due to charging and drifts in the FIB processing. To address and map out these problems, a set of different cavities with feature sizes between 2 and 80 μm and radii of curvature between 2 and 1000 μm was produced. For each feature, an optimisation process as presented in the workflow graphic in Fig. 4.5 in the previous chapter was followed, which for the largest features comprised of three iterations.

The desired shape used in the FIB machining followed an ellipsoidal profile.¹ The milled features were designed to have a depth around 500 nm, which in combination with the range of RoCs gives the above quoted feature sizes. A problem encountered with the relatively old FIB (the FEI FIB200 was installed in 1999), was the digitisation of the dwell times caused by an old analog-to-digital converter in the beam steering electronics. The result was, that in combination with the finite number of maximal points in the stream file the dwell times necessary to produce the large features showed step-like clipping behaviour. This in turn lead to ripples at the bottom of the largest features. I will discuss the impact of these macroscopic surface inhomogeneities at the end of this section.

The CO₂ laser treatment was applied to the features directly after the FIB process. For this the samples were transported to München in gel boxes and the correct laser settings had to be found and optimised. As large parts of this process are irrelevant for this thesis, I omit the details except remarking that there is a separate research report that documents them.²

¹The exact function for the profile is given in Eq. A.5 of the mathematical compendium.

²"Surface optimisation of FIB-milled microcavities via CO₂ -Laser ablation", written by the author of this thesis in October 2015.

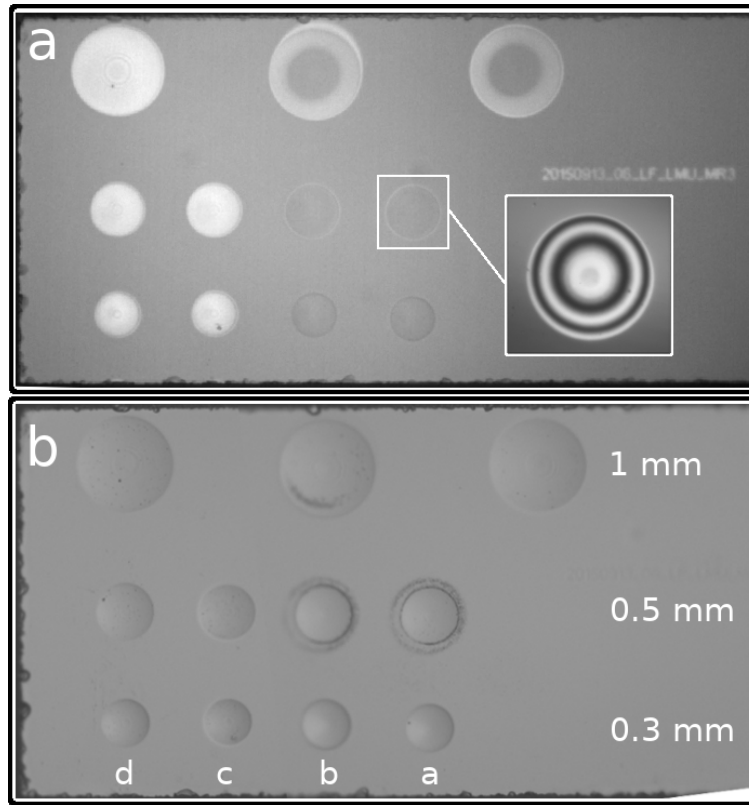


FIGURE 5.1: **Large radius of curvature features.** Optical micrographs of concave FIB milled features on a silica substrate. a) Plinth after FIB milling and CO₂ laser ablation applied to features in column a and b. Inset: White-Light-Interferometer (WLI) image of feature with RoC = 500 μm. b) Features after dielectric coating. The nominal radius of curvature for the features in each row is the same and given at the side of the image.

The visual impact of the laser treatment on FIB milled fused silica substrates is striking. Fig. 5.1a shows a plinth with two columns of untreated (left) and two columns of smoothed (right) features. The laser treatment converts the white surface aspect into a grey, substrate like appearance. This property indicates a decrease in surface roughness leading to a reduced amount of scattering, originally causing the white aspect in the as-milled case. The inset in panel a shows a WLI image of one concave feature, showing typical interference rings. From the length dependence of the interference pattern one can deduce the topography of the concave feature.

Fig. 5.1b shows the same plinth after dielectric coating.³ Here the difference in surface appearance has vanished, but CO₂-laser treated features show signs of microripples at the edge of the treated regions (particularly visible for the features with $R = 0.5$ mm).

³The samples were sent to LaserOptik GmbH for an Ion Beam Sputtering (IBS) coating with a central wavelength of 578 nm. The nominal values for the absorption loss δ_{abs} and transmission T were $\delta_{\text{abs}} = 10$ ppm and $T = 30$ ppm.

The topography of the features was characterised via AFM and WLI measurements both after the FIB milling and the CO₂ laser ablation. Figure 5.2 shows a comparison between these measurements of a wide range of features. To this end, the original FIB milled (CO₂-smoothed) shape is plotted with a continuous (dashed-dotted) line in the top panel. The profile of each feature is plotted relative to a horizontal dashed line of the same colour, which is offset for each feature for better visualisation. To obtain the radius of curvature of the feature, an elliptoidal surface is fitted to the WLI data and the result appears in the legend of the figure.⁴

It is evident, that the laser treatment removes material from the center, as expected from the indentations obtained by calibration laser pulses. The removal leads to an additional macroscopic smoothing of the shape, particularly visible for the larger features shown in the top right panel of Fig. 5.2. Deviations from the desired shape due to charging induced beam aberration were found to be negligible, as was ascertained by comparison of features milled with a progressively randomised order of the stream file points.⁵

The ripples due to the digitisation in the FIB electronics mentioned before are most prominent for the largest, unsmoothed features. Here the central region of the feature profile shows steps, which would lead to aberrations in the wavefront of a cavity mode. Note that most of the steps disappear after the smoothing. The data presented is obtained by taking a cross section of a 2D WLI map of the surface profile and is sufficient to characterise the surface, as the features are azimuthally symmetric within very good approximation.

The lower panel of Fig. 5.2 shows AFM measurements of one of the smallest features milled with RoC = 4 µm before (left) and after (right) the CO₂ smoothing. As can be seen, the FIB-milling produces accurate shapes with sharp edges which can be efficiently smoothed by laser application without large changes in feature depth.

5.1.3 Surface roughness

To quantify the surface roughness, AFM measurements in the clean room at the LMU were made before and after the laser treatment. A small central 5×5 µm² region was chosen to evaluate the local surface roughness. I followed the standard procedure to obtain the surface roughness, which is to subtract a high-order polynomial from the surface data to remove the macroscopic shape and analyse the resulting height distribution statistically (see Fig. 5.3). For some smaller features this field of view is sufficient to contain the whole feature, enabling the assessment of the feature topography on the basis of the same data.

⁴The function for the fit is the same as used for the feature creation, given in Eq. A.5 of the mathematical compendium.

⁵In more detail, the milling order was varied from building the feature from left to right with a randomisation length of a few micrometer to a full randomisation of the milling order. As the difference between the obtained topographies was negligible, the conclusion was drawn that charging of the silica surface, which was anticipated to lead to FIB beam aberrations, posed no problem.

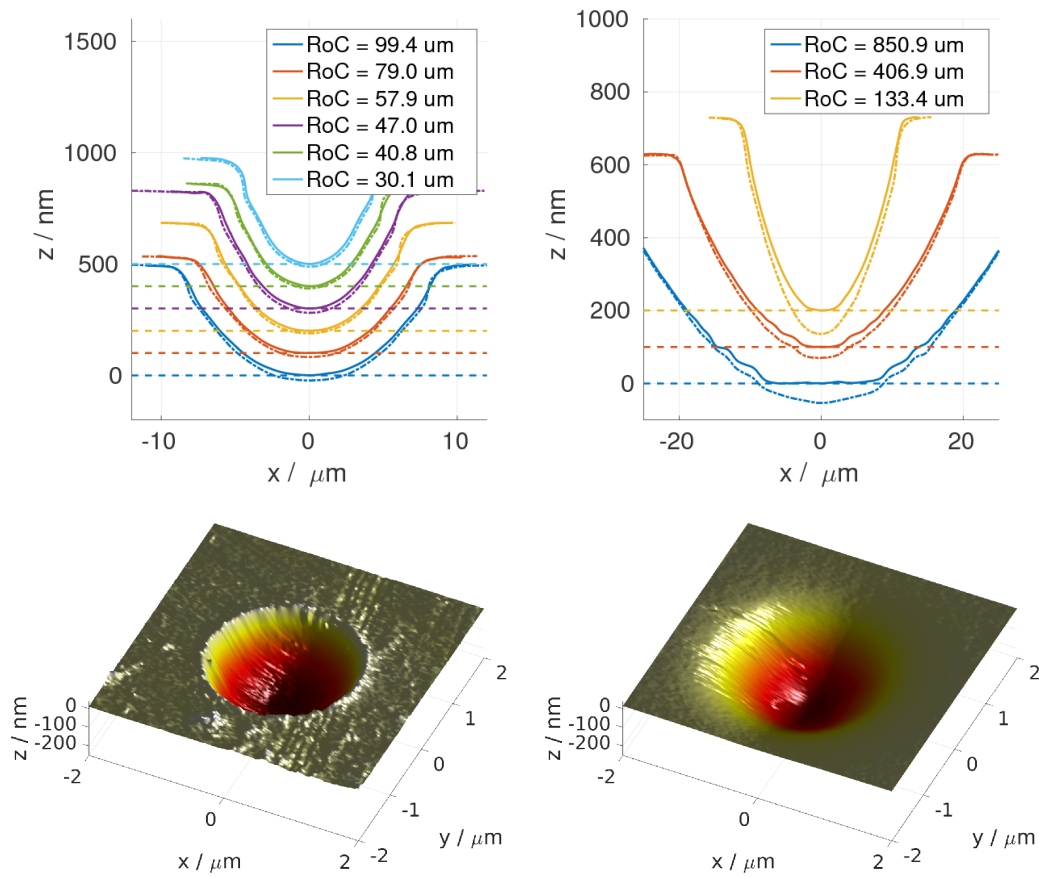


FIGURE 5.2: **Characterisation of FIB-milled and CO₂ laser smoothed features.** Top: Line cut through WLI data of multiple features. The original FIB fabricated surface (solid line) is compared with the smoothed shape (dashed-dotted line). The laser treatment has lead to a more pronounced indentation and a smoothing of large length scale components is apparent. Bottom: AFM measurements of small feature with $\text{RoC} = 4 \mu\text{m}$ before (left) and after (right) the CO₂ laser smoothing. The sharp edges are removed by the laser treatment without large changes in the feature depth.

Table 5.1 summarises the results of the AFM measurements. The quality of the AFM tip was controlled by measuring the surface of a super polished mirror with a nominal surface roughness of $\sigma = 0.25 \text{ nm}$. Fig. 5.3 presents a subset of the datasets, summarising the general findings in exemplary plots of the surface height (left) and the radially averaged power spectral density (PSD, right) for the three different types of samples: The as-FIB-milled surface, the post-laser treatment FIB milled surface and the reference mirror. For the reference $\sigma = 0.22 \text{ nm}$ was found, which is in reasonable agreement with the nominal value and confirms the quality of the tip and the reference mirror. Note that the ordinate in all three rows has the same scaling to allow direct comparison. The pre-treated FIB surfaces exhibits roughness values around $\sigma = 0.7 \text{ nm}$ with some exceptions which are probably caused by some dirt on the sample. A striking improvement could be found when measuring the post-treated surfaces with σ values ranging from 0.22 to 0.49 nm, the mean value from 8 different features being $\sigma = 0.36 \pm 0.10 \text{ nm}$. The PSD shows a similar trend:

RoC / μm	RMS after FIB / nm	RMS after smoothing / nm
8	0.63	0.49
20	1.7	0.30
30	0.70	-
60	0.53	0.36
80	0.59	-
100	0.84	-
500	0.61	0.31
1000	0.60	0.22

TABLE 5.1: **Surface roughness of concave features after CO₂ ablation.** AFM surface roughness measurements for features with different radius of curvature before and after after CO₂ smoothing. A reduction in surface roughness after the laser treatment is apparent. In particular the data confirms a surface roughness of $\sigma_{\text{Trichet}} = 0.8 \text{ nm}$ reported before for FIB milled features by Trichet [88].

The main difference before and after the smoothing is the decrease in lower spatial frequency portions after the smoothing and a reduction of the involved amplitudes by almost an order of magnitude.

According to the theory presented in Section 3.3.4, only the region below $1/\lambda = 1.73 \mu\text{m}^{-1}$ accounts for the relevant roughness components - which for the presented surfaces contains the largest contributions of the height distribution (the ordinate is in log-form). It is therefore a good approximation to use the surface roughness values obtained from the statistical average presented above to compute roughness induced light scattering.

A noteworthy phenomenon is that features which are directly adjacent to regions that had undergone laser treatment show an increased roughness, in some cases as high as $\sigma = 2 \text{ nm}$. This effect was not studied thoroughly, but a general rule to avoid closely spaced features to prevent any re-deposition induced roughness in the future is advisable on the basis of these findings.

5.1.4 Optical characterisation

To gain further insight into the surface quality of the fabricated features, an open cavity setup was assembled as described in the previous chapter. The cavity consisted of a planar mirror (superpolished substrate S-05106 from LaserOptik GmbH) and a concave feature as outlined before. In the following I use a shorthand notation for each cavity consisting of the RoC in micrometers, the column on the plinth (as defined in 5.1b) and the subscript S if the surface has been smoothed (i.e. 1000b_S for the top cavity in the third column in Fig. 5.1b with a RoC of 1 mm which has been smoothed or 300d for the bottom cavity in the first column with a RoC of 300 μm which has not been treated with the CO₂ laser).

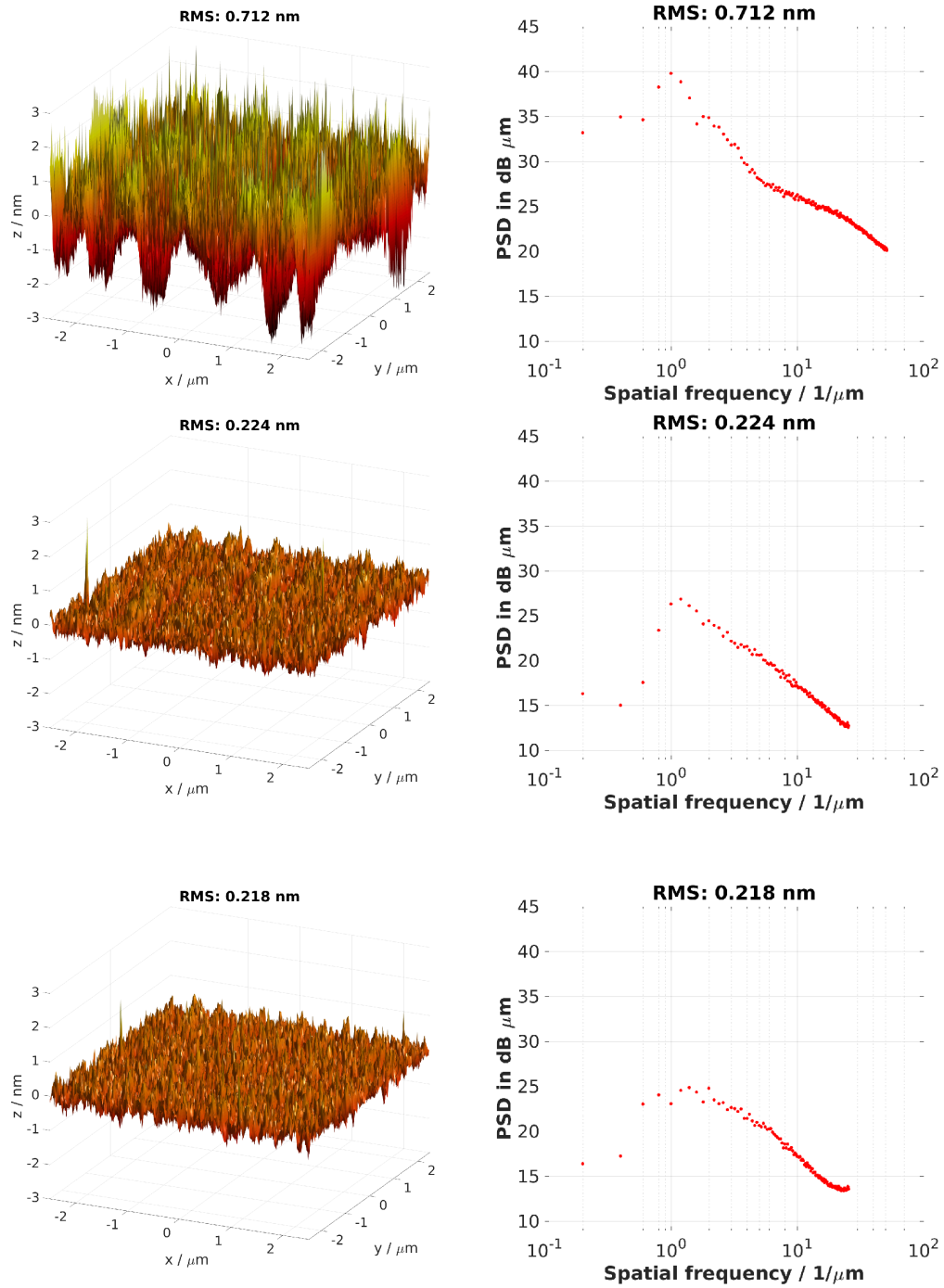


FIGURE 5.3: **Surface roughness of concave features.** AFM measurements of a $5 \times 5 \mu\text{m}^2$ region from the center of the concave feature to determine the surface roughness. Left column shows topography after subtraction of a high-order polynomial, right column presents the radially averaged power spectral densities. Top: FIB-milled surface, Middle: FIB-milled surface after laser treatment, Bottom: Super-polished mirror as reference

5.1.5 Cavity ringdown results for short cavities

To obtain data that allow to judge the optical properties of the mirrors I deploy a cavity ringdown experiment as outlined in the previous chapter. By using a beam splitter in the collection optics path, both cavity spectra and the temporal order of cavity photons can be recorded. Thus it is possible to ascertain the cavity length for each measurement by evaluating the free spectral range $\Delta\lambda = \lambda_2 - \lambda_1$ (with $L = \frac{\lambda_1\lambda_2}{2\Delta\lambda}$). To enable this even for short cavities where $\Delta\lambda > 50$ nm, the super-continuum filter (SuperChrome) is set to a broad window (> 50 nm), allowing to populate multiple modes. The cavity length is then adjusted to position a $\text{TEM}_{0,0}$ mode around the central wavelength $\lambda = 578$ nm and the excitation linewidth is reduced for the time resolved photon collection (i.e. to only collect photons from the $\text{TEM}_{0,0}$ mode in question).

Fig. 5.4 shows the results of this procedure for three different cavity lengths (short cavity length at the top to large cavity length at the bottom). The right image in each row shows the cavity spectrum when illuminated with a broad linewidth, allowing to measure $\Delta\lambda$ and to ascertain that the cavity is positioned optimally with regards to both excitation and collection spot. The high extinction ratio between $\text{TEM}_{n+m=1}$ and $\text{TEM}_{n+m=0}$ is only achieved by using single mode fibers for both excitation and collection and by careful optimisation.⁶ The left image in each row shows the same cavity spectrum for a narrow excitation linewidth in the bottom panel and the time resolved photon trace with a fit to the data in the top panel. The fit is obtained as outlined in Section 4.1.1. I can thus associate a cavity lifetime with each cavity length and calculate the finesse from this data.⁷

While this procedure (single scan) guarantees high quality data as each cavity length is optimised manually, it is very time consuming. Because of this, a second measurement (length scan) is performed, in which the cavity is opened with a stepper motor while illuminated with a narrow linewidth excitation source (≈ 5 nm). At each point both time traces and cavity spectra are recorded, such that a graph $\tau(L)$ or $\mathcal{F}(L)$ can be produced.

Fig. 5.5 presents the results of the single scan measurements for a range of cavities in the left panel. The dashed line corresponds to the resolution limit of the SPAD (i.e. a finesse corresponding to $\tau = 50$ ps). The finesse values for a wide range of cavity lengths are presented and show a general trend of $\mathcal{F} \approx 4 \times 10^4$ at short cavity lengths decreasing for longer cavity lengths to values around 10^4 . While this trend is true for smoothed cavities, all time traces for non-smoothed features resulted in cavity lifetimes below the resolution limit of the SPAD.

⁶Note that the populated modes are the cavity modes where $n + m$ is even. Here the maximum of the electric field lies in the center of the feature. The odd cavity modes ($n + m$ is odd) are barely visible between the even ones as small transmission peaks.

⁷The corresponding equations are given in Section 4.1.4.

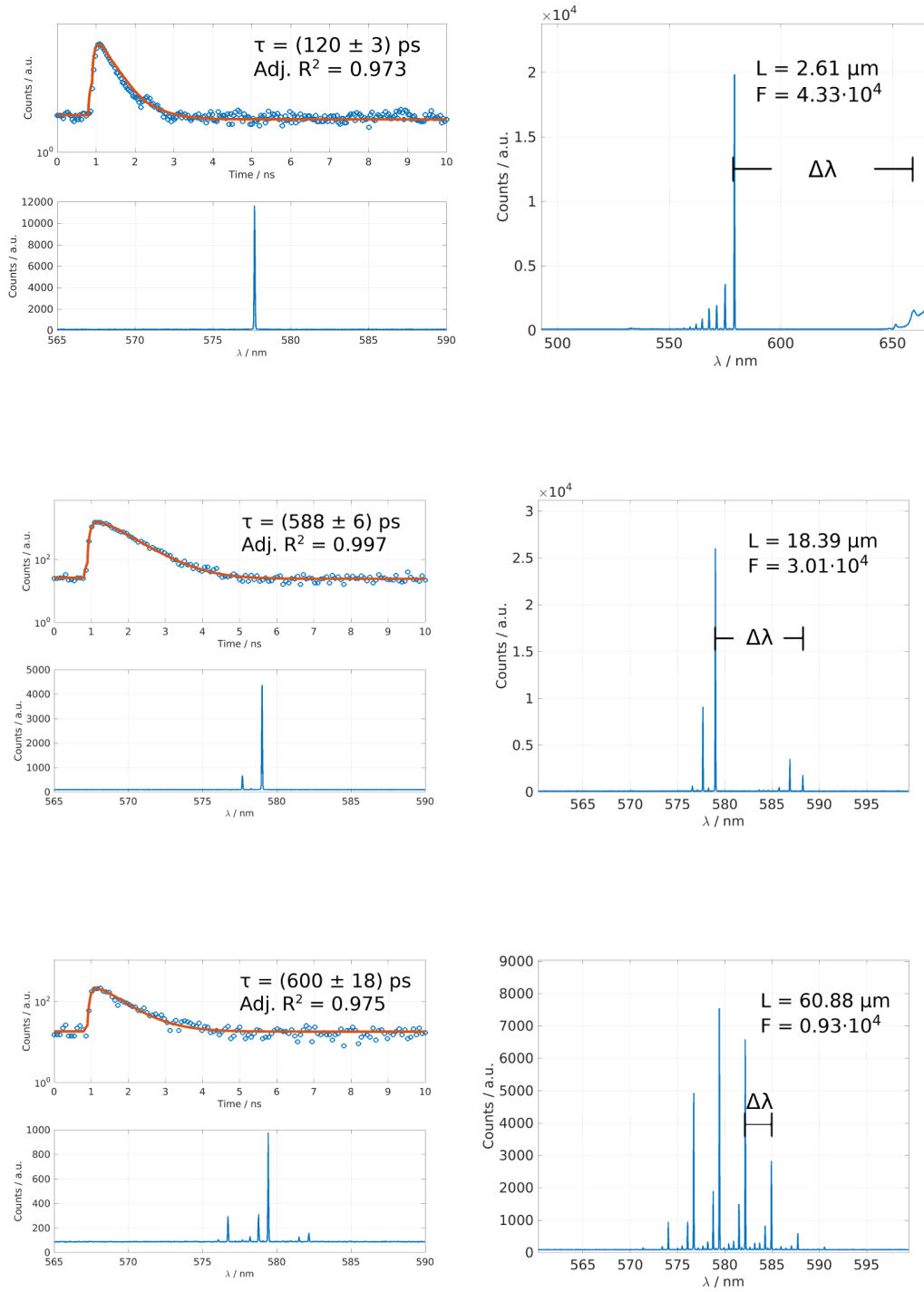


FIGURE 5.4: **Cavity spectra and time resolved photon traces.** The data corresponds to the 1000b_S cavity for three different cavity lengths (top to bottom). Each row shows a broad illumination spectrum (left column, bottom panel) together with the respective time resolved photon signal (left column, top panel). Each time trace is fitted and the time constant is plotted alongside it. The cavity length is obtained from the free spectral range such that the length dependence of the finesse can be mapped out.

While the single scan measurement allowed to quantify the finesse and thus the surface roughness of the concave features, a smaller stepsize lengthscan was used to investigate systematic deviations in cavity light confinement. The right panel of Fig. 5.5 shows finesse data for the 1000b_S cavity obtained by automatically scanning the cavity length with a stepper motor. The dashed line once again denotes the resolution limit of the SPAD.

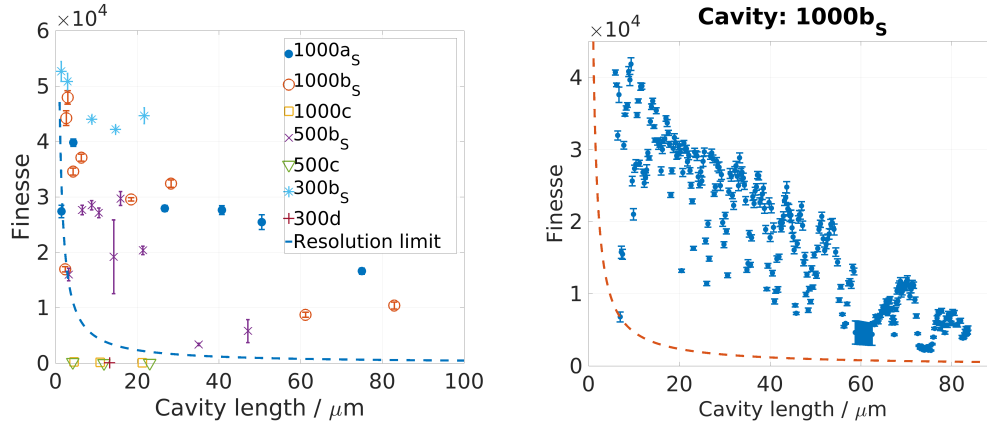


FIGURE 5.5: **Cavity characterisation by ringdown measurements.** Finesse values for a range of cavities as a function of the cavity length derived from cavity ringdown measurements. Left panel: Results from single scan measurements. Right panel: Results obtained by automatically scanning the cavity length for the 1000b_S cavity.

These datasets give a more detailed account of the finesse variations but contain more noise as well. The reason for this is the stochastic nature of collecting the light from multiple cavity modes: Photons from the TEM_{0,0} will exhibit a longer lifetime compared to the light stemming from higher transverse modes. As the cavity length is varied automatically, multiple modes come in to resonance with the light source populating the cavity modes. This effect is particularly strong for small cavity lengths. At larger mirror separations it is less pronounced, as $\Delta\lambda$ no longer exceeds the excitation linewidth, and the variations in the data reflect the average change of the populated TEM_{0,0} modes.⁸ The difference in lifetime for the higher transverse modes depends mostly on diffraction losses due to the larger electric field mode profile on the concave mirror.

5.1.6 Discussion

The presented data allows to quantify the peak finesse at about $\mathcal{F} = 5 \times 10^4$, which corresponds to a total loss of 126 ppm per round trip.⁹ Of this loss $2\delta_{\text{abs}} + 2T +$

⁸For all cases, the population of the TEM_{0,0} modes is optimised by alignment of the excitation and collection spot after single mode fibers.

⁹The relation between finesse and roundtrip losses is given in Eq. 3.14 and can be approximated to $\mathcal{F} = 2\pi/\delta$ for low roundtrip losses ($\delta \ll 1$).

$\delta_{\text{scatt},1} = 100$ ppm are due to the IBS coating (parameters given above) and the scattering off the superpolished mirror.¹⁰ The remaining 26 ppm are the scattering losses caused by the smoothed mirror and correspond with Eq. 3.19 to a surface roughness of $\sigma \approx 0.24$ nm. This result is in excellent agreement with both the AFM data presented above and the coating parameters, which were communicated by the company that fabricated the dielectric coating.

Some of the cavities were not usable because of impurities in the coating or dirty surfaces (in parts visible in Fig. 5.1). The finesse of the unsmoothed cavities could not be specified optically as the measured lifetimes were below the 50 ps resolution of the SPAD. At short cavity lengths ($q < 10$), the linewidths of the cavity modes remained resolution limited (linewidth below 30 pm as measured with SG 1), which results in bounds of $4 \times 10^3 < \mathcal{F} < 2 \times 10^4$ and a surface roughness of $0.7 \text{ nm} < \sigma < 1.8 \text{ nm}$. A likely, but not proven scenario is that both gold residues and redeposition from the laser ablation process further deteriorated the surface of the substrates.

While the single scan measurements produced high quality spectra and time traces which allowed a determination of the finesse with good accuracy, the automated length scans provide data for further analysis. In particular the datasets for cavities 1000a_S, 1000b_S and 300b_S showed systematic behaviour at cavity lengths $L > 25 \mu\text{m}$, of which I have presented the finesse trace for cavity 1000b_S in Fig. 5.5. The lengthscales of the dips in finesse and the ‘ripples’ in the mirror surface, that can be related to the cavity length by the mode waist $w_0 = \sqrt{\frac{\lambda L}{\pi}} \left(\frac{R}{L} - 1\right)^{\frac{1}{4}}$, are of a similar magnitude. A likely origin of the periodically decreasing optical confinement is thus an increased round trip loss caused by diffraction off the surface ripples, where the phase profile of the cavity mode and the mirror surface mismatch. To confirm this theory, one could run mode mixing calculations with the topographic data of the concave features. Since these ripples are caused by a low-spec FIB and will be removed in future work, this investigation is of low importance however. The modemixing formalism presented in the next section addresses the relation between diffraction loss and the topography of the mirror.

¹⁰With $\sigma_{\text{sp}} = 0.21$ nm one evaluates Eq. 3.19 and obtains $\delta_{\text{scatt},1} = 20$ ppm.

5.2 Coupled open-access microcavities

The following section explores the advanced fabrication capabilities that the FIB milling offers. As pointed out in the literature review, FIB milling allows nanometric control over the topography of the concave mirror. This capability is used here to create coupled cavities forming a photonic molecule with varying degrees of coupling between the photonic states as introduced in Chapter 2 [95, 96, 99]. More in detail, this section describes the experimental formation of strongly coupled ‘super-modes’ in the open-access geometry and compares the findings with results from an analytical model using the modemixing formalism introduced in Section 3.3.6. Two identical cavities are gradually merged moving from two uncoupled oscillators (features fully separated) to a single one (features fully merged). In between, the hybridisation of the fundamental mode as well as the first four transverse excited states is analysed. Moreover, taking advantage of the intrinsic tunability of the open cavity approach, the anti-crossing behaviour of this strongly coupled system is demonstrated by simply changing the angle between the two mirrors. A large part of this section has been written with Dr. Aurélien Trichet and has been published in the peer-reviewed journal *Laser & Photonics Reviews* under the title “Spectral engineering of coupled open-access microcavities” in December 2015 [121].

5.2.1 Chip design

We chose the shape of a single cavity to be the isophase surface of a Gaussian mode, introduced in Chapter 3. We keep this formulation for radial displacements that extend well beyond the paraxial approximation. This approach provides us with an analytical form as well as a smooth shape which is ideal to prevent any crack formation during the growth of the DBRs, which was a problem of sharp edged features such as the ones shown in Fig. 5.2 in the bottom left panel. The phase of a Gaussian cavity mode with $m = n = 0$ at a position (x, y, z) is given by:

$$\phi(x, y, z) = \frac{k(x^2 + y^2)}{2R(z)} - \arctan\left(\frac{z}{z_R}\right) + kz \quad (5.1)$$

where the parameters have been defined in Chapter 3. In order to confine the light, the cavity length L has to be smaller than the radius of curvature R on axis. In this study, we have used a RoC of $6 \mu\text{m}$ for a targeted cavity length in the middle of the stability range, ie. $L = 3 \mu\text{m}$. With this set of parameters, the mode waist w_0 is of the order of 800 nm , which leads to a single cavity mode volume of $5 \times \lambda^3$. To obtain the surface coordinate z_ϕ as a function of (x, y) of the isophase surface, one has to solve the following equation:

$$\phi(x, y, z_\phi) = \phi(0, 0, L) = kL - \arctan\left(\frac{1}{\sqrt{\frac{R}{L} - 1}}\right) \quad (5.2)$$

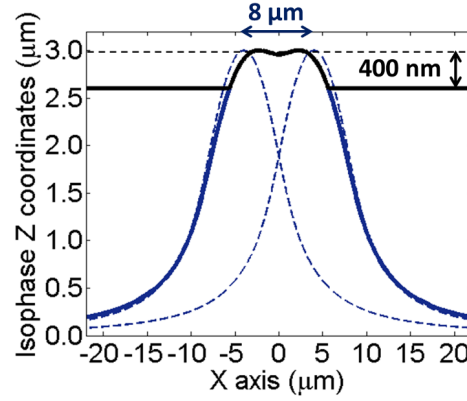


FIGURE 5.6: **Coupled cavity shape.** Gaussian mode isophase. The dashed lines correspond to the isophase for two independent cavities separated by $8\text{ }\mu\text{m}$, the solid blue line to the sum of each independent isophase (Eq. 5.4) taking the normalisation factor into account. The black solid line gives the patterned shape which includes only the last 400 nm of the coupled cavity shape.

The coupled cavity shape $\Delta(x, y)$ is constructed by adding two surfaces defined by the function $z_\phi(x, y)$ separated by a distance d (blue dashed lines on Fig. 5.6a) which leads to the equations:

$$\Delta(x, y) = Z(x, y) \frac{L}{Z_{\max}} \quad (5.3)$$

$$Z(x, y) = z_\phi(x - d/2, y) + z_\phi(x + d/2, y) \quad (5.4)$$

where $\frac{L}{Z_{\max}}$ is a normalisation term that keeps the maximum length of the coupled cavities constant. As long as there is a saddle point in between the two cavities, $Z_{\max} \approx L$ and the normalisation factor is close to unity. However, when the saddle point disappears, the normalisation factor keeps a constant length for the new structure created. For the cavities presented in this study, these two cases are delimited by a separation $d = 7.6\text{ }\mu\text{m}$. We use the shape given by the function $\Delta(x, y)$ as an input of our Matlab function to create the stream file for the FIB200. The lateral extension of the feature is dictated by its depth that we choose to be 400 nm . For a single cavity, a depth of 400 nm corresponds to a diameter around $5.5\text{ }\mu\text{m}$, which is 7 times larger than the expected waist. Therefore, above 99.99% of the mode is contained within the feature. The normalisation term in Eq. 5.3 enables the comparison between each feature since the respective fundamental mode energies will be close to each other.

Starting from flat silica substrates from UQG Optics, we pattern one of them with the FIB200 as outlined in Section 4.2.1 to produce concave templates with the shape given above. These templates are then coated with a Distributed Bragg Reflector (DBR) at the Thin Film Facility of the Department of Physics (University of Oxford) via sputter deposition. In this work, we used 10 pairs of $\text{SiO}_2/\text{TiO}_2$ giving a

macro-reflectivity above 99.7% at the center wavelength of $\lambda = 637$ nm, corresponding to a maximum achievable finesse $\mathcal{F} \sim 1000$. We are thus interested in a different regime compared to the data presented before. Here the finesse of the cavity modes is largely irrelevant and our focus lies on the spectral position and relative branching of the different modes.

In order to study the gradual coupling behavior between two cavities, we produced chips with 13×13 features with varying inter-cavity distance d . Fig. 5.7a displays a FIB micrograph of these features on a silicon substrate, silica being non-conductive. In this example, the parameter d is scanned from $d = 10$ μm along the x axis (left cavity) to $d = 10$ μm along the y axis (right cavity), going through fully merged cavity for $d = 0$ μm along both axes. The spectral properties of the fully merged cavities and separated ones are expected to be similar since they feature the same depth (400 nm) and radius of curvature ($R = 6$ μm). Measurements were taken on a sample with $13 \times 13 = 169$ features, resulting in increments in the cavity separation parameter d of $d_{\text{step}} = 118$ nm.

5.2.2 Experimental setup

The experimental setup used to characterise the coupled cavities is the room temperature cavity assembly presented in Chapter 4 in the laser transmission mode. The cavities are placed in proximity to the eucentric height of the kinematic mount, since this configuration enables us to tune the relative angle between two adjacent coupled cavities without inducing significant cavity length changes (see Fig. 5.7c).

Initially the absolute cavity length is set to 3 μm using a white light transmission experiment (see Fig. 5.7b). For the characterisation, a continuous wave TOPTICA laser DL100 with a fixed wavelength of $\lambda = 637$ nm (linewidth < 1 MHz) is focused with an aspheric lens (focallength = 5 cm) onto the chip. In this way the spot size is always bigger than the cavity contour allowing mode matching even to the higher transverse modes with $m + n > 0$. Since the fundamental mode energy changes significantly as a function of d , we do not have an absolute measurement of the cavity length. Therefore, each mode observed experimentally is referred to with its energy difference from the ground (bonding) state (see Fig. 5.7d). The length scale for this sweep is obtained by traversing successive ground states, for which the cavity length differs by $\frac{\lambda}{2}$.

By spatially selecting specific cavities, we can record the transmission spectrum as a function of cavity length. With this method, each maximum transmission peak is associated with a spatial wavefunction imaged onto a CCD allowing us to count the number of nodes and anti-nodes along the x and y direction, and therefore, properly identify each mode. Another way of obtaining this spectral and spatial information is used in a later section, where the normal mode splitting is demonstrated. There we used the fluorescence of a dense layer of quantum dots to populate the cavity

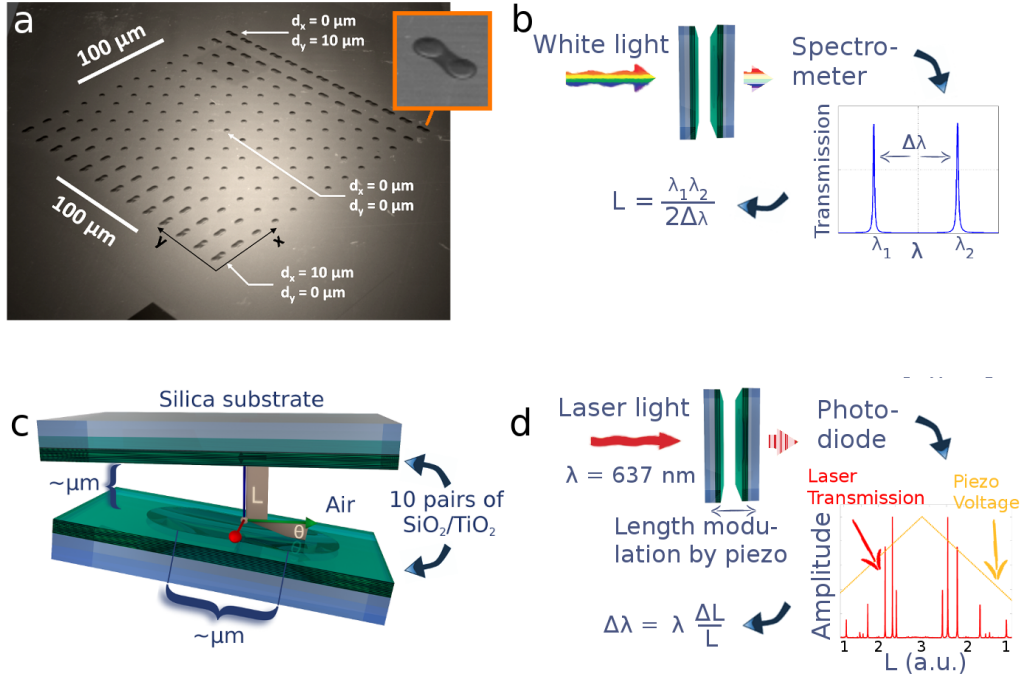


FIGURE 5.7: **Chip design and setup for the coupled cavities.** a) FIB micrograph of coupled cavities templates. From bottom to top the distance d between the two features is changed from $d = (10, 0) \mu\text{m}$ over $(0, 0) \mu\text{m}$ to $(0, 10) \mu\text{m}$. Inset: Zoom into marked area showing coupled cavity feature with more details. b) Length initialisation routine with white light transmission. c) Experimental setup showing control over cavity length L and angle θ between the two mirrors. d) Laser transmission and equivalence between length and spectral sweep.

modes, which is conceptually similar to positioning a broad-linewidth, red lamp between the mirrors.

5.2.3 Mode formation theory and modelling

In the modemixing formalism introduced in Chapter 3 solutions of the electric field distribution for a cavity environment are found by solving the eigenvalue equation $\mathbb{M}|\Psi_i\rangle = \gamma_i|\Psi_i\rangle$, where $\mathbb{M}$ is the modemixing matrix which describes coupling between modes upon a single round trip within the cavity. For the purpose of modelling the coupled cavity a set of the first 500 basis states $\mathbb{H}_{q,m,n}(x, y, z)$ ordered by increasing $m + n$ value is chosen. For an azimuthally invariant cavity those modes are $(m + n + 1)$ -fold degenerate but slight deviations lift the degeneracy and produce energy differences between the states. Each of these states has a further twofold polarisation degeneracy.

Due to the elongation of the cavity profile in one dimension we truncate the basis set at $n + m = 15$ in the perpendicular direction allowing modes of order up to $n + m = 38$ in the elongated direction. For feature separations above $d = 8 \mu\text{m}$ we further change the origin of the basis set to co-align with the left feature. Care was taken that both methods produced the same results for an overlapping region $8 \mu\text{m}$

$< d < 8.5 \mu\text{m}$. To introduce further aspects of the real cavity environment such as the angle between the mirrors, $\Delta(x, y)$ was deformed by applying rotation matrices inducing a tilt by angle θ around the x axis (Fig. 5.7b). It can be shown that the paraxial approximation holds for a single cavity with the parameters that define the basis states ($L \simeq 3 \mu\text{m}$ and $R = 6 \mu\text{m}$). The same is true for the studied coupled cavity modes, since their waist is larger than in the single cavity case, thus guaranteeing a smaller divergence.

The convergence of the process is evident by the fast decaying contributions of higher order modes in the composition of the eigenstates of $\mathbb{M}$, leading to an accurate representation of the actual field distribution. The calculation of the matrix elements is facilitated by the symmetry of the system, allowing the integration to be done in one quadrant only.¹¹ The method is based on MATLABs quad2d routine with absolute and relative error bounds of 10^{-12} and 10^{-10} respectively running on a parallel pool with 4×8 workers each running at 2.6 GHz.

This procedure leads to spectral and spatial determination of the mode properties as described in Section 3.3.6. The full spectrum of the different cavity separation states is obtained by looping over d in 250 nm increments with a finer mesh of 62.5 nm in the coupled regime for $6.8 \mu\text{m} < d < 8 \mu\text{m}$. At each d value the spectrum of eigenvalues and eigenvectors of the corresponding modemixing matrix $\mathbb{M}$ is analysed, leading to the identification of the low energy modes in question. The spectral position (finesse) is obtained by analysing the phase (magnitude) of the eigenvalue γ_i and the spatial wavefunction follows from the composition of the eigenvector $|\Psi_i\rangle$.

5.2.4 Mode hybridisation

Figure 5.8 shows the mode hybridisation process that links the cavity states while merging. The modes shown correspond to a longitudinal quantum number $q = 9$ or a cavity length around $L \simeq 3 \mu\text{m}$. The evolution of the modes from fully separated to merged is given by the rules $(m, n)_+ \rightarrow (2m, n)$ and $(m, n)_- \rightarrow (2m + 1, n)$. Here the subscripts $+$ and $-$ denote the in and out-of-phase relation between the two bare modes. The rule is illustrated in Fig. 5.8a, where the real part of the wavefunction for the first bonding and anti-bonding state is plotted alongside microscope images of the coupled cavity feature. Fig. 5.8c depicts experimental and theoretical spectral information of the first six modes relative to the ground state $m + n = 0$. The premise that fully separated ($d = 10 \mu\text{m}$) and merged ($d = 0 \mu\text{m}$) cavities display the same mode structure is found to be only approximately correct for our system due to the long distance influence of the added shapes $z_\phi(x - d/2, y)$ and $z_\phi(x + d/2, y)$ on each other. For separations $d \rightarrow \infty$, the mode structure coincides.

¹¹The symmetry properties of Hermite-Gauss modes are discussed in Section B.5 of the physical compendium.

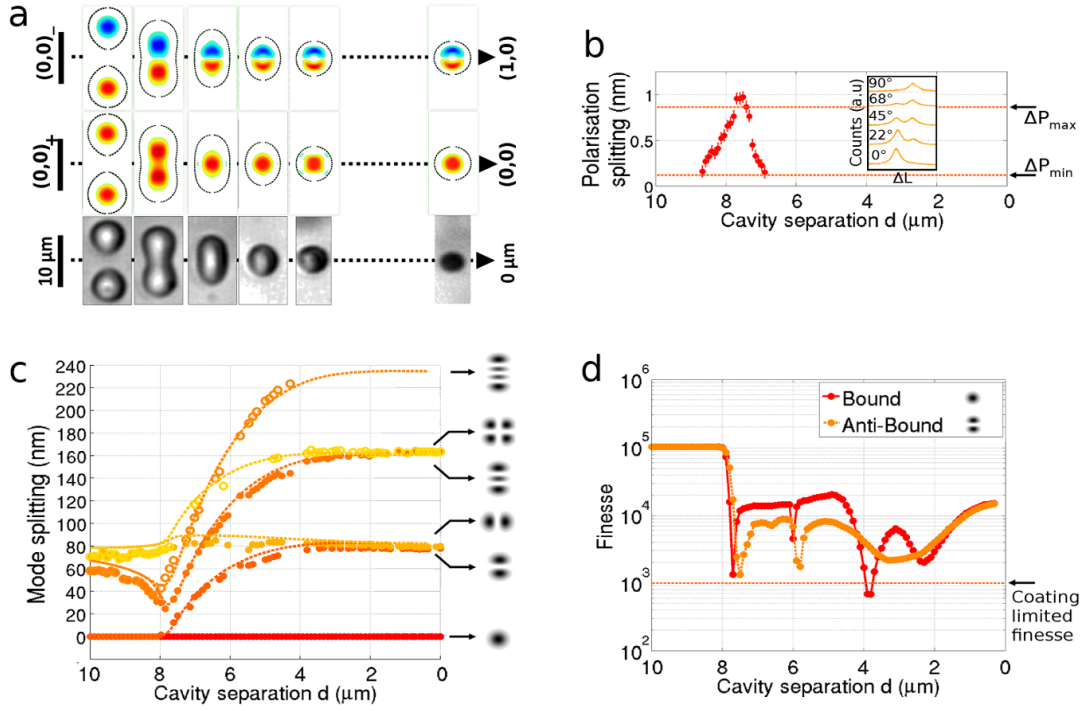


FIGURE 5.8: **Mode hybridisation for coupled cavities.** The hybridisation follows the formation rule $((m, n)_+, (m, n)_-) \rightarrow ((2m, n), (2m + 1, n))$ for merging features. a) Real part of the wavefunction showing the hybridisation of the first bonding and anti-bonding states (upper two rows), and microscope images of the respective coupled cavity feature (lower row). b) Experimentally resolved polarisation splitting of the first bonding state, leaving two peaks with mutually orthogonal polarisation (inset). $\Delta P_{\min}$ denotes the linewidth resolution limit, $\Delta P_{\max}$ is calculated with formula (3) from [122] for $\epsilon = 1$. c) Experimental results (dots) obtained by a laser transmission experiment and theoretical values (dashed lines) derived with modemixing formalism. Theoretical mode positions are shifted towards bigger d values by 350 nm (see text). d) Theoretical finesse values for the first bonding and anti-bonding states obtained with modemixing formalism. The dips correspond to resonances with higher transverse modes of same (m, n) parity for lower q values (as reported in [123]).

For $d = 0 \mu\text{m}$, the effective radius of curvature measured via the transverse mode splitting is given by Eq. 3.24 which gives a value of $(6 \pm 0.1) \mu\text{m}$ in excellent agreement with the fabrication method input parameters. Starting with a cavity separation of $d = 10 \mu\text{m}$ a pronounced splitting between the modes $(1, 0)$ and $(0, 1)$ is observed. The in- and out-of phase modes of the two branches stay degenerate down to $d = 8.1 \mu\text{m}$. For a separation d below $8.1 \mu\text{m}$ the degeneracy is lifted and the coupling between bonding and anti-bonding state grows. For higher n states this process sets in later and the splitting is less pronounced. In between $d = 6 \mu\text{m}$ and $d = 8 \mu\text{m}$, the mode energy decreases for higher m modes due to the decrease of the confining transverse potential. For smaller d the modes gradually evolve to the single deformed cavity case and display a gradually declining splitting with full recovery of the $(m + n + 1)$ -fold degeneracy for $d = 0 \mu\text{m}$.

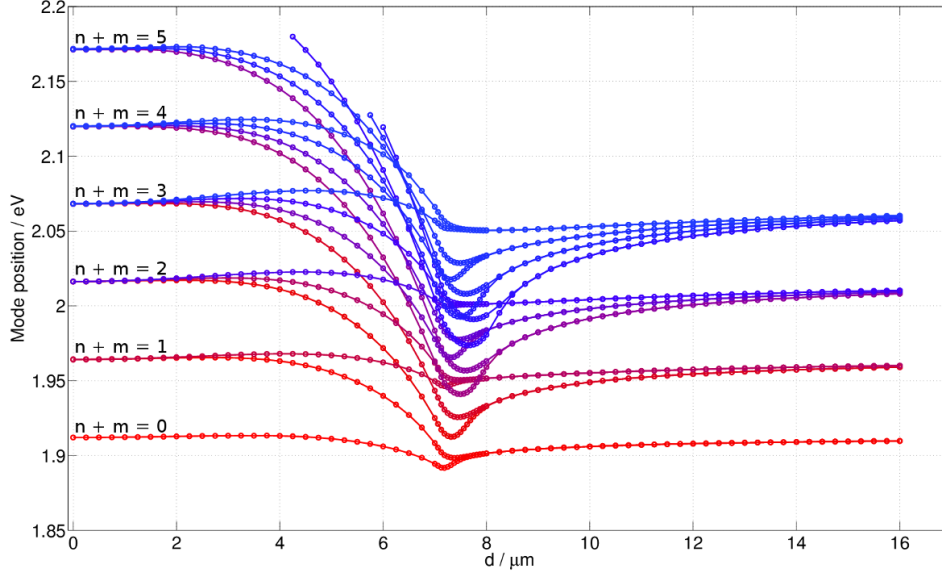


FIGURE 5.9: **Absolute energy position of modes in coupled cavities obtained by the modemixing formalism.** The cavities merge from right to left according to the hybridisation rule given above: $((m, n)_+, (m, n)_-) \rightarrow ((2m, n), (2m + 1, n))$. A central dip in the energy of all modes marks the transition regime, where the central saddle point first appears and then disappears for increasing d , in essence increasing the transverse mode area and thus decreasing the confinement.

Experimental and theoretical values show qualitative agreement with slight deviations in the horizontal position. This mismatch could be accounted for by shifting the theoretical curve in Fig. 5.8c and 5.8d by 350 nm towards larger d values.

We propose that this mismatch stems from the neglected penetration depth into the DBR ($L_{\text{DBR}} \approx 900$ nm) in the modemixing theory. Theoretically a decrease of the effective length of the cavity leads to a decreased mode waist on the curved mirror and to smaller inter-modal coupling, effectively shifting the curve towards smaller d values. With this compensation we obtain quantitatively well matched mode splittings across the whole d parameter range.

Fig. 5.9 shows the mode branching for a larger set of the first 20 modes with longitudinal mode index $q = 9$. Here d increases from left to right, so that states gradually merge according to the formation rule given above from right to left. The data stems from the modemixing calculations and contains similar information as Fig. 5.8c. Instead of giving the mode position relative to the ground state, here the absolute mode position is used. Interestingly the mode energies show a pronounced dip at cavity separations $d \approx 7.5$ μm . It is caused by the larger transverse area accessible to the mode for concave shapes in the transitory regime with a central saddle point. Apart from this, the evolution of the mode energies are quite pleasing to observe.

In general each of the modes is twofold degenerate with respect to polarisation.

Fig. 5.8b shows the lifting of this degeneracy for the first bonding state for intermediate d values between $d = 7.0 \mu\text{m}$ and $d = 8.6 \mu\text{m}$, where the eccentricity of the concave shape is maximal, leaving two well distinguishable cross-polarised peaks (see inset of Fig. 5.8b). Below and above these values no polarisation induced splitting is observed within the linewidth resolution limit given by the coating limited finesse values of ≈ 1000 (limit shown by $\Delta P_{\min}$).

The evolution of the splitting with d tends to rule out a birefringence originating from the coating. In addition, we have checked over identical samples that the lower energy mode is always polarized perpendicularly to the coupling direction. We therefore attribute the splitting to nonparaxial field components along the longitudinal axis of the cavity as described in [122]. This effect is large in the structure studied here due to the small radius of curvature compared to reference [122]. The maximal value of the splitting were taken from [122], and gives $\Delta P_{\max}$ by evaluating $\Delta P = \frac{\epsilon^2 \lambda}{4\pi k R}$ for the eccentricity $\epsilon = 1$. As seen in Fig. 5.8c, this prediction is in good agreement with our measurement for highly elliptical cavities ($d \simeq 7.5 \mu\text{m}$). At this position, the coupled cavity profile transitions from saddle shaped to elliptical. For both higher and lower d values, the splitting rapidly decreases below the linewidth resolution limit.

Fig. 5.8d depicts finesse values of the first bonding and anti-bonding state. By application of the modemixing formalism each mode was assigned a finesse by equating $\mathcal{F}_i \approx \frac{2\pi}{1-\gamma_i^2}$, where γ_i is the eigenvalue corresponding to the eigenmode in question [112].¹² The magnitude of the eigenvalue γ_i thus accounts for diffraction effects - in particular $1 - \gamma_i^2$ quantifies the loss of intensity of mode i after one roundtrip. The experimental limit is given by the dashed line and shows that the coating is the limiting factor for our system. The higher valued diffraction limits show a decrease for intermediary d values with several sharp dips in between before reaching maximal values for d above $7.5 \mu\text{m}$. Because of the finite numerical accuracy given by the modemixing approach I capped the maximal finesse values at $\mathcal{F} = 10^5$ corresponding to mirror losses of 30 ppm. The general trend of the values shown is a result of the long distance influence of the two added concave shapes causing larger feature sizes on the high d end thus reducing diffraction losses. This effect vanishes for larger d values where the finesse returns to the values reported for $d = 0 \mu\text{m}$.

The intermediary dips occur at positions where the respective mode is in resonance with a higher transverse mode of lower q which has the same parity. In this manner the bonding state $(q, 0, 0)$ has a dip at $d = 3.85 \mu\text{m}$ where it is in resonance with the $(q - 1, 2, 2)$ state. This phenomenon has recently been reported for single cavities by Benedikter et al. [123]. Experimentally the resolution of these dips was not possible due to the relatively low coating-limited finesse (dashed line

¹²I used this expression before to determine the finesse of a cavity on the basis of its surface roughness. In general any round trip loss leads to a larger denominator and thus a decreased finesse as is apparent from the definition in Section 3.3.2.

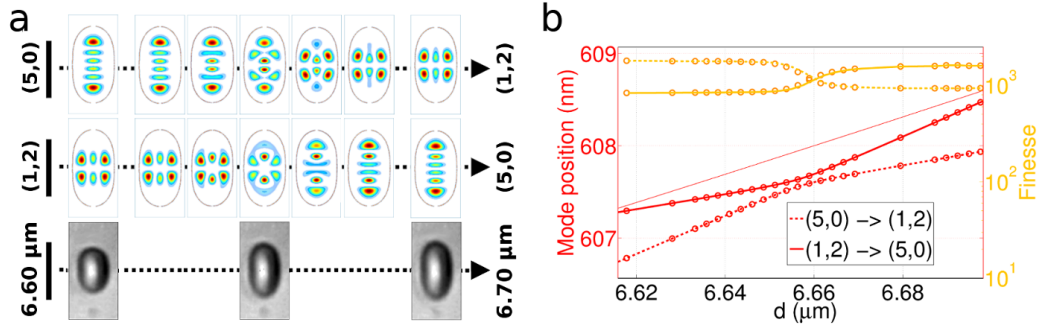


FIGURE 5.10: **Cavity mode anti-crossing.** Avoided crossing of higher transverse cavity modes with same (m, n) parity, $(1, 2)$ and $(5, 0)$, obtained by modemixing analysis as the cavity separation is tuned across the resonance position. a) Spatial wavefunction showing gradual interchange of the mode identity. b) Spectral position (left ordinate) and finesse (right ordinate) demonstrating the avoided level crossing. The third red line corresponds to mode $(3, 1)$ in single cavity notation.

in Fig. 5.8d) - an obstacle which could be overcome by increasing the reflectivity of the DBRs, allowing values as high as $\mathcal{F} \approx 5 \times 10^4$, as demonstrated in the section before. Following the mode evolution for higher excited transverse states the modemixing formalism predicts avoided crossings between modes of same (m, n) parity. One of these anticrossings occurs between state $(1, 2)$ and $(5, 0)$ in single cavity notation around $d \simeq 6.31 \mu\text{m}$ with a splitting of $\hbar\Omega = 0.26 \text{ meV}$. Fig. 5.10 shows the analysis of this phenomenon, depicting the spatial wavefunctions (a), the mode positions (b, left ordinate) and the mode finesse (b, right ordinate) as obtained with the modemixing formalism by looping over d in 2.5 nm increments. The gradual exchange of the mode identity given by its finesse and spatial wavefunction is accompanied by an avoided level crossing in the spectral domain. One could plot the composition of each mode, as I have done for strongly coupled polariton states in Chapter 3. Mathematically the process is equivalent - but here two photonic modes couple strongly and so the mixed states do not carry distinct properties derived from electronic wavefunctions and the resulting state remains a pure cavity mode. Because of this, the splitting in this strongly coupled system is referred to as normal mode splitting, in contrast to electronic systems where the term Rabi splitting is used.

5.2.5 In-situ control of the coupling strength

The wide length tunability of open-access microcavities allows a degree of in-situ control over the mode overlap and therefore inter-cavity coupling strength. In this set of experiments, the cavity length is scanned over the full stability range to extract spectra for coupled modes as a function of longitudinal mode number. Fig. 5.11a and b present these logarithmic spectra stacked on top of each other for $d = 7.77 \mu\text{m}$ and $d = 7.41 \mu\text{m}$. The bonding state mode position is used as a reference point set to 0 nm . Each spectrum is labelled with its respective cavity length for this ground

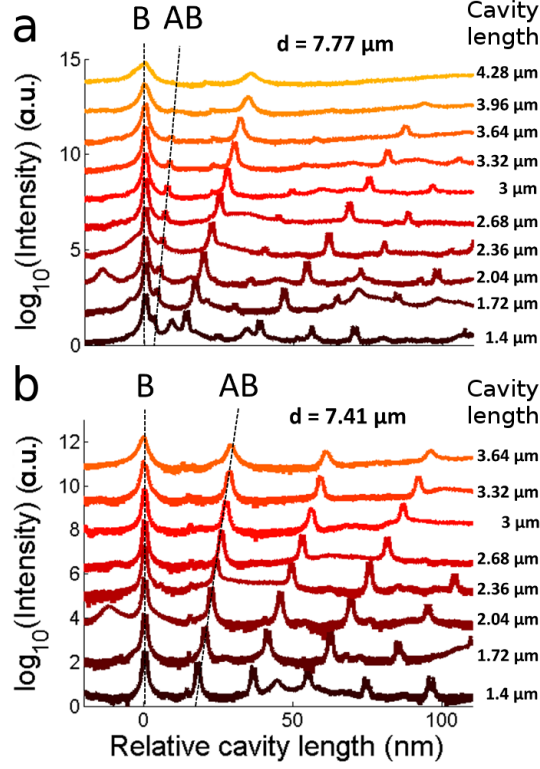


FIGURE 5.11: Logarithmic transmission spectra for different cavity lengths (equivalent to longitudinal mode number q) for a feature separation of a) $d = 7.77 \mu\text{m}$ and b) $d = 7.41 \mu\text{m}$. The experimental curves are shifted with respect to each other for clarity. The bonding (B) and anti-bonding (AB) states are highlighted with the black dashed lines. The absolute cavity length at the B state is given on the right hand side of the figure.

state on the right side of Fig. 5.11a and b. The smallest optical cavity length achieved is $1.4 \mu\text{m}$ which is the smallest length attainable without putting the mirrors into contact (including the DBR penetration depth). Above $L \approx 4 \mu\text{m}$, the cavity mode linewidth increases significantly because of diffraction losses [112]. For $L = 3 \mu\text{m}$ the mode spacing corresponds to the values shown in Fig. 5.8b for the respective d parameter. In both Fig. 5.11a and b, the bonding (B) and anti-bonding (AB) states are highlighted with black dashed lines.

The splitting between these two states is increasing with the absolute cavity length. This is consistent with the fact that the mode waists, and therefore the mode overlap, is increasing for larger length leading to an increased inter-modal coupling. A similar behaviour can be observed for higher excited states as well. For the cavity with $d = 7.77 \mu\text{m}$ (respectively $d = 7.41 \mu\text{m}$), the splitting is then tuned from 2.7 nm to 8.6 nm (respectively 17.7 nm to 28.3 nm) by steps of 0.8 nm (respectively 1.7 nm).

5.2.6 Normal mode splitting of cavity modes

To populate cavity modes with photons, a luminescing material can be placed between the mirrors. Here an ensemble of core-shell CdSe/ZnS quantum dots (Lumi-dot 640 from Sigma Aldrich) were embedded into a thin spin-coated PMMA film on

the planar mirror.¹³

After initialising the setup to a similar cavity length as above ($L \simeq 3 \mu\text{m}$) with a white light transmission experiment, a PicoQuant LDH-D-C-470 laser with $\lambda = 470 \text{ nm}$ and continuous wave mode is focused at a single cavity with moderate power densities of $\simeq 1000 \text{ W/cm}^2$ to excite the quantum dots and cause emission into the cavity modes around $\lambda = 640 \text{ nm}$. By adapting the cavity length such that the $m + n = 0$ mode is positioned at $\lambda = 640 \text{ nm}$ the relative mode spacing to higher excited states is determined with Lorentzian fits to the mode peaks in the cavity emission spectrum, which is recorded with a spectrometer.

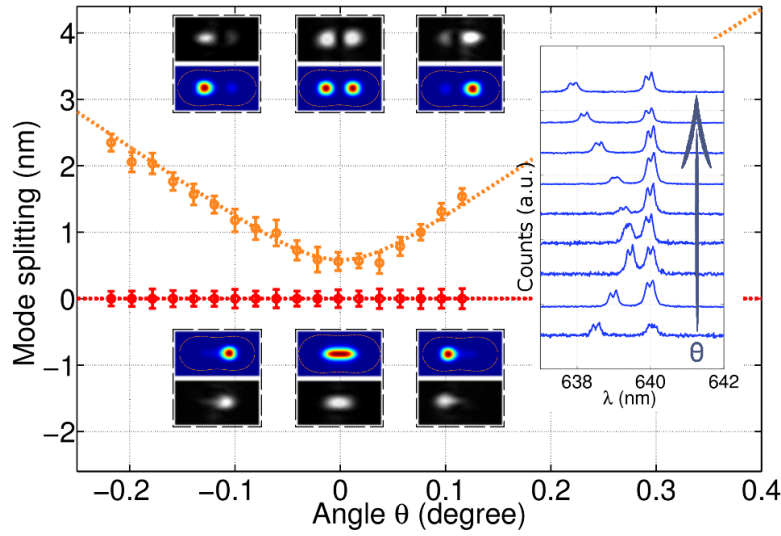


FIGURE 5.12: **Cavity mode anti-crossing by angular tuning between the two mirrors.** Mode splitting of ground $(0, 0)$ and first excited $(1, 0)$ (bonding and anti-bonding) state for coupled cavity with $d = 7.45 \mu\text{m}$ showing anti-crossing behaviour when tuning the angle between the two mirrors (see 5.7c for a schematic of the experiment). The dots correspond to experimental results with linewidths given by the error-bars and agree well with the theory (lines). The small insets depict the spatial wavefunction for the two modes as observed experimentally (grey colourscale) and predicted theoretically via modemixing (blue-red colourscale). The large inset shows a selection of the original spectra; each mode is polarisation split due to the eccentricity of the cavity (comp. with Fig. 5.8b).

In order to prove that the cavities are strongly coupled and that the spectral splittings are not just an effect of the cavity shape, we demonstrate the characteristic anti-crossing behaviour between the ground state and first excited state. This experiment is performed simply by changing the angle between the two mirrors, thus varying the relative length of the two cavities. This experiment was performed for a separation parameter $d = 7.45 \mu\text{m}$ and for the angular range $-0.25^\circ < \theta < 0.15^\circ$ (see Fig. 5.7c for visualisation). For each angle, the length of the cavity was adjusted to fix the ground state $n + m = 0$ at the spectral position $\lambda = 640 \text{ nm}$. Each mode was split

¹³The deposition procedure is described in Section 4.2.2.

by 0.3 nm into two orthogonally polarised peaks due to the cavity eccentricity and was fitted with a double Lorentzian function (see the large inset in Fig. 5.12). The width and the position of the two peaks showed the same behaviour and contain the same information, which is plotted in Fig. 5.12 as a function of the angle θ . The dots denote the mean value of the fitted peaks and the error-bars give their respective linewidths. The continuous line is the result obtained with the modemixing formalism with rotation matrices $\mathbb{R}_x(\theta)$ applied to modulate the mirror shape $\Delta(x, y)$. As the angle is scanned, the anticrossing behaviour is clearly observed.

For Fig. 5.12, the normal mode splitting $\hbar\Omega$ exceeds the linewidth of the cavity modes $\hbar\Gamma$ by a factor of two, implying $\Omega > \Gamma$ as is required for the strong coupling regime as discussed in Section 3.4.3. For large separation parameters d , the strong coupling regime vanishes where $\Omega \approx \Gamma$, which corresponds to a separation of $d = 8.1 \mu\text{m}$.

Further pictorial confirmation of the accurate description by the modemixing formalism is given by the spatial wavefunctions obtained theoretically (red-blue colourscale insets) and experimentally (grey colourscale insets). The images show clearly the hybridisation between individual cavity modes for tuning through the avoided crossing. The same behaviour is seen for higher excited supermodes, which show less pronounced angular sensitivity the higher the excitation number m in the elongated direction is.

5.3 Conclusions of the bare cavity characterisation

In this chapter I have shown a number of improvements of the FIB milled open-access microcavities over the situation established by previous publications [86, 88]. By employing a combined fabrication process with FIB milling and CO₂ ablation I showed large radius of curvature features ($R \approx 1 \text{ mm}$) with a low surface roughness allowing high finesse values ($\mathcal{F} \approx 5 \times 10^4$).

In a second study I demonstrated the photonic qualities of coupled open-access microcavities with mode volumes around $5 \times \lambda^3$. Furthermore I have presented experimental results from coupled cavities in which the inter-cavity spacing is varied and compared the results with predictions obtained by a modemixing formalism. As with other coupled systems, the strongly coupled character of the bonding and anti-bonding states is demonstrated by the mode anti-crossing. By making use of the degrees of freedom which the open-access cavity provides in-situ (length and angular tuning), the coupling between individual cavity modes of the system can be controlled.

This work shows the ability to engineer the mode structure of coupled open-access cavities as a fundamental building block for photonic devices. Such photonic molecules have direct implications for the study of coupled quantum systems. For

example they are attractive for the study of polariton blockade effects and the creation of ultrafast single photon sources. Furthermore it establishes a platform to investigate non-linear phenomena such as phase transitions of light and the transport of excitations in complex systems. ¹⁴

¹⁴The original publication Ref. [121] contains the relevant references, which are outside of the scope of this thesis.

6 Planar cavity strong coupling

The last chapter explored the photonic properties of open cavities in the plano-concave geometry. We have seen that for small radii of curvature (here $R = 6 \mu\text{m}$) the transverse mode spacing Δ^t is of order 10 nm at 640 nm or 30 meV.¹ For larger values of R , Δ^t decreases rapidly as described by Eq. 3.24. To make use of such a cavity one has to work with cavity linewidths below the transverse mode spacing - otherwise the modes blur into each other and the mode volume deteriorates.

In the following chapter I present strong coupling experiments at room temperature. The excitonic states that the cavity mode couples to have linewidths around 50 meV. In the context of strongly coupled system, one strives to match the linewidths of photonic mode and exciton state, as described in Chapter 3 before. This, and the transverse mode spacing argument given above, motivated the use of planar cavities for the experiments in this section. In fact a reflector such as a silver layer of 50 nm on both resonator sides is sufficient to produce cavity modes with a linewidth in the range of 30 meV at short cavity lengths, thus eliminating the need for DBRs.

In the following I use such a ‘poor man’s’ cavity to couple planar cavity modes to the strong optical transitions in the two-dimensional transition metal dichalcogenide (TMDC) WS_2 , which exhibits significant potential for optoelectronic devices. The first study investigates the coupling properties and length dependence of the emerging polariton state. In the second part I combine the 2D TMDC with an organic dye to create hybrid polariton states with mixed excitonic properties from both materials which can be influenced with an applied electric field. A third study rounds up this chapter by showing that collective polariton states can be created in ensembles of colloidal nanoplatelets, thus coherently coupling the excitons of multiple particles. On the basis of the coupling strength and the density of the nanoparticles it is possible to work out the individual transition dipole moment and find confirmation of the previously proposed giant oscillator strength (see Section 2.1.1). The findings presented in this section are largely applicable to FIB-milled cavities as well, but would require smaller excitonic linewidths typically obtained by cooling the sample.

¹The relation between the linewidth in energy ΔE and wavelength $\Delta\lambda$ at a central wavelength λ is given by $\Delta E = hc\Delta\lambda/\lambda^2$.

6.1 Room-temperature exciton-polaritons with two-dimensional WS₂

In Chapter 2 I have reviewed previous room-temperature experiments approaching the strong coupling regime with transition metal dichalcogenides and have pointed out that well resolved exciton-polaritons have yet to be achieved. The lack of clear evidence for this important technological feature and the introduction of the open planar cavity as a means to achieve exciton-polaritons, in contrast to the prevailing monolithic concept, motivates this section. Thus I present a study of monolayer WS₂ coupled to an open Fabry-Pérot cavity at room-temperature, in which polariton eigenstates are unambiguously displayed. By showing that in-situ tunability of the cavity length results in a maximal Rabi splitting of $\hbar\Omega_{\text{Rabi}} = 70 \text{ meV}$, exceeding the exciton linewidth, the polariton formation is proven. Additionally I use the transfer matrix model introduced in Section 3.4.2 appropriate for the large linewidth regime to model the measured data. Furthermore an investigation of the polariton distribution as a function of cavity detuning and coupling strength is presented. The findings establish a platform towards integrated polariton devices at room temperature suitable for spinoptronics and strongly correlated phenomena. Large parts of the data presented in this section have been published in the peer-reviewed journal Scientific Reports under the title “Room-temperature exciton-polaritons with two-dimensional WS₂” in September 2016 [114].

6.1.1 Experimental methods

The open microcavity used for the work in this chapter consists of two opposing flat mirrors, a large dielectric DBR with 10 pairs of SiO₂, TiO₂ (refractive indices 1.45 and 2.05 respectively) with central wavelength of $\lambda = 637 \text{ nm}$ and a smaller silver mirror with a thickness of 50 nm and a reflectivity of $R = 95\%$, deposited via thermal evaporation (Fig. 6.1b). I use the room temperature open cavity setup introduced in Section 4.2.3, which allows both positioning of the silver mirror relative to the WS₂ flake and electrical control of the cavity length. The WS₂ flakes are grown via chemical vapour deposition (CVD) as described in Ref. [51] by a collaborating group from the Department of Materials and transferred onto the dielectric mirror stack, which has a low refractive-index terminated configuration to provide an anti-node of the electric field at the mirror surface and thus optimal coupling to the monolayer.² The flakes have lateral dimensions exceeding 100 μm (Fig. 6.1a) and are transferred with a PMMA helper layer. More information about the transfer process and the sample preparation can be found in Section 4.2.2.

Note that the lower reflectivity mirror (here a silver mirror) dominates the optical confinement within a cavity, as described in Section 3.3.2, resulting here in a

²This is the reason for the use of the DBR mirror. In the third study of this chapter I use a silver-silver cavity, as the thickness of the active layer exceeds the wavelength of the light.

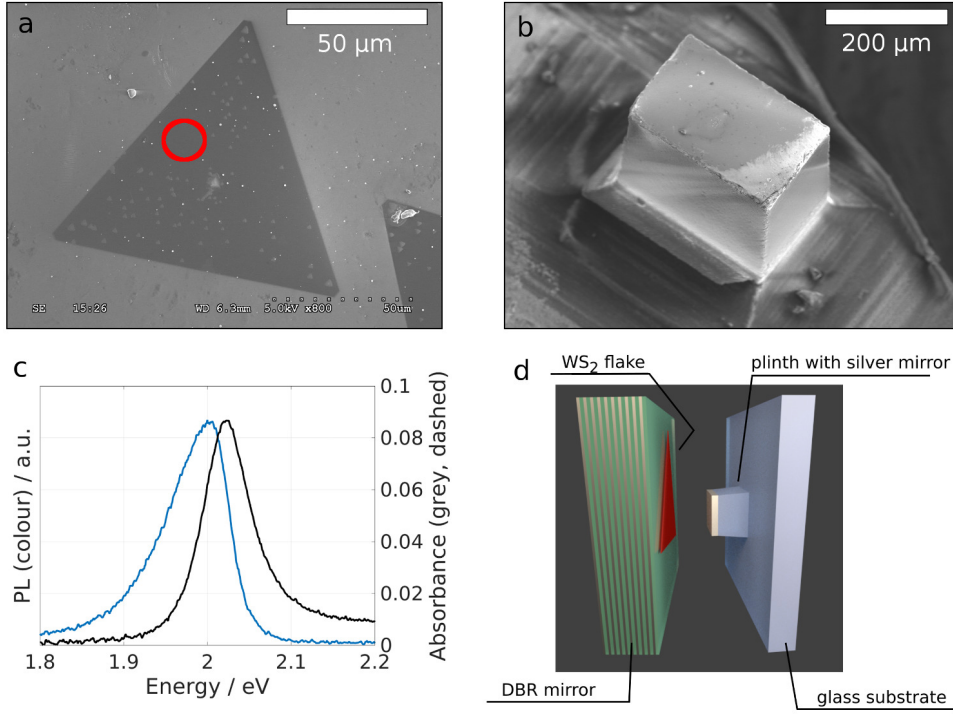


FIGURE 6.1: **WS₂ in an open microcavity.** a) SEM micrograph of a triangular monolayer WS₂ flake transferred onto a DBR mirror. b) Elevated silica plinth with a silver coating forming one side of the microcavity. c) Absorbance (black) and photoluminescence (blue) spectra after off-resonant, continuous wave excitation ($\lambda_{\text{exc}} = 473 \text{ nm}$) of marked region in a. d) Schematics of cavity setup: The left side consists of a DBR with 10 pairs of SiO₂/TiO₂ with single WS₂ flakes transferred to the low refractive-index terminated surface. The cavity is formed by positioning a silver mirror opposite the DBR.

cavity finesse of $\mathcal{F} \approx 50$.³ After non-resonant excitation with a $\lambda = 473 \text{ nm}$ laser at power densities around $\rho_{\text{exc}} = 1500 \frac{\text{W}}{\text{cm}^2}$ the WS₂ flakes show strong neutral exciton emission at 2.01 eV with little, spatially varying contribution from the charged exciton state at 1.98 eV (see Fig. 6.1c), which is attributed to a non-uniform excess electron background [124]. By positioning the silver plinth over a region of the DBR mirror which holds monolayer WS₂ and reducing the distance between the two mirrors below $L \approx 5 \mu\text{m}$, stable cavity modes interacting strongly with the WS₂ excitons appear in a transmission experiment.

The data presented in the following is the result of multiple months of work, in whose span the cavity system was improved successively.⁴ In particular a multitude of similar datasets was recorded, of which only a small fraction appears in this exposition.

³A low finesse of $\mathcal{F} \approx 50$ corresponds to roundtrip losses around 10 %.

⁴The initial cavity setup consisted of two DBR mirrors without lateral tunability. Over the course of the experiments a DBR-Gold and Silver-Silver cavity were used, before converging on a DBR-Silver setup which gave the best results.

6.1.2 Exciton-polariton states in a tunable cavity

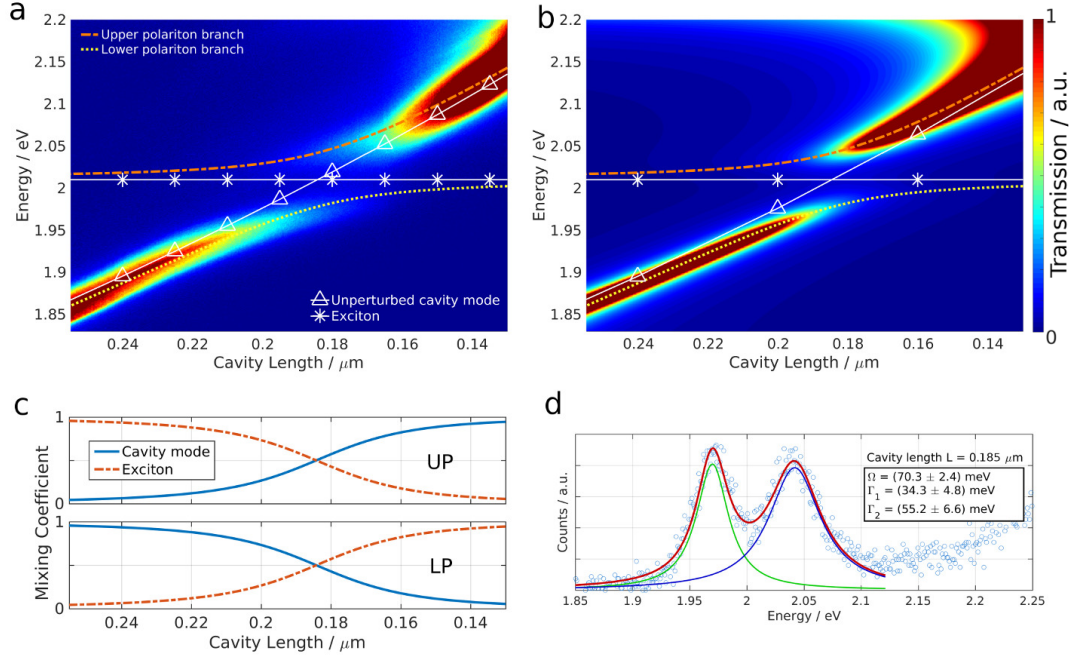


FIGURE 6.2: **Polariton dispersion at room temperature.** a) Transmission spectra as the cavity length is swept, showing typical polariton dispersion. The white continuous lines show the energy of the unperturbed cavity mode (triangles) and the exciton (stars). The energy of the coupled system, the two polariton branches are shown with the coloured, dashed lines. b) Transmission spectra as cavity length is swept obtained by transfer matrix modelling. The dispersion lines from a) are overlaid. c) Photonic and excitonic fractions of upper (UP) and lower (LP) polariton branch. d) Transmission spectrum at maximal photon-exciton mixing revealing a Rabi Splitting of $\Omega_{\text{Rabi}} = 70 \text{ meV}$.

Fig. 6.2a shows successively acquired transmission spectra for different cavity lengths tracking the mode with longitudinal mode number $q = 3$.⁵ The cavity length is decreased from left to right from 260 nm to 130 nm which leads to a change in cavity mode energy moving from 1.85 eV to 2.15 eV. The exciton energy of the monolayer WS_2 stays constant at 2.01 eV (white lines in Fig. 6.2a). These two states are the uncoupled photon and exciton states, which couple in the system and show a typical avoided level crossing, forming the upper (UP) and lower polariton (LP) branch (coloured and dashed lines). Fig. 6.2b shows the calculated transmission spectra obtained with a numerical transfer matrix method with the experimental absorption data for the WS_2 monolayer as an input. The modelled thickness of the flake is 0.8 nm with a peak absorbance of the lowest energy exciton transition of $A = 0.09$, as inferred directly from optical absorption measurement.⁶ The absorption

⁵Compared with the previous chapter, a lower q value is achieved here because the DBR is replaced by a silver mirror which has no penetration depth, i.e. there are only evanescent components of the electric field below the silver surface. For the configuration presented here the total penetration depth is $L_{\text{pen}} = 750 \text{ nm}$ (comp. with expressions given in Ref. [125].)

⁶Similar values can be found in the literature in Ref. [48].

curve was converted to complex refractive index values with a classical Lorentz oscillator model, neglecting the continuum of states above the bandgap energy. The results of the TMM calculations are in excellent agreement with the experimental data presented in Fig. 6.2a.

Analytically the strongly coupled system can be described by the coupled-oscillator Hamiltonian introduced in Section 3.4.5

$$H_{\text{Int}} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} E_{\text{cav}} & \frac{\Omega_{\text{Rabi}}}{2} \\ \frac{\Omega_{\text{Rabi}}}{2} & E_{\text{exc}} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (6.1)$$

The eigenstates of the equation represent superpositions of the bare states, photonic mode and exciton, which are referred to as exciton-polaritons. The coefficients α^2 and β^2 quantify the contribution of photonic and excitonic part respectively, and are plotted in Fig. 6.2c. As the cavity mode is tuned through the exciton energy the lower (upper) polariton branch switches from photon- (exciton)-like to exciton- (photon)-like. Fig. 6.2d contains a vertical slice through the data presented in Fig. 6.2a at the crossing point of exciton and photon energy. The Rabi splitting is evaluated to $\hbar\Omega_{\text{Rabi}} = (70 \pm 2)$ meV from a fit to the data using two Lorentzian lineshapes. The splitting is fully resolved, since the individual linewidths of upper and lower polariton branch are (55 ± 7) meV and (34 ± 5) meV respectively, both smaller than $\hbar\Omega_{\text{Rabi}}$. Note that the cavity mode linewidth increases from ≈ 30 meV to ≈ 60 meV across the energy window presented in Fig. 6.2 even without the presence of an absorber due to the edge of the stop-band of the DBR which is centered around 1.95 eV ($\lambda = 637$ nm). The Rabi splitting thus exceeds both bare state linewidths and, in particular, their difference - a requirement for a strongly coupled systems as described in Section 3.4.3.

6.1.3 Fitting routine

To describe the acquired data, each spectrum is fitted with two Lorentzian peaks with linewidth Γ_1 and Γ_2 and a common amplitude A weighted by the photonic coefficient α^2 for the two polariton branches. To apply the model given by Eq. 6.1, the energy of the unperturbed cavity mode has to be known, which can be deduced as follows: The cavity length for every acquired spectrum is obtained by measuring the unperturbed cavity mode position from a region without a monolayer of WS₂, which I call monitor mode in the following. This is achieved by recording the data from multiple regions of the spectrometer CCD at the same time, thus acquiring multiple datasets of spatially differing cavity modes of the same scan. The unperturbed cavity mode energy is now known⁷ for every frame such that the fit function contains three fixed parameters (the background count rate b , the energy of the exciton E_{exc} and cavity mode E_{cav}) and four parameters to be fitted with Matlabs non-linear

⁷The cavity mode energy is defined up to a small constant, which might arise due to an angle within the cavity, resulting in a cavity length difference between the monitor and active cavity mode.

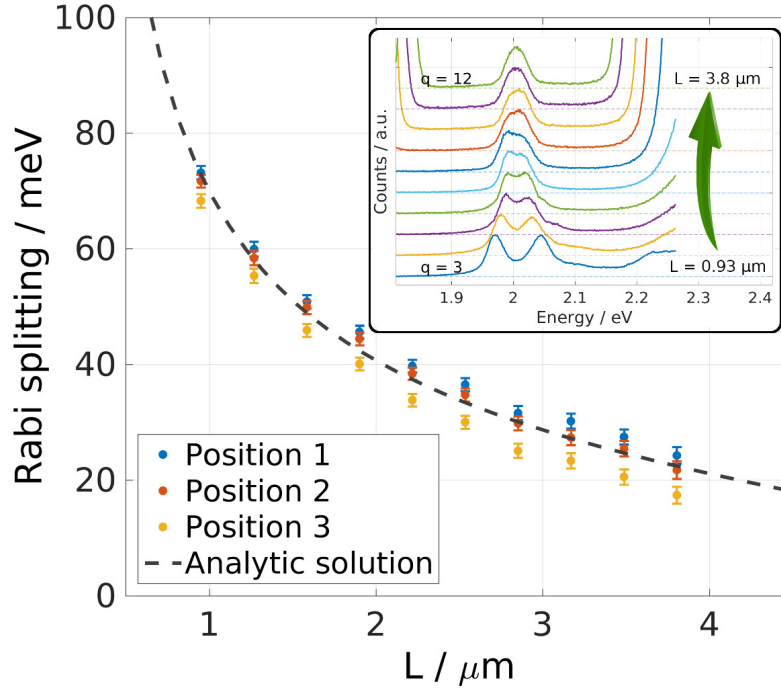


FIGURE 6.3: **Varying the Rabi splitting.** Rabi Splitting for different longitudinal cavity modes ($q = 3, \dots, 12$). Symbols show experimentally obtained values for three different positions on the WS_2 flake with corresponding uncertainty. The dashed line corresponds to the analytic expression shown in Eq. 6.2, derived in the Suppl. Materials. The inset depicts transmission spectra for the different longitudinal mode indices stacked vertically for better visualisation.

least-squares algorithm (the amplitude A , the linewidth of both polariton states Γ_1 and Γ_2 and the Rabi splitting Ω_{Rabi}).

Now the peak positions of both polariton states emerge from the diagonalisation of Eq. 6.1. The analytical expression is rather lengthy and can be found as Eq. B.57 in the physical compendium. To fit one dataset, one has to iterate through each frame corresponding to a different cavity length and perform the fit. The typical procedure is to fit several frames close to the anticrossing point to obtain an accurate estimate of Ω_{Rabi} to then fix this parameter and perform the fits for all spectra.

6.1.4 Length tunability

The open-access design of the microcavity allows for opening the cavity freely, which gives access to different longitudinal mode numbers q (thus performing a cavity scanning experiment as outlined in Section 4.1.5). For increasing cavity length (increasing q) the coupling strength between cavity mode and the WS_2 monolayer decreases. Fig. 6.3 presents data obtained by evaluating the polariton dispersion for the first ten accessible longitudinal mode numbers ($q = 3, \dots, 12$). The Rabi splitting $\hbar\Omega_{\text{Rabi}}$ is obtained as one parameter of the fitting procedure outlined above and

plotted as symbols in Fig. 6.3. The inset in Fig. 6.3 displays the transmission spectra at the crossing point for the different longitudinal mode indices. The dashed line shows the analytic solution for the Rabi splitting derived by solving Maxwell's equations for the specific cavity geometry. I have presented parts of the solution in the introductory Section 3.4.2, the full derivation is reproduced in Section B.7 of the physical compendium.⁸ Thus:

$$\hbar\Omega(L) = 2\hbar\sqrt{V^2 - \frac{1}{4}(\gamma - \kappa)^2} \quad (6.2)$$

$$\begin{aligned} \kappa &= \frac{1 - \sqrt{R}}{\sqrt{R}} \frac{c}{2n_c L_{\text{eff}}} \\ V^2 &= \frac{1 + \sqrt{R}}{\sqrt{R}} \frac{kdWc}{2n_c^2 L_{\text{eff}}} + \frac{kdW}{2n_c} (\kappa + \gamma) + \left(\frac{kd\epsilon_B c}{2L_{\text{eff}} n_c^2 \sqrt{R}} \right)^2 \end{aligned} \quad (6.3)$$

Here R is the mirror reflectivity (here $R_{\text{Silver}} \ll R_{\text{DBR}}$, so that I can set $R = R_{\text{Silver}}$), $L_{\text{eff}} = L + L_{\text{DBR}}$ (L is the geometric cavity length, L_{DBR} is the effective length of the DBR [109]), κ, γ are the cavity and exciton half-widths (HWHM), c the speed of light, n_c the refractive index within the cavity, d the width of the monolayer ($d = 0.8$ nm), $k = \frac{E_{\text{exc}}}{\hbar c}$, ϵ_B the dielectric background and W is a parameter proportional to the oscillator strength of the WS_2 monolayer. ϵ_B and W can be directly obtained from the dielectric function of monolayer WS_2 [48], thus the system has no free parameter. For the fit to the data presented in Fig. 6.3 it is sufficient to measure the absorbance of the flake, which shows slight spatial variations for the sample presented here, and obtain W by comparing the two dielectric functions (of the form derived using the linear response theory in Section 3.4.1).

Comparing the solutions of Eq. 6.3 with expressions found by Savona et al. [126]

$$\gamma_{p_{\text{Sav}}} = \frac{1 - \sqrt{R}}{\sqrt{R}} \frac{c}{n_c L_{\text{eff}}} \quad \& \quad V_{\text{Sav}}^2 = \frac{1 + \sqrt{R}}{\sqrt{R}} \frac{\Gamma_0}{n_c L_{\text{eff}}} \quad (6.4)$$

one identifies a few differences. Here Γ_0 is proportional to the oscillator strength of the quantum well. κ matches the published photonic linewidth, the difference in the denominator stems from the different cavity geometry. The published form of V^2 lacks the two last terms in the truncated solution [109, 126]. The first correction term $\frac{kdW}{2n_c} (\kappa + \gamma)$ is small for small linewidths $\kappa + \gamma \ll \frac{2c}{n_c L_{\text{eff}}}$, but for room temperature polariton applications it becomes sizable. For the data presented here it corrects the value for V^2 by 7% for $L_{\text{eff}} = 1 \mu\text{m}$ and by 25% for $L_{\text{eff}} = 4 \mu\text{m}$. The second term $\left(\frac{kd\epsilon_B}{2L_{\text{eff}} n_c^2 \sqrt{R}} \right)^2$ is small for large cavity lengths and low refractive indices of the thin dispersive medium, i.e. for $\frac{kd\epsilon_B^2}{4L_{\text{eff}} n_c^2} \ll W$. In the present case, where $\epsilon_B = 21$ is large [48], it adds about 28% for $L_{\text{eff}} = 1 \mu\text{m}$ and 7% for $L_{\text{eff}} = 4 \mu\text{m}$ to the value of V^2 (see Fig. 6.4 inset). Fig. 6.4 shows the difference of these expressions. The black

⁸For symmetry reasons I have set $\gamma_x = \gamma_r \gamma_p = \kappa$ in the derivation, which I restitute here.

dashed line shows $\Omega \propto \frac{1}{\sqrt{L_{\text{eff}}}}$, the blue continuous line depicts the analytic solution without truncation of terms in higher order of d , the red dashed line corresponds to the truncated solutions from Eq. 6.3 and the yellow dashed line shows the solution from Savona et al. [126] (Eq. 6.4). Parameters are chosen as for the fit to the data. In particular I chose $W = 21\gamma = 588 \text{ meV}$. I have included the experimental data from one position from the main text to demonstrate the difference in slope and magnitude to the solution given by Eq. 6.4. Note that the model predicts a larger coupling for small cavity lengths, in particular I estimate a Rabi splitting of $\approx 180 \text{ meV}$ for a $L_{\text{eff}} = \frac{\lambda}{2} = 310 \text{ nm}$ cavity.

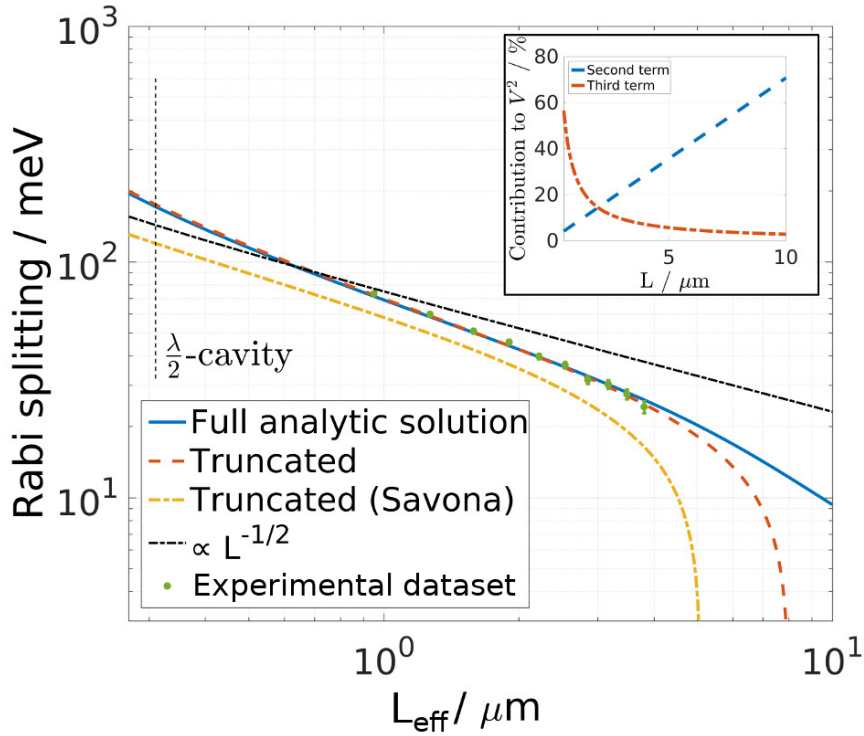


FIGURE 6.4: **Rabi splitting Ω as obtained by different analytical expressions.** The black dashed line shows $\Omega \propto \frac{1}{\sqrt{L_{\text{eff}}}}$, the blue continuous line depicts the analytic solution without truncation of terms in higher order of d , the red dashed line corresponds to our truncated solutions from Eq. 6.3, the yellow dashed line shows the solution from Savona et al. [126] (Eq. 6.4). The green dots are experimental values as presented in the main text. Parameters have the numeric value: $\epsilon_B = 20$, $\gamma = 28 \text{ meV}$, $R = 0.95$, $k_x = 2 \text{ eV}$, $k_p = 2 \text{ eV}$, $d = 0.8 \text{ nm}$, $n_c = 1$, $W = 21\gamma$ (see [48] for choice of ϵ_B & W).

6.1.5 Exciton-polariton population

Interestingly the change in cavity length and the subsequent modulation of the Rabi splitting has stark consequences for polariton dynamics. When performing an optical transmission experiment polariton states are probed by coupling to the photonic component, which leads to the typical changes in intensity across a branch. A different way to populate exciton-polariton states is to optically pump the excitons

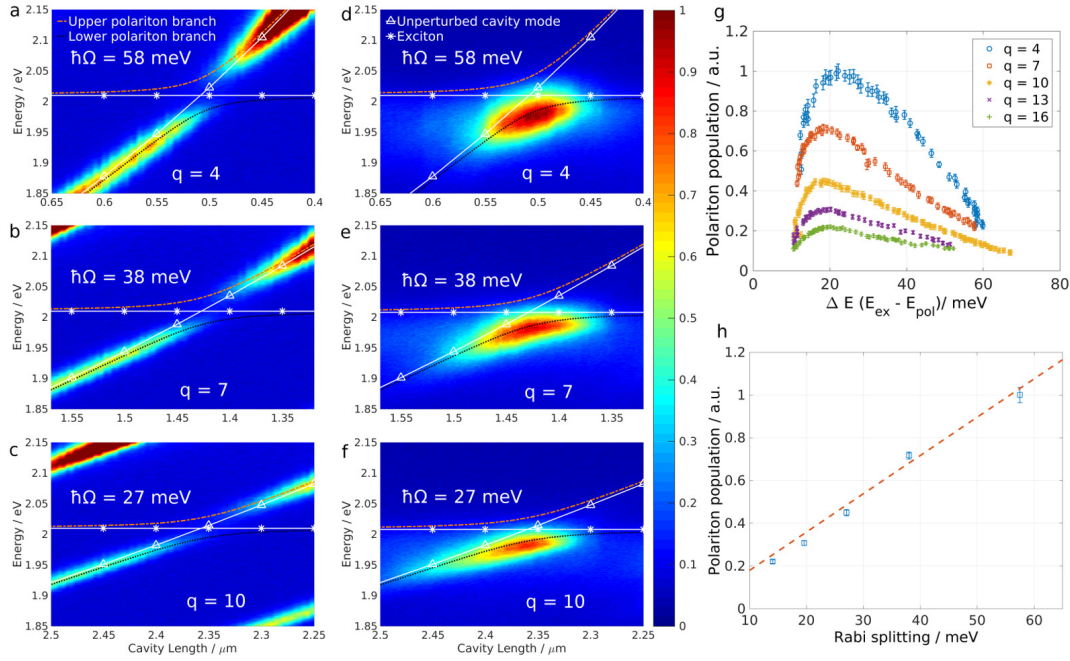


FIGURE 6.5: **Polariton population with off-resonant pump.** Transmission (a-c) and PL (d-f) spectra as cavity length is swept, traversing different longitudinal modes ($q = 4, 7, 10$). For PL measurements the sample is excited off-resonantly with a ($\lambda_{\text{exc}} = 473$ nm) continuous-wave laser. The lines show the dispersion of the uncoupled (white) and coupled system (colour) as in Fig. 6.1. g) Polariton population as obtained from Lorentzian lineshape fits to the PL data for $q = 4, 7, 10, 13$ and 16 . h) Maximal polariton population as a function of the Rabi splitting $\hbar\Omega$. Dashed line shows a linear dependence to guide the eye.

non-resonantly, causing scattering and direct radiative pumping. Figs. 6.5a-c display white lamp transmission data for higher q values $q = 4, 7$ and 10 , showing a decreasing degree of coupling. The overlaid lines depict the uncoupled (white, continuous) and coupled (colour, dashed) dispersions as before (comp. Fig. 6.2). For the datasets presented in Figs. 6.5d-f the cavity length is scanned in the same way as for the transmission datasets, but here the sample is excited with a $\lambda = 473$ nm continuous wave laser. The resulting spectra show that only the central region of the lower polariton branch is populated. In particular the intensity and shape of the emission along the branch varies for different longitudinal mode numbers for the same laser irradiation. It is thus a function of the Rabi splitting. Note that the modulation of the incident laser power due to the change in cavity length is negligible, as the pump wavelength is far below the stopband of the mirror through which the monolayer is excited.

Fig. 6.5g shows the polariton population for $q = 4, 7, 10, 13$ and 16 as a function of the energy difference ΔE between polariton branch and exciton energy ($\Delta E = E_{\text{exc}} - E_{\text{LP}}$). It is obtained by fitting a Lorentzian lineshape to the PL data presented in Figs. 6.5d-f and scaling the obtained amplitudes by the inverse of the square of

the photonic fraction α for the respective polariton branch. In general the lower polariton branch is populated slowly while its energy approaches the exciton energy from below. The population reaches a maximum between $15 \text{ meV} < \Delta E < 30 \text{ meV}$ and decreases rapidly for $\Delta E \rightarrow 0$. The absolute polariton population number is not the same for different longitudinal cavity modes and decreases for a smaller Rabi splitting. In fact Fig. 6.5h shows the maximum polariton population as a function of the associated Rabi splitting, revealing a linear dependence. This trend could be explained by the scattering rate from exciton reservoir to polariton state, which is approximately proportional to the energy difference between the two states [127] and governs the polariton population in the steady state. The upper polariton branch stays unpopulated for all cases.

The off-resonant pump leads to excitation high in the conduction band of the WS_2 monolayer which is followed by a rapid thermalisation, creating an exciton bath which then populates the lower polariton branch [14, 128]. Two known pathways for populating processes are the direct radiative decay channel, whose rate is proportional to the photonic coefficient α of the LPB and the phonon-assisted scattering of excitons into the LPB which is proportional to the excitonic coefficient β [129]. On the other hand there are multiple relaxation pathways for polaritons: the direct radiative decay proportional to α dominating for large ΔE , exciton-electron scattering proportional to β [18] and exciton-exciton annihilation [130] proportional to β^2 . The processes proportional to powers of β result in the fast decay of polaritons for small ΔE . The quantitative description of this system bears potential for further studies. Furthermore the presented system could allow for the investigation of exciton mediated non-linear phenomena [131, 132] such as dissipative phase transitions [133] and strongly correlated states exhibiting superfluidity [134] and Bose-Einstein condensation [135, 136].

6.1.6 Conclusion

To conclude this section, I have demonstrated strong coupling between photonic cavity modes and excitons in two-dimensional atomically-thin WS_2 at room temperature. The coherent exchange of energy between those two constituents results in the formation of exciton-polaritons with a Rabi splitting of $70 \pm 3 \text{ meV}$. Monolayers of WS_2 represent a promising candidate for polariton based devices due to their large exciton binding energies allowing for room temperature operation and very large oscillator strengths. I have demonstrated in situ control over the coupling strength and derived an analytic expression describing the length dependence. By studying the PL of the device it was further shown that the coupling strength directly influences the polariton population dynamics.

6.2 Electrically tunable organic-inorganic hybrid polaritons

In the previous section I have shown exciton-polaritons in a cavity with monolayer WS_2 . In general the excitonic component of the polariton state provides a finite Coulomb scattering cross section, such that the different types of exciton found in organic materials (Frenkel) and inorganic materials (Wannier-Mott) produce polaritons with different interparticle interaction strength. In this section I explore a hybrid polariton state with distinct excitons from two different materials. Technologically such a scheme provides a potential route towards in-situ control of nonlinear behaviour. I demonstrate a device in which hybrid polaritons are displayed at ambient temperatures, the excitonic component of which is part Frenkel and part Wannier-Mott, and in which the dominant exciton type can be switched with an applied voltage. The device consists of an open microcavity containing both organic dye and a monolayer of the transition metal dichalcogenide WS_2 . Large parts of the data presented in this section have been published in the peer-reviewed journal *Nature Communications* under the title “Electrically tunable organic-inorganic hybrid polaritons with monolayer WS_2 ” in January 2017 [137].

6.2.1 Hybrid polaritons

As touched upon in the introduction of this section, in general two different types of excitons are distinguished - the Frenkel and the Wannier-Mott exciton. The Frenkel exciton is characterised by its strong binding energy (order of 1 eV) and large oscillator strength [138]. However, a small Bohr radius (~ 1 nm) and relatively low mobility ($\sim 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) make for weak exciton-exciton interaction cross sections. Wannier-Mott excitons generally have lower binding energies (a few meV) and smaller oscillator strengths but larger scattering cross sections. For the class of two-dimensional transition metal dichalcogenides (TMD) the exciton classification is not trivial since the exciton binding energy can be as high as 700 meV [124]. However, due to their crystalline structure the carrier mobility is large ($\sim 40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [139], the Coulomb interaction in the confined plane is strong and the wavefunction is of Wannier-Mott type (i.e. with an extension over a large number of unit cells)[140].

Engineering polariton states for nonlinear effects in compact optoelectronic devices remains a major challenge. A possible pathway towards controlling the physical properties of polaritons within a device is the use of hybrid polariton states [141, 142]. Such states combine excitonic properties from different materials, thus creating polaritons with properties beyond those that can be created by any single material. The superposition weight of their components can be modified in-situ by changing the resonance condition between the different excitons and the cavity mode.

6.2.2 Experimental methods

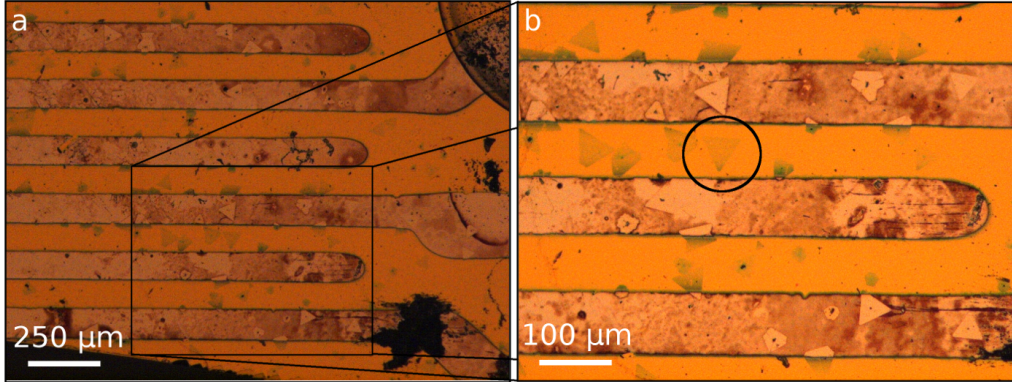


FIGURE 6.6: **Optical microscope images of WS_2 flakes on a DBR with electrodes.** a) Large field of view (x20) showing the individual silver electrodes, which are connected to either side. b) Zoom (x50) into region marked in a, showing randomly aligned WS_2 flakes on top of the silver electrodes. The circle marks one of the flakes used for this study.

The cavity setup is the same as in the previous section. To enable electrical control within the cavity, silver electrodes with a width and a spacing of $90\ \mu\text{m}$ are thermally evaporated on top of the DBR, as shown in Fig. 6.6. This process is facilitated by masking a region of the DBR with a laser processed foil defining the electrode shape. The thickness of these electrodes is similar to the thickness of the silver layer on the small opposing mirror, approximately $50\ \text{nm}$. The WS_2 flakes are grown and transferred as described in the previous section and the introductory Section 4.2.2. Here the silver electrodes are evaporated first, hence resulting in a random distribution of WS_2 flakes relative to the electrodes. As the average size of a WS_2 flake is $80\ \mu\text{m}$ about 90% of the flakes overlap partially with the silver electrodes (see Fig. 6.6). The results presented below were obtained from a flake which was not in contact with the electrodes, thus ensuring purely electrostatic tuning. The electrodes have a length of $\approx 1\ \text{cm}$ and were connected to thin wires with conducting silver paint at the respective ends.

Experimentally a cavity mode in the region of these electrodes would be spectrally broader and the number of round-trips would be reduced due to the additional absorption of the second silver interface. For the data that I present below the effect that such broadening would have can be estimated:

Given the cavity length of around $500\ \text{nm}$ and the reflectivity of the silver mirror $R = 0.95$, we can equate an effective mode area $A = \frac{\pi L \lambda}{1-R} \approx 19.5\ \mu\text{m}^2$, as derived in [143]. This area translates to a mode radius of $r \approx 2.5\ \mu\text{m}$. Since the region of the sample from which I obtained the results is more than $15\ \mu\text{m}$ from the next silver electrode, the effect from the electrode on the cavity mode is negligible.

The electrodes were pairwise connected to a Keithley 2400 to apply voltages and monitor the current. Care was taken that for the datasets presented, the full voltage was applied and the respective current limits were not exceeded. Fig. 6.7 shows the

absorption lineshape of the WS₂ flake for various applied voltages. The occurrence of trion (or charged exciton) states in atomically flat TMDCs has been reported previously [144, 145]. By applying an electric field to deplete a region of the material from electrons, it is possible to change the Fermi level and thus the spectral weight and position of both the neutral exciton (X^0) and charged exciton (X^-) states [18, 124, 144, 146]. Such electrical control can thus be used to vary the absorption profile. Fig. 6.7 shows the absorbance of an exemplary WS₂ flake for different applied voltages. As the Fermi level is raised for increasing positive biases the spectral weight of the absorption profile shifts towards the charged exciton X^- .

As Fig. 2(a) in Ref. [124] shows, the trion can be quenched by applying a negative gate voltage. The zero bias level of weight in neutral and charged exciton is dependent on the intrinsic doping of the WS₂ flake, which is thought to be a result of the growth and transfer method. On the CVD grown samples of this study I have found variations of X^- contribution on one flake and even larger variations when comparing multiple flakes. In general the X/X^- ratio found for the sample is similar to bias values between -30 V and 0 V in Fig. 2(a) in Ref. [124]. To demonstrate the strong coupling to a cavity mode I chose a region with minimal trion contribution.⁹ The reasoning behind this was, that with more trionic contribution the polariton linewidth increases, the asymmetry between upper and lower polariton branch increases and the Rabi splitting is less obvious.

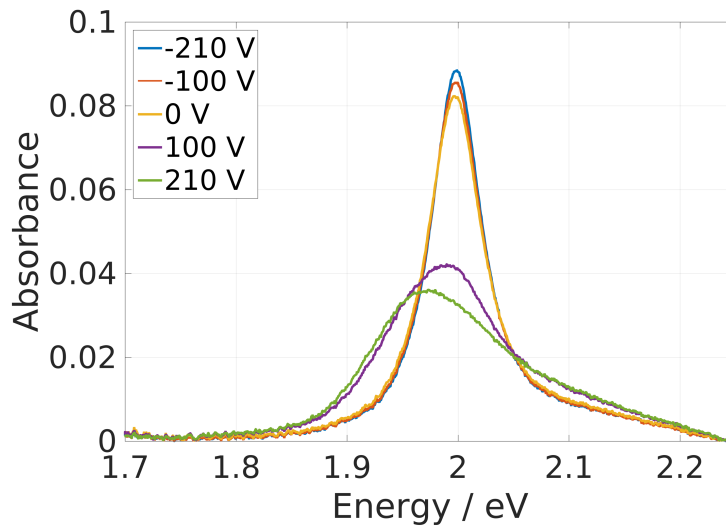


FIGURE 6.7: **Electrical control over the absorption profile of monolayer WS₂.** WS₂ absorption profile as a function of the applied voltage. For large negative voltages the neutral exciton X^0 state dominates the profile (depletion of free electrons), while for the opposite bias the spectral weight shifts towards the charged exciton X^- (abundance of free electrons).

⁹The trion content can be judged from the absorption lineshape for negative applied voltages presented in Fig. 6.9.

The other active component of the hybrid system, the organic dye TDBC¹⁰, was introduced on the opposing silver mirror by dissolving J-aggregated TDBC in an aqueous solution with 5 weight percent gelatine. The solution was then spin coated onto the small silver mirror, giving a polymer, dye layer of approximately 300 nm. A strongly coupled system on the basis of organic dyes is well known in the literature [14, 147]. Fig. 6.8 shows the Rabi splitting for a fixed cavity length as a function of the concentration of the dye TDBC. When plotted as a function of the square root of the concentration the linear relationship is visible. By varying the concentration of TDBC in the aqueous solution it is thus possible to optimise the hybridisation between WS₂ and organic excitons, which mainly depends on the energy difference and oscillator strength of both exciton states.

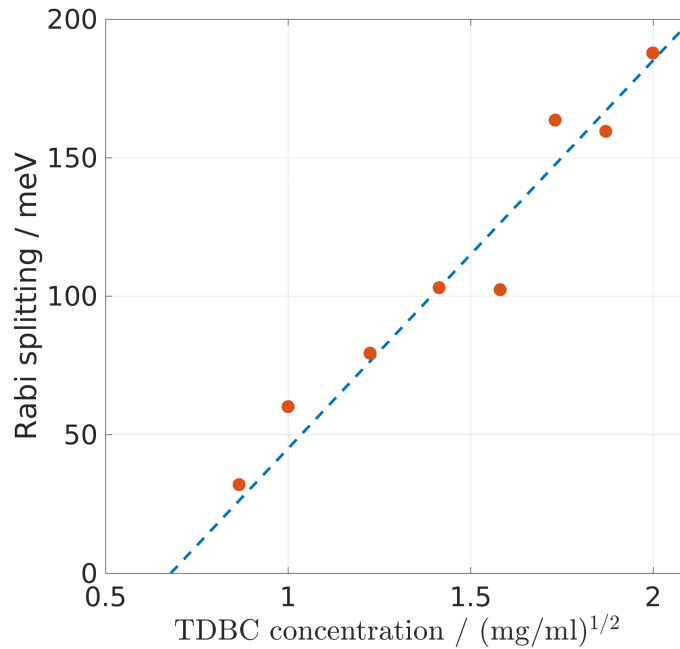


FIGURE 6.8: **Polaritons with the organic component TDBC.** Rabi splitting as a function of the square root of the TDBC concentration for a fixed cavity length, revealing a linear dependence when plotted against the square root of the dye concentration. This dataset was taken by Dr. David Coles and is reproduced with his courtesy.

6.2.3 Hybrid polariton states in the experiment

Fig. 6.9a-c shows the cavity consisting of a distributed Bragg reflector (DBR) with WS₂ flakes on the low refractive index terminated side and a small silver mirror covered with a thin layer of the organic dye. In this experiment a smaller silver mirror was chosen, such that it could be positioned between two electrodes. When the cavity mode energy is tuned between the two exciton energies, it couples simultaneously to both exciton types thereby creating hybrid organic-inorganic polariton

¹⁰In chemists notation 1,1'-diethyl-3,3'-di(4-sulfobutyl)-5,5',6,6'-tetrachlorobenzimidazolocarbo-cyanine.

states. The WS_2 layer is placed between two electrodes such that an applied voltage perturbs the energy of the Wannier-Mott excitons and thereby modifies the composition of the hybrid polariton state. The change in the spectral position alters the relative mixing of Frenkel and Wannier-Mott excitons within polariton states, thus allowing for in situ control of polariton properties such as mobility and scattering cross section.

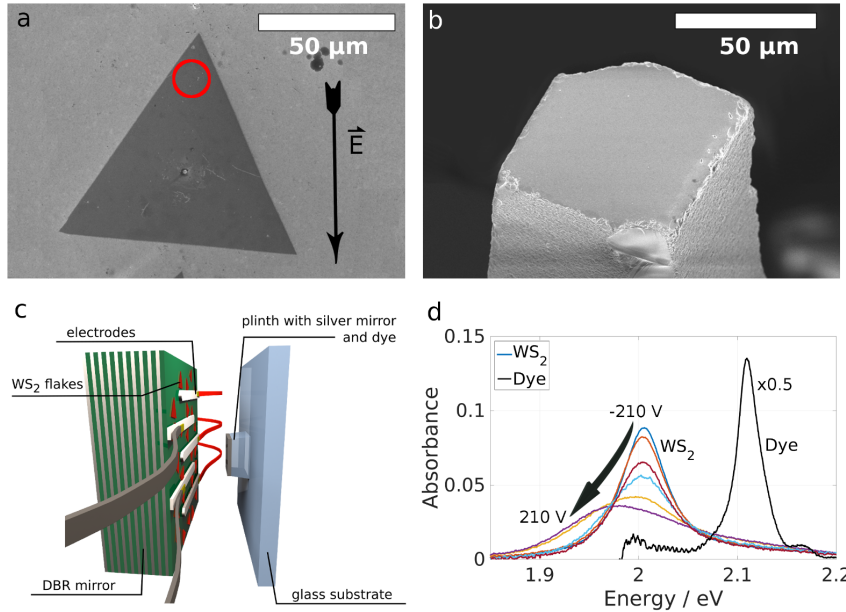


FIGURE 6.9: **Two-dimensional WS_2 between electrodes in an optical microcavity.** a) SEM-micrograph of a monolayer WS_2 flake deposited on SiO_2 terminated DBR, forming one side of the optical microcavity. The arrow denotes the direction of the applied electric field and the red circle the area from which the data was obtained. b) SEM image of the opposing cavity side, a silver mirror on a silica plinth. c) Sketch of the two mirrors with silver electrodes on the surface of the DBR giving electrical tunability within the cavity. d) Absorbance of atomically-thin WS_2 for various applied voltages obtained from the position marked with a red circle in a (colour) and the organic dye TDBC (black, scaled by factor 0.5).

Both the organic dye and the inorganic WS_2 monolayer absorb strongly in the visible, with narrow, excitonic absorption peaks at $E_F = 2.11 \text{ eV}$ and $E_{\text{WM}} = 2.01 \text{ eV}$ respectively. Placed in an electric field, the WS_2 absorption peak position is additionally tunable within approximately 20 meV to the red for electric field strengths of $E = 2.33 \times 10^4 \text{ Vcm}^{-1}$ as discussed above (see Fig. 6.9d).

Here we use the effect to change the WS_2 absorption peak position, amplitude and width within the cavity to alter a polariton state. This polariton state is of hybrid nature, combining Wannier-Mott (WM) excitons formed in the inorganic component WS_2 and Frenkel (F) excitons in the organic J-aggregated dye TDBC. The system of one cavity mode simultaneously coupled to two excitonic transitions can be described by a matrix equation similar to Eq. 3.35 and the treatment in the previous

section:

$$H |\Psi\rangle = \begin{pmatrix} E_c & V_F & V_{WM} \\ V_F & E_F & 0 \\ V_{WM} & 0 & E_{WM} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = E |\Psi\rangle \quad (6.5)$$

Here V_F and V_{WM} are the interaction potentials between the cavity mode and F- and WM excitons.

The state $|\Psi\rangle$ is defined by the three coefficients α , β and γ , which quantify the contribution of photon, F- and WM-exciton respectively. Each of the three eigenstates forms a polariton branch, whose photonic part can be readily observed spectroscopically. Fig. 6.10a shows the dispersion of these branches. As the cavity length is decreased from $L = 0.57 \mu\text{m}$ to $L = 0.39 \mu\text{m}$ the cavity mode energy increases according to $E_c = \frac{qhc}{2L}$, where $q = 4$ is the longitudinal mode index (white continuous line, $\times$).¹¹ As it traverses the exciton energies at E_{WM} (white continuous line, $*$) and E_F (white continuous line, Δ), an anti-crossing is visible which is indicative of the strongly coupled nature of the system. In this way, coupled eigenstates to Eq. 6.5 are formed which we call the lower, middle and upper polariton branch (LP, MP and UP). The constituent uncoupled components for these branches quantified by α^2 (cavity mode), β^2 (F exciton) and γ^2 (WM exciton) are shown in Fig. 6.10b.

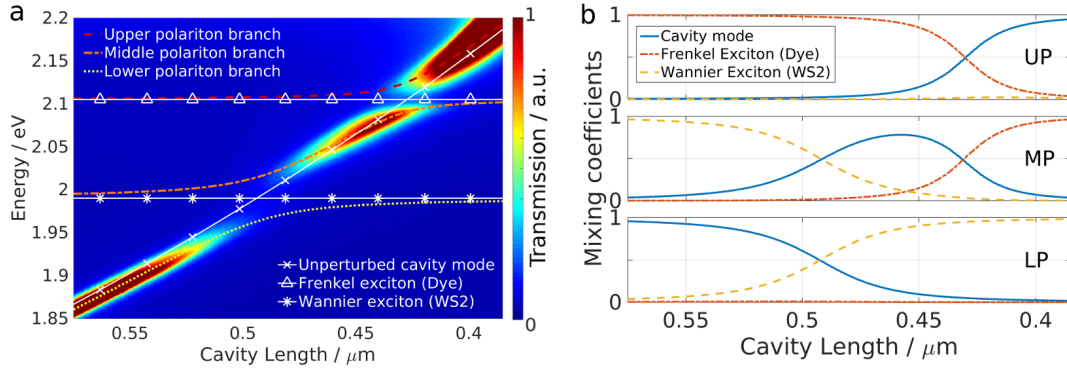


FIGURE 6.10: Transmission spectra of hybrid polariton state. a) Successive transmission spectra of hybrid WS₂-TDBC microcavity for decreasing cavity length from left to right. The white, continuous lines correspond to the uncoupled energies of Frenkel-exciton (TDBC, triangles), Wannier-Mott exciton (WS₂, stars) and cavity mode (crosses). The dashed lines in colour show the dispersion for the coupled system consisting of the three polariton branches, lower polariton (LP, yellow, - -), middle polariton (MP, orange, - -) and upper polariton (UP, red, - -), where the terms in brackets denote the name of the state, the line colour and the line style respectively. b) Photonic (cavity mode, blue, continuous), Frenkel-excitonic (TDBC, red, - -) and Wannier-Mott-excitonic (WS₂, yellow, - -) contribution to the three polariton branches LP, MP and UP for the dispersion plotted in a.

¹¹The electric field intensity decays slowly in the DBR and the system thus has an effective penetration length of $L_{\text{pen}} = 750 \text{ nm}$, similar to the data presented in the previous section.

The nature of the LP (UP) branch transits from photonic (F-excitonic) to WM-excitonic (photonic) as the cavity length is decreased. The more interesting MP branch changes from WM-excitonic to F-excitonic nature for decreasing mirror separation. For cavity lengths in the region $0.525 \mu\text{m} > L > 0.425 \mu\text{m}$, its photonic fraction increases and together with the two excitons, a hybrid polariton state is formed.

6.2.4 Fitting procedure and error propagation

The hybrid polariton study is based on similar transmission data sets as presented in Fig. 6.10. Before proceeding to demonstrate the voltage control over the state, here I want to shed light on the data processing and treatment of experimental uncertainties. Both have a significant impact on the results of this study, because the numbers quantifying the hybridisation of a polariton state depend critically on the coupling strength and details of its dispersion. Thus each data set is acquired and analysed by the following procedure, which deviates slightly from the fitting routine outlined in the previous section:¹²

- The sequence of transmission spectra is acquired by sweeping the voltage of the piezo microactuator, varying the cavity length. The actual cavity length for each frame is obtained by fitting a Lorentzian profile to the unperturbed cavity mode for either the same longitudinal mode (with index $q = 4$ and for energies below $E = 1.85 \text{ meV}$) or the the next one (with index $q = 5$, if the $q = 4$ mode has energies above $E = 1.85 \text{ meV}$). The value of q can be obtained for each dataset from the free spectral range, which then allows the absolute cavity length to be expressed as $L_{\text{cav}} = \frac{qhc}{2E}$, where E is the mode energy.
- Each frame is fitted with Lorentzian lineshape peaks to obtain the position of the individual polariton branches (Fig. 6.11a shows a subset of 20 points with their associated uncertainty as errorbar, increased by a factor of 30 for better visibility).
- The analytic form of the three equations for UP, MP and LP is found by diagonalising Eq. 6.5.¹³ The three expressions are simultaneously fitted to the obtained peaks with Matlab's nonlinear least squares algorithm. Fig. 6.11b shows all positions from the previous step (points with errorbars) and the fitted dispersion (continuous lines).
- In a first round, the four parameters (E_f , E_w , V_f , V_w) are shared in the fitting procedure and obtained as parameters after the fit. In a second round the parameters governing the position and the interaction strength of the dye (E_f ,

¹²The reasons for this deviation is the slightly more complex system: Regions above and below the WS₂ flake were not accessible to record unperturbed cavity modes due to a smaller silver mirror (depicted in Fig. 6.9b), which in turn was necessary to avoid contact with the silver electrodes. Another difference is the polariton state, which consists of three branches, requiring a careful fitting procedure.

¹³The rather lengthy expression is similar to the one presented in Eq. B.55 in the physical compendium.

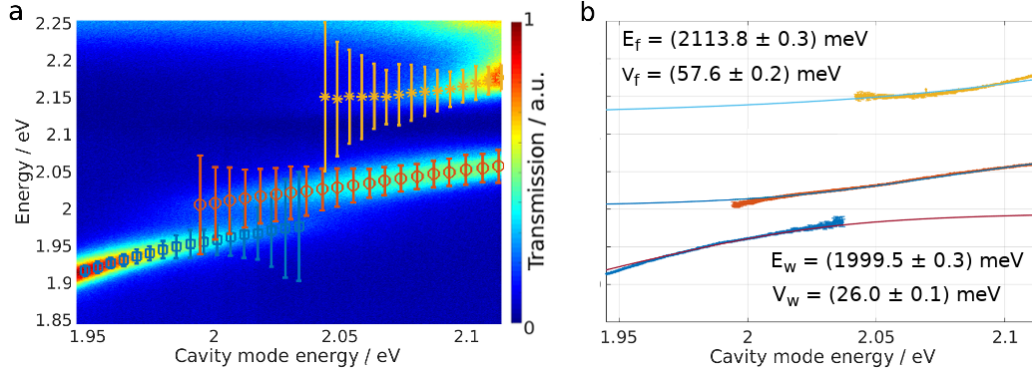


FIGURE 6.11: **Example for transmission spectra fitting procedure.** a) Fitted transmission peaks with error bars superimposed on raw transmission data for different cavity mode energies. Each peak is fitted with a Lorentzian profile. Here only 20 points are shown and the errorbar is increased by a factor of 30 for better visibility. b) Dispersion as given by Eq. 6.5 fitted to the peak positions presented in a. Here each fitted point is drawn with the normal errorbar size. The fit is performed after obtaining three separate equations for UP, MP and LP from diagonalisation of Eq. 6.5 and proceeding with a non-linear least squares algorithm with shared parameters E_f , E_w , V_f and V_w .

V_f) are fixed to a common value obtained by averaging their respective values from the first round.

- The covariance matrix M_{cov} is obtained for each fit. Through diagonalisation of Eq. 6.5 one obtains the eigenvectors, whose components represent the mixing coefficients after proper normalisation. The respective values for point A and B (which will be introduced in the next section) of these values is directly obtained by plugging in the parameters found above. The uncertainty for each of the coefficients is obtained by constructing the Jacobian $J_{ij}^f = \frac{\partial f_i}{\partial x_j}$, where f_i is the respective expression for the polariton fraction and x_j is one of the parameters found above. The uncertainties u can now be calculated from $u = \sqrt{\text{diag}(JM_{\text{cov}}J^t)}$.

6.2.5 Electrical control over polariton composition

Fig. 6.12a-c show the hybrid polariton system with a higher concentrated dye for different applied voltages of -210 V, 110 V and 210 V respectively, as measured by taking successive transmission spectra for varying cavity lengths. As the strength of the interaction between dye and cavity mode is increased, the photonic fraction in the middle polariton branch is decreased and the hybridisation between both excitons is stronger (for the data presented in Fig. 6.10 $\beta^2 = \gamma^2 \approx 10\%$ for a cavity length of $L = 0.455 \mu\text{m}$). By variation of the concentration of the dye it is thus possible to control the composition of the polariton branches, in particular the middle polariton branch. When relying on the photonic part of a polariton state for detection, a reduced overlap between both excitons is desirably. For applications, where

the exciton hybridisation is the only important parameter, a larger dye concentration might be desirable.

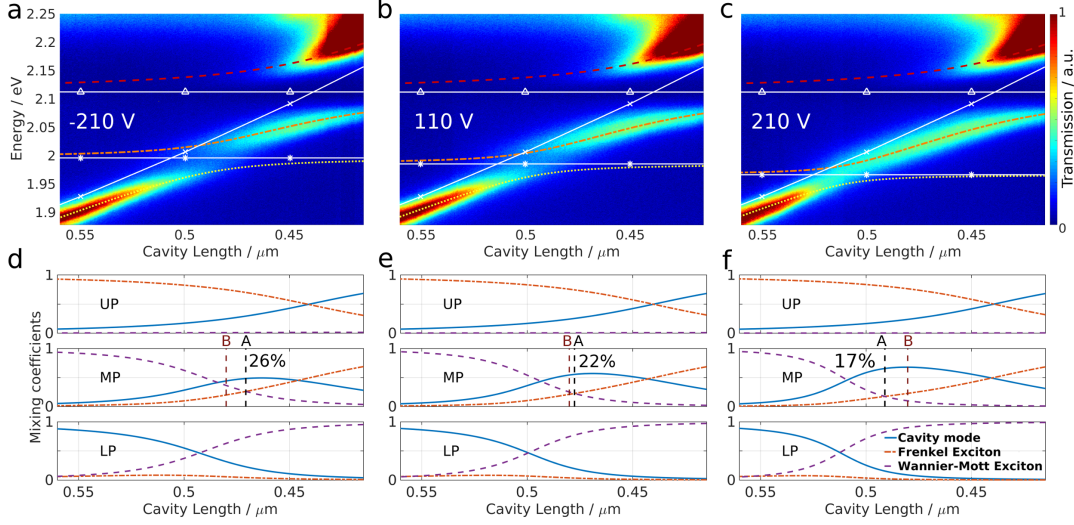


FIGURE 6.12: Electrically controlled hybridisation of Frenkel- and Wannier-Mott-excitons in a polariton state. a-c) Successive transmission spectra of hybrid WS_2 -TDBC microcavity for decreasing cavity length from left to right and different applied voltages of -210 V, 110 V and 210 V for a, b and c respectively. The white, continuous lines correspond to the uncoupled energies of Frenkel-exciton (TDBC, triangles), Wannier-Mott exciton (WS_2 , stars) and cavity mode (crosses). The dashed lines in colour show the dispersion for the coupled system consisting of the three polariton branches, lower polariton (LP, yellow, - -), middle polariton (MP, orange, - -) and upper polariton (UP, red, - -), where the terms in brackets denote the name of the state, the line colour and the line style respectively. d-f) Photonic (cavity mode, blue, continuous), Frenkel-excitonic (TDBC, red, - -) and Wannier-Mott-excitonic (WS_2 , purple, - -) contribution to the three polariton branches LP, MP and UP for the dispersions plotted above respectively. Two points A (black dashed line) and B (red dashed line) mark cavity lengths at which: A) Frenkel- and Wannier-Mott-exciton contribution to the middle polariton branch is equal, B) the cavity length is $L = 0.48 \mu\text{m}$ and the dominant exciton contribution can be swapped electrically. The numerical value displayed in the MP panel as a percentage gives the value of Frenkel- and Wannier-Mott-exciton contribution β^2 and γ^2 at point A.

I shall define two points of interest along the dispersion curve: Point A corresponds to the cavity length at which the middle polariton branch has equal weights of F- and WM-exciton, and is labelled in Fig. 6.12d-f (middle panels). Point B stands for a fixed cavity length of $L = 0.480 \mu\text{m}$, which I will show corresponds to a cavity length where I can electrically switch the MP state from having a dominant Wannier-Mott exciton component to a dominant Frenkel exciton component.

By applying an external electric field, E_{WM} and the corresponding absorption amplitude and linewidth are modified leading to a change in the polariton mixing coefficients. As the applied voltage is increased from -210 V to 110 V (210 V), the Rabi splitting about the Wannier-Mott exciton decreases from $2V_{\text{WM}} = 57 \text{ meV}$ to

46 meV (35 meV) and E_{WM} shifts from 1.997 eV to 1.987 eV (1.968 eV). The absorption linewidth of the WM-excitonic transition increases such that the splitting is not resolvable for applied voltages above 150 V (see Fig. 6.12c). The Rabi splitting about the Frenkel exciton energy is $2V_{\text{F}} = 115$ meV for all applied voltages. For the same change in voltage the excitonic weight at point A changes from $\beta^2 = \gamma^2 = 26\%$ to 22% (17%) while the photonic fraction increases from $\alpha^2 = 48\%$ to 56% (66%). At the same time the cavity length corresponding to point A shifts from $L = 0.471 \mu\text{m}$ to $0.478 \mu\text{m}$ ($0.492 \mu\text{m}$). At point B the composition of the polariton swaps from $\beta^2 = 20\%$, $\gamma^2 = 36\%$ to $\beta^2 = 21\%$, $\gamma^2 = 25\%$ ($\beta^2 = 23\%$, $\gamma^2 = 10\%$) while α^2 increases from 44% to 54% (67%) as the applied voltage is changed from -210 V to 110 V (210 V), therefore the dominant exciton component within the MP branch switches from Wannier-Mott to Frenkel with increasing voltage.

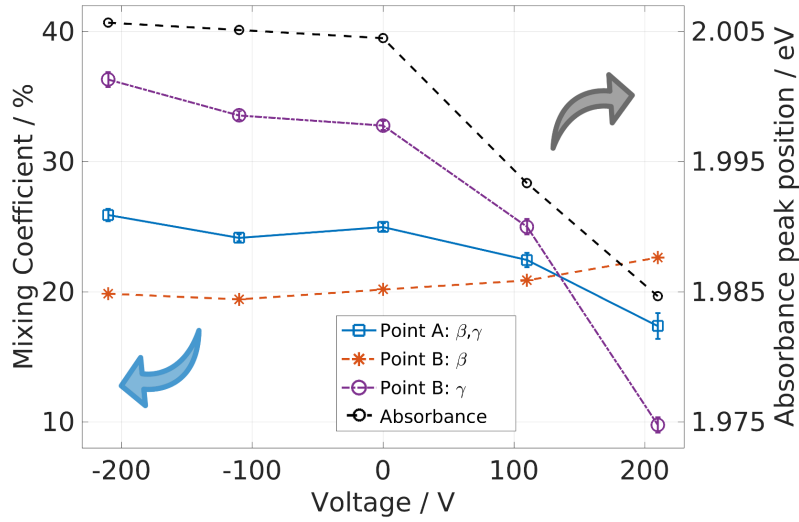


FIGURE 6.13: **Electrical control over polariton composition.** Frenkel- and Wannier-Mott-exciton fraction β and γ in hybrid polariton state for different applied voltages (colour, symbols, left ordinate, blue arrow) and interpolated absorbance peak position of WS_2 outside the cavity (black, dashed, right ordinate, grey arrow). The exciton fractions are shown for two points, where point A corresponds to the cavity length at which $\beta = \gamma$ (maximal mixing) and point B to a fixed cavity length of $L = 0.48 \mu\text{m}$. The errorbars were obtained by fitting the polariton dispersion (Eq. 6.5) to the transmission data and are of similar size as the symbols. The absorbance peak positions were acquired by fitting a Gaussian lineshape to the absorbance shown in Fig. 6.9.

Fig. 6.13 shows the changes in polariton composition as a function of the applied voltage for more intermediate voltages. The black dashed line is obtained by fitting the absorption peaks presented in Fig. 6.9d with a Gaussian lineshape and interpolating the central energy (right ordinate). The datapoints quantifying the polariton composition are the result of fits of the polariton dispersion given by Eq. 6.5 to the transmission data shown in Fig. 6.12a-c as described in the previous section. It is

evident that the change in the hybrid polariton composition stems from the altered WM-exciton state, which can be controlled electrically in the above stated manner.

The j-aggregate exciton energy can be shifted in an electrical field through the Stark effect, but it requires field strengths of about 10^6 V/cm for a 20 nm shift,¹⁴ whereas the field strengths that I obtained in the experiment were about 2.33×10^4 V/cm. The data gives experimental evidence of this, since the Frenkel exciton energy remained unchanged (within the uncertainty of the Lorentzian lineshape fit) for any applied electric field.

Complementary to the data set shown above, I include the results from a different WS₂ flake, demonstrating similar electrical control of the hybridisation. Fig. 6.14 presents the summary of the electrically controlled hybridisation for this flake. While the degree of hybridisation is slightly different for this flake, the overall phenomenon is the same and the dominant exciton component in the hybrid polariton state can be swapped electrically.

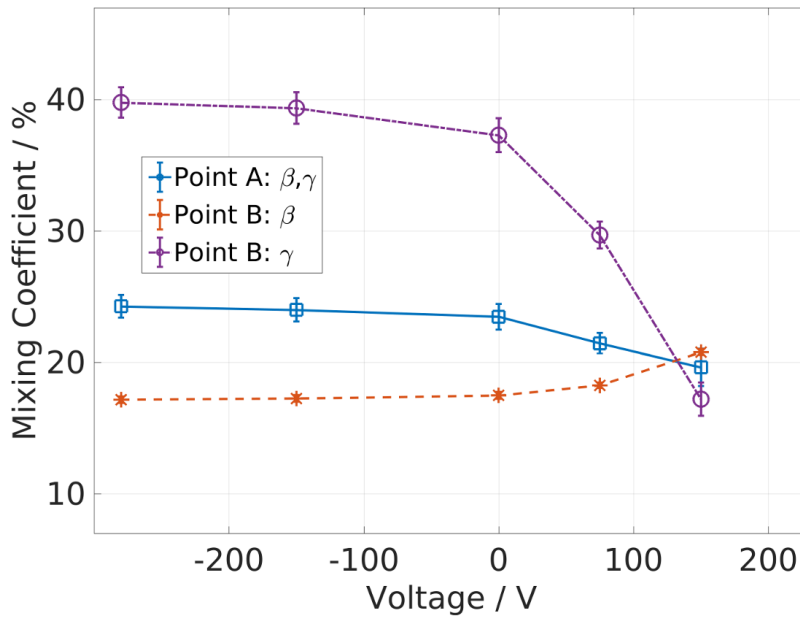


FIGURE 6.14: **Electrical control over composition of polaritons for a second WS₂ flake.** Frenkel- and Wannier-Mott-exciton fraction β and γ in hybrid polariton state for different applied voltages (colour, symbols, left ordinate) and absorbance peak position of WS₂ outside the cavity (black, dashed, right ordinate). The exciton fractions are shown for two points, where point A corresponds to the cavity length at which $\beta = \gamma$ (maximal mixing) and point B to a fixed cavity length of $L = 0.475 \mu\text{m}$.

¹⁴As determined through previous electroabsorption measurements by Dr. David Coles (unpublished).

6.2.6 Putting the results into context

In addition to the electrical tuning of the polariton state, the open cavity allows to bring higher longitudinal modes with decreasing exciton-photon coupling into resonance as presented before. The effect of such lower coupling would be a different mixing of the polariton components, thus allowing further control over the hybrid state.

The change in absorption peak position and lineshape in response to the change in applied voltage originates from the local change in electron density. This effect has been described previously for the PL lineshape [124, 146, 148] and more recently for the absorption spectrum of TMDCs [18, 144]. It is attributed to a combined result of Coulomb scattering, Pauli blocking and Coulomb screening which causes a transfer of oscillator strength from neutral (X^0) to charged (X^-) exciton together with a shift in energy of both states (see [18, 144] for a more detailed description). In the presented system with a laterally applied field without direct carrier injection I make use of the abundance of electrons commonly found in WS_2 and $MoSe_2$ flakes [146, 148], whose distribution across the flake can be altered with the electric field. Due to the geometry of the system, the steady state of this distribution is reached on a millisecond timescale. The slow speed is attributed to the occurrence of scattering defects in the transferred monolayer, caused by locally induced strain and impurities reducing the mobility. Improvements in sample preparation such as the embedding of single TMDC layers within quasi non-interacting hBN heterostructures together with a back-gated electric field geometry would allow for fast switching times, limited with the current technology by the high resistance and therefore the high RC constant of the measurement circuit [149]. Advances in contacting two-dimensional semiconductor layers up to the ohmic contact would remedy this situation [150].

While the transition from X^0 to X^- with increased electron density is well understood [144, 151], the impact such change has on exciton-polariton states is non-trivial and the topic of current research [18, 152]. Due to the fermionic nature of a trion state, the trion-trion interaction is stronger than the purely exciton mediated non-linearity [153], which would make trion-polariton systems attractive for observing strongly correlated phenomena obeying Fermi-Dirac statistics.

6.3 Strong exciton-photon coupling with colloidal nanoplatelets in an open microcavity

After presenting two studies of exciton-polaritons in monolayer TMDCs, in the following section I will explore the collective polariton-state in ensembles of colloidal semiconductor nanoplatelets (NPLs). NPLs exhibit quantum size effects due to their thickness of only few monolayers, together with strong optical band-edge transitions facilitated by large lateral extensions. Here I demonstrate room temperature strong coupling of the light and heavy hole exciton transitions of CdSe nanoplatelets with the photonic modes of an open planar microcavity, which has not been described for this system before. Vacuum Rabi splittings of 66 ± 1 meV and 58 ± 1 meV are observed for the heavy and light hole excitons respectively, together with a polariton-mediated hybridisation of both transitions. I analyse the polariton dispersion and probe the state population after off-resonant, optically pumped excitation. By measuring the concentration of platelets in the film I compute the transition dipole moment of a nanoplatelet exciton to be $\mu = (575 \pm 110)$ D. Large parts of the data presented in this section have been published in the peer-reviewed journal *Nano Letters* under the title “Strong exciton-photon coupling with colloidal nanoplatelets in an open microcavity” in October 2016 [154].

6.3.1 Experimental methods

Since I have presented strongly coupled systems in the planar open cavity geometry before, I keep the experimental introduction at this point very brief. The NPLs are drop-cast from solution on a silver mirror, where they form a dense film and can be introduced in the multi-purpose room temperature open cavity setup, with a mirror alignment as depicted in Fig. 6.16c,f.¹⁵ In the process of drying residual oleic acid acting as a passivating ligand assists in creating a homogeneous film with a thickness of approximately 700 nm. Note that the film is thicker than $\lambda = 550$ nm, allowing to couple to randomly dispersed dipoles in the film on the surface of a metallic mirror, which enforces an alectric node on its surface. Fig. 6.15 shows the topography of the edge of the dried spot as obtained with an AFM (Fig. 6.16d-e similarly show SEM images of the film).

Figure 6.16a shows a TEM micrograph of dispersed platelets. While platelets towards the edges of the agglomeration tend to lay flat of the substrate, other platelets are stacked and lay sideways. The platelets have an average length of $L_x = 32.5 \pm 2.5$ nm, a width of $L_y = 8.2 \pm 0.9$ nm and a thickness of $L_z = 1.36$ nm, obtained by taking the inter-plane distance along the 100 direction (13.6 Å) and 4.5ML of CdSe.

¹⁵More details about the deposition method and sample preparation are given in Section 4.2.2.

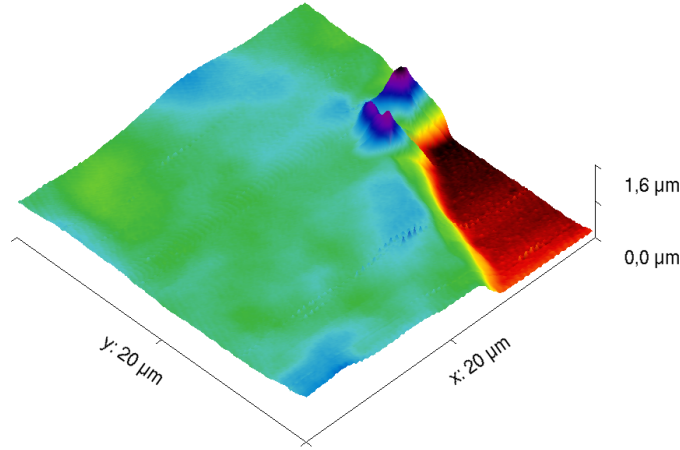


FIGURE 6.15: **AFM image of nanoplatelet film.** The data was acquired close to the edge of the film, showing a clearly defined edge with a homogeneous film. (comp. with Fig. 6.16e).

More details about the synthesis of the CdSe nanoplatelets will be presented after the main results, as the description does not add to the exposition of the main data. Fig. 6.16b shows the photoluminescence and absorbance lineshape of the platelets. For the PL experiments the sample is excited with a continuous wave GaN diode laser with $\lambda = 405$ nm at power densities around $\rho_{\text{exc}} = 1000 \frac{\text{W}}{\text{cm}^2}$.

6.3.2 Collective polariton states

The optical absorption spectrum of the nanoplatelets displayed in Fig. 6.16b reveals two transitions, which correspond to the lower energy heavy hole (hh) exciton with $E_{\text{hh}} \approx 2.42$ eV and the higher-energy light hole (lh) exciton with $E_{\text{lh}} \approx 2.56$ eV.¹⁶ These states have binding energies of $R_{\text{hh}} = (178 \pm 34)$ meV and $R_{\text{lh}} = (259 \pm 3)$ meV respectively [155].

The cavity length dependent optical transmission of the nanoplatelet-cavity system is shown in figure 6.17a. For the maximum cavity length of $L \approx 1.62$ μm a transmission peak corresponding to the lower polariton branch (LPB) is visible at 2.3 eV, which moves to higher energy with reducing the cavity length (note the reversed x -axis of 6.17a). As the LPB peak approaches the energy of the hh exciton at 2.42 eV, a second transmission peak, corresponding to the middle polariton branch (MPB), of energy 2.45 eV appears above E_{hh} . The LPB and MPB energies display an anticrossing about E_{hh} . As the cavity length is decreased further, a third higher energy transmission peak above E_{lh} appears (the upper polariton branch (UPB)) which undergoes an anticrossing with the MPB about E_{lh} .

¹⁶I have presented similar absorption spectra from the literature in Section 2.1.1.

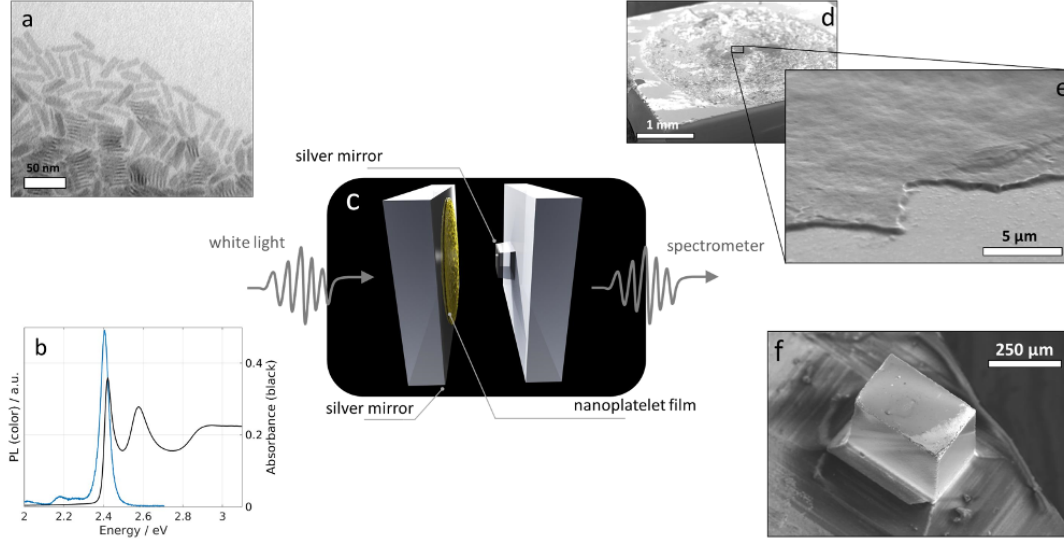


FIGURE 6.16: **CdSe nanoplatelets in an open microcavity.** a) TEM image of dispersed CdSe nanoplatelets. Some stacked platelets are visible towards the bottom laying sideways. b) Photoluminescence (color) and absorbance (black) of a CdSe nanoplatelet film deposited by dropcasting from solution. c) Experimental setup: Open-access microcavity consisting of two opposing, freely positionable silver mirrors. d) SEM micrograph of silver mirror (left side of cavity) with e) dropcast nanoplatelet film. f) SEM micrograph of fused silica plinth coated with 50 nm of silver (right side of cavity).

This system of one cavity mode simultaneously coupled to two excitonic transitions is described by the Hamiltonian introduced in the previous section in Eq.

6.5

$$H |\Psi\rangle = \begin{pmatrix} E_{\text{cav}} & V_{\text{hh}} & V_{\text{lh}} \\ V_{\text{hh}} & E_{\text{hh}} & 0 \\ V_{\text{lh}} & 0 & E_{\text{lh}} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = E |\Psi\rangle \quad (6.6)$$

where V_{hh} and V_{lh} are the interaction potentials between the cavity mode and heavy and light hole excitons. The state $|\Psi\rangle$ is then defined by the three coefficients α , β and γ , which quantify the contribution of photon, hh exciton and lh exciton respectively, familiar from the hybrid system presented before.

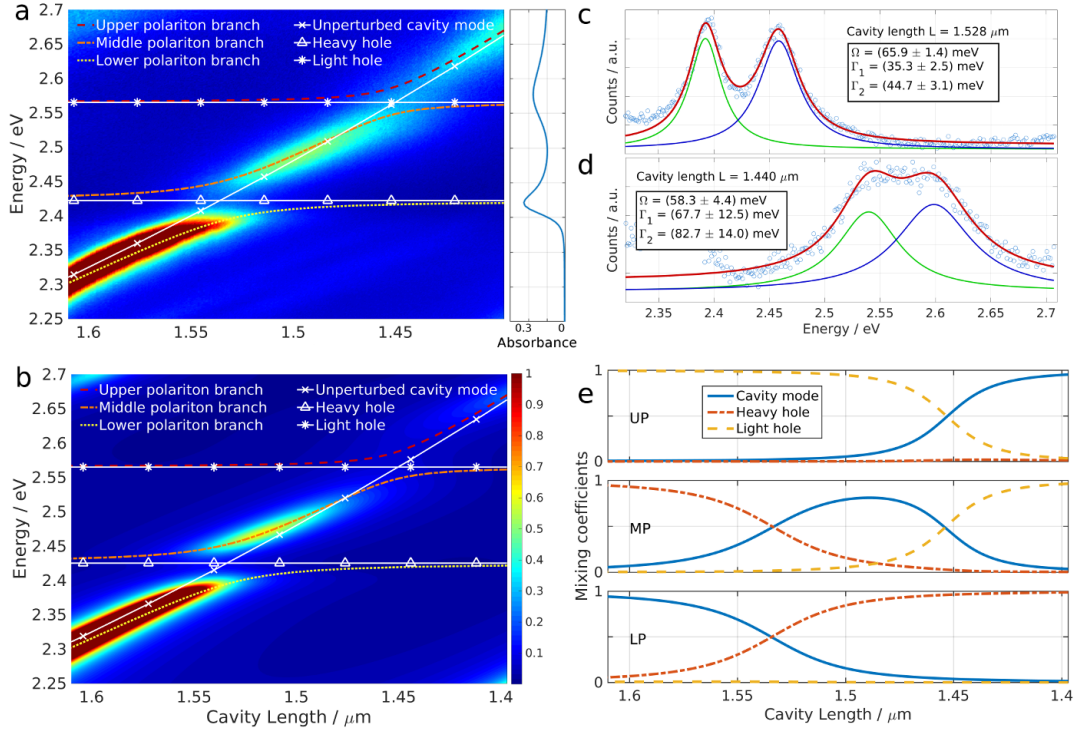


FIGURE 6.17: Transmission spectra and polariton composition for a dense NPL film in an open microcavity. The transmission spectra are normalised and presented as the cavity length is decreased from left to right, obtained experimentally (a) and by transfer-matrix calculations (b). The bare light and heavy hole exciton energies and the unperturbed cavity mode are overlaid in white, the polariton branches obtained from the Hamiltonian H (Eq. 6.6) in color. The avoided crossing around the heavy hole transition is resolved fully with a Rabi splitting of $66 \pm 1 \text{ meV}$, the broad linewidth of the higher energy light hole exciton prevents the resolution of the corresponding splitting, but mode position and intensity clearly indicate the coupling. c) and d) Transmission spectra for cavity lengths $L = 1.528 \mu\text{m}$ and $L = 1.440 \mu\text{m}$ respectively and fits with two Lorentzians revealing the Rabi splitting for the heavy hole and light hole transition. e) Square of coefficients α , β and γ showing the hybridisation of photonic mode and excitonic transitions as obtained from diagonalisation of Eq. 6.6. The three different subplots correspond to the upper (UP), middle (MP) and lower (LP) polariton branches (from top to bottom).

Using the known values of E_{hh} , E_{lh} and E_{cav} , and treating V_{hh} and V_{lh} as free variables, I fit equation 6.6 to the observed polariton dispersion as described in the previous section.¹⁷ At the crossing between unperturbed cavity and exciton energy the polaritons are half-light, half-matter quasi-particles. The splitting at this point is the Rabi splitting which corresponds to twice the interaction potential $\hbar\Omega_{\text{hh(lh)}} = 2V_{\text{hh(lh)}}$. In the system the splitting is well resolved for the heavy hole exciton, where I obtain $\hbar\Omega_{\text{hh}} = 66 \pm 1 \text{ meV}$ with linewidths of $\Gamma_{\text{LP}} = 35 \pm 3 \text{ meV}$ and $\Gamma_{\text{MP}} = 45 \pm 3 \text{ meV}$ for lower and middle polariton branch respectively. The light hole transition shows a similar avoided crossing with $\hbar\Omega_{\text{lh}} = 58 \pm 4 \text{ meV}$ but the corresponding linewidths of $\Gamma_{\text{MP}} = 68 \pm 13 \text{ meV}$ and $\Gamma_{\text{UP}} = 83 \pm 14 \text{ meV}$ for

¹⁷ E_{cav} is obtained as described in the previous section.

middle and upper polariton branch respectively result in a splitting that is not fully resolved. The linewidths and splitting values are obtained by fitting two superposed Lorentzian lineshapes to the transmission spectra at the maximal photon-exciton mixing point (see Fig. 6.17c-d), which correspond to vertical cuts through the data presented in Fig. 6.17a at cavity lengths $L \approx 1.53 \mu\text{m}$ and $L \approx 1.44 \mu\text{m}$.

As outlined before, Eq. 6.6 allows to determine the polariton mixing coefficients as a function of cavity length, as shown in Fig. 6.17e. For a longitudinal cavity mode with mode number q ¹⁸ the LPB is largely photon like for cavity lengths $L > 1.53 \mu\text{m}$, becoming more hh exciton-like as the cavity mode energy crosses the exciton energy. The UPB similarly is lh exciton-like when the cavity length $L > 1.44 \mu\text{m}$, becoming more photon-like for smaller cavity lengths. Meanwhile, the MPB has hh and lh exciton-like character when close in energy to the hh and lh exciton energies respectively. For cavity lengths $1.53 \mu\text{m} > L > 1.44 \mu\text{m}$ it has mostly photonic character, however, it also is composed of approximately 10% of both exciton states, hence it is a hybrid polariton state with exciton contributions from both the lh and hh transition. Note that in a transmission experiment, light couples into and out of the cavity via the polariton photon component resulting in greater visibility of photon-like polariton states and observation of a mode structure as shown in Fig. 6.17a.

Fig. 6.17b shows the modelled dispersion curves obtained by Transfer-Matrix-Modelling with the experimentally obtained absorption for the nanoplatelet film. The modelled thickness of the film is 700 nm (see Fig. 6.15 for AFM data) with a peak absorbance of the heavy hole transition of $A = 0.35$, as inferred directly from optical absorption measurement. The absorption curve was converted to complex refractive index values with a classical Lorentz oscillator model for both transitions, neglecting the continuum of states above $E = 2.8 \text{ eV}$. The modelled transmission through the device is in excellent agreement with the experimental data presented in Fig. 6.17a.

6.3.3 Additional cavity spectra

To allow a critical analysis of the presented data, Fig. 6.18 shows transmission spectra corresponding to vertical slices through Fig. 6.17a for different cavity lengths. The presentation as 2D plots demonstrates the avoided level crossing about the hh (Fig. 6.18a) and lh exciton energy (Fig. 6.18b).¹⁹ The latter is not fully resolved, as the exciton and cavity linewidth exceed the Rabi splitting slightly (see values above.)

¹⁸The longitudinal mode number in Fig 6.17a-e is $q = 6$. Note that the cavity is composed of two silver mirrors and thus exhibits a negligible penetration depth of the electric field into the mirrors.

¹⁹In particular the series give a better representation of how the data is aquired, as each spectrum appears on the screen for a few seconds while the next spectrum is acquired after the cavity length is changed.

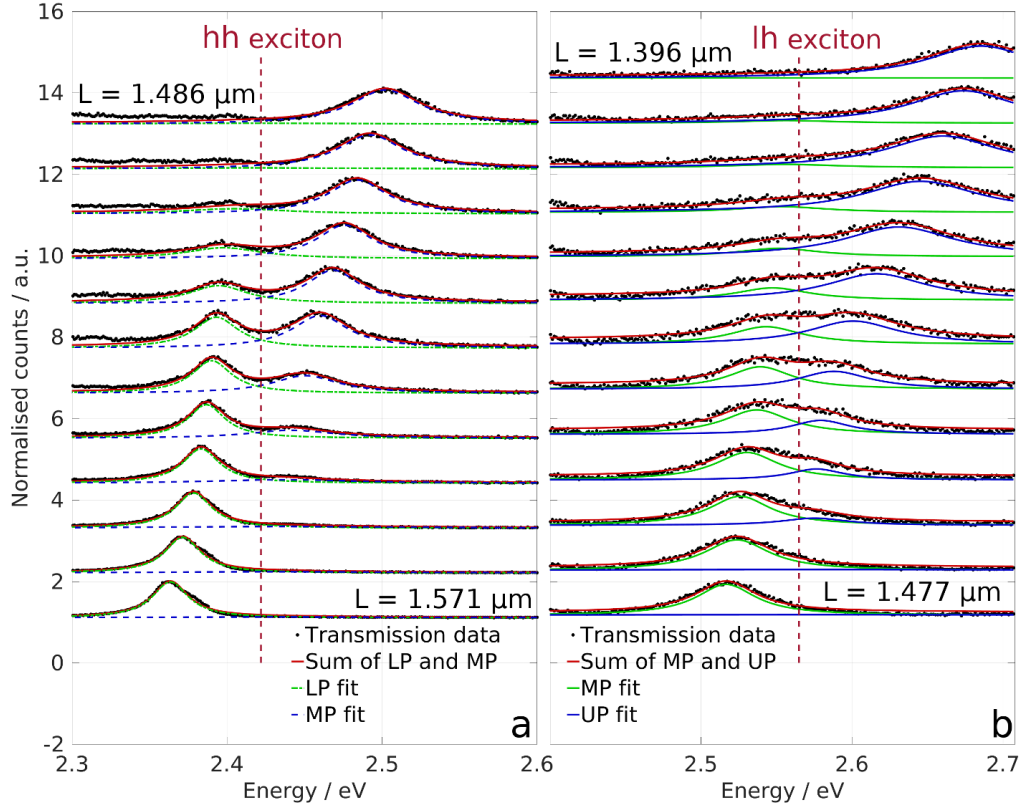


FIGURE 6.18: **Single cavity transmission spectra.** a) Cavity transmission spectra for decreasing cavity length from bottom to top, corresponding to vertical slices through the data presented in Fig. 6.17. Each spectrum is fitted with two superposed Lorentzian lineshapes to obtain the position and the linewidth of the polariton states. A clear anticrossing about the heavy hole exciton energy can be observed. b) Equivalent data for the light hole exciton transition, demonstrating that the splitting is not fully resolvable given the linewidths of exciton and cavity mode.

Each peak is fitted with a sum of two Lorentzian lineshapes and the central position and linewidth for the hh anticrossing is plotted in Fig. 6.19a. For reference to the previously presented raw transmission data in Fig. 6.17, I have superposed the same theoretical polariton dispersion on this dataset, demonstrating the excellent agreement.

In general, polariton properties are given by a weighted average of the properties of its constituents, ie. the polariton linewidth is the sum of the excitonic linewidth times the excitonic coefficient β^2 , γ^2 and photonic linewidth multiplied by α^2 divided by two ($\Gamma_{\text{pol}} = \frac{\Gamma_{\text{exc}}\beta^2 + \Gamma_{\text{cav}}\alpha^2}{2}$).

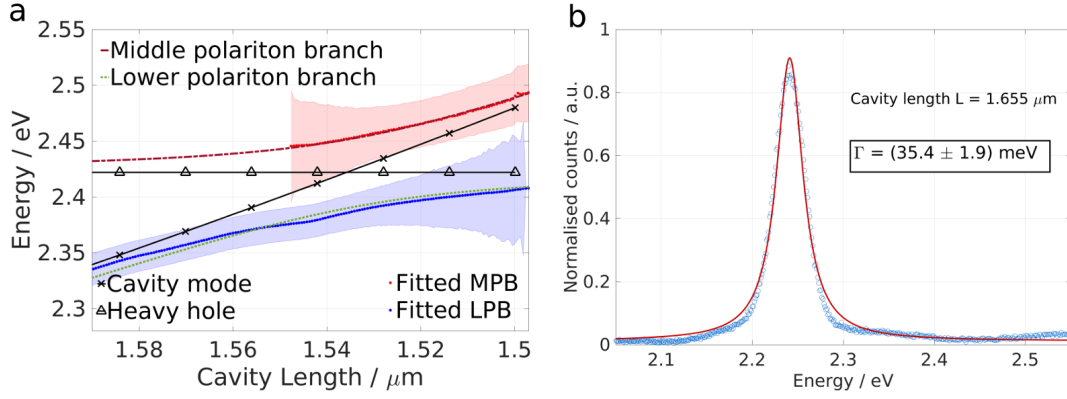


FIGURE 6.19: **Fitted polariton dispersion and cavity lineshape.** a) Polariton dispersion about the heavy hole exciton energy as obtained by the fits shown in Fig. 6.18. The vertical extent of the shaded area around the datapoints corresponds to the fitted linewidth of the Lorentzian lineshape. b) Transmission spectrum at a cavity length $L = 1.66 \mu\text{m}$, where the cavity mode energy is far from both exciton energies. The fit shows a FWHM of $\Gamma = 35 \text{ meV}$, corresponding to a cavity Q-factor of $Q = 64$.

To investigate the polariton linewidths, it is thus important to understand the cavity mode linewidth, which for the silver cavity is $\Gamma_{\text{cav}} \approx 35 \text{ meV}$ at an energy of 2.23 eV (see Fig. 6.19b) and broadens as the reflectivity of silver decreases for higher energies. The reason for the poor resolution of the lh coupling is a combination of the reduced reflectivity of the silver mirror²⁰ for the energy above 2.5 eV and a weaker oscillator strength and broader linewidth of the lh exciton in comparison with the hh exciton. Reasons for this are additional relaxation paths from lh to the lower energy hh-exciton (comp. with Suppl. Materials, Sect. E of Ref. [155]).

6.3.4 Single platelet transition dipole moment

If the number of randomly aligned platelets N coupled to the mode is known, it is possible to deduce the transition dipole moment μ of a single platelet from Eq. 3.32 derived in Chapter 3:²¹

$$\hbar\Omega = \frac{1}{3}\mu\sqrt{N}\left(\frac{2\hbar\omega}{\varepsilon_0 n_{\text{eff}}^2 V_{\text{eff}}}\right)^{\frac{1}{2}} \quad (6.7)$$

Here $\hbar\omega$ is the exciton energy, n_{eff} is the effective refractive index within the cavity and V_{eff} is the electric field mode volume. Thus I can then infer the dipole moment of the excitonic transition of a single platelet from the respective Rabi splitting. The appropriate relations and derivation of the number of platelets in the film are given

²⁰I discuss the implications of the reduced mirror reflectivity on the mode linewidth in Section B.12.3 of the physical compendium.

²¹Note that the prefactor ξ can be averaged to $\xi = 1/3$ for random dipole orientations and in general two orthogonal polarisations of photons contribute to the coupling.

in Section B.12 of the physical compendium, as their exposition is slightly lengthy:

$$\begin{aligned}
 N &= (3.9 \pm 1.5) \times 10^5 \\
 \mu_{\text{hh}} &= (1.92 \pm 0.37) \times 10^{-27} \text{ C m} = (575 \pm 110) \text{ D} \\
 \mu_{\text{lh}} &= (1.70 \pm 0.35) \times 10^{-27} \text{ C m} = (509 \pm 104) \text{ D}
 \end{aligned} \tag{6.8}$$

This compares to transition dipole moments of 100 D found in epitaxially grown GaAs quantum dots [156] and 21 to 210 D in InGaN quantum dots with a diameter of 5.2 nm [157]. The lateral dimensions of the platelets studied here are $L_x = 32.5 \pm 2.5 \text{ nm}$ and $L_y = 8.2 \pm 0.9 \text{ nm}$ as obtained by TEM microscopy. These results confirm the giant oscillator strength associated with the large exciton coherence area found in CdSe nanoplatelets [155, 158].

6.3.5 Photoluminescence from NPL exciton-polaritons

Fig. 6.20a shows the cavity length dependent photoluminescence collected at normal incidence, following non-resonant high energy excitation with a continuous wave laser with $\lambda = 405 \text{ nm}$. Bright emission from the lower polariton branch at cavity lengths between $1.6 \mu\text{m}$ and $1.5 \mu\text{m}$ is observed, corresponding to a LPB energy of 2.3 eV to 2.4 eV . Some weak residual PL is also visible at the energy of the nanoplatelet PL (shown to right of Fig. 6.20a). This signal results from the recombination of excitons that are not coupled to the cavity mode, some of which leaks directly through the mirrors. Emission from the MPB and UPB is not visible, as has previously been shown to be a result of fast relaxation pathways between polariton and lower lying exciton states [159].

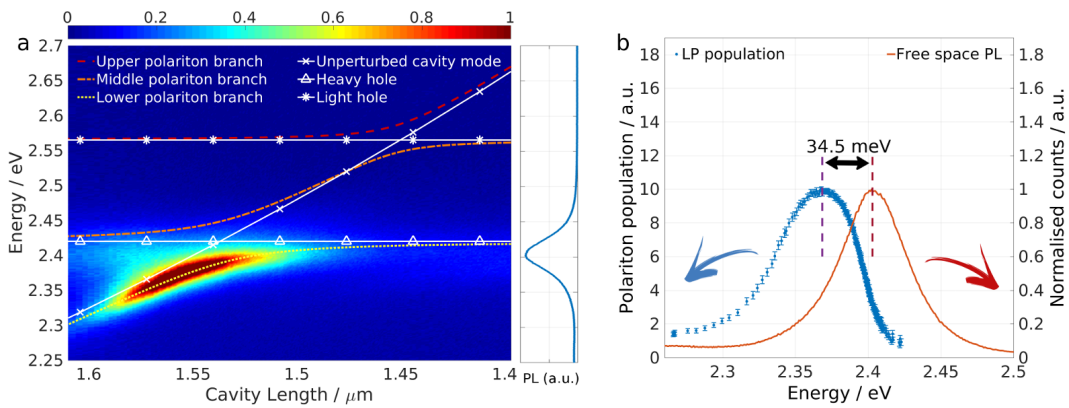


FIGURE 6.20: **Photoluminescence and polariton population after optical pumping of CdSe NPLs.** a) Photoluminescence intensity of polariton branches as cavity length is varied. Sample is excited off-resonantly with a continuous wave laser with $\lambda = 405 \text{ nm}$. b) Normalised polariton population obtained from experimental data by scaling each frame with the corresponding inverse of the square of the photonic coefficient α .

To convert the measured intensity into the polariton population one scales the photoluminescence intensity of the lower polariton state (ie. the area below the peak, as will be discussed below) with the square of the inverse of the photonic coefficient α of the polariton branch. The converted data allows to see changes in the polariton population along the dispersion, as shown in Fig. 6.20b, blue circles with errorbars. A shift of $\Delta E = 34.5$ meV between the peak position of free space PL and polariton population is visible.

Fig. 6.21 shows additional PL spectra derived from the data presented in Fig. 6.20a. The normalised polariton population is obtained as described before with the help of the photonic coefficient α (Fig. Fig. 6.21a). Note that before scaling the PL intensity to obtain the polariton population, the uncoupled exciton emission (i.e. the PL spectrum at shortest cavity length) is subtracted. Fig. 6.21b displays a selection of cavity spectra for decreasing cavity length from bottom to top, corresponding to vertical slices through the data presented in Fig. 6.20a.

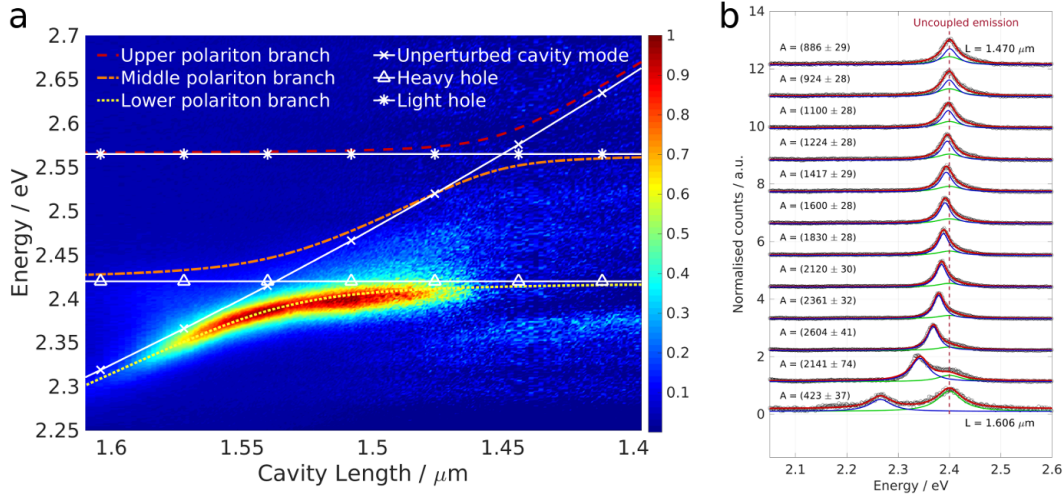


FIGURE 6.21: **Exciton-polariton population after non-resonant excitation.**

a) Normalised polariton population obtained from experimental data presented in Fig. 6.20a by scaling each frame with the corresponding inverse of the square of the photonic coefficient α (conversion between PL intensity and polariton population). Note that before scaling the PL intensity to obtain the polariton population, the uncoupled exciton emission (i.e. the PL spectrum at shortest cavity length) is subtracted. b) Selection of cavity spectra for decreasing cavity length from bottom to top, corresponding to vertical slices through the data presented in Fig. 6.20a. Each spectrum is fitted with a sum of two Lorentzian lineshapes (red), one at the position of the lower polariton state (blue line) and one for the uncoupled exciton emission at an energy of 2.4 eV. The latter one is kept fixed (in all three parameters amplitude, width and position) for all fits. The data presented in Fig. 6.20b is obtained by taking the area of the LP state (blue line, numerical values for A given to the left of each frame), converting it to the polariton population as above and plotting it against the energy of the LP state.

Each spectrum is fitted with a sum of two Lorentzian lineshapes (red), one at the position of the lower polariton state (blue line) and one for the uncoupled exciton emission at an energy of 2.4 eV. The latter one is kept fixed (in all three parameters amplitude, width and position) for all fits. The data presented in Fig. 6.20b is obtained by taking the area of the LP state (blue line), converting it to the polariton population as before and plotting it against the energy of the LP state. Note that the shift in peak position which results from this scaling is small (≈ 5 meV).

6.3.6 Discussion

I distinguish two different population pathways for the polariton state: optical pumping and thermally assisted scattering. In optical pumping the radiative decay of uncoupled excitons directly populates the photonic component of polariton states,

however there must be an energetic overlap between the exciton emission and polariton and a fraction of the excitons within the cavity must remain uncoupled. The small Stokes shift of 12 meV [155] therefore limits this population mechanism to polariton states close to the exciton energy [160–162]. Thermally assisted relaxation into the polariton state is akin to normal band-edge relaxation and relies on a phonon bath to absorb the additional energy. The coupling to the phonon background is proportional to the square of the excitonic component of the polariton state [129, 163]. The large shift ΔE observed in the system therefore suggests that polariton states are primarily populated by phonon-assisted scattering rather than through ‘optical pumping’ from uncoupled exciton decay.

In summary, I have demonstrated the strong coupling between photonic cavity modes and excitons in quasi-two-dimensional colloidal nanoplatelets. The coherent exchange of energy between those two constituents results in the formation of hybridised exciton-polaritons at room temperature with a vacuum Rabi splittings of 66 ± 1 meV and 58 ± 1 meV associated with the heavy hole and light hole exciton transitions respectively. I found that the polariton states are emissive due to the high fluorescence quantum yield of the nanoplatelets, and that polariton states appear to mostly be populated through an optical pumping from uncoupled exciton states.

Nanoplatelets represent a promising candidate for polariton based devices due to their large exciton binding energies allowing for room temperature operation. Compared to other colloidal nanoparticles, they are more efficient light absorbers and could become an integral part of future photonic devices.

7 Single photon sources in open microcavities

The ability to produce single, indistinguishable photons on demand is of fundamental importance for emerging quantum technologies [164]. The ‘cleanest’ way to study systems emitting single quanta is to perform single atom experiments in completely vacated cavity chambers. Over the years much effort has been invested to create ionic traps in which one can store single ionised atoms for almost indefinite times.

Naturally these systems have been analysed and large parts of CQED effects were first described in experiments with atoms.¹ For single atoms STIRAP (stimulated Raman scattering involving adiabatic passage) has been used to produce ‘on-demand’ photon emission, allowing a stream of a few single photon pulses from one single atom, triggered by the detection of a first photon emitted from the cavity. Coherence times over minutes and almost noise free data characterise this realm and quantum information algorithms have been applied here for the first time [165, 166]. The problem with this artificial environment is for one the large cost and effort maintaining it but to an equal extend the lack of scalability.

While single emitters like colour centres, single ions, single molecules and single nanocrystals all emit single photons (with restrictions for large QDs and NPLs), their availability and coherent emission is uncontrollable in normal environments. CQED offers a rich set of tools to attain the level of control necessary and can be used to guide the emission of the photon into specific directions by funnelling them through specific cavity modes. Focusing on indistinguishable single photon sources from condensed matter systems, good results are obtained from epitaxially grown InGa/GaAs quantum dots [167] and the best results to date have been achieved with resonant s-shell pumping [168].² They demand complex fabrication methods, expensive experimental conditions and exhibit a lack of tunability and scalability similar to cold atoms however.

Current research thus aims at improving those constraints with new materials and tunable cavity environments. With this in mind the following chapter presents single photon emission from a quantum dot and a single emitter in the two-dimensional material WSe₂. In contrast to the previous chapter, we now return to FIB milled microcavities to enhance the single emitters:

¹The books by Haroche [52] or Meystre and Sargent [53] allow comprehensive overviews.

²All such systems have to be cooled down below 25 K and are typically fabricated in monolithic structures, as shown in Chapter 2.

In a first section I present a room temperature experiment with single CdSe/ZnS quantum dots, where a two-fold Purcell enhanced radiative lifetime is demonstrated. As the linewidth of the emitter is relatively broad, here the effective Q of the system is low and thus the low mode volume in the λ^3 regime is vital. In a second study, a single photon emitter hosted by a WSe₂ monolayer is incorporated into a range of optimised FIB milled cavities at low temperatures to obtain a more systematic understanding of the effect the cavity has on the emitter. Here an effective Purcell factor of 7.8 is demonstrated and the saturation countrate is increased five-fold when compared to the emission into free space.

7.1 Purcell enhanced emission from single QDs at room temperature

The following section explores how a FIB milled microcavity modulates the spontaneous emission of a single CdSe/ZnS core shell quantum dot. The cavity environment causes enhanced emission into spectrally narrow modes which can be tuned by varying the cavity length. By temporally resolving the PL from the system after pulsed excitation the excited state lifetime is obtained and an effective Purcell enhancement of a factor of 2 for the shortest cavity lengths with mode volumes around $1 \mu\text{m}^3$ is found. This result, obtained at room temperature with a broad emitter ($\Gamma \approx 50 \text{ meV}$), shows how a small mode volume cavity can be used for spectral modulation of single emitters and represents an important step in the technological application of open microcavities. The data in this section has been presented to a public audience at the Quantum Dot Day conference in Cambridge in January 2015.

7.1.1 Experimental methods

To show room temperature Purcell modulations, I employ the multi-purpose room temperature cavity setup introduced in Chapter 4. The cavity consists of two dielectric mirrors, the featured mirror with a dielectric coating of 20 pairs of SiO₂/Ta₂O₅ resulting in a reflectivity of $R = 99.997\%$ and the planar mirror with a coating with 10 pairs of SiO₂/TiO₂ with $R = 97.3\%$ and a low refractive index last layer, ensuring an electric field antinode at the mirror surface. The asymmetric configuration of the mirror reflectivities results in almost 100% of the photons to be emitted out of the planar side of the cavity.³ The quantum dots (Lumidot 640 CdSe/ZnS core shell quantum dots from Sigma Aldrich) were diluted and spin coated onto the planar mirror as described in Section 4.2.2. Through iteration a dilution was found which gave sufficient single quantum dots while still providing good chances of coupling

³For a cavity with mirror reflectivities R_i and $1 - R_i \ll 1$ we can approximate the total transmission through side i with $T_i^{\text{tot}} = \frac{1-R_i}{1-R_1R_2}$ (by summing the reflected and transmitted parts and assuming a resonant cavity mode). For the presented configuration we thus obtain $T^{\text{tot}} = 99.89\%$ through the lower reflectivity cavity mirror.

to a dot when ‘randomly’ changing the lateral position of the planar mirror relative to the concave feature. The cavity is initialised as before with a white light transmission experiment. For PL measurements the system is excited non-resonantly with a pulsed laser with $\lambda = 473 \text{ nm}$ at excitation densities of $\rho_{\text{exc}} = 1000 \text{ W/cm}^2$. The light is then detected by either a spectrometer or a SPAD as described in Section 4.2.2.

Fig. 7.1a shows a graphic impression of the microcavity with single QDs dispersed on the planar mirror side (red spheres). Without the cavity environment the spectrum of a single QD has a Lorentzian lineshape as shown in Fig. 7.1b, exhibiting a linewidth of roughly $\delta\lambda_{\text{em}} = 18 \text{ nm}$ or 50 meV .⁴ The linewidth is broadened by phonon scattering and spectral diffusion on a single QD level⁵ and much larger than the linewidth of a cavity mode.

In contrast to the second study presented in this Chapter, the single emitter nature of the QD was not verified with a HBT measurement. The reason for this was the poor countrate of the system ($\approx 900 \text{ Hz}$ on average on both SPADs after the fiber splitter, with peak counts of $\approx 2500 \text{ Hz}$), which rendered the data acquisition very tedious. This is a clear shortcoming of the data presented here, however: Strong indicators of a single emitter are the Lorentzian lineshape, the sensitivity of the cavity emission on the transverse QD position, the blinking behaviour shown in the next paragraph and the monoexponential decay of the excited state demonstrated in the next subsection.

A similar single QD spectrum appears much different when placed within a cavity. Here the emission predominantly occurs in well defined cavity modes, as shown in Fig. 7.1e, where a single QD is positioned within a cavity with $R = 7 \mu\text{m}$.

⁴The linewidth is typical for single CdSe/ZnS QDs at room temperature, with large QD-to-QD variations as reported by Ref. [169].

⁵The natural linewidth for an emitter with a lifetime of $\tau \approx 10 \text{ ns}$ is below $1 \mu\text{eV}$.

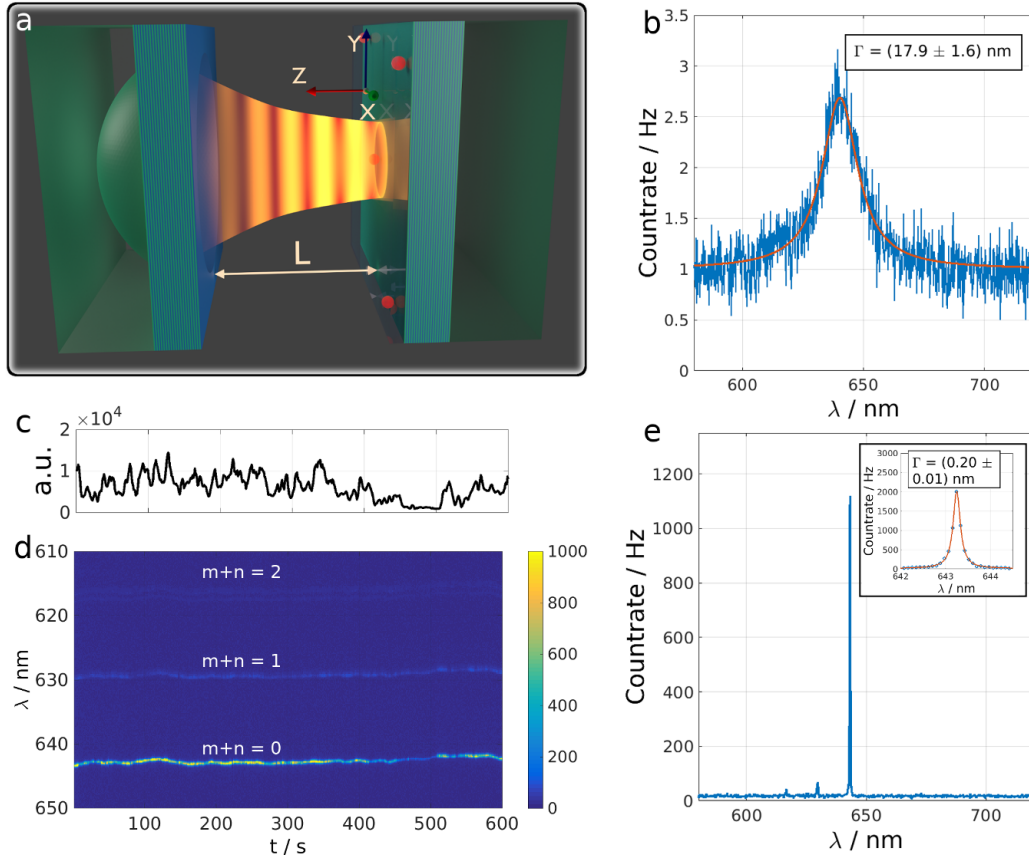


FIGURE 7.1: **Single CdSe/ZnS core-shell QDs in an open microcavity.** a) Artistic impression of the cavity. A highly diluted solution of CdSe/ZnS quantum dots is spin coated onto the planar mirror, which is freely positionable opposite a mirror with concave FIB milled features. b) PL spectrum from single QD when excited non-resonantly with $\lambda = 473$ nm. c) Time trace of integrated PL counts from a single QD. The trace exhibits typical blinking, indicative of single QD emission. d) Time trace of single QD emission into a cavity with $R = 7 \mu\text{m}$. Additional to the main $\text{TEM}_{0,0}^6$ mode, the first two excited transverse modes are populated as well, exhibiting a split spectrum indicative of a slightly elliptical cavity. e) Single QD spectrum in an open microcavity with $R = 7 \mu\text{m}$.

Three modes of the $q = 6$ mode family are visible - the $\text{TEM}_{0,0}$ mode at 643 nm is dominating the emission and the two higher excited states $\text{TEM}_{m+n=1}$ at 630 nm and $\text{TEM}_{m+n=2}$ at 617 nm contain less than 5% of the emission. The cavity mode linewidth is measured to be $\delta\lambda_{\text{cav}} = (0.20 \pm 0.01) \text{ nm}$ or $(0.6 \pm 0.03) \text{ meV}$, thus placing the experiment firmly in the bad emitter regime of cavity coupling where $\delta\lambda_{\text{em}} \gg \delta\lambda_{\text{cav}}$. The good alignment of the emitter relative to the cavity mode is apparent as the $\text{TEM}_{m+n=1}$ mode is suppressed relatively to the lineshape presented in panel b. Since the next section shows a similar system with improved alignment capabilities I will discuss this lateral alignment there - here it suffices to point out that the quantum dot is positioned within good accuracy opposite of the center of the concave feature. Panels c and d of Fig. 7.1 show time traces of the system; panel c shows the accumulated counts of the $\text{TEM}_{0,0}$ mode and panel d exhibits a series

of spectra with a larger spectral range, obtained with an acquisition time of 1 s. The jitter in spectral mode position is a consequence of variations in cavity length in the room temperature cavity setup - it amounts to a displacement of less than 1.7 nm in 10 min of acquisition time without systematic drifts.⁶ This jitter is not the reason for the fluctuations in accumulated counts displayed in panel c - instead I attribute it to the commonly found blinking behaviour of single nanoparticles thought to be a result of spectral diffusion and changes in passivating surface states. For this experiment I took the blinking behaviour and the sensitivity of the cavity mode structure on the lateral position of the planar mirror (indicative of a point like light source) as evidence for a single emitter. In the next section I will present more reliable data by recording the second order autocorrelation function in an HBT setup. The spectral details presented in Fig. 7.1d further imply a slight ellipticity of the concave FIB milled shape. This follows by noting that the $m + n = 2$ modes are not degenerate, but split by about 1.2 nm (compare with the discussion of coupled cavities in Chapter 5).

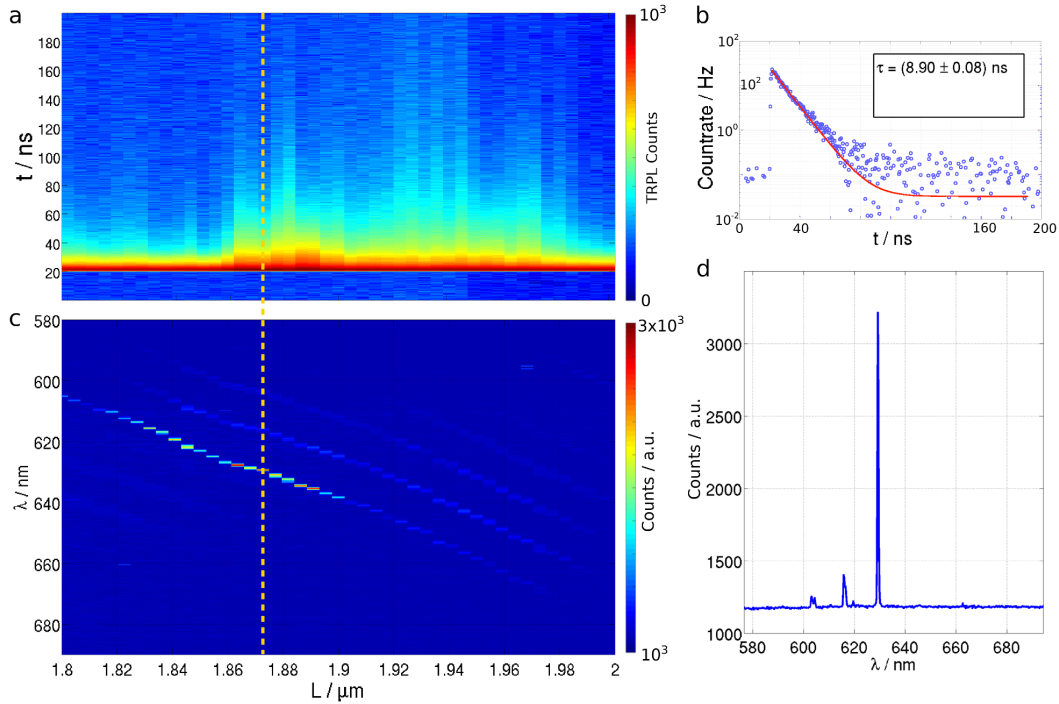


FIGURE 7.2: **Time resolved single QD emission in an open microcavity.**

a) Series of TRPL traces from single QD cavity emission. Each TRPL trace is normalised and the logarithm of the trace is plotted for better comparison. The corresponding spectra are plotted below in c). The cavity length is increased from left to right such that the mode energy of the $q = 6$ mode family traverses the quantum dot emission. b) and d) Single TRPL trace with monoexponential fit and spectrum of frame marked with the yellow dashed line in panel a and c.

⁶The distribution of cavity mode positions has a mean value of 642.60 nm and a standard deviation of 0.39 nm.

7.1.2 Time resolved single QD emission in a cavity

Further to the spectral characteristics of the system, I investigate how photons are emitted in time. Fig. 7.2 displays data of the main experimental mode of this section - a cavity length scan with both spectral and time resolved photon detection (as introduced in Section 4.1.5). Fig. 7.2a, c show the TRPL and spectral data as the cavity length is increased from left to right such that the $q = 6$ cavity mode family traverses the emission of the single QD. The frames in both plots coincide vertically and each frame in panel a is normalised for better visual comparison. Panels b,d show a single TRPL trace and spectrum for the frame indicated with a yellow dashed line in the left panels. The TRPL data is fitted with a monoexponential decay after background subtraction - note that in this experiment no deconvolution of the instrument response function was necessary as the measured lifetimes were substantially longer than the timing resolution of the SPAD used ($\tau \approx 10$ ns). Note furthermore that a long pass filter with an edge wavelength of $\lambda = 620$ nm was positioned in front of the SPAD, removing most of the autofluorescence and laser light from the detected photons. This filter is the reason for the abrupt increase of TRPL counts at a cavity length of $L = 1.86$ μm .

The decay constants obtained by the fit to the TRPL data are plotted in Fig. 7.3a, aligned with the spectra shown before in panel b. The individual spectra and TRPL fits are shown in Panel c to allow the graphic verification of the changes in lifetime that the change in cavity length has. The three panels correspond to the colour coded three dashed lines in the left plot - the left inset in each panel shows the cavity spectrum and the right inset the TRPL data with fitted lifetime τ . As the cavity length is increased the measured lifetimes increase from $\tau = 9$ ns to $\tau = 25$ ns.

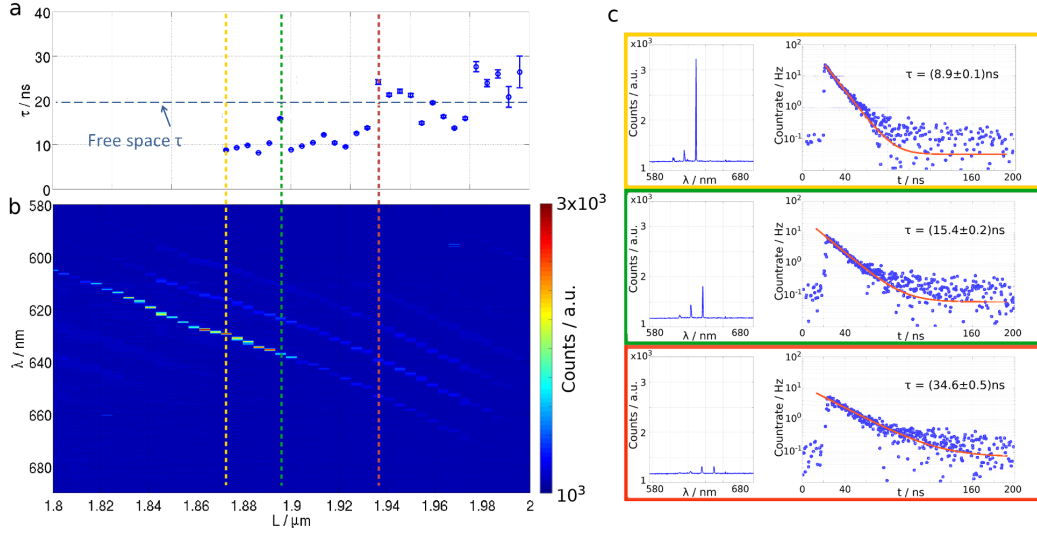


FIGURE 7.3: **A closer look at the first accessible mode family.** a) and b) Excited state lifetime and cavity spectra from single QD as presented before. Here only data from the first cavity mode family with $q = 6$ is shown. c) Single TRPL traces and spectra corresponding to the three indicated frames in panel a and b.

A more comprehensive picture of the effect is given in Fig. 7.4. Here the same data is plotted for a larger cavity length scan - from left to right four cavity mode families cross the emission of the QD. Fig. 7.4a presents a summary of the found values for τ and allows the comparison with the free space lifetime (blue dashed line) and the theoretical prediction (red dashed line).

For the theoretical prediction the expression for the effective Purcell factor is evaluated as given by Eq. 3.42 and 3.43. The cavity-emitter system has an effective Q -value of $Q_{\text{eff}} = \frac{\lambda}{\delta\lambda_{\text{em}} + \delta\lambda_{\text{cav}}} = 36$ and a mode volume of $V \approx 1 \mu\text{m}^3$ at the shortest cavity length of $L \approx 1.9 \mu\text{m}$ with a longitudinal mode number of $q = 6$.⁷ The resulting effective Purcell factor equates to $F'_{\text{theo}} = 1.8 \pm 0.3$ and decreases for longer cavity lengths. The red-dashed line in Fig. 7.4a is obtained by evaluating F'_{theo} for the larger mode volumes implied by the optical cavity length.

Fig. 7.4c shows the single QD lineshape already presented in Fig. 7.1b, aligned vertically to the wavelength axis of panel b. As the cavity modes are scanned across the emitter lineshape, they are populated depending on the electric field structure of the mode and the emission strength of the QD. Note that as the cavity is opened, a minor lateral movement between both mirrors takes place whereby the $m + n = 1$ cavity mode gains in intensity relative to the $m + n = 0$ mode when comparing the $q = 6$ and the $q = 8$ cavity mode family.

⁷Note that I give the optical cavity length in this section, as it is most relevant to quantify the cavity mode volume.

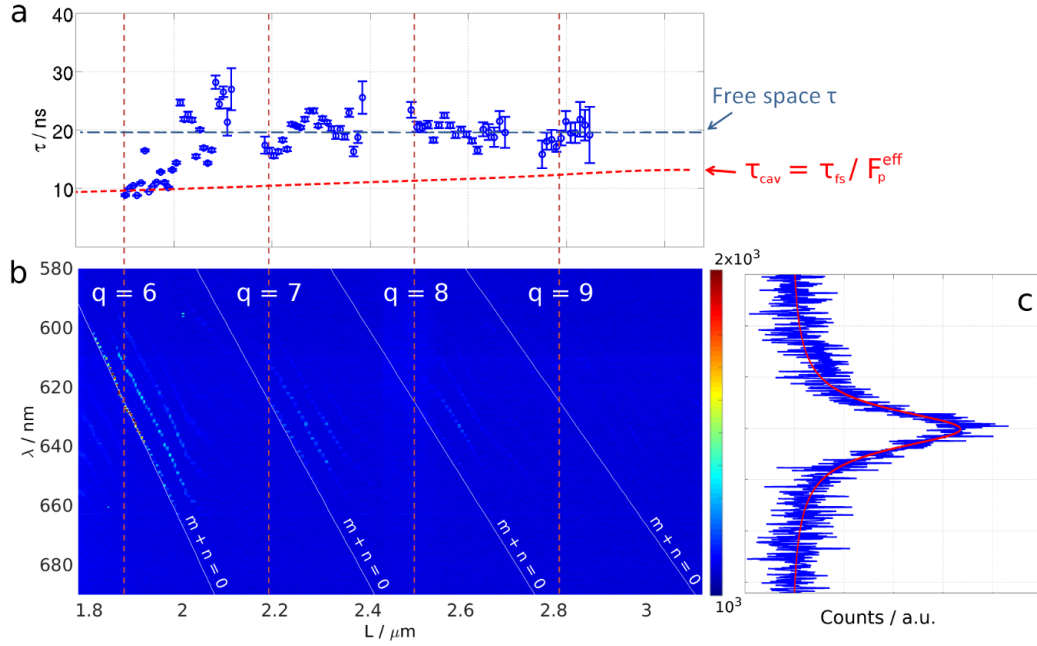


FIGURE 7.4: **Purcell modulation of single QD excited state lifetime.** a) Excited state lifetimes of single QD as obtained from monoexponential fits to the TRPL data. The blue and red dashed line give the free space and theoretical excited state lifetime. b) Series of cavity spectra as cavity length is increased from left to right. The individual frames are horizontally aligned with the lifetime data in panel a. The $\text{TEM}_{0,0}$ modes for the four different q families are marked with a thin white line to guide the eye. c) Single QD PL spectrum aligned to the wavelength scale of panel b.

7.1.3 Discussion

The change in cavity length strongly modulates the measured TRPL lifetimes. The experimental results are in good agreement with the theoretical prediction for the shortest cavity length, evidencing a maximal effective Purcell factor of 2, implying a quantum efficiency η of the quantum dot close to unity.⁸

While for the first mode family with $q = 6$ the recorded lifetimes range between 8 ns and 28 ns, the measured τ -values converge to the free space value with a decreasing modulation amplitude for higher longitudinal modes. The same effect has been discussed recently by Kaupp et al. for NV-centers in metallic open cavities [79]. The data presented here reveals a secondary modulation within each mode family which is not visible in Ref. [79]. I attribute it to the influence of the transverse modes, fully defined in the cavity system which has a high finesse of $\mathcal{F} = 550$ in comparison.

The suppression in decay rate which leads to a value of τ exceeding the free space lifetime further suggests that the solid angle of the cavity mode subtends a large

⁸For an emitter with radiative quantum efficiency $\eta = \frac{\gamma_{\text{rad}}}{\gamma_{\text{rad}} + \gamma_{\text{non-rad}}}$, the quantum efficiency is given as $\eta = \frac{F'_{\text{exp}} - 1}{F'_{\text{theo}} - 1} = \frac{F_{\text{exp}}}{F_{\text{theo}}}$, where F'_{exp} is the measured effective Purcell factor.

fraction of the solid angle accessible to the emitter, thus reducing the effective Purcell factor to values of $F_p^{\text{eff}} < 1$.⁹ As the cavity is opened, this effect is lost quickly and the τ values for $q > 7$ have converged to the free space lifetime within the accuracy of the experiment.

The data presented in this section evidence the small mode volumes accessible with open-access FIB milled cavities. The reported Purcell factor of 2 attests to the remarkable capability to modulate a broad emitter at room temperature by relatively facile means. The presented system thereby establishes the open FIB milled cavity as a viable platform for multi-purpose photonic devices, which allow in situ modulation and enhancement of the emission from single emitters.

⁹The theoretical basis for this effect is derived in Section B.9 of the physical compendium.

7.2 Microcavity enhanced single photon emission from two-dimensional WSe₂

Recently quantum light emission has been observed from localised excitons in exfoliated WSe₂. As part of developing optoelectronic devices the control of the radiative properties of such emitters is an important step. Here I report the coupling of an exciton state in WSe₂ to the photonic modes of open microcavities at cryogenic temperatures. I use a range of radii of curvature in the plano-concave cavity geometry with mode volumes in the λ^3 regime, giving Purcell factors of up to 8 while increasing the photon flux five-fold. The findings presented here may add to versatile monolayer based, ultra-bright single photon sources for a wide range of applications in nanophotonics and quantum information technologies.

7.2.1 Introduction

Single photon emission has been observed from a range of systems such as single atoms, point defect in crystals, quantum dots and localised excitons in a multitude of materials. Recently two-dimensional semiconductors have attracted increased attention because of their strong interaction with light owed to a direct bandgap transition with a strong transition dipole moment of the delocalised exciton [45, 47, 57]. Of these, the transition metal dichalcogenide WSe₂ has been found to contain single defects with weakly bound excitons, stable at cryogenic temperatures below 15 K, emitting quantum light with impressive brightness and stability as introduced in Section 2.1.2 [54–56, 58]. In particular the localised excitons can be created with nanometric precision [59], exhibit strain tunability [60] and the hosting two-dimensional material allows for integration into ultra-compact, charge tunable devices [45, 150].

In this section I describe the integration of a single photon emitting localised exciton hosted within a monolayer of WSe₂ into a range of open-access cavities and show that the coupling to the matter and the emission properties can be controlled with high precision.

7.2.2 Monolayer WSe₂ on a DBR

The plano-concave microcavity consists of two opposing silica substrates, coated with a DBR comprising 13 pairs of SiO₂/TiO₂ with a reflectivity above 99.95% at the center wavelength of $\lambda = 740$ nm. To insert the localised exciton state into the cavity, the mechanically exfoliated WSe₂ monolayer is transferred onto the planar mirror with a dry stamping process as described in Section 4.2.2. Most of the deposited material consisted of several layers of WSe₂, only a few monolayer flakes with extensions over a few micrometers could be obtained in one exfoliation process and were found via optical microscope inspection (see Fig. 7.5a,b).

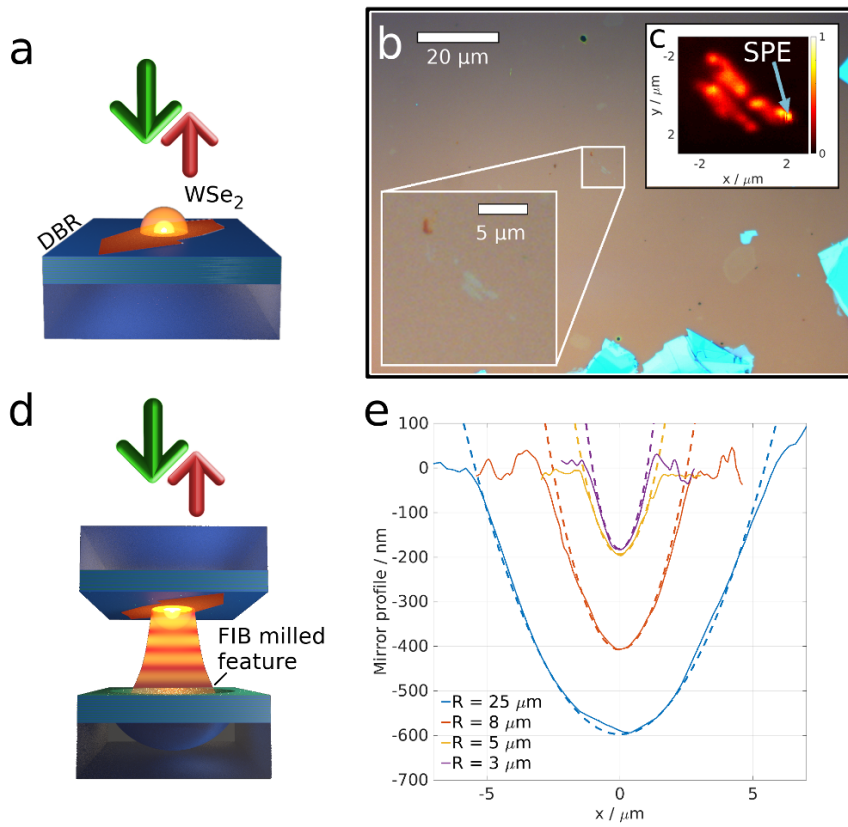


FIGURE 7.5: **Monolayer WSe₂ in an open microcavity.** a) A WSe₂ monolayer on a DBR mirror showing single photon emission from localised spots after excitation with a green laser. b) Optical microscope images of WSe₂ flakes on a mirror, deposited with a dry transfer method. Multilayer WSe₂ appears as blue-silver region. c) Spectrally filtered PL signal (740 nm–760 nm) from the same flake as in b) in a confocal microscope at 4 K. The arrow points to a spot which shows single photon emission with a resolution limited spot-size of 600 nm. d) The open-access microcavity is formed by flipping the sample such that the DBR stacks points downwards and positioning a mirror with concave features opposite it. In this configuration the sample is excited below the stopband of the mirrors with a green laser and emission is collected through the flat mirror. e) AFM crosssections of concave features forming one side of the microcavities, showing a range of radii of curvature.

The monolayers showed PL from both delocalised neutral excitons and bright, localised and spectrally narrow emitters visible below 15 K (see PL map Fig. 7.5c). The bright spots could be identified as single photon emitters (SPEs) with emission wavelengths around 750 nm, similar to the emission wavelengths reported in the literature [54–56].

To obtain a localised cavity mode (in the geometry shown in Fig. 7.5d), another mirror with FIB-milled concave features with varying radii of curvature was positioned opposite of the SPE. Fig. 7.5e shows cross sections of the concave features obtained with an AFM, demonstrating a range of radii of curvatures between 3 μm and 25 μm which were used in this study. Both mirrors forming the cavity were mounted in a tube within a liquid helium dewar, which provides optical access to

the sample in the custom-built confocal microscope presented before for low temperature applications. The planar mirror was positioned facing downwards onto a large sample mount movable in three dimensions to vary the field of view and focus. Within this sample mount another stack of five piezo actuators (translation in three dimensions, tilt and rotation) provided the ability to align and position the featured mirror facing upwards relative to the planar mirror. A more detailed exposition of the experimental setup and the equipment utilised to acquire the data is given in Section 4.2.4.

7.2.3 Monolayer WSe₂ in open microcavities

Fig. 7.5a displays the sample facing upwards, allowing for direct off-resonant excitation and collection of the PL. The inset in Fig. 7.5b shows a PL map of the same region as shown in the optical microscope images in the main plot, containing broad emission from most of the flake and a localised spot belonging to a single photon emitting defect with a FWHM of ~ 600 nm (marked with an arrow in Fig. 7.5c). For the PL map, the sample was excited with a continuous wave laser with $\lambda_{\text{exc}} = 532$ nm and spectral filtering in the collection optics to collect only photons between 740 nm and 760 nm. The particular single photon emitter (SPE) which is studied here has a central energy of $E_{\text{SPE}} = 1.64$ eV and linewidth of $\Gamma_{\text{SPE}} \approx 500$ μ eV (see Fig. 7.6a). While its spectral position has been stable over weeks, its brightness displayed fluctuations which increased with increased excitation power.

To align the SPE opposite of the concave feature, the multilayer parts of the WSe₂ visible in the optical microscope image in Fig. 7.5b were used as ‘landmarks’, since their outline in a white lamp transmission image was visible even when the mirror was flipped. Another fruitful strategy was to use a high excitation power¹⁰ resulting in autofluorescence from the mirrors and emission from the delocalised excitons from the rest of the WSe₂ flake, facilitating the recording of cavity modes even for situations where no SPE emission could be obtained. With gradual optimisation of the position of the desired SPE opposite of a concave FIB milled feature the coupling to the cavity mode could then be enhanced. To position the same emitter into a different cavity, the cavity length was first increased to about $L \approx 3$ μ m to move the planar mirror freely, move the desired concave feature to the center of the field of view and repeat the above procedure to align the SPE to the new cavity environment.

Fig. 7.6b displays spectra from four different cavities for the TEM_{0,0} mode brought into resonance with the SPE. To ascertain the correct cavity length and transverse position relative to the SPE, the cavity length was varied with one of the piezo microactuators and the PL spectrum (without any filtering) was collected. Fig. 7.6c,d shows two such cavity length scans, demonstrating bad transverse alignment (Fig. 7.6c) and optimal transverse alignment (Fig. 7.6d) of the $q = 6$ longitudinal mode to the SPE. The plots show PL spectra from the cavity system as the cavity length is

¹⁰With excitation power around $P_{\text{exc}} \approx 1$ mW.

decreased from left to right, for a given transverse position of the SPE to the concave feature.

The quality of the lateral alignment can be assessed on the basis of the coupling of different transverse modes to the SPE. Since the electric field of the first transverse mode ($m + n = 1$) has a node in the center of its transverse electric field distribution, the optimal coupling to the SPE evidences itself with a minimal PL intensity for the first transverse mode and maximal intensity of the $m + n = 0$ mode. For Fig. 7.6c the intensity of the $\text{TEM}_{n+m=1}^6$ mode is comparable to the $\text{TEM}_{n+m=0}^6$ mode, which is thus a sign a slightly misplaced emitter from the center of the cavity. The ratio of emission of the $\text{TEM}_{n+m=0}^6$ to the $\text{TEM}_{n+m=1}^6$ mode in Fig. 7.6d is very large however, indicative of a well aligned single emitter within a cavity.¹¹ Note that the axes of the piezo microactuators show some crosstalk leading to varying lateral coupling quality for successive longitudinal modes.

The different radii of curvature of the concave mirror lead to a different confinement of higher excited states. Thus the transverse mode spacing increases with decreasing radius of curvature, which is visible in the spectra plotted in Fig. 7.6b for four different cavities with $R = 25, 8, 5$ and $3 \mu\text{m}$. To make these states visible in the PL spectrum in Fig. 7.6b the excitation power was increased well above saturation to $\approx 1 \text{ mW}$. Such large excitation powers cause both autofluorescence from the mirrors and emission from the delocalised exciton as pointed out before, which I used here to populate the first transverse mode to ascertain the transverse mode spacing. The three subplots in Fig. 7.6b show a more detailed spectrum of the $\text{TEM}_{0,0}$ mode for the three smallest cavities. In particular the linewidth of the smallest RoC cavity shows a substantial deviation from a Lorentzian lineshape, originating from diffraction losses at the edge of the feature and deviations of the desired concave profile. Additionally the spectrum of the $R = 3 \mu\text{m}$ cavity only exhibits the $\text{TEM}_{0,0}^5$ mode, which I ascertained by scanning the cavity length over the next longitudinal mode family ($q = 6$). This is indicative of a very shallow feature which does not allow confined transverse modes.¹²

¹¹The mode waist of the $\text{TEM}_{n+m=0}^6$ mode is roughly 500 nm for the presented cavity, with a similar spacing between the two electric field maxima of the $\text{TEM}_{n+m=1}^6$ mode.

¹²The depth of the feature is about 150 nm as shown in Fig. 7.5e.

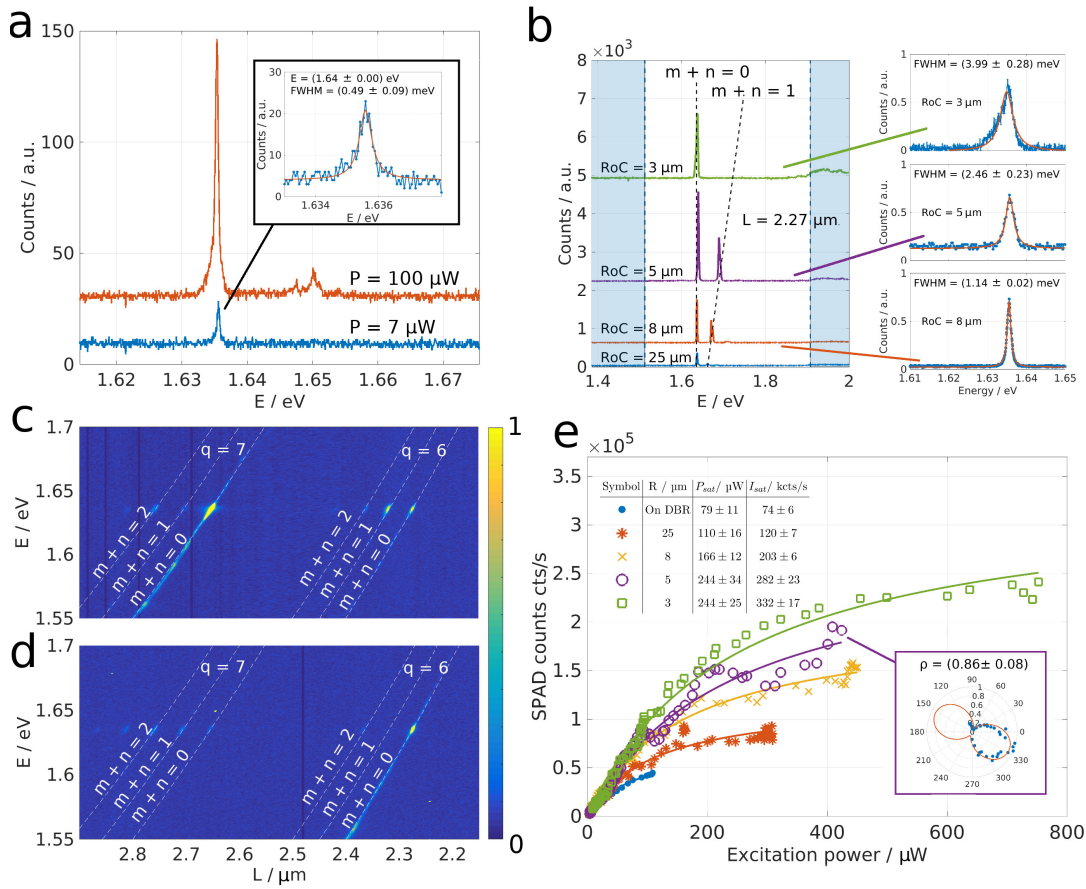


FIGURE 7.6: **Emission of a WSe₂ SPE in open microcavities.** a) Emission from spot marked in Fig. 7.5c for two different excitation powers P with $\lambda_{\text{exc}} = 532 \text{ nm}$. The inset shows the lineshape of the emission spectrum at the lower power. b) Spectra of the cavity system for four different radii of curvature of the plano-concave resonator. For the concave feature with $R = 25, 8 \mu\text{m}$ ($R = 5, 3 \mu\text{m}$) the $\text{TEM}_{0,0}^6$ ($\text{TEM}_{0,0}^5$) mode is brought into resonance with the SPE and the system is irradiated above saturation such that higher transverse ($m + n > 0$) modes of the same longitudinal mode family are visible. The insets to the right show the inhomogeneous lineshape of the fundamental mode for three cavities with a radius of curvature of $3 \mu\text{m}$, $5 \mu\text{m}$ and $8 \mu\text{m}$ from top to bottom. The shaded regions to the left and right of the main plot mark the end of the stop band of the mirrors. c) PL spectra of cavity with $R = 8 \mu\text{m}$ as a function of the cavity length. The cavity is misaligned with respect to the SPE and thus the $\text{TEM}_{m+n=1}^6$ mode is populated. d) Same as in c with an aligned cavity. Now the $\text{TEM}_{0,0}^6$ is primarily populated and the $\text{TEM}_{m+n=1}^6$ remains dark. e) The saturation curves of the SPE in free space and aligned to the fundamental mode of different cavities. The table to the upper left summarises the parameters obtained from the saturation fits. The bottom inset shows the linearly polarised nature of the emission from the RoC = $5 \mu\text{m}$ cavity.

The SPE shows typical saturation behaviour as the excitation power is increased (see Fig. 7.6e). Care is taken to collect only emission from the $\text{TEM}_{0,0}$ mode of the different cavities. A first sign of a modulation of the emission properties of the SPE due to the presence of the cavity, the Purcell effect, is the change in saturation counts

in the four different photonic environments, which increases roughly five-fold from $I_{\text{sat}} = (74 \pm 6)$ kcts/s at $P_{\text{sat}} = 79 \mu\text{W}$ to $I_{\text{sat}} = (332 \pm 17)$ kcts/s at $P_{\text{sat}} = 244 \mu\text{W}$ (see table in inset in Fig. 7.6e). The emission is linearly polarised with a degree of polarisation of $p = (0.86 \pm 0.08)$, shown in the bottom inset for the cavity with a RoC of $4 \mu\text{m}$.

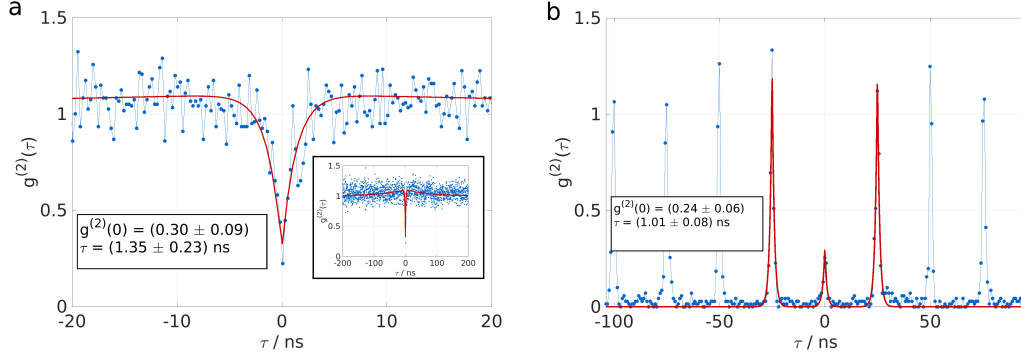


FIGURE 7.7: **Single photon emission from WSe₂ in an open cavity.** Second order correlation function obtained in a Hanbury-Brown and Twiss setup on emission from the TEM_{0,0}⁶ mode of the RoC = $3 \mu\text{m}$ cavity with a) continuous wave excitation and b) pulsed excitation with $f_{\text{rep}} = 40$ MHz at saturation power. The inset in a) shows the same data on a larger timescale, demonstrating a weak signature of photon bunching.

Additional to the typical saturation curve, the photon statistics of the emission should show anti-bunching as the evidence for single photon emission. To prove this, Fig. 7.7a,b show the second order autocorrelation function $g^{(2)}(\tau)$ for both continuous wave (a) and pulsed excitation (b) with $f_{\text{rep}} = 40$ MHz at $\lambda_{\text{exc}} = 532$ nm below saturation. I have acquired data from all cavities and consistently obtained $g^{(2)}(0)$ values below 0.25 without background subtraction. The data presented in Fig. 7.7 stems from emission from the smallest cavity with a RoC of $3 \mu\text{m}$ without background subtraction. We have observed signs of bunching on larger timescales of approx. 75 ns (see inset in Fig. 7.7a). The weak bunching characteristics could be indicative of a long-lived shelving state, however an alternative origin was identified previously in the spectral jittering of the emitting state [54]. For the pulsed measurement, the $g^{(2)}(0)$ value is obtained as the ratio of the areas of the central peak to the other peaks. Note that the time constant in both autocorrelation measurements is roughly $\tau = 1$ ns, shown later to be a result of the Purcell enhancement of the small cavity.

The radiative decay rate of the excited state of the SPE can be measured more directly by detecting the time between excitation pulse and photon emission in a time resolved photoluminescence (TRPL) experiment. Fig. 7.8a shows this data for the four different cavities. The dataset with the longest lifetime τ (slowest radiative decay rate $\gamma = \frac{1}{\tau}$) was taken for the situation depicted in Fig. 7.5a with the SPE located on the DBR emitting into the half-space above. The data reveals a lifetime of $\tau_{\text{fs}} = (4.3 \pm 0.2)$ ns in this case. Bringing another mirror into a position opposite of

it forms the cavity and alters the density of optical states, into which the emitter can irradiate.

The other datasets in Fig. 7.8a show the TRPL signal from the SPE tuned into resonance with the $\text{TEM}_{0,0}$ modes of the four different cavities. The numeric values of the decay rate are plotted in the inset as a function of the radius of curvature of the concave feature (left ordinate) and compared with the theoretical Purcell enhancement given by $F_{\text{theo}} = 3\lambda^3 Q / (4\pi^2 V)$ (right ordinate), where Q is the effective quality factor and V is the mode volume as introduced before.

Fig. 7.8b presents additional datapoints, obtained by decreasing the cavity length from left to right, such that the energy of the $\text{TEM}_{0,0}^6$ ($\text{TEM}_{0,0}^5$) mode traverses the SPE energy for concave features with $R = 25, 8 \mu\text{m}$ ($R = 5, 3 \mu\text{m}$). The two insets show fits to the TRPL data, in which the instrument response function of the single photon detector has been convoluted with a monoexponential function, giving the time constant τ . The left inset displays data from the SPE emitting into the half-space above the planar mirror, the left one data from the SPE tuned into resonance with the $\text{TEM}_{0,0}^5$ mode of the $R = 5 \mu\text{m}$ cavity. The data in the main plot is obtained by similar fits and shows a dip in lifetime (or a peak in the radiative decay rate) as the cavity lengths of the four different cavities are tuned, such that the $\text{TEM}_{0,0}$ mode is spectrally scanned across the SPE emission. While the presence of all cavities has a marked influence on the lifetime, the largest RoC cavity results in a minimal lifetime of $\tau = (1.22 \pm 0.07) \text{ ns}$ and the best enhancement is seen for the $R = 5 \mu\text{m}$ cavity, where the lifetime is $\tau = (0.55 \pm 0.03) \text{ ns}$.

Fig. 7.8d displays a series of spectra for the same cavity length changes as in Fig. 7.8b for the $R = 5 \mu\text{m}$ cavity. As the separation between the mirrors is decreased the energy of the cavity mode increases and traverses the SPE, with the resonant case depicted in the middle inset in the lower panel (light blue, dashed line). The left (right) subplot of the lower panel marked with a red dashed line (green dashed line) show spectra, where the cavity mode is detuned from the emitter to lower (higher) energies.

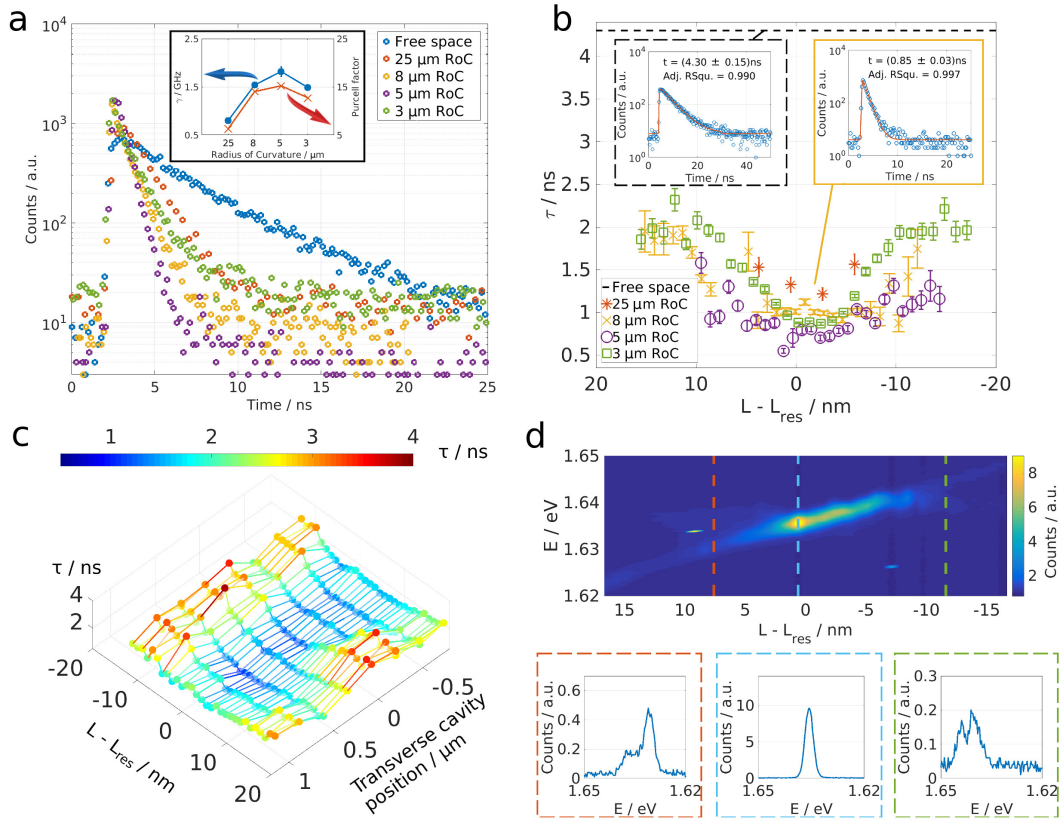


FIGURE 7.8: a) Time-resolved photoluminescence from SPE in four different cavities and in free space showing Purcell enhancement of the radiative decay. Inset: Largest radiative decay constant measured for the respective radius of curvature and theoretical Purcell enhancement. b) The lifetime as the cavity length is varied such that the $\text{TEM}_{0,0}$ traverses the SPE for four different cavities. The free space lifetime is obtained by the fit in the left inset and marked with the dashed black line in the main plot. The right inset shows the fit to the time resolved PL signal from the SPE in the $R = 5$ μm cavity on resonance. c) Effect of spatial detuning: Lifetime of SPE in $R = 3$ μm cavity as a function of both the cavity length and the cavities transverse position relative to the SPE. d) Top panel: PL spectra from SPE in the $R = 5$ μm cavity as the cavity length is varied. The horizontal position coincides with the data presented in Fig. 7.8b. Lower panel: Three selected spectra from data presented above, corresponding to the vertical, dashed lines in the top plane plot. Note the scale difference when comparing the middle plot on resonance with the two detuned cases (differing by a factor of 20 and 50 respectively).

Along with the spectral alignment of the emitter to the cavity mode, the position of the emitter in the electric field of the mode is another critical parameter for the Purcell effect. While the placement of the monolayer at the surface of the planar DBR with a low refractive index termination ensures longitudinal alignment to an antinode of the mode, the transverse position is a parameter which can be optimised experimentally in situ (as demonstrated in Fig. 7.6c). Fig. 7.8c shows the effect that such spatial detuning has on the magnitude of the Purcell enhancement. In the figure I have plotted the lifetime as a function of both spectral (cavity length) and spatial

detuning (along an arbitrary direction of the azimuthally symmetric concave cavity parallel to the mirror surface). While the lifetime values for small spatial detunings range from $\tau = 0.9$ ns to $\tau = 3.4$ ns the Purcell effect causes lower variations for large spatial detunings, where the lifetimes lay in the range of $\tau = 1.5$ ns to $\tau = 3.0$ ns.

$R_{\text{phys}} / \mu\text{m}$	$R_{\text{opt}} / \mu\text{m}$	$\Gamma_{\text{cav}} / \text{meV}$	Q_{eff}	V/λ^3	F'_{theo}	F'_{exp}
25	26.5	2.15	607	7.35	7.3	3.44
8	14.7	1.14	970	5.26	15.0	6.62
5	7.6	2.46	545	2.72	16.2	7.81
3	-	3.99	361	-	-	6.4

TABLE 7.1: **Quantitative evaluation of the coupling of single photon emitters in WSe₂ to low modevolume cavities.** Purcell-effect related quantities for the SPE coupled to the TEM_{0,0}⁶ (TEM_{0,0}⁵) mode of four cavities with $R = 25, 8 \mu\text{m}$ ($R = 5, 3 \mu\text{m}$) at $L \approx 2.3 \mu\text{m}$ ($L \approx 1.9 \mu\text{m}$). R_{phys} and R_{opt} are the radii of curvature obtained by AFM measurement (comp. Fig. 7.5e) and as inferred from the transverse mode spacing in the analytic Gaussian beam description. Γ_{cav} , Q_{eff} and V are the mode linewidth, effective quality factor of the cavity-emitter system and mode volume, which result in the effective theoretical value for $F'_{\text{theo}} = \frac{3\lambda^3 Q_{\text{eff}}}{4\pi^2 V} + 1$. F'_{exp} denotes the measured ratio of the excited state lifetime outside and within the cavity $F'_{\text{exp}} = \frac{\tau_{\text{fs}}}{\tau_{\text{cav}}}$. The missing values in the bottom row could not be obtained, because no transverse modes were available to calculate R_{opt} .

Tab. 7.1 summarises the most important quantities for the four different cavities. The first column shows R_{phys} , the physical radius of curvature as measured with an AFM (see Fig. 7.5e). R_{opt} , the parameter in the second column, is the radius of curvature obtained from the transverse mode spacing as given by Eq. 3.24. It describes the effective confining potential and has been reported before to exceed the nominal RoC for small curvatures [88]. Γ_{cav} , Q_{eff} and V are the cavity mode FWHM linewidth, quality factor and volume that I infer from the optical radius of curvature. With these values I can calculate the effective Purcell factor $F'_{\text{theo}} = F_{\text{theo}} + 1 = \frac{3\lambda^3 Q_{\text{eff}}}{4\pi^2 V} + 1$ and compare it to the experimental value $F'_{\text{exp}} = \frac{\tau_{\text{fs}}}{\tau_{\text{cav}}}$.

7.2.4 Discussion

The saturation excitation power P_{sat} and countrate I_{sat} depend on the radiative decay rate γ_r only and should thus show enhancements proportional to the Purcell factor. The data presented in the table in Fig. 7.6e supports this theory weakly and suggests severe losses from the cavity mode, as can be seen by the following reasoning:

- The same lens with an $\text{NA} = 0.82$ was used for both the cavity coupling and free-space experiments. In the free-space experiment with the SPE emitting

into the halfspace above the mirror this results in a collection efficiency of $\eta_{fs} = 42.8\%$.¹³

- The divergence of the cavity modes in this study is below $\theta_{div} = 0.4$, which suggests that all the light is collected from the cavity mode irradiating through the planar mirror side. Since the reflectivity of both DBRs is the same, we obtain a collection efficiency of $\eta_{cav} = 50\%$ for emission out of the cavity.
- Assuming $P_{sat} \propto F'_{theo}$ we find a ratio of $\frac{2P_{sat}}{P_{sat fs} F'_{theo}} = 44\%, 30\%, 41\%$ and 48% for the four cavities from largest to smallest.
- For the I_{sat} values we calculate a similar ratio, but subtract it from 1 to obtain losses (ie. deviations from the theoretically enhanced free-space saturation counts) of $\delta_{DBR}(758nm) = 1 - \frac{I_{sat} \eta_{cav}}{I_{sat fs} \eta_{fs} F'_{theo}} = 70\%, 77\%, 71\%$ and 59% for the four cavities in the same order.

The spread in these values thus confirms the theory of proportionality only weakly. The losses at the DBR interface are attributed to an increased surface roughness and/or contamination from the backside, where the mirror was attached to the sample holder. Note that the cavity linewidth exceeds the emitter linewidth for all cavities. Even though we see such losses our cavity setup still increases the photon flux of the SPE by 900% and increases the frequency of single photon emission by a factor of 7.8 when compared to irradiation into free space.

This number compares with a theoretically predicted Purcell enhancement of $F'_{theo} = 16.2$, approximately twice of what I have found experimentally. In fact the ratio of F'_{theo}/F'_{exp} is 2.1, 2.3 and 2.1 for the three cavities with RoC 25 μm , 8 μm and 5 μm respectively, evidently showing a similar ratio between prediction and experimental result. The reason for the systematic discrepancy is therefor likely to be related to the properties of the emitter, not the cavity system. A reduced radiative quantum efficiency of $\eta \approx 40\%$ would, for example, explain the results.¹⁴ The data presented in this section is under preparation of being published with a more thorough investigation of the emitter orientation and quantum efficiency.

7.2.5 Conclusion

To conclude this section, I have presented a single photon emitter hosted by the transition metal dichalcogenide WSe₂ coupled to a range of FIB milled microcavities with mode volumes in the λ^3 regime. I have shown an enhancement of the spontaneous emission rate by an effective Purcell factor of 7.8 for a cavity with a radius of curvature of $R = 5 \mu m$ together with full spectral and spatial tunability. Coupling to

¹³The collection efficiency is given by $\eta_{fs} = 2 \frac{\Omega_{NA}}{4\pi} = 1 - \sqrt{1 - (NA/n)^2}$, where Ω_{NA} is the solid angle subtended by the lens, n is the refractive index of the medium between mirror and lens and the factor 2 arises from the reflection off the mirror.

¹⁴As introduced previously the quantum efficiency is given as $\eta = \frac{F'_{exp} - 1}{F'_{theo} - 1} = \frac{F_{exp}}{F_{theo}}$.

the cavity has increased the saturation countrate from $74 \frac{kcts}{s}$ on the mirror surface to $332 \frac{kcts}{s}$ within the cavity, an almost five-fold enhancement.

The results presented in this chapter highlight the capabilities of open-access microcavities to increase the quality of single photon emitters, both in terms of photon count rates and spectral purity. By allowing in-situ movements of both mirrors the approach offers a promising route towards wavelength tunable, modular and bright single photon sources for a wide range of applications in quantum information technology. Challenges of the approach are the relatively complex experimental setup and the susceptibility to mechanical vibration, which is at the center of current optimisation.

8 Closing perspective

In summary I have presented improvements of the fabrication of FIB milled microcavities, allowing a finesse around 5×10^4 and nanometric control over wide ranges of mirror shapes. A study of coupled cavities evidenced this ability and showed that the open cavity platform enables in-situ tuning of the photonic coupling parameters, a prerequisite for tunable cavity arrays with different dimensionalities and geometries.

In Chapter 6 I have demonstrated that both monolayer WS_2 and CdSe nanoplatelets can be embedded within an open microcavity to reach the strong coupling regime, where the nature of the exciton state itself is changed. In fact, by increasing the electric field per photon, collectively coupled exciton-polariton states emerged which exhibit properties such as ultra-light restmasses and finite Coulomb scattering cross sections. By fully resolving the Rabi splitting, the strong coupling regime was verified unambiguously. The open cavity allows to access different levels of exciton-photon detuning in-situ, enabling further studies of polariton dynamics and the role of phonon assisted scattering within the polariton state. In a second study a hybrid organic-inorganic polariton state was created, bearing potential for the creation of optical switches and the control of exciton-mediated nonlinearities.

In the concluding experimental Chapter 7 I showed that FIB milled microcavities exhibiting small electric field mode volumes around λ^3 can be used to change the optical density of states accessible to exciton states, resulting in Purcell enhanced emission by factors of up to 2 at room temperature and 8 at low temperature. The perturbative coupling thus allowed striking modulation of the spontaneous emission process, with a magnitude exceeding previous literature results of similar systems presented in Section 2.2.1.

8.1 Outlook

The findings presented in this thesis advance the understanding in a mostly application oriented field of nanophotonics. Here one strives to establish light sources, sensors and optical switches by combining nanomaterials with suitable dielectric environments. Both the open cavity system and the novel materials introduced in this thesis may contribute towards future nanophotonic devices.

The FIB milling has been shown to be suitable for the creation of large curved features. Here the milling beam was optimised, such that the surface of the cavity exhibited roughness values around $\sigma = 0.7 \text{ nm}$, which could be improved to $\sigma =$

0.3 nm by CO₂ laser ablation. For certain applications, such as photonic Bose-Einstein condensation [170, 171], the photonic potential landscape is of major importance for the thermalisation of photons and both the mirror shape and the local surface roughness could be engineered to create vortices and to control the condensation of light.

On the other hand, high finesse cavities such as the ones presented in Chapter 5 are used as sensors in microfluidic channels to detect single nanoparticles [91] and, as shown in the last chapter, to enhance single photon emission. Current research in this field entails the search for other materials that exhibit single photon emission at elevated temperatures - a good example of a recent success in this regard are single defect sites in hexagonal boron nitride exhibiting narrow linewidths and megacounts at room temperature [172]. The aim is to create customer-ready, modular open-cavity systems allowing single photon emission with finite spectral tunability. Over the last years, the nitrogen vacancy center in diamond has been thoroughly researched and might be the first emitter in such modular cavity devices.

Regarding the extension of the coupled cavity system, a future research direction is to create arrays with different dimensions which could be used to create topological insulators and to investigate other nonlinear phenomena such as phase transitions of light and strongly correlated states. For this, an excitonic component would need to be introduced into the cavity. Another challenging pathway is to employ intercavity quantum interferences to produce single photons via the unconventional photon blockade [94, 173].

For a sufficiently strong electric field per photon one enters the strong coupling regime. The collective exciton-polariton state in such systems bears particular interest for fundamental research. It is attractive for a range of nonlinear devices such as threshold-less polariton lasers, to create ultra-compact Bose-Einstein condensates and, with a two-dimensional material, investigate dimensionally frustrated electron-gas systems [18]. The relatively young field of valleytronics harbours additional research directions: Here additional degrees of freedom of electronic states, such as spin and valley, are used to encode and process information [174, 175].

Slightly more device oriented, the hybrid polariton state could be used for energy transfer between the excitonic constituents. By contacting the inorganic component, excitations originating in the organic part (due to the larger oscillator strength) could be extracted after scattering within the hybrid polariton state. For biological systems, a polariton induced shift of the energy levels involved in photosynthesis could be used to bypass certain components in the photosynthesis cascade such as the baseplate, resulting in an increased photosynthesis efficiency or artificial selection pressures [14, 176].

To conclude, the open cavity platform developed in this thesis introduces a versatile platform for future experiments and devices. While CdSe QDs are well established in the literature, novel nanomaterials such as nanoplatelets and two-dimensional transition metal dichalcogenides have only recently been described and bear considerable potential for nanophotonic devices. The open microcavity approach allows to control individual quantum states in condensed matter systems at elevated temperatures.

A Mathematical compendium

A.1 Distributions

Gaussian:

$$\mathcal{G}_{\mu,\sigma}(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2} \quad (\text{A.1})$$

Lorentzian or Cauchy distribution:

$$\mathcal{L}_{\mu,\gamma}(x) = \frac{2}{\pi\gamma \left[1 + \left(\frac{x-\mu}{\gamma/2}\right)^2\right]} = \frac{1}{\pi} \frac{(\gamma/2)}{(\gamma/2)^2 + (x-\mu)^2} \quad (\text{A.2})$$

Poisson distribution:

$$P_{\langle n \rangle}(n) = e^{-\langle n \rangle} \frac{\langle n \rangle^n}{n!} \quad (\text{A.3})$$

A.2 Advanced mathematical operations

Convolution:

$$\begin{aligned} (f * g)(t) &\stackrel{\text{def}}{=} \int_{-\infty}^{\infty} f(\tau) g(t - \tau) d\tau \\ &= \int_{-\infty}^{\infty} f(t - \tau) g(\tau) d\tau. \end{aligned} \quad (\text{A.4})$$

A.3 Topographic functions:

Elliptoidal surface:

$$z(x, y) = b - L \left(1 - \frac{(x - x_c)^2 + (y - y_c)^2}{LR} \right)^{\frac{1}{2}} + L \quad (\text{A.5})$$

Here L is the nominal cavity length and R the radius of curvature.

A.4 Trigonometric relations

$$\arctan(a) - \arctan(b) = \arctan\left(\frac{a-b}{1+ab}\right) \quad (\text{A.6})$$

$$\arctan\left(\frac{a}{b}\right) = \arccos(\pm(1 + (a/b)^2)^{-\frac{1}{2}}) \quad (\text{A.7})$$

B Physical compendium

B.1 Electrodynamics

Inside a medium Maxwell's equations read

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = \rho_{\text{free}}(\mathbf{r}, t) \quad (\text{B.1a})$$

$$\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0 \quad (\text{B.1b})$$

$$\nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{\partial}{\partial t} \mathbf{B}(\mathbf{r}, t) \quad (\text{B.1c})$$

$$\nabla \times \mathbf{H}(\mathbf{r}, t) = \frac{\partial}{\partial t} \mathbf{D}(\mathbf{r}, t) + \mathbf{J}(\mathbf{r}, t) \quad (\text{B.1d})$$

These equations introduce relations between vectors which are macroscopic averages over volumes containing multiple atoms. While effects related to the magnetic field $\mathbf{H} = \mathbf{B}/\mu_0 - \mathbf{M}$ are of lesser importance for this work, more space will be devoted towards a comprehensive description of the electric fields and their interaction with matter. This treatment bases on the understanding that each electric field causes a magnetic field and vice versa as described by Eq. B.1c and B.1d. The electric displacement field $\mathbf{D}(\mathbf{r}, t)$ is related to the electric field $\mathbf{E}(\mathbf{r}, t)$ by

$$\mathbf{D}(\mathbf{r}, t) = \varepsilon \varepsilon_0 \mathbf{E}(\mathbf{r}, t) = (1 + \chi_e) \varepsilon_0 \mathbf{E}(\mathbf{r}, t) = \varepsilon_0 \mathbf{E}(\mathbf{r}, t) + \mathbf{P}(\mathbf{r}, t) \quad (\text{B.2})$$

with the relative permittivity ε , the linear electric susceptibility χ_e and the induced polarisation density $\mathbf{P}(\mathbf{r}, t) = \chi_e \varepsilon_0 \mathbf{E}(\mathbf{r}, t)$. The susceptibility of a material thus describes the strength of the material response to an electric field, in other words it quantifies the ability of the material to be polarised. It is useful to introduce these additional quantities as they facilitate the macroscopic description of interaction with matter, ie. how light is absorbed and transmitted in a material. If the z-axis is chosen arbitrarily as the propagation direction, the wave equation that directly follows from Maxwell's equation B.1c and B.1d describes a wave oscillating with a term $e^{i(kz - \omega t)}$. Here the wavenumber and the frequency of the wave are related by the speed of light $\omega/k = c/n = c/\sqrt{\varepsilon} = (\mu_0 \varepsilon_0 \varepsilon)^{-\frac{1}{2}}$, where $n = \sqrt{\varepsilon}$ is the complex refractive index of the medium.¹ The amplitude of the polarisation density can be a complex quantity, where the imaginary part describes attenuation or gain effects and the real part the phase velocity in the medium, ie. the index of refraction. More specifically one

¹ A material with unit relative magnetic permeability μ is assumed at this point.

can write the amplitude of the polarisation density as

$$\mathcal{P} = N\mu X = \varepsilon_0(\chi' + i\chi'')E_0 \quad (\text{B.3})$$

where N is the number of systems per unit volume, μ is the dipole moment of a single system and X is a complex dimensionless amplitude which varies little in an optical period for typical materials.

B.2 Transfer-matrix method

Maxwell's equation in a spatially homogeneous medium with refractive index n can be combined to give the well known wave equation for the electric field (a similar equation can be obtained for the magnetic field):

$$\nabla^2 \mathbf{E}(\mathbf{r}, t) = \frac{1}{c^2} \frac{d^2}{dt^2} \mathbf{E}(\mathbf{r}, t) \quad (\text{B.4})$$

The wave equation can be further simplified assuming monochromatic light, resulting in a solution of the form $\mathbf{E}(\mathbf{r}, t) = \epsilon \mathbf{E}(\mathbf{r}) \exp(i(\omega t + \varphi))$ with ϵ the polarisation vector, $k = |\mathbf{k}| = \frac{\omega}{c} = \frac{2\pi}{\lambda}$ the magnitude of the wavenumber and φ a phase offset. For the amplitude $\mathbf{E}(\mathbf{r})$ one obtains the time-independent Helmholtz equation

$$(\nabla^2 + n^2 \mathbf{k}_0^2) \mathbf{E}(\mathbf{r}) = 0 \quad (\text{B.5})$$

with the vacuum wavenumber $\mathbf{k}_0 = \frac{\mathbf{k}}{n}$ and $k_0 = |\mathbf{k}_0| = \frac{2\pi}{\lambda_0}$. Without loss of generality one commonly sets $\mathbf{k}_0 \parallel \hat{\mathbf{z}}$ to obtain $\partial_z^2 E = -k_0^2 n^2 E$ for the field amplitude in z -direction. A general form of the solution for waves in this direction is

$$E(z) = A^+ e^{ikz} + A^- e^{-ikz} \quad (\text{B.6})$$

A^+ and A^- are the amplitudes of forward and backward travelling waves. For the transition from a medium with refractive index n_1 to one with n_2 one defines the amplitude reflection and transmission coefficients:

$$r = \frac{A_1^-}{A_1^+} \quad \& \quad t = \frac{A_2^+}{A_1^+} \quad (\text{B.7})$$

To solve the boundary conditions for multiple interfaces it is convenient to define a transfer matrix $\mathcal{T}$, which propagates the wave across a homogeneous layer. Such a matrix can be obtained by choosing a convenient basis set. One possibility is to define

a vector composed of the electric and magnetic field:²

$$\Phi(z) = \begin{pmatrix} E(z) \\ \frac{1}{ik_0} \partial_z E(z) \end{pmatrix} \quad (\text{B.8})$$

A matrix $\mathcal{T}_a$ that enforces the propagation through a layer with refractive index n and thickness a ($\mathcal{T}_a \Phi|_{z=0} = \Phi|_{z=a}$) in this basis has the form:

$$\mathcal{T}_a = \begin{pmatrix} \cos(ka) & \frac{i}{n} \sin(ka) \\ in \sin(ka) & \cos(ka) \end{pmatrix} \quad (\text{B.9})$$

We can now describe the light propagation within the simplest resonator, a quasi one-dimensional cavity with two (planar) mirrors with reflectivity $R_1 = |r_1|^2$ and $R_2 = |r_2|^2$ (see schematic in Fig. 3.4). Such a resonator is sometimes called a Fabry-Pérot etalon for historic reasons. The vector that $\mathcal{T}_L$ propagates are given by Eq. B.8. The relation between A^+ and A^- at each mirror is given by the definition of the reflection coefficient and thus (with arbitrary $\mathfrak{c} \in \mathbb{C}$):

$$\begin{pmatrix} \cos(kL) & \frac{i}{n} \sin(kL) \\ in \sin(kL) & \cos(kL) \end{pmatrix} \begin{pmatrix} 1 + r_1 \\ n(r_1 - 1) \end{pmatrix} = \mathfrak{c} \begin{pmatrix} 1 + r_2 \\ n(1 - r_2) \end{pmatrix} \quad (\text{B.10})$$

The choice of coefficients for the vectors on each side of the cavity enforces the correct reflection, i.e. attenuation and phase jump. Eliminating $\mathfrak{c}$ one obtains

$$r_1 r_2 e^{i2kL} = 1 \quad (\text{B.11})$$

which is the main resonator equation.

B.3 Gaussian-beam cavity modes

With the stability parameter $g_i = 1 - \frac{L}{R_i}$ one obtains:

$$z_R = \frac{L\sqrt{g_1 g_2 (1 - g_1 g_2)}}{g_1 + g_2 - 2g_1 g_2} \quad w_0 = \sqrt{\frac{\lambda z_R}{\pi}} = \sqrt{\frac{\lambda L}{\pi}} \left(\frac{g_1 g_2 (1 - g_1 g_2)}{(g_1 + g_2 - 2g_1 g_2)^2} \right)^{\frac{1}{4}} \quad (\text{B.12a})$$

$$z_1 = \frac{-Lg_2(1 - g_1)}{g_1 + g_2 - 2g_1 g_2} \quad w_1 = w(z_1) = \sqrt{\frac{\lambda L}{\pi}} \left(\frac{g_2}{g_1(1 - g_1 g_2)} \right)^{\frac{1}{4}} \quad (\text{B.12b})$$

$$z_2 = \frac{Lg_1(1 - g_2)}{g_1 + g_2 - 2g_1 g_2} \quad w_2 = w(z_2) = \sqrt{\frac{\lambda L}{\pi}} \left(\frac{g_1}{g_2(1 - g_1 g_2)} \right)^{\frac{1}{4}} \quad (\text{B.12c})$$

²Sometimes a basis of forward and backwards travelling waves is more appropriate, see for ex. [109].

B.4 Cavity lineshape

In the following the electric field transmitted by a resonator is calculated as shown in Fig. 3.4. One assumption is that there are no absorption or scattering losses at the mirror interface, thus $r_i^2 + t_i^2 = 1$. For an electric field amplitude E^{in} incident from the left of the resonator the transmitted field can be obtained:

$$\text{First :} \quad E_1^{\text{out}} = E^{\text{in}} t_1 e^{i\phi} t_2 = E^{\text{in}} t_1 t_2 e^{i\phi} \quad (\text{B.13})$$

$$\text{n-th:} \quad E_n^{\text{out}} = E_{n-1}^{\text{out}} \frac{-r_2}{t_2} e^{i\phi} (-r_1) e^{i\phi} t_2 = E_{n-1}^{\text{out}} r_1 r_2 e^{i2\phi} \quad (\text{B.14})$$

Now the field contribution after the n -th round trip transmission is known (note that we assume dielectric mirrors where a reflected field picks up a phase of π). ϕ is the phase that light propagating across the cavity with length L acquires. Summing up all terms with the help of the geometric series one obtains for the total electric field:

$$E^{\text{out}} = \sum_{n=1}^{\infty} E_n^{\text{out}} = E^{\text{in}} t_1 t_2 e^{i\phi} \sum_{n=0}^{\infty} \left(r_1 r_2 e^{i2\phi} \right)^n = \frac{E^{\text{in}} t_1 t_2 e^{i\phi}}{1 - r_1 r_2 e^{i2\phi}} \quad (\text{B.15})$$

For the intensity ratio between incoming and outgoing field one thus finds the Airy distribution [177]:

$$A^{\text{out}}(\phi) = \frac{I^{\text{out}}}{I^{\text{in}}} = \frac{|E^{\text{out}}|^2}{|E^{\text{in}}|^2} = \frac{(1 - R_1)(1 - R_2)}{(1 - \sqrt{R_1 R_2})^2 + 4\sqrt{R_1 R_2} \sin^2 \phi} \quad (\text{B.16})$$

B.4.1 Canonical quantisation

As the scope of this thesis is centered around the interaction between light and matter, the quantisation of electric and magnetic field that is a standard exercise in quantum mechanics is presented at the bare minimum. An in depth derivation can be found in many text books (eg. [103, 105]). For the purpose of quantisation, let's suppose a finite cubic volume of space with volume $V = L^3$. A standing electric field polarised in x-direction and with wavenumber k , propagating parallel to the z-axis (all without loss of generality) will obey the boundary condition $kL = 2\pi q$ and can be written as

$$E(z, t) = \hat{\mathbf{x}} X(t) N \sin(kz) \quad (\text{B.17})$$

Here $X(t)$ is an arbitrary field amplitude and N is a constant that will be determined later. Note that Maxwell's equation Eq. B.1d in the absence of currents directly results in the corresponding magnetic field $B(z, t) = \hat{\mathbf{y}} \frac{k \dot{X}(t)}{c^2} N \cos(kz)$. From the classical electromagnetic energy density $\epsilon = (\epsilon_0 E(z, t)^2 + B(z, t)^2 / \mu_0) / 2$ one can

directly write the Hamiltonian:

$$\mathcal{H} = \frac{1}{2} \int_V dV \left(\epsilon_0 E(z, t)^2 + \frac{B(z, t)^2}{\mu_0} \right) \quad (\text{B.18})$$

$$= \frac{1}{4} \epsilon_0 N^2 V \left(X^2 + \frac{k^2 \dot{X}^2}{c^2} \right) = \frac{1}{2} \left(\omega^2 X^2 + \dot{X}^2 \right) \quad (\text{B.19})$$

In the last step I have set $N^2 = 2\omega^2/\epsilon_0 V$. The Hamiltonian of the electromagnetic field (for one mode with wavenumber k and polarisation $\epsilon = \hat{\mathbf{x}}$) is thus formally equivalent to a classical harmonic oscillator (which has unit mass in this example). Since the harmonic oscillator is well known both in classical and in quantum mechanics a comparison between the two is instructive at this point. The quantum analogue reads

$$\mathcal{H} = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) \quad (\text{B.20})$$

where $a^\dagger, a$ are the creation and annihilation operators satisfying the bosonic commutation relation $[a, a^\dagger] = 1$. Formally there is an equivalence between this commutation relation and the canonical commutation relation in quantum mechanics $[X, m\dot{X}] = i\hbar$, which is one way to express the uncertainty principle. Indeed one can write X and $\dot{X}$ in terms of the a and $a^\dagger$ operators and obtains the electric field as:

$$E(z, t) = \hat{\mathbf{x}} E_\omega \left(a + a^\dagger \right) \sin(kz) \quad (\text{B.21})$$

where the prefactors have been summarised in E_ω . The electric field can then be interpreted as an operator - the creation operator $a^\dagger$ creates a photon in the mode with wavenumber k and polarisation ϵ and the annihilation operator a destroys it. To represent the whole electric field one sums this expression over all modes and polarisations and forwards and backwards travelling waves. Building on these interpretations of quantum mechanics for electromagnetism E_ω can be identified as the ‘electric field per photon’ in a mode with volume V and frequency $\nu = \omega/2\pi$:

$$E_\omega = \left(\frac{\hbar\omega}{2\epsilon_0 V} \right)^{\frac{1}{2}} \quad (\text{B.22})$$

B.5 Modemixing-formalism

Note that the matrix $\mathbb{A}$ ($\mathbb{B}$) is symmetrical, that is $\mathbb{A}_{s,t} = \mathbb{A}_{t,s}$ ($\mathbb{B}_{s,t} = \mathbb{B}_{t,s}$). For concave shapes with inversion symmetries in both x - and y -direction one has $\Delta_b(x, y) = \Delta_b(x, -y)$ and $\Delta_b(x, y) = \Delta_b(-x, y)$, so an integration over quadrant I is sufficient. A further reduction in complexity of the problem can be made by analysing the symmetry of the basis states. For Hermite-Gauss modes as given in Eq. 3.7 the field in the transverse plane is modulated by the Hermite polynomials $H_n(x)$. They have the symmetry property $H_n(x) = (-1)^n H_n(-x)$, thus the conclusion is that the

overall integral is given by

$$I_{tot} = (1 + (-1)^{n_s+n_t} + (-1)^{n_s+n_t+m_s+m_t} + (-1)^{m_s+m_t}) I \quad (\text{B.23})$$

where I is the integral $\mathbb{B}_{s,t}$ over quadrant I and $(n_{s(t)}, m_{s(t)})$ are the transverse excitation numbers of the basis states $\psi_{s(t)}$. In particular the integral vanishes for certain combinations of $(n_{s(t)}, m_{s(t)})$ where:

$$(-1)^{n_s+n_t} + (-1)^{n_s+n_t+m_s+m_t} + (-1)^{m_s+m_t} = -1$$

Thus in many cases no integration needs to be performed for symmetry reasons. This condition gives a tiled structure of $\mathbb{M}$ and substantially reduces the amount of work necessary for the integration.

This procedure fully defines the $N \times N$ matrix $\mathbb{M}$. The dimension N of $\mathbb{M}$ depend on the number of basis states - in general a sensible choice of basis states for a given cavity environment will reduce the number of dimensions required for a good mode representation substantially.

The eigenstates Ψ_i of the eigenvalue equation $\mathbb{M}\Psi_i = \gamma_i\Psi_i$ will be a linear superposition of the basis states: $\Psi_i = \sum_j C_j\psi_j$. The weights C_j can be computed as the components of the eigenvectors of $\mathbb{M}$ and thus quantify the contribution of the respective basis state to the eigenstate. The quality of the mode representation, that is the convergence of the model, can be judged by the decay of higher excited state contribution in the composition of the eigenstates. Another important parameter is the eigenvalue γ_i of the mode Ψ_i . It is interesting to notice that $|\gamma_i|$ gives the losses per round trip (which are directly connected to the finesse) while the phase of γ_i relates to its spectral position.

The phase angle ϕ_i of the complex number γ_i is given by $\phi_i = \arctan(\frac{\text{Im}(\gamma_i)}{\text{Re}(\gamma_i)})$. Setting the cavity length to L and introducing a phase detuning parameter $\delta\phi_i$ one finds for every eigenvector that:

$$2kL + 2\phi_i + \delta\phi_i = 2q\pi \quad (\text{B.24})$$

where $q \in \mathbb{N}^+$. For resonant modes the phase detuning should vanish, so $\delta\phi_i = 0$ and the corresponding resonance wavelength λ_i is approximated by:

$$\lambda_i = \frac{\lambda}{1 + \frac{\phi_{\gamma_i}\lambda}{2\pi L}} \quad (\text{B.25})$$

B.6 Linear response theory

Suppose a monochromatic electric field of the form

$$E(t) = E_0(e^{-i\nu t} + e^{i\nu t}) \quad (\text{B.26})$$

incident on an atom. The atom in this most simple description can be modelled as an infinitely heavy positively charged nucleus with a surrounding negative charge cloud (ie. an electron) which is allowed to oscillate about its equilibrium position. For small deviations the equation of motion reads

$$m \frac{d^2}{dt^2} x(t) + 2m\beta \frac{d}{dt} x(t) + m\omega^2 x(t) = eE(t) \quad (\text{B.27})$$

which corresponds to a damped oscillator driven by the electric field with frequency ν . β is the damping parameter whose physical origin is discussed in the main text, ω the eigenfrequency of the oscillator, e is the charge of the cloud (ie. charge of the electron) and m its mass. Once the system has reached a steady state, $x(t)$ will oscillate with the same frequency as the driving field, which motivates the Ansatz $x(t) = A^- x_0 e^{-i\nu t} + A^+ x_0 e^{i\nu t}$, with x_0 a real amplitude and $A^\pm$ a complex modulation. Substituting the Ansatz into Eq. B.27 one obtains for the amplitudes:

$$A^- = \frac{E_0 e / (2\nu m x_0)}{(w^2 - \nu^2) / (2\nu) - i\beta} \quad \& \quad A^+ = (A^-)^* \quad (\text{B.28})$$

For near resonant excitation $|\omega - \nu| \ll \omega + \nu$ and one can approximate $\omega^2 - \nu^2 \approx 2\nu(\omega - \nu)$. How does one incorporate this response of a single oscillator into the macroscopic description of matter with the electric susceptibility and induced polarisation introduced in Section B.1? By comparing the complex amplitude A^- with Eq. B.3 and noting that classically the dipole moment is given as $\mu = ex_0$ one identifies $X = A^+$.³ One thus writes the electric susceptibility χ_e of a material characterised by N damped oscillators per unit volume as

$$\chi_e = \frac{Ne^2}{2\varepsilon_0 m \nu} \frac{1}{(\omega - \nu - i\beta)} = \frac{Ne^2}{2\varepsilon_0 m \nu} \frac{\omega - \nu + i\beta}{(\omega - \nu)^2 + \beta^2} \quad (\text{B.29})$$

B.7 Linear response theory within the transfer matrix method

The problem of finding the resonant modes in the cavity is reduced to finding the amplitude reflection coefficient r as defined in Fig. 3.9. Having found r one can compute the cavity dispersion by solving ($k_c = n_c k$)

$$\begin{pmatrix} \cos(k_c L) & \frac{i}{n_c} \sin(k_c L) \\ i n_c \sin(k_c L) & \cos(k_c L) \end{pmatrix} \begin{pmatrix} 1 + r_1 \\ n_c(r_1 - 1) \end{pmatrix} = A \begin{pmatrix} 1 + r \\ n_c(1 - r) \end{pmatrix} \quad (\text{B.30})$$

The choice of coefficients for the vectors on each side of the cavity ensures the correct reflection conditions, i.e. attenuation and phase jump. Eliminating A one finds

$$r_1 r e^{i2k_c L} = 1 \quad (\text{B.31})$$

³Mathematical rigour would demand associating A^+ with the complex conjugate of X as the amplitude for the positive frequencies. For the current exposition it is sufficient to focus on one branch of the frequencies and refer the reader to [53] p. 10 et sqq. for a more in-depth discussion.

For ideal dielectric mirrors $r_1 = r = 1$ and thus the well known Fabry-Perot resonance condition $k_c L = \pi q$ emerges, q being an integer. Now the problem is reduced to finding r . Taking the right side of the sketch in Fig. 3.9 one starts with ($k_w = n_w k$)

$$\begin{pmatrix} \cos(k_w d) & \frac{i}{n_w} \sin(k_w d) \\ i n_w \sin(k_w d) & \cos(k_w d) \end{pmatrix} \begin{pmatrix} 1 + r \\ n_c(1 - r) \end{pmatrix} = A \begin{pmatrix} 1 + r_2 \\ n_w(1 - r_2) \end{pmatrix} \quad (\text{B.32})$$

By eliminating A and solving for r one finds:

$$r = \frac{n_c - n_w + e^{i2k_w d}(n_c + n_w)r_2}{n_c + n_w + e^{i2k_w d}(n_c - n_w)r_2} \quad (\text{B.33})$$

This expression is further reducible if a certain form for r_2 is assumed. If $r_2 = 1$, as for a perfect dielectric reflector, it reads:

$$r = \frac{n_c \cos(k_w d) + i n_w \sin(k_w d)}{n_c \cos(k_w d) - i n_w \sin(k_w d)} \quad (\text{B.34})$$

Substituting this expression into Eq. B.31, assuming a thin layer ($|k_w d| \ll 1$) and setting $r_1 = 1$:

$$n_c \sin(k_c L) + n_w k_w d \cos(k_c L) = 0 \quad (\text{B.35})$$

A very succinct expression can be obtained by evaluating this equation close to the cavity mode resonance ($\cos(k_c L) \approx 1, \sin(k_c L) \approx n_c(k - k_p)L$, with k_p being the wavenumber on resonance):

$$n_c^2(k - k_p)L + n_w^2 k d = 0 \quad (\text{B.36})$$

Now n_w , the complex refractive index of the dispersive thin layer, can be introduced to find the dispersion of the resonant modes. The dielectric function of a system of Lorentz oscillators has been derived above (Section B.6):

$$\varepsilon(k) = \varepsilon_B - \frac{W}{c(k - k_x) + i\gamma_x} \quad (\text{B.37})$$

where W is proportional to the oscillator strength of the material, k_x is the wavenumber of the oscillator resonance and γ_x is the oscillator HWHM linewidth.

For the remainder of this section note that $\hbar = c = 1$. Putting $n_w = \sqrt{\varepsilon(k)}$ into Eq. B.36 one obtains:

$$n_c^2(k - k_p + i\gamma_p)L + \left(\varepsilon_B - \frac{W}{k - k_x + i\gamma_x} \right) k d = 0 \quad (\text{B.38})$$

At this stage a term $i\gamma_p$ has been introduced for the finite linewidth of the cavity mode. Of course this is artificial at this point and γ_p will be derived later in terms of the reflectivity R of the mirrors. By assuming that k varies little over the extent of the thin dispersive layer, in other words the factor $k d$ is constant ($k d = k_d d$), one can

solve the equation for k and finds by neglecting higher orders in d :

$$k_{1,2} = \frac{1}{2} (k_p + k_x - i(\gamma_p + \gamma_x)) \pm \sqrt{\frac{Wk_d d}{Ln_c^2} + \frac{1}{4}(k_p - k_x + i(\gamma_x - \gamma_p))^2} \quad (\text{B.39})$$

Now the question is, what shape the artificially introduced cavity linewidth γ_p has in terms of the mirror reflectivity. To this end one sets $r_1 = \sqrt{R}$ and follows the above procedure again. Lengthy solutions for $k_{1,2}$ are found in which one identifies:

$$\begin{aligned} \gamma_p &= \frac{1 - \sqrt{R}}{\sqrt{R}} \frac{1}{2n_c L} \\ V^2 &= \frac{k_d d W}{4n_c^2 L} \left(\frac{3 + \sqrt{R}}{\sqrt{R}} + 2Ln_c \gamma_x \right) + \left(\frac{k_d d \epsilon_B}{2Ln_c^2 \sqrt{R}} \right)^2 \\ &= \frac{1 + \sqrt{R}}{\sqrt{R}} \frac{k_d d W}{2n_c^2 L} + \frac{k_d d W}{2n_c} (\gamma_p + \gamma_x) + \left(\frac{k_d d \epsilon_B}{2Ln_c^2 \sqrt{R}} \right)^2 \end{aligned} \quad (\text{B.40})$$

In this terms of higher order in d have been neglected, except for one term proportional to ϵ_B^2 , and $k_d d \epsilon_B \ll n_c$ has been assumed.

B.8 Electronic density of states

B.8.1 3D

In three dimensions the volume of a state in $\mathbf{k}$ -space is $V_{3D} = (2\pi/L)^3$, where L is the side length of the quantisation volume. The differential volume dV between a sphere with radius $|\mathbf{k}|$ and $|\mathbf{k} + d\mathbf{k}|$ is easily found in spherical coordinates ($k = |\mathbf{k}|$):

$$dV_{3D} = 4\pi k^2 dk$$

The density of states is now given as (each state can be occupied twice with opposing spin)

$$\rho_{3D}(k)dk = 2dV_{3D}/V_{3D} = \frac{k^2 L^3}{\pi^2} dk \quad (\text{B.41})$$

Or, since one is interested in the availability of energy states and $E = \hbar^2 k^2 / 2m$ (one assumes a unit quantisation volume):

$$\rho_{3D}(E)dE = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE \quad (\text{B.42})$$

B.8.2 2D

In two dimensions the volume of a state in $\mathbf{k}$ -space is $V_{2D} = (2\pi/L)^2$, where L is the side length of the quantisation volume. The differential volume dV between a disk

with radius $|\mathbf{k}|$ and $|\mathbf{k} + d\mathbf{k}|$ can be similarly given as:

$$dV_{2D} = 2\pi k dk$$

As a function of energy the density of states reads:

$$\rho_{2D}(E)dE = \frac{m}{\pi\hbar^2}dE \quad (\text{B.43})$$

One thus obtains a constant density of states for each new energy level E_i , which can be formally written with the Heavyside function θ_H as:

$$\rho_{2D}(E)dE = \frac{m}{\pi\hbar^2} \sum_i \theta_H(E - E_i)dE \quad (\text{B.44})$$

B.8.3 1D

The derivation follows analogous to the 2D case to obtain:

$$\rho_{1D}(E)dE = \left(\frac{2m}{\pi\hbar^2}\right)^{\frac{1}{2}} \sum_i \left(\frac{n_i\theta_H(E - E_i)}{\sqrt{E - E_i}}\right) dE \quad (\text{B.45})$$

Here a degeneracy factor n_i has been introduced, which accounts for the fact that multiple state arrangements may have the same energy.

B.8.4 0D

For zero-dimensional point like confinement, the density of states consists of delta function like peaks for each discrete state. Higher states will be degenerate, the first excited state of the idealised quantum box for example has a degeneracy of three.

B.9 A closer analysis of the Purcell effect

To add to the understanding of the Purcell effect this section sheds light on a nuance common to the quantum theory. Above it was shown how the vacuum field fluctuations give a mean electric field of $E_0 = \left(\frac{\hbar\omega}{2\varepsilon_0 V}\right)^{\frac{1}{2}}$ per mode with volume V . In the next step the density of states was used to describe the mode. Equivalent to this description one could as well use the density of states for free space and show that the cavity directly enhances the electric field E_0 by a factor of the finesse $\mathcal{F}$ (at resonance). More accurately one can analyse an Airy function very similar to the one given for the cavity transmission in Eq. 3.5 for the cavity internal field amplification, which then leads to the same Lorentzian spectral lineshape as the one phenomenologically introduced above.

The main text treated the concept of an optical density of states to describe the spontaneous emission process. Here this picture is extended by a closer look at how

the emitter couples to the surrounding states. Note that the Purcell factor derived in Eq. 3.42 describes the change in spontaneous emission rate as if it would only couple to the cavity mode. As such it describes both suppression and enhancement of the emission rate. In most optical cavity systems this is only an approximate description however, since the emitter can as well emit into the solid angle of free space not subtended by the cavity mode or has access to other leaky modes in the DBR. To conceptualise the simultaneous coupling to such different optical environments one can take the spontaneous emission per unit angle and frequency as given by Fermi's Golden rule.

Lets start with writing down the spontaneous emission rate per unit angle and frequency for a dipole aligned along the $\hat{y}$ direction (which will be generalised later). Assigning the $\hat{x} - \hat{y}$ plane as the conceptual surface on which our E-field with direction $\hat{e}_r$ impinges it is straightfoward to use the basis of s and p-polarised light $\hat{s}$ and $\hat{p}$ for the vectorial description of the electric field. $\hat{s}$ is perpendicular to the plane of incidence and $\hat{p}$ parallel to it - both $\hat{s}$ and $\hat{p}$ are perpendicular to $\hat{e}_r$, as Maxwell's equation demand. For this particular choice the three vector are the basis vectors for spherical coordinates, namely $\hat{s} = \hat{e}_\varphi$ and $\hat{p} = \hat{e}_\theta$, expressed in cartesian coordinates as:

$$\hat{e}_r = \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix}, \quad \hat{e}_\theta = \begin{pmatrix} \cos \theta \cos \varphi \\ \cos \theta \sin \varphi \\ -\sin \theta \end{pmatrix}, \quad \hat{e}_\varphi = \begin{pmatrix} -\sin \varphi \\ \cos \varphi \\ 0 \end{pmatrix} \quad (\text{B.46})$$

With this choice the dipole matrix element $\mathcal{V}_{i \rightarrow f} = e \langle f | \mathbf{r} \cdot \mathbf{E} | i \rangle$ introduced in Eq. 3.29 can be evaluated with the same assumption that the electric field is constant over the extent of the wavefunctions of initial and final state. In the basis of $\hat{s}$ and $\hat{p}$ polarised waves⁴ the dot product $\mathbf{r} \cdot \mathbf{E}$ can be evaluated (with $\mathbf{r} = \hat{y}$):

$$\Gamma_\Omega(\omega, \theta, \varphi) = \frac{2\pi}{\hbar^2} \mu_{i \rightarrow f}^2 E_0^2 \frac{\omega^2}{\pi^2 c^3} \frac{1}{4\pi} \begin{pmatrix} \cos^2(\varphi) \\ \sin^2(\varphi) \cos^2(\theta) \end{pmatrix} \quad (\text{B.47})$$

$$= \frac{3}{8\pi} \Gamma_{i \rightarrow f}^{\text{fs}}(\omega) \begin{pmatrix} \cos^2(\varphi) \\ \sin^2(\varphi) \cos^2(\theta) \end{pmatrix} \quad (\text{B.48})$$

where $E_0 = \left(\frac{\hbar\omega}{2\varepsilon_0}\right)^{\frac{1}{2}}$ was used for the vacuum electric field in free space. The prefactor $\frac{3}{8\pi}$ combines the two polarisations, the solid angle 4π and the beforehand averaged factor $\xi = \frac{1}{3}$ for free space. In fact it can be checked by integrating over the full solid angle

$$\Gamma = \int_\Omega d\Omega \Gamma_\Omega \cdot (\hat{s} + \hat{p}) = \frac{3\Gamma_{i \rightarrow f}^{\text{fs}}}{4} \left(1 + \frac{1}{3}\right) = \Gamma_{i \rightarrow f}^{\text{fs}} \quad (\text{B.49})$$

⁴The states $\hat{s}$, $\hat{p}$ are represented by the vectors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

as expected for emission into free space. This formulation now allows to specify both the solid angle of emission and the electric field strength at the position of the emitter. The particular choice of dipole alignment along the $\hat{\mathbf{y}}$ direction was however only chosen for exposition purposes and can be generalised.

For the description of open cavities one aligns the optical axis to the $\hat{\mathbf{z}}$ direction. The complexity of our dipole coupling can be reduced by requiring azimuthal symmetry (ie. invariance in $\hat{\mathbf{e}}_\varphi$ direction): In this case the angle between dipole $\mathbf{er}$ and $\hat{\mathbf{x}}\text{-}\hat{\mathbf{y}}$ plane α is a sufficient parameter to characterise the system and $\mathbf{r} = (0, \cos(\alpha), \sin(\alpha))^T$ can be chosen without loss of generality. For the cavity mode in the plano-concave geometry one can use the Gaussian beam parameters introduced in Sec. 3.2.2. In particular the mode can be idealised as a cone with opening angle $\theta_d = \frac{\lambda}{\pi w_0}$ along the $\hat{\mathbf{z}}$ direction. The idea is to treat dipole emission into the solid angle defined by this cone as emission into the cavity mode - the rest of the solid angle is associated with free space emission. The total emission rate is then given as

$$\begin{aligned}\Gamma &= \int_{\Omega_{\text{cav}}} \mathbf{\Gamma}_{\Omega_{\text{cav}}}^{\text{cav}} \cdot (\hat{\mathbf{s}} + \hat{\mathbf{p}}) d\Omega + \int_{\Omega_{\text{fs}}} \mathbf{\Gamma}_{\Omega_{\text{fs}}}^{\text{fs}} \cdot (\hat{\mathbf{s}} + \hat{\mathbf{p}}) d\Omega \\ &= \int_0^{2\pi} d\varphi \int_0^{\theta_d} \sin(\theta) d\theta \mathbf{\Gamma}_{\Omega_{\text{cav}}}^{\text{cav}} \cdot (\hat{\mathbf{s}} + \hat{\mathbf{p}}) + \int_0^{2\pi} d\varphi \int_{\theta_d}^{\frac{\pi}{2}} \sin(\theta) d\theta \mathbf{\Gamma}_{\Omega_{\text{fs}}}^{\text{fs}} \cdot (\hat{\mathbf{s}} + \hat{\mathbf{p}}) \\ &= \Gamma_{i \rightarrow f}^{\text{cav}}(\omega) + (1 - \zeta) \Gamma_{i \rightarrow f}^{\text{fs}}(\omega)\end{aligned}\tag{B.50}$$

Where the parameter ζ has been introduced which quantifies the fraction of the solid angle subtended by the cavity mode. The analytic form for $\Gamma_{i \rightarrow f}^{\text{fs}}$ and $\Gamma_{i \rightarrow f}^{\text{cav}}$ has been given in Eq. 3.41.

The effective Purcell factor in the cavity can now be defined as

$$F_P^{\text{eff}} = \frac{\Gamma_{i \rightarrow f}^{\text{cav}}(\omega_0) + (1 - \zeta) \Gamma_{i \rightarrow f}^{\text{fs}}(\omega_0)}{\Gamma_{i \rightarrow f}^{\text{fs}}} = F_P + 1 - \zeta\tag{B.51}$$

For most open cavity results, ζ can be neglected and the effective Purcell factor is given as $F_P^{\text{eff}} = F_P + 1$. Another parameter which is often used is the β -factor for a specific cavity mode, which is defined as the ratio between the emission into that mode and the total emission:

$$\beta = \frac{\Gamma_{i \rightarrow f}^{\text{cav}}(\omega_0)}{\Gamma_{i \rightarrow f}^{\text{cav}}(\omega_0) + (1 - \zeta) \Gamma_{i \rightarrow f}^{\text{fs}}(\omega_0)} = \frac{F_P}{F_P + 1 - \zeta}\tag{B.52}$$

B.10 Dressed states

The photonic creation and annihilation operators $a^\dagger$ and a work on photon states which are elements of an infinite dimensional space. For a two level system, similar operators σ_+ and σ_- can be defined that act on the states $|a\rangle$ and $|b\rangle$ and have the form $\sigma_+ \equiv |a\rangle \langle b|$ and $\sigma_- \equiv |b\rangle \langle a|$. To investigate the coupling between the quantised photon bath and the two level system one assumes that the transition between

ground state $|b\rangle$ and excited state $|a\rangle$ with energy difference $\hbar\omega$ is mediated by the absorption and emission of one photon with frequency ν . Now the total Hamiltonian $\mathcal{H}$ of the system can be written as:

$$\mathcal{H} = \hbar\nu(a^\dagger a + \frac{1}{2}) + \hbar\omega\sigma_z + \hbar g(a^\dagger\sigma_- + a\sigma_+) \quad (\text{B.53})$$

Here σ_z is defined as $\sigma_z \equiv |a\rangle\langle a| - |b\rangle\langle b|$ and g is the coupling rate between photon reservoir and two-level system. Note that with writing down the Hamiltonian in this form terms such as $a^\dagger\sigma_+$ and terms with multiple $a^\dagger$ or a operators have been neglected (the first omission corresponds to the rotating wave approximation, the second one to neglected higher order photon absorption and emission events).

In a further step the Hamiltonian decomposes into a sum of Hamiltonians $\mathcal{H}_n$ ($\mathcal{H} = \sum_n \mathcal{H}_n$) acting on the n -quanta manifold $\{|n, a\rangle, |n+1, b\rangle\}$. In the basis of this subset⁵ one finds (with the detuning $\delta = \omega - \nu$):

$$\frac{1}{\hbar}\mathcal{H}_n = \nu(n + \frac{1}{2})\mathbb{1} + \frac{1}{2} \begin{pmatrix} \delta & 2g\sqrt{n+1} \\ 2g\sqrt{n+1} & -\delta \end{pmatrix} \quad (\text{B.54})$$

In the absence of coupling $g = 0$, this Hamiltonian is diagonal and the energy eigenstates of the system are the bare states $|n, a\rangle$ and $|n+1, b\rangle$. With finite coupling $g > 0$ however, the system will have new eigenstates $|n, +\rangle$ and $|n, -\rangle$ which can be expressed as linear superpositions of the bare states. After diagonalisation of Eq. B.54 one obtains the energy and composition of the new states:

$$E_n^\pm = \hbar\nu \left(n + \frac{1}{2} \right) \pm \frac{1}{2} \hbar \mathcal{V}_n \quad \text{with} \quad \mathcal{V}_n = \sqrt{4g^2(n+1) + \delta^2} \quad (\text{B.55})$$

$$\begin{pmatrix} |n, +\rangle \\ |n, -\rangle \end{pmatrix} = \begin{pmatrix} \cos(\vartheta_n) & -\sin(\vartheta_n) \\ \sin(\vartheta_n) & \cos(\vartheta_n) \end{pmatrix} \begin{pmatrix} |n, a\rangle \\ |n+1, b\rangle \end{pmatrix} \quad \text{with} \quad \tan(\vartheta_n) = \frac{2g\sqrt{n+1}}{\mathcal{V}_n - \delta} \quad (\text{B.56})$$

Here the Rabi frequency $\mathcal{V}_n$ has been introduced, which quantifies the energy transfer between the systems. Another quantity that simplifies the diagonalisation is the angle ϑ_n which allows to express the dressed states as a rotation of the bare states. Interestingly the energy of the dressed states $E_n^\pm$ and the Rabi frequency $\mathcal{V}_n$ depends on the number of quanta in the system - it actually forms a ladder of states, which is often referred to as Jaynes Cummings ladder. Fig. B.1 shows the energy structure of the ladder (top panel) and the composition of the lower polariton state (bottom panel).

⁵The states $|n, a\rangle, |n+1, b\rangle$ are represented by the vectors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

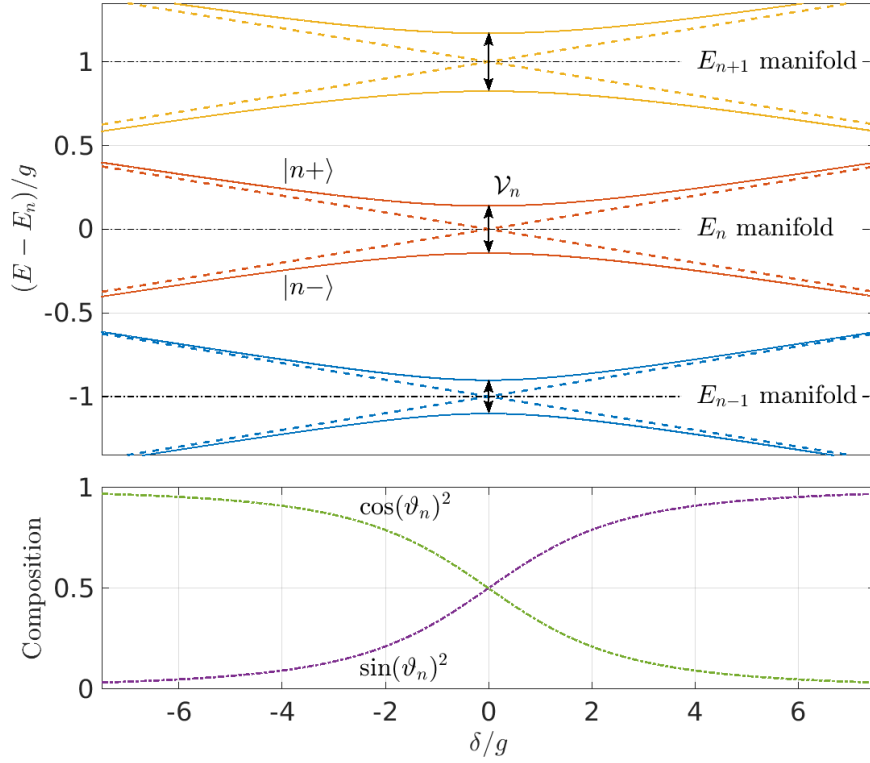


FIGURE B.1: **Dressed state energy levels and composition.** Top panel: Bare state energies (dashed lines) and dressed state energies (continuous lines) for three manifolds with $n-1$, n and $n+1$ quanta. Bottom panel: Weight of bare states composing the lower polariton state of the n -quantum manifold $|n, -\rangle$. The upper polariton state $|n, +\rangle$ has the same composition with interchanged sin and cos terms.

The dashed (continuous) lines show the bare (dressed) states. In the case of zero coupling ($g = 0$) both states would coincide and $\vartheta_n = 0$ regardless of the detuning δ . Since a finite coupling $g > 0$ was assumed, each E_n -manifold is split - the bare state energies do not cross, which is called an avoided level crossing.

B.11 Analytical description of polariton dispersion

The spectrum $S(x)$ of a strongly coupled system composed of the bare states with energies E_{cav} and E_{exc} can be described phenomenologically by modelling each polariton branch with width Γ_1, Γ_2 with a Lorentzian $\mathcal{L}_{\mu_i, \Gamma_i}(x)$ (Eq. A.2) and using the energy dispersion given by Eq. B.55 ($\mu_i = E^\pm$). Furthermore each polariton state is

weighted by its photonic fraction, parametrised by the angle ϑ in Eq. B.56.

$$S(x) = \frac{\sin\left(\arctan\left(\frac{\hbar\Omega_{\text{Rabi}}}{E_{\text{cav}} - E_{\text{exc}}}\right)/2\right)^2 A\Gamma_1/(2\pi)}{(\Gamma_1/2)^2 + \left(x - \frac{1}{2}\left(E_{\text{cav}} + E_{\text{exc}} - \sqrt{\hbar^2\Omega_{\text{Rabi}}^2 + (E_{\text{cav}} - E_{\text{exc}})^2}\right)\right)^2} + \frac{\cos\left(\arctan\left(\frac{\hbar\Omega_{\text{Rabi}}}{E_{\text{cav}} - E_{\text{exc}}}\right)/2\right)^2 A\Gamma_2/(2\pi)}{(\Gamma_2/2)^2 + \left(x - \frac{1}{2}\left(E_{\text{cav}} + E_{\text{exc}} + \sqrt{\hbar^2\Omega_{\text{Rabi}}^2 + (E_{\text{cav}} - E_{\text{exc}})^2}\right)\right)^2} + b \quad (\text{B.57})$$

Here x is the dependent variable, ie. the energy at which the spectrum is evaluated, A is an arbitrary amplitude and b a constant background term.

B.12 Nanoplatelet analysis

B.12.1 Synthesis of CdSe nanoplatelets

Synthesis of CdSe nanoplatelets emitting around 515 nm: In a three-neck round bottom flask 170 mg of Cadmium Myristate, 24 mg of Selenium powder (99,999%) and 15 ml Octadecene (ODE) were introduced and degassed under vacuum for 30 min at 120 °C. Then the temperature was raised gradually up to 240 °C under Argon flow. When the solution turns orange (around 210 °C) 90 mg of Cadmium Acetate were swiftly added to the reaction. After 10 min of the reaction time the heating mantle was removed and 2.5 ml of Oleic Acid were injected. When the solution had cooled down to 80 °C 15 ml of Hexane were added. The CdSe nanoplatelets were then separated by selective precipitation.

B.12.2 Elementary analysis in CdSe NPL

The concentration of the CdSe NPL has been determined with inductively coupled plasma optical emission spectrometry (ICP-OES). Two measurements of the same sample has been performed and the average has been used to determine the concentration of the CdSe NPL. The results can be summarized in the following table :

Element	Avg	Stddev	%RSD
Cd ₁	1.304 ppm	0.003279	0.2514
Se ₁	0.6582 ppm	0.002482	0.3771
Cd ₂	1.281 ppm	0.002070	0.1616
Se ₂	0.6536 ppm	0.001062	0.1625
Cd	1.2925 ppm	0.002674	0.2065
Se	0.6560 ppm	0.001772	0.2698

TABLE B.1: Results of inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of CdSe nanoplatelet solution.

The concentration of the CdSe NPL has been determined using the Selenium atoms because the solution has an excess of cadmium oleate.

B.12.3 Cavity linewidth

The linewidth of a cavity mode composed of two mirrors with reflectivity R and separation L is given by:⁶

$$\Gamma_{\text{cav}} = \frac{1 - R}{R} \frac{c}{n_c L} \quad (\text{B.58})$$

Here n_c is the effective refractive index within the cavity. With the wavelength dependent refractive index of silver taken from [178] and the mode energy dependence on the cavity length $E_{\text{cav}} = \frac{q\hbar c}{2L}$, Γ_{cav} can be plotted as a function of the cavity length for the longitudinal mode index $q = 6$ (see Fig. B.2). The graph shows the steep increase in cavity linewidth for cavity lengths below $1.3 \mu\text{m}$ and demonstrates that the above reported linewidth is compatible with the theory.

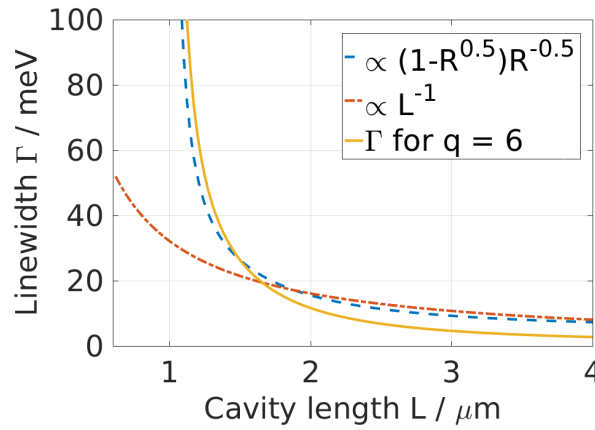


FIGURE B.2: **Linewidth of cavity with two silver mirrors.** The linewidth is given as a function of the cavity length for longitudinal mode number $q = 6$ (yellow continuous line). The blue dashed line shows the dependence on the silver mirror reflectivity only, the red dashed dotted line the effect of the mirror separation.

B.12.4 Measuring the dipole moment

In the following the procedure to obtain the dipole moment of a single nanoplatelet in the platelet film is described. The Rabi splitting for an ensemble of N randomly aligned dipoles with transition dipole moment μ is given as [179] (comp. with Eq. 3.1):

$$\hbar\Omega = \frac{1}{3}\mu\sqrt{N} \left(\frac{2\hbar\omega}{\varepsilon_0 n_{\text{eff}}^2 V_{\text{eff}}} \right)^{\frac{1}{2}} \quad (\text{B.59})$$

Here $\hbar\omega$ is the exciton energy, n_{eff} is the effective refractive index within the cavity and V_{eff} is the electric field mode volume. The factor $\frac{1}{3}$ is obtained by evaluating the

⁶As derived in Eq. 3.12 of the theoretical foundations.

integral:

$$\begin{aligned} \langle \vec{\mu} \cdot \hat{E} \rangle &= \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \sin(\theta) d\theta \cos^2(\theta) \mu \\ &= \frac{\mu}{2} \int_0^\pi \sin(\theta) \cos^2(\theta) d\theta = \frac{1}{3} \mu \end{aligned} \quad (\text{B.60})$$

The thickness of the drop casted nanoplatelet film has been measured with an AFM to $d = 693 \pm 77$ nm (see Fig. 6.15a). The effective refractive index $n_{\text{eff}} = 1.3$ is thus obtained in accordance with the TMM calculations by taking the weighted average of the refractive index of the film and air within the cavity ($n_{\text{film}} = 1.5$, mainly composed of oleic acid). To compute V_{eff} , the expression for the effective mode volume for a planar cavity is taken from [143] as

$$V_{\text{eff}} = \frac{\pi L^2 \lambda}{1 - R} \approx 560 \lambda^3 = 75 \mu\text{m}^3 \quad (\text{B.61})$$

with $\lambda = \frac{2\pi c}{\omega} = 511$ nm and the mirror reflectivity $R = 0.95$.

Now, the only missing parameter is the number of platelets N coupled to the mode. To obtain it, firstly the average size of nanoplatelets is estimated on the basis of a TEM micrograph $L_x = 32.5 \pm 2.5$ nm, $L_y = 8.2 \pm 0.9$ nm and $L_z = 1.36 \pm 0.05$ nm. Secondly the concentration of selenium atoms in solution is measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), from which a concentration of $c_{\text{sol}}^{\text{NPL}} = 0.890 \pm 0.002 \mu\text{M}$ is inferred. To compare this volume concentration of platelets in solution $c_{\text{sol}}^{\text{NPL}}$ to the volume concentration in a dried film $c_{\text{film}}^{\text{NPL}}$, the weight difference $\Delta m = 6.24$ mg of a drop of $V_{\text{sol}} = (10 \pm 0.18) \mu\text{L}$ before and after evaporation V_{dry} of the solvent hexane with the known density of $\rho_{\text{hex}} = 654.8 \frac{\text{mg}}{\text{ml}}$ is measured. Note that the uncertainty in the volume pipetted ($\sigma_V = 1.8\%$) dominates the error for the end result. With this one finds the volume concentration of platelets in the dried film $c_{\text{film}}^{\text{NPL}}$ as:

$$c_{\text{film}}^{\text{NPL}} = c_{\text{sol}}^{\text{NPL}} \frac{V_{\text{sol}}}{V_{\text{dry}}} = c_{\text{sol}}^{\text{NPL}} \frac{V_{\text{sol}}}{V_{\text{sol}} - \frac{\Delta m}{\rho_{\text{hex}}}} = 21.26 c_{\text{sol}}^{\text{NPL}} = 18.9 \pm 6.9 \mu\text{M} \quad (\text{B.62})$$

With the platelet dimensions ($V_{\text{NPL}} = L_x L_y L_z$) above this concentration translates into a volume fraction f_V of platelets in the film of (N_A is the Avogadro number):

$$f_V = c_{\text{film}}^{\text{NPL}} N_A V_{\text{NPL}} = (0.5 \pm 0.2)\% \quad (\text{B.63})$$

For the number of platelets coupled to the cavity mode this equates to :

$$N = \frac{V_{\text{eff}}}{L} d c_{\text{film}}^{\text{NPL}} N_A = \frac{\pi L \lambda}{1 - R} d c_{\text{film}}^{\text{NPL}} N_A = (3.9 \pm 1.5) \times 10^5 \quad (\text{B.64})$$

Taking this value and using $\hbar\Omega = (65.9 \pm 1.4)$ meV Eq. B.59 is solved for μ to obtain:

$$\mu = 3 \left(\frac{\varepsilon_0 n_{\text{eff}}^2 V_{\text{eff}}}{2\hbar\omega} \right)^{\frac{1}{2}} \frac{\hbar\Omega}{\sqrt{N}} = (1.92 \pm 0.37) \times 10^{-27} \text{ C m} = (575 \pm 110) \text{ D} \quad (\text{B.65})$$

Note that the value for μ is independent of the exact choice for the mode volume (and thus the mirror reflectivity) since:

$$\begin{aligned} \mu &= 3 \left(\frac{\varepsilon_0 n_{\text{eff}}^2 V_{\text{eff}}}{2\hbar\omega} \right)^{\frac{1}{2}} \frac{\hbar\Omega}{\sqrt{N}} = 3 \left(\frac{\varepsilon_0 n_{\text{eff}}^2 V_{\text{eff}}}{2\hbar\omega} \right)^{\frac{1}{2}} \frac{\hbar\Omega\sqrt{L}}{\sqrt{V_{\text{eff}}dc_{\text{film}}^{\text{NPL}}N_A}} \\ &= 3 \left(\frac{\varepsilon_0 n_{\text{eff}}^2}{2\hbar\omega c_{\text{film}}^{\text{NPL}}N_A} \right)^{\frac{1}{2}} \left(\frac{L}{d} \right)^{\frac{1}{2}} \hbar\Omega \end{aligned} \quad (\text{B.66})$$

Assuming a two level system with energy difference $\Delta E = \hbar\omega$ and transition dipole moment μ , the radiative lifetime τ of the heavy-hole exciton can be expressed as [179]:

$$\tau = \frac{3\pi\epsilon_0\hbar c^3}{\omega^3\mu^2} \quad (\text{B.67})$$

With μ as found above this expression results in $\tau = (1.3 \pm 0.5)$ ps. Similarly the oscillator strength f of the transition can be expressed as:

$$f = \frac{2m\omega}{3\hbar}\mu^2 = (280 \pm 107) \quad (\text{B.68})$$

where m is the reduced mass of the exciton. These results confirm the giant oscillator strength associated with the large exciton coherence area reported previously [155].

C Thesis word cloud

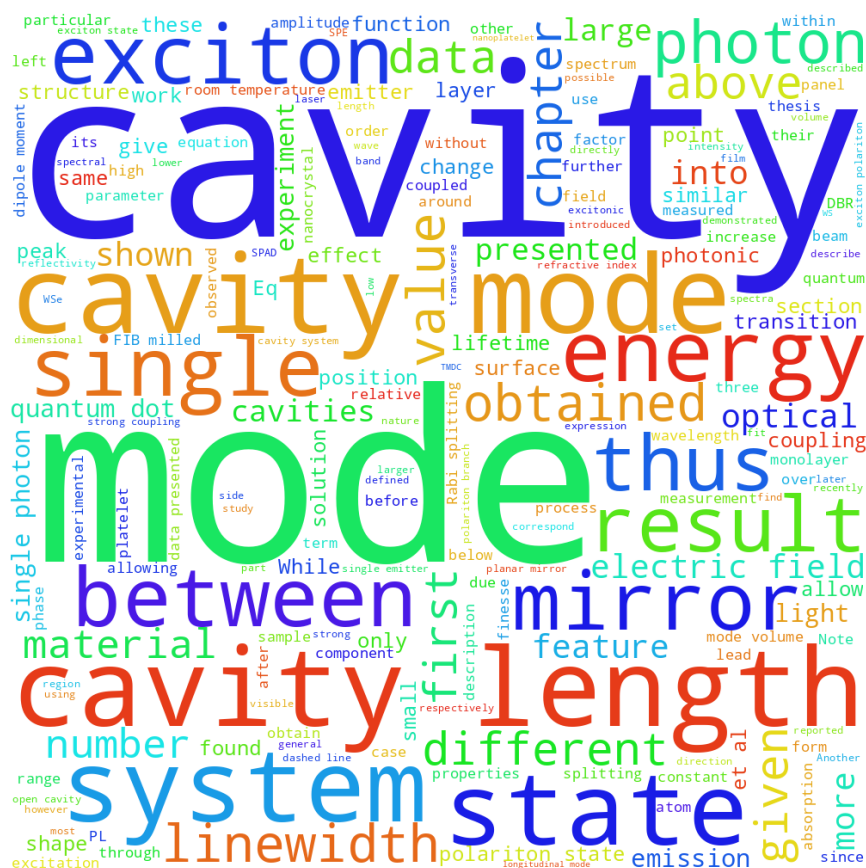


FIGURE C.1: The thesis as a word cloud.

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