

Dissertation

Leonora Christina Sewidan

Influence of post-processing treatments on single-photon emission of hexagonal boron nitride point defects

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**Influence of post-processing treatments on
single-photon emission of hexagonal boron nitride
point defects**

Von der Fakultät für Elektrotechnik, Informationstechnik, Physik
der Technischen Universität Carolo-Wilhelmina zu Braunschweig

zur Erlangung des Grades einer Doktorin

der Naturwissenschaften (Dr. rer. nat.)

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aus Flensburg

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Abstract

Single-photon emitters (SPEs) in hexagonal boron nitride (hBN) have emerged as promising candidates for scalable, room-temperature quantum photonics due to their bright emission, chemical robustness, and ease of integration into on-chip architectures. Despite this potential, the microscopic origin of many hBN emitters remains uncertain, and the influence of post-processing treatments on their optical performance is not yet fully understood. This thesis addresses these challenges by systematically studying the photophysical properties of hBN point defects and evaluating how selected post-processing treatments (PPTs) modify their emission behavior.

Specifically, the focus in this work are point defects in hBN nanoflakes and the effect of ozone treatment and high-temperature annealing in different atmospheres on the measured characteristics. The characterization is performed in terms of their single-photon capabilities, photon flux, and stability. These characteristics are compared in the treated samples with those observed in the untreated samples. A statistical analysis of the characteristics measured on 577 untreated emitters and 383 emitters from post-processed samples is presented. The results show that, although no improvement in stability is achieved, the single-photon purity improves significantly with the applied treatments, therefore leading to a greater availability of stable single-photon emitters compared to the untreated samples.

To contextualize the experimental results, the extracted emitter properties – such as zero-phonon line positions, lifetimes, and Debye–Waller factors – are compared with density functional theory (DFT) predictions available in the hBN defect database, enabling the identification of several plausible defect structures, with a focus on carbon-based configurations.

In addition, a relative calibration of two single-photon avalanche diode (SPAD) detectors using a selected hBN single-photon emitter is presented. Together, these findings provide new insight into the optical behavior of hBN point defects, the role of post-processing in modifying their quantum emission, and the suitability of hBN emitters as reference sources in detector characterization.

Kurzfassung

Einzelphotonenemitter in hexagonalem Bornitrid (hBN) haben sich aufgrund ihrer hohen Hel-
ligkeit, chemischen Stabilität und der einfachen Integration in photonische On-Chip-Strukturen
als vielversprechende Kandidaten für Anwendungen in den Quantentechnologien bei Raumtem-
peratur erwiesen. Trotz dieses Potenzials ist der mikroskopische Ursprung vieler hBN-Emitter
sowie der Einfluss von Nachbehandlungsverfahren auf ihre optischen Eigenschaften bislang nicht
vollständig geklärt. Diese Arbeit adressiert diese Herausforderungen durch eine systematische
Untersuchung der photophysikalischen Eigenschaften von Punktdefekten in hBN-Nanoflakes
und ein Vergleich der Auswirkungen ausgewählter Post-Processing-Behandlungen auf deren
Emissionsverhalten.

Im Mittelpunkt dieser Arbeit stehen Punktdefekte in hBN-Nanoflakes und der Einfluss von
Ozonbehandlung sowie Hochtemperaturannealing in verschiedenen Atmosphären auf die gemesse-
nen Eigenschaften. Die Charakterisierung umfasst die Einzelphotonengüte, den Photonenfluss
und die Stabilität der Emitter. Diese Eigenschaften werden zwischen behandelten und un-
behandelten Proben verglichen. Eine statistische Analyse von 577 Emittlern unbehandelter
Proben und 383 Emittlern aus nachbehandelten Proben zeigt, dass zwar keine Verbesserung der
Stabilität erreicht wird, jedoch die Einzelphotonengüte durch die angewandten Behandlungen
deutlich steigt, was zu einer höheren Verfügbarkeit stabiler Einzelphotonenemitter führt.

Um die experimentellen Ergebnisse einzuordnen, werden die extrahierten Emissionseigenschaften
– wie Zero-Phonon-Linien (ZPL), Lebensdauern und Debye-Waller-Faktoren – mit DFT Vorher-
sagen aus der hBN-Defektdatenbank verglichen, was die Identifizierung mehrerer plausibler
Defektstrukturen ermöglicht, insbesondere solcher mit Kohlenstoffbezug.

Darüber hinaus wird eine relative Kalibrierung zweier Single-Photon-Avalanche-Diode-(SPAD)-
Detektoren unter Verwendung eines ausgewählten hBN-Einzelphotonen-Emitters vorgestellt.
Insgesamt liefern diese Ergebnisse neue Einblicke in das optische Verhalten von hBN Punktde-
fekten, die Rolle von Nachbehandlungen bei der Modifikation ihrer Quanteneigenschaften sowie
die Eignung von hBN-Emittlern als Referenzquellen für die Detektorkalibrierung

List of publications

Parts of this work have been published in the following articles:

- L. Sewidan, H. Georgieva, P. Tieben, A. W. Schell, M. López, & S. Kück. (2024). "Characterization of hexagonal boron nitride quantum emitters for application in quantum radiometry". Journal of Physics: Conference Series, 2864(1). <https://doi.org/10.1088/1742-6596/2864/1/012013>
- L. Sewidan, E. Redolfi, H. Georgieva, J. Forneris, M. López, & S. Kück. (2025). "Characterization of hexagonal boron nitride quantum emitters in nanoflakes after post-processing treatments". Proc. SPIE 13368, 2D Photonic Materials and Devices VIII, 133680E (19 March 2025). <https://doi.org/10.1117/12.3041882>

Further publications:

- H. Georgieva, P. Stepanov, L. Sewidan, A. Pishchagin, M. López, & S. Kück. (2024). Metrological characterization of a commercial single-photon source with high photon flux emission. METROLOGIA, 61(5), Article 054001. <https://doi.org/10.1088/1681-7575/ad615e>

List of Abbreviations

BP	band pass
BS	beam splitter
CVD	chemical vapor deposition
CW	continuous wave
DAQ	data acquisition
DBS	dichroic beam splitter
DFT	density-functional-theory
DW	Debye-Waller
FWHM	full width at half maximum
hBN	hexagonal boron nitride
HBT	Hanbury-Brown and Twiss
LL	laser line
LP	long pass
MM	multi-mode
NA	numerical aperture
ND	neutral density
NF	notch filter
ODMR	optically detected magnetic resonance
PL	photoluminescence
PPT	post-processing treatment
PSB	phonon sideband
PSF	point-spread function
QE	quantum emitter
SEM	standard error of the mean
SM	single-mode
SPAD	single-photon avalanche diode
SP	short pass
SPE	single-photon emitter
SPS	single-photon source
WFL	wide-field lens
ZPL	zero-phonon line

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1 Introduction

Over the past decade, the demand for reliable single-photon generation has increased sharply due to the rapid development of quantum technologies. Solid-state platforms such as semiconductor quantum dots, color centers in diamond, and single molecules have established themselves as robust single-photon sources and are already used across a broad range of applications, including magnetic-field sensing, super-resolution microscopy, and quantum radiometry. This heightened interest is closely linked to the emergence of the “quantum age,” in which quantum optical systems underpin secure communication protocols, quantum metrology, and the foundations of quantum information processing. In particular, quantum key distribution (QKD) relies on the transmission of individual photons to prevent eavesdropping, while long-distance quantum communication further requires quantum repeaters to overcome photon loss in optical fibers.

At its core, quantum information science is based on using quantum mechanical objects for encoding, communication and measuring information. Here, quantum systems offer computational and communication advantages that cannot be achieved with classical devices, enabling both speedups in specific algorithms and fundamentally secure information transfer [1, 2].

A key technological requirement for these applications is the development of room-temperature single-photon sources (SPSs) with high brightness, photostability, and narrow spectral emission. Such sources greatly simplify device integration and reduce operational complexity, accelerating their adoption in practical quantum technologies [3–5].

Defects in hexagonal boron nitride (hBN) have emerged as promising SPS candidate. As a layered van-der-Waals material with a wide bandgap (6eV), hBN hosts optically active point defects that exhibit bright and stable single-photon emission even at ambient conditions. The two-dimensional nature of hBN offers several advantages: enhanced light extraction, compatibility with heterogeneous material stacks, and straightforward integration into on-chip photonic structures. Additionally, hBN can be grown over large areas, exfoliated to few-layer thicknesses, and processed using standard microfabrication techniques, making it attractive for scalable quantum photonics.

However, a major challenge remains: the microscopic origin of many hBN emitters is still under active investigation, and emitter properties vary strongly between samples and fabrication conditions. Post-processing treatments (PPTs) – such as thermal annealing, ion irradiation, and ozone exposure – are commonly employed to activate, modify, or stabilize defects, yet their specific effects on emitter formation and optical performance are not fully understood. Understanding how PPTs influence emitter creation, stability, spectral properties, and overall reproducibility is therefore essential for both fundamental defect identification and reliable integration into quantum devices.

This thesis aims to address some these challenges by systematically studying the effect of PPTs on commercially available hBN nanoflakes – one of the most common platforms for hBN.

In this work, I present the characterization of several hBN single emitters in commercial nano-flakes after different post-processing treatments. I show the comparison of their spectral properties, single-photon purity, photon flux and optical stability between untreated emitters and emitters after different post-processing treatments (PPTs). The PPTs performed are ozone treatment and thermal annealing in different atmospheres and at different temperatures, which, according to literature, are supposed to increase the photon emission stability of the hBN emitters [6, 7].

2 Theoretical background

2.1 Single photon sources

A photon is defined as the smallest unit of electromagnetic radiation. The concept of quantizing the electromagnetic field was first described by Planck in 1900 [8] to explain black-body radiation, who called the discrete energy packets "quanta". The discovery of the photoelectric effect by Einstein continued this idea in 1905 [9], when he discovered that electrons are emitted from metal when illuminated by light. From this, he gathered that atoms must absorb the energy from light in distinct packages, calling each one "light quantum" (or "Lichtquant"). The word "photon" itself was first introduced by Gilbert Lewis in 1926 [10] before Dirac formally described the quantization of light in 1927 [11], providing the theoretical framework for the quantum nature of light.

Then, a groundbreaking experiment by Hanbury Brown and Twiss in 1956 defined the field of quantum optics, when they noticed that the signal of light from a star measured at two photomultiplier tubes was correlated [12]. Classical wave theory did not explain this type of correlation, while treating the detection process with quantum mechanics offered a possible explanation.

After the invention of the laser in the 1960s, Glauber described new states of light with statistical properties different from classical light in 1963 [13]. Finally, experimental proof of the existence of non-classical quantized light was shown by Kimble, Dagenais and Mandel in 1977 [14] when demonstrating photon antibunching for the first time, thereby giving rise to the concept of the single-photon source (SPS).

2.1.1 Working principle

An ideal single-photon source emits one single photon in a time interval defined by the user through the excitation mode ("on-demand"). The probability of emitting only a single photon is 100% and the probability of multi-photon emission is 0%.

2.1.1.1 Classification

Generally, sources can be divided into two categories: probabilistic and deterministic sources [1, 15, 16].

Probabilistic single-photon sources are based on optical nonlinearity and generally rely on the creation of photon pairs via processes such as spontaneous parametric down-conversion and spontaneous four-wave mixing. Deterministic single-photon sources, on the other hand, describe emission from a single emitter, such as single atoms, ions, molecules, color-centers or quantum dots.

The classification of these groups as deterministic and probabilistic refers to the underlying

photon-emission process. Here, deterministic means that the emission is triggered by a controllable event, such as the excitation process that theoretically guarantees the emission of a photon. These terms are mostly used to distinguish the categories, as real sources include losses and deterministic sources become more probabilistic in real-world operation [1, 15].

In this work, the focus will be on the deterministic type of emitter. The emission principle of these emitters remain largely the same, even as the material and energy systems differ from each other. Fig. 2.1 shows the general process of a simple two level energy system: a trigger is used to excite an atom from the ground state $|g\rangle$ to an excited (higher energy) state $|e\rangle$. A trigger can be optical or electrical, but in most applications it is a laser. This transition is shown as a black arrow. The atom remains in the excited state for a distinct period of time (radiative lifetime τ_r), before it relaxes back to the ground state (dashed arrow). Since $|e\rangle$ has a higher energy than $|g\rangle$, the excess energy is released in the form of a photon with the energy

$$E = h \cdot \nu, \quad (2.1)$$

where h is the Planck constant and ν the frequency that corresponds to the distinctive transition between the two states. The frequency can also be expressed as the wavelength λ through the relation $c = \lambda \cdot \nu$ where c is the speed of light.

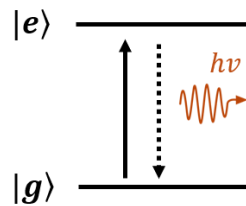


Figure 2.1: Sketch of a two-level energy system of a single emitter. The emitter in the ground state $|g\rangle$ is excited by an external trigger, such as a laser pulse, and transitions into a higher energy state $|e\rangle$ (solid black arrow). When transitioning back into the ground state (dashed arrow), energy is released in the form of a photon (red arrow).

The atom has to be excited again before another photon can be emitted. In reality, energy systems are more complex than the one shown in Fig. 2.1, because of coupling to local electronic states of neighboring atoms or vibrational modes, as well as further energy levels that the excited atom can transition to.

2.1.1.2 Optically active defects in crystals

To understand the electronic states that influence the energy levels in solids, one first needs to understand the band theory of solids (i. e. crystals) [17]. Atoms in solids are very close to each other and therefore, the outer orbitals containing the valence electrons overlap and interact, thus forming broad energy bands instead of discrete energy states. One of the most important optically active solid materials to consider are semiconductors.

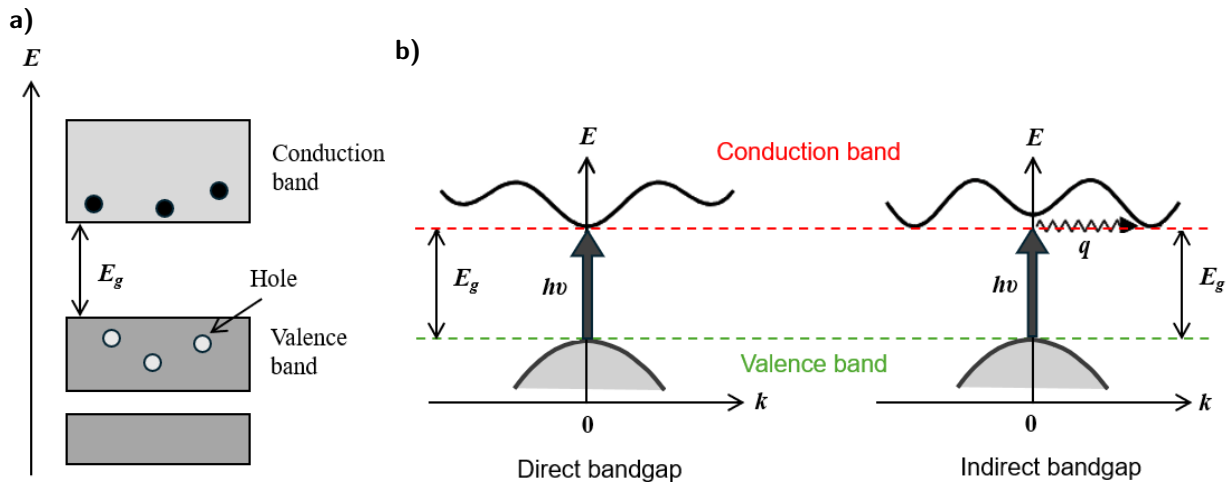


Figure 2.2: Schematic energy-level diagram for a semiconductor. **a)** The valence bands (gray) are filled with valence electrons. The unfilled conduction band is separated by an energy gap. Electrons can be excited across the gap to the conduction band, leaving positively charged empty states called holes in the valence band. **b)** Comparison of interband transitions in direct (left) and indirect (right) bandgap materials. The green line indicates the maximum valence band energy, the red marks the conduction band minimum. In a direct bandgap material, these energies line up ($k = 0$) and the electrons can transition freely, while the maximum and minimum do not line up for an indirect bandgap material ($k \neq 0$). To transition, a phonon has to be emitted or absorbed (q) (reproduced from [17]).

The valence electrons form bands and at 0 K, the bands are filled up, with the last band to be filled called valence band. An unfilled band called the conduction band is separated from the valence band by an energy gap E_g called the bandgap. At higher temperatures, electrons can be excited from the valence band to the conduction band, which creates holes in the valence band with a positive charge (as shown in Fig. 2.2a). The electrons in the conduction band and the holes in the valence band behave like particles and can carry electrical current. Introducing impurities into a crystal structure can control the populations of the free electrons and holes. This process is called doping.

Bandgaps are separated into two categories: direct and indirect. In a semiconductor with a direct bandgap, an electron in the conduction band can recombine directly with a hole in the valence band by emitting a photon; the valence band maximum and conduction band minimum occur at the same position (see Fig. 2.2b). In an indirect-bandgap semiconductor, the electrons can only recombine with holes indirectly in a process that involves a quantized lattice vibration (phonons) and therefore they have lower optical transition probabilities. In this case, the conduction band minimum does not occur in the same zone as the valence band maximum. The term position or "zone" in this context refers to inherent symmetries in semiconductor crystals, which - when broken down into the smallest unit - is called primitive cell or Brillouin zone [16, 17].

Insulator crystals typically have large bandgaps and therefore resist electron movement – however, imperfections in the crystal lattice can lead to vacancies and enable movement. This kind

of defect is called a color center, since these type of insulator crystals are typically colorless but exhibit color when defects are present [17].

Vibrational modes of the crystal cause further broadening of the electronic states of the dopant atoms. The trapped electrons couple to vibrations in the crystal and therefore broadening absorption and emission lines into distinct, often continuous bands (phonon side bands). Importantly, the formation of vibrational bands is different from the previously described process of electronic bands, which arises from the overlapping orbitals whereas the phonon side bands arise from the vibrational modes [6, 16, 17].

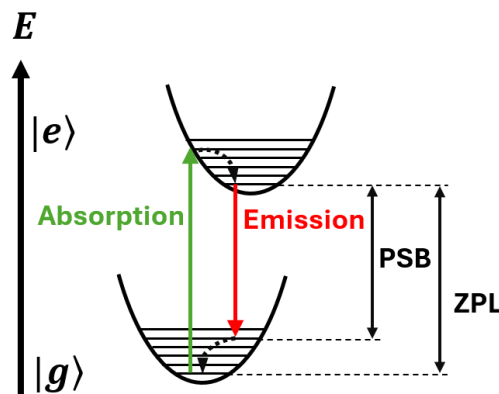


Figure 2.3: Sketch of potential energy of a two level system with vibronic transitions. An atom in the ground state is excited to a higher vibrational mode of the excited state (green arrow). The atom relaxes to the lowest vibrational state, then emits a photon and enters a vibrational mode of the ground state (red arrow). The energy of the emitted photon corresponds to either a phonon side band (PSB) or the zero-phonon line (ZPL).

Fig. 2.3 demonstrates the previously introduced two-level system with additional vibrational modes. An atom in the ground state $|g\rangle$ will absorb an incoming photon and transfer to an excited state $|e\rangle$ (green arrow). Excess energy is dissipated into vibrational modes of the crystal lattice and the atom relaxes into the lowest vibrational state of the excited state $|e\rangle$ (black dashed arrow), which is followed by the emission process (red arrow). Depending on which vibrational mode the atom is in after emission, additional relaxation to the equilibrium of the ground state $|g\rangle$ occurs. The emitted photon will have a wavelength matching one of the distinct bands, where return to the lowest vibrational mode corresponds to the wavelength of the zero-phonon line (ZPL), while the rest corresponds with the phonon side bands (PSB). Vibrational relaxation (relaxation from high to the lowest vibrational mode) leads to an energy loss with the difference between absorption and emission energies known as the Stokes shift.

2.2 Photon statistics

Before going into more detail about specific optical defects in materials, it is important to understand the nature of quantum light. What essentially separates quantum light sources from classical light sources is the difference in their statistical nature as first described by

Glauber [13]. In this section, the most important differences are highlighted by first describing the simplest case, a monochromatic beam with frequency ν and constant intensity I . In this case, the photon flux Φ can be described as

$$\Phi = \frac{I \cdot A}{h\nu} = \frac{P}{h\nu}, \quad (2.2)$$

where A is the area of the beam and P is the optical power. The photon flux is therefore defined as the average number of photons that pass through an area per time (generally photons per second)[16]. A detector is needed to measure this light beam. Photon-counting detectors generally work by converting an incoming photon into a charge carrier and then using an avalanche process to amplify that single charge into a measurable voltage pulse [1]. One of their most important characteristics is the quantum efficiency η , which is the ratio of the photon counts to the number of incident photons. For an average photon flux, the average number of counts during a measurement interval T is given by

$$N = \eta \cdot \Phi \cdot T = \frac{\eta \cdot P \cdot T}{h\nu} \quad (2.3)$$

From this, we can obtain the count rate $\mathcal{R}$, which is the average number of counts divided by the measurement time (counts per second):

$$\mathcal{R} = \frac{N}{T} = \Phi\eta = \frac{\eta P}{h\nu}. \quad (2.4)$$

When using a coherent light source with constant intensity, while the average photon count rate is constant, the discrete nature of photons means that for very short time intervals the photon number fluctuates. The average number of photons $\bar{n}$ in a beam of the length L is

$$\bar{n} = \frac{\Phi L}{c}. \quad (2.5)$$

When this beam of light is divided into N segments (with N being very large), the probability of finding a photon in any segment is given by $p = \bar{n}/N$. So what is the probability $\mathcal{P}(n)$ of finding n photons in a beam of length L containing N segments? When assumed that n segments will contain one photon and all other segments no photons, this probability can be modeled using a binomial distribution:

$$\mathcal{P}(n) = \frac{N!}{n!(N-n)!} \left(\frac{\bar{n}}{N}\right)^n \left(1 - \frac{\bar{n}}{N}\right)^{N-n}. \quad (2.6)$$

With $N \rightarrow \infty$ and series of expansion we obtain a Poissonian distribution [2, 16]:

$$\mathcal{P}(n) = \frac{\bar{n}^n}{n!} e^{-\bar{n}}. \quad (2.7)$$

This type of a perfectly stable classical light source therefore follows a Poissonian distribution, which describes an inherently random process that only returns integer values. The randomness

originates from the $N \rightarrow \infty$ segments with an equal probability to find a photon in each one. The task of a non-classical light source is to convert this into an output pulse containing exactly one photon – in a way that the probability to emit one photon is one ($\mathcal{P}(n = 1) = 1$) and probability to emit anything other than one photon is zero ($\mathcal{P}(n \neq 1) = 0$) [2].

The Poisson distribution is distinctly characterized by its mean value $\bar{n}$. Fig. 2.4 shows the Poisson distributions for a mean value of 0.1 and 1 and we can see that even for $\bar{n} = 0.1$ there remains a non-zero chance for $n = 2$.

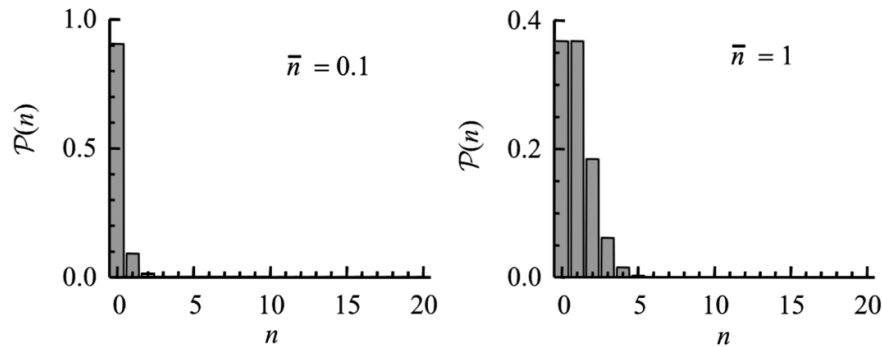


Figure 2.4: Poisson distributions for the main values 0.1 and 1 (adapted from [16]).

Another characteristic of the Poisson distribution is that the standard deviation Δn is given by

$$\Delta n = \sqrt{\bar{n}}. \quad (2.8)$$

This is in contrast to sub-Poissonian statistics where $\Delta n < \sqrt{\bar{n}}$ and super-Poissonian statistics where $\Delta n > \sqrt{\bar{n}}$. This is shown in Fig. 2.5, where the three different distributions are shown for a mean photon number of $\bar{n} = 100$. The distribution of super-Poissonian light is broader and the sub-Poissonian is less broad in contrast to the Poissonian distribution.

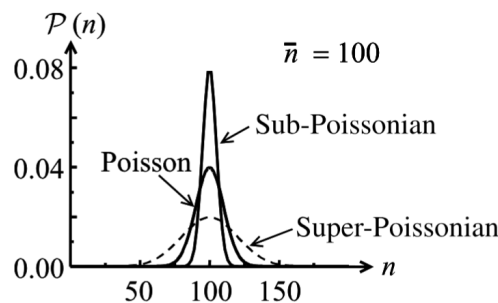


Figure 2.5: Comparison of the distributions of different photon statistics. For a mean photon number $\bar{n} = 100$, Poissonian, sub-Poissonian and super-Poissonian distributions are shown (taken from [16]).

Since the Poissonian distribution describes a stable, coherent light source, the super-Poissonian distribution describes light sources with higher fluctuations and time-varying light intensities such as thermal light and partially coherent light (partially coherent light has classical intensity fluctuations on a time scale determined by coherence time, see Sec. 2.4).

On the other hand, sub-Poissonian light describes a light source with less fluctuations. This has to be non-classical, since the stable, coherent light source is the perfect classical light source as described above.

The classical light source can be divided into equally small pieces where only a fraction contains a photon. The non-classical light source instead can be considered as a light beam where the distance between photons corresponds to identical time intervals (as opposed to random time intervals). Measuring this beam for a time T would then always render the same photon count for each measurement due to the lack of randomness (see Fig. 2.6).

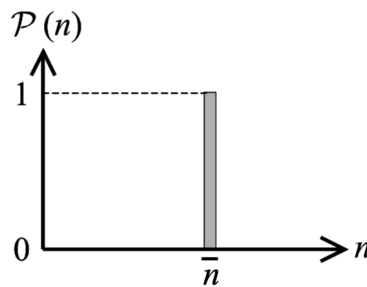


Figure 2.6: Statistic of the photon count for a non-classical light source with a fixed time interval Δt between photons that is measured for a period T (taken from [16]).

This type of light can be generated but its detection is complicated by experimental constraints. With lowered detection efficiency, some photons will remain undetected. Therefore the regularity of time intervals between photons will be lost to random sampling, thus approaching random time intervals for high optical losses.

There are three main factors that contribute to optical losses: inefficient collection from the source, low transmission and low detection efficiencies of the detectors. The non-classical light source emits photons in all directions, but not all these photons are collected (inefficient collection). The photons that are collected then pass through different optical components which can introduce low transmission due to absorption, reflection and scattering. Finally, the remaining photons reach the detector, where low quantum efficiency leads to more losses. When these losses are high, the photon statistics degrade and the sub-Poissonian light will approach Poissonian statistics. It is therefore important to reduce losses as much as possible.

2.3 Hanbury Brown and Twiss Interferometer

The principle to investigate the correlation of a beam of light at two detectors came from Hanbury Brown and Twiss (HBT). As astronomers, they wanted to measure the diameter of stars with an new kind of intensity interferometer: they used two separate mirrors to collect starlight and focus the two beams on two different photomultiplier tubes. The photocurrents are then correlated. The main principle behind the HBT experiment is that intensity fluctuations of a light source are related to its coherence: if the light measured by the two detectors is coherent (either spatially or temporally), then the intensity fluctuations are correlated to each other [16].

Fig. 2.7 shows the basic experimental setup to realize this measurement. The incoming light is equally divided into two paths by a 50/50 beam splitter. The photons impinge on the detectors (D1 and D2) and generate electrical pulses each time a photon is detected. The detectors are connected to a counter, where the output pulse of D1 acts as a start signal while the pulse from D2 functions as the stop signal. The counter registers the number of pulses and the time between them. This is plotted in a histogram, where the number of events is plotted against the time delay in between the pulses.

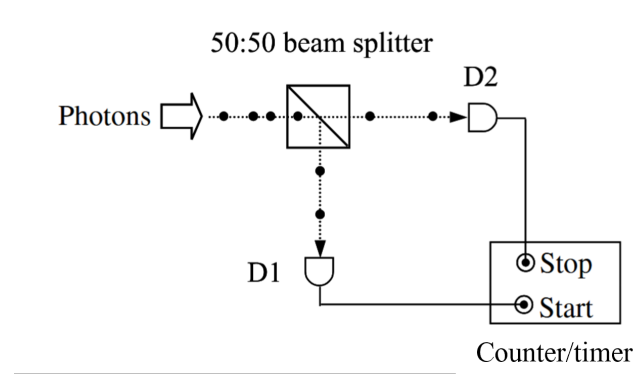


Figure 2.7: Sketch of the Hanbury Brown and Twiss (HBT) experiment. A beam of light (photons) is divided equally by a 50/50 beam splitter and guided to two separate detectors (D1 and D2). The output signals of the detectors are correlated to each other by a counter, which measures the number of pulses and the time between a pulse from D1 (start) and a pulse from D2 (stop) (taken from [16]).

When considering the input light classically, several photons can arrive at the same time (in bunches). The beam splitter will divide the photons. One half is directed to D1 and the other half to D2, where they will - with high probability - arrive at the same time. This means that at $\tau = 0$, there will be a large number of events, whereas for increasing delay times τ , the number of events will decrease.

However, when considering a non-classical light source, photons will arrive after another with a fixed time in between arrivals (provided the optical losses are kept to a minimum, see section 2.2). When a photon arrives at the beam splitter, it will be either guided to D1 or D2, where it will register as the start pulse. At this point ($\tau = 0$) there is a 0% probability of simultaneously generating a stop pulse at the other detector, since only a single photon arrived. Therefore, no events will be recorded at $\tau = 0$; only when a second photon arrives at the other detector, an event will be recorded. This means that with increasing delay time, the number of events will increase.

These two cases are classified as bunched and anti-bunched light, respectively. While the HBT experiment does not provide complete photon number statistics, it allows one to place an upper bound on the multi-photon generation rate [2] and gives information about what type of light source is being measured.

A coherent Poissonian light source is neither bunched nor anti-bunched since the time interval

between the photons is random and therefore the probability of obtaining a stop pulse is the same for all delay times [16, 18, 19].

2.4 Second order correlation function

The classifications of bunched and anti-bunched light introduced in the previous section is based on the second-order correlation function. It characterizes intensity fluctuations [16, 19] and is defined as

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle}, \quad (2.9)$$

where $I(t)$ is the intensity at time t , $I(t+\tau)$ the intensity after a time delay τ and $\langle \rangle$ denotes the time average.

When coherent light is detected by two detectors, the intensity fluctuations will be correlated to each other [16]. There are two aspects of coherence: spatial and temporal coherence. Spatial coherence refers to the wave's phase at different points in space, whereas temporal coherence refers to the phase at different points in time. The coherence time τ_c refers to the time in which the phase of the wave remains stable. It follows that for $\tau \gg \tau_c$, the intensity fluctuations at times t and $t+\tau$ will be uncorrelated, because the light between the two detectors is no longer temporally coherent. In that case

$$g^{(2)}(\tau \gg \tau_c) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2} = \frac{\langle I(t) \rangle^2}{\langle I(t) \rangle^2} = 1. \quad (2.10)$$

However, if $\tau \ll \tau_c$ the fluctuations at the detectors at these times will be correlated and for $\tau = 0$:

$$g^{(2)}(0) = \frac{\langle I(t)^2 \rangle}{\langle I(t) \rangle^2}. \quad (2.11)$$

If the intensity of a light source is time dependent (e. g. in thermal sources), then at $\tau = 0$ [16, 19, 20]:

$$g^{(2)}(0) \geq 1 \quad (2.12)$$

$$g^{(2)}(0) \geq g^{(2)}(\tau) \quad (2.13)$$

These equations stipulate that the second-order coherence can never exceed its value at zero time delay where the minimum is 1. This applies to all forms of classical light. Again, the easiest case to consider is a coherent, monochromatic (Poissonian) light source with a time independent intensity I_0 . Since the intensity is constant at all time delays, plugging the intensity into Eq. 2.9 yields $g^{(2)}(\tau) = 1$.

For a light source with time-varying intensity (thermal light), it must be true that $\langle I(t)^2 \rangle > \langle I(t) \rangle^2$, because squaring before taking the average exaggerates the intensity fluctuations above the mean value [16]. With Eq. 2.11 it therefore follows that $g^{(2)}(0) > 1$. On large time scales, Eq. 2.10 shows that this value will eventually drop to 1 and therefore describes bunched light. The third case cannot be described by classical behavior and therefore describes the non-classical anti-bunched light. Eq. 2.12 describes the conditions for classical light; however, as already laid out in the previous section, non-classical light should show anti-bunching, which means

$$g^{(2)}(0) < 1 \quad (2.14)$$

$$g^{(2)}(0) < g^{(2)}(\tau). \quad (2.15)$$

This violates the classical conditions and is therefore proof of a quantum light source.

A graphical representation of these cases can be seen in Fig. 2.8. The graph shows the $g^{(2)}(\tau)$ value plotted against the time delay τ [18]. The Poissonian source is represented as a dashed line at $g^{(2)}(\tau) = 1$. The thermal, super-Poissonian light source is shown as a solid black line with bunching to $g^{(2)}(0) = 2$ and for longer time delays decreasing to $g^{(2)}(\tau) = 1$. The anti-bunched, sub-Poissonian light with $g^{(2)}(0) = 0$ is shown in Fig. 2.8 as a gray line.

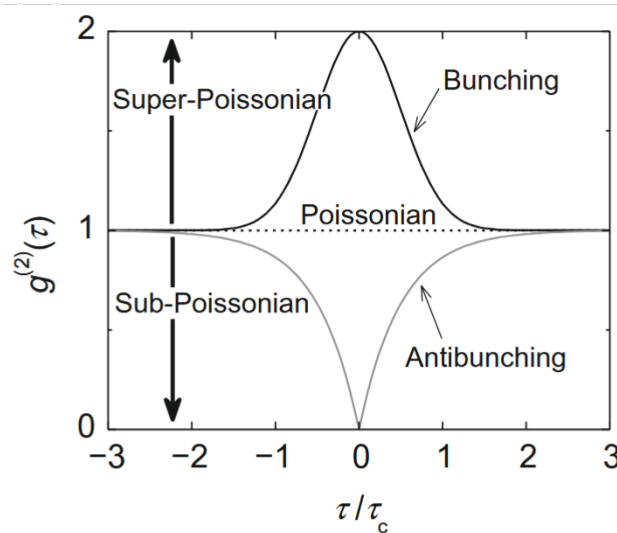


Figure 2.8: Second-order correlation showing the relation between sub-, super- and Poissonian photon statistics and antibunching and bunching. The x-axis shows the time delay and the y-axis the normalized $g^{(2)}(\tau)$ value. τ_c is the coherence time of the bunched/antibunched sources. Plotted are ideal cases for the three different light sources: a thermal, partially-coherent source (black), a coherent source (dashed) and a single-photon source (gray) (taken from [18]).

Most single-photon-sources will exhibit both anti-bunching and sub-Poissonian photon statistics. However, an anti-bunched source does not necessarily have sub-Poissonian photon statistics, since a source could exhibit anti-bunching on short and bunching on longer time scales

[18].

While the classical interpretation of the $g^{(2)}(\tau)$ is defined in terms of intensity fluctuations of the incident light, for non-classical cases, the $g^{(2)}(\tau)$ function is defined by coincidences between photon counting events. This interpretation requires photon number states, which are given by the quantum theory of light. In quantum mechanics, the well-known concept of the harmonic oscillator can be used to describe quantized energy. Each of these quanta have a specific value with the difference between levels of energy given by Eq. 2.1. Fig. 2.9 depicts this concept of distinct energy levels in a potential well with wave functions that correspond to vibrational states. The lowest point of the potential represents the lowest possible energy value, also known as zero point energy [21].

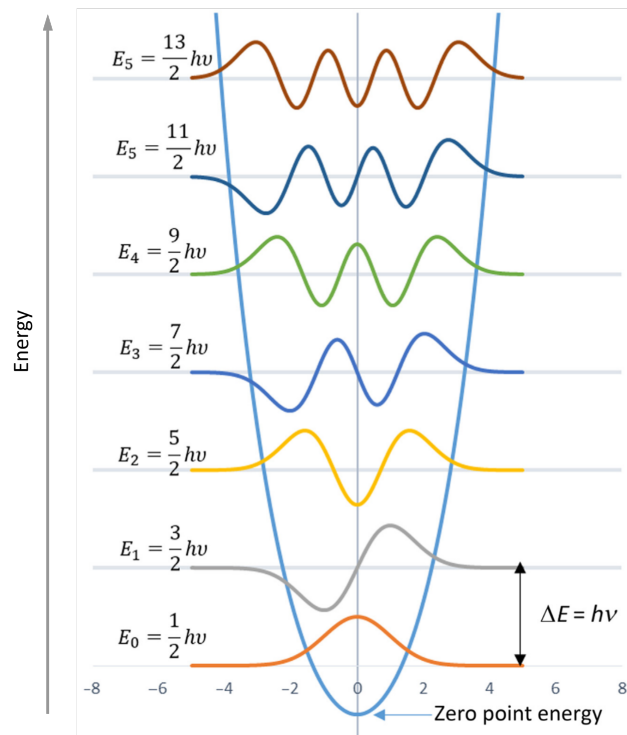


Figure 2.9: Potential well for a quantum harmonic oscillator. The allowed quantum states are spread equally along the y-axis which depicts the energy. The shape of the stationary wave functions correspond to each vibrational level (adapted from [21]).

The general equation for the energy levels is given by:

$$E_n = \left(n + \frac{1}{2}\right) h\nu \quad (2.16)$$

where n is the number of the quanta (also written as $|n\rangle$, denoting a quantum state).

Therefore, to obtain a higher state of energy, a photon of the energy $h\nu$ has to be added and similarly, to get to a lower state, the energy has to be reduced by the same amount. In quantum mechanical notation, this is achieved by the so-called ladder operators that raise or lower the energy of a quantum system. The creation operator $\hat{a}^\dagger$ essentially creates a quantum of energy by raising the system from state $|n\rangle$ to $|n+1\rangle$ and the annihilation operator $\hat{a}$ lowers the system

to $|n-1\rangle$. They can be defined by the equations

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle; \quad \hat{a}|n\rangle = \sqrt{n}|n-1\rangle. \quad (2.17)$$

The factors $\sqrt{n+1}$ and $\sqrt{n}$ on the right-hand side of the equations ensure the correct normalization.

Any quantum state needs to fulfill its eigenvalue equation. This means when an operator acts on a quantum state (i. e. wave function or eigenstate), it results in the same eigenstate multiplied by a constant (the eigenvalue). When measuring a physical variable (observable) of an eigenstate, the measured value will always correspond to its eigenvalue.

By applying both creation and annihilation operators to the eigenstate $|n\rangle$ (also called Fock state), it can be seen that $\hat{a}^\dagger\hat{a}|n\rangle = n|n\rangle$. We can therefore define a number operator $\hat{n}$ with $\hat{n} = \hat{a}^\dagger\hat{a}$ which fulfills the eigenvalue equation $\hat{n}|n\rangle = n|n\rangle$, where n is the eigenvalue.

The $g^{(2)}(\tau)$ function in this quantum interpretation has to be defined based on the coincidences between photon counting events instead of intensity fluctuations as in Eq. 2.9 and can be re-written as

$$g^{(2)}(\tau) = \frac{\langle n_1(t)n_2(t+\tau) \rangle}{\langle n_1(t) \rangle \langle n_2(t+\tau) \rangle} \quad (2.18)$$

where n_1 and n_2 are the number of photons at detector 1 and 2 (see Fig. 2.7). With the photon number operator $\hat{n}$, this can be written as

$$g^{(2)}(0) = \frac{\langle \hat{a}_1^\dagger \hat{a}_2^\dagger \hat{a}_2 \hat{a}_1 \rangle}{\langle \hat{a}_1^\dagger \hat{a}_1 \rangle \langle \hat{a}_2^\dagger \hat{a}_2 \rangle}. \quad (2.19)$$

This can be simplified to

$$g^{(2)}(0) = \frac{\langle \hat{n}(\hat{n}-1) \rangle}{\langle \hat{n} \rangle^2} \quad (2.20)$$

An in-depth mathematical description of this simplification and the derivation of these equations can be found in [16, 18, 22].

Finally, Fock states (as eigenstates) have a fixed photon number with no fluctuation [22], therefore the average $\langle \rangle$ is not needed for a single experiment and Eq. 2.20 can be written as

$$g^{(2)}(0) = \frac{n(n-1)}{n^2} = 1 - \frac{1}{n}. \quad (2.21)$$

For an ideal single-photon source, there should only be one photon at a time (Fock state with $n=1$) which means Eq. 2.21 has a value of zero (see Fig. 2.8). For a source emitting two photons ($n=2$), $g^{(2)}(0) = 0.5$. Therefore, to describe a single-photon source, the $g^{(2)}(0)$ value has to be between 0.5 and 0. This definition of an imperfect single-photon source is proposed in the "Single-Photon Sources and Detectors Dictionary" [15] and is therefore used in this work

when referring to a single-photon emitter (SPE). After this theoretical overview of single-photon statistics, the next section will focus on single-photon emitters in specific material systems.

2.5 Hexagonal boron nitride

There are numerous physical systems that have been investigated as deterministic single-photon sources, including single atoms, quantum dots, single ions, single molecules, color centers in diamond, semiconductor nanocrystals, and atomic defects in two-dimensional materials [1, 23, 24]. Systems such as single atoms, ions, and quantum dots typically require cryogenic temperatures, which limits their practicality and scalability. Room-temperature operation, on the other hand, introduces challenges such as spectral broadening caused by stronger electron–phonon interactions (see Section 2.1.1.2). Some diamond color centers, such as silicon- or tin-vacancy defects (SiV and SnV, respectively), are notable exceptions, exhibiting narrow emission even at room temperature [1]. However, the high refractive index and three-dimensional crystal geometry of diamond make efficient photon extraction difficult without additional optical structures such as solid-immersion lenses – though this has improved with the advent of nanodiamond hosts [1, 25].

Two-dimensional van der Waals materials, such as hexagonal boron nitride (hBN) and tungsten diselenide (WSe₂), provide an attractive alternative. Their structure allows for defects close to the surface, facilitating photon collection while maintaining relatively narrow emission linewidths [23]. Nevertheless, emission from WSe₂ is typically only observable up to ~ 35 K, whereas hBN hosts emitters that remain optically active from cryogenic temperatures to well above room temperature – even up to 800 K [23].

Another key parameter for practical applications is photostability. Organic molecules often suffer from permanent photobleaching at room temperature, while diamond color centers and defects in 2D materials exhibit more robust stability. The emitter lifetime is equally important, as it determines the maximum achievable photon emission rate. Typical lifetimes range from $< \sim 1$ ns for semiconductor quantum dots, 1–2 ns for SiV centers in diamond, and ~ 4 ns for single molecules (DBT in anthracene), to 2–6 ns for hBN defects [3, 23, 26, 27].

The nitrogen-vacancy (NV[−]) center in diamond has a relatively long lifetime of about 10–20 ns with high photostability and therefore remains a benchmark system for room-temperature single-photon emission and spin-based quantum applications. However, the more difficult light extraction and their broad spectrum with a low amount of emission into the ZPL motivates the exploration of alternative platforms in two-dimensional materials like hexagonal boron nitride (hBN) [6, 23, 25, 28].

Boron nitride (BN) was first discovered in 1842 by W. H. Balmain who prepared it using boric acid and potassium cyanide [29]. He described the compound as white powder that is "infusible, insoluble, even when heated [...]; it is not altered upon exposure to air".

Its first commercial application came only a century later, when Union Carbide and Carborun-

dum prepared it in its hexagonal form on a large-scale basis in the 1950s [30, 31]. The interest in boron nitride for industry arose due to several properties: it is chemically inert, has a very high melting point at ambient pressure ($> 2500\text{ }^{\circ}\text{C}$) [31–34] and its chemical structure makes it a solid-state lubricant. The lubricant property arises from weak van-der-Waals forces between layers; consequently, the layers can slide over each other under shear stress, providing low friction [35, 36].

In application, BN can therefore be used e. g. in high-temperature components (from ceramics to heat-dissipating material in micro-chips), as lubricant in high-temperature or extreme environments (in vacuum or space), coatings, and in cosmetics due to its white color. Furthermore, it is non-wetting and can withstand molten glass and silicone-/metal melts [31]. In its cubic form, boron nitride exhibits extreme hardness comparable to diamond [37]. Fig. 2.10 shows two scanning electron microscope images of different boron nitride samples [31, 33]; one is showing the plate-like flakes of hexagonal boron nitride powder (a), the other cubic BN crystals (b).

Hexagonal boron nitride also displays high thermal conductivity and acts as an insulator of electricity [31, 38].

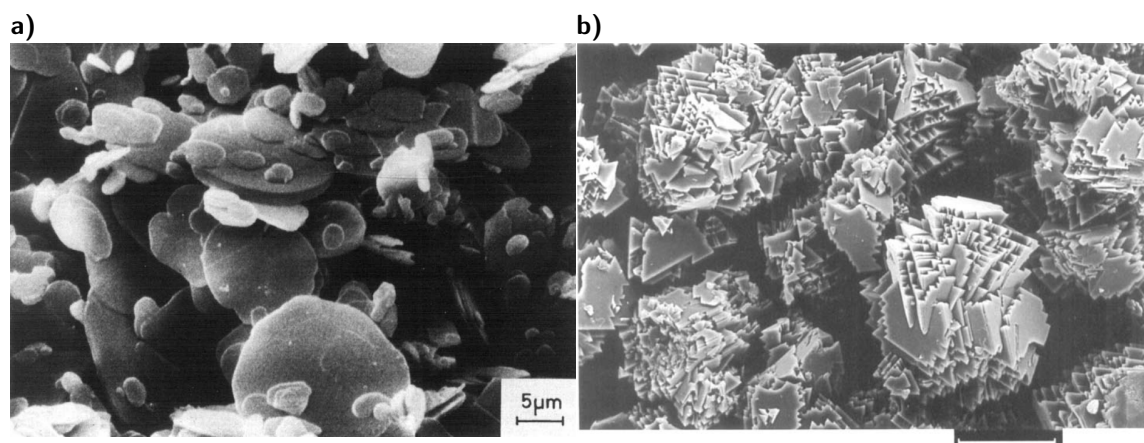


Figure 2.10: SEM pictures of boron nitride: **a)** shows flakes from hexagonal boron nitride powder (taken from [31]) and **b)** shows cubic boron nitride crystals where the marker represents $30\text{ }\mu\text{m}$ (taken from [33]).

2.5.1 Structural properties

Hexagonal boron nitride is a two dimensional material that consists of boron and nitrogen atoms which are bound to each other through covalent bonds into a planar lattice [39]. Several of these layers can bond through van-der-Waals interactions and form stacks (see. Fig. 2.11a). This leads to a highly anisotropic material with strong in-plane interactions but weak out-of-plane lattice energy [28, 40].

The unit cell is hexagonal, leading to a honeycomb structure of the crystal (see Fig. 2.11b). The most common stacking is called AA' stacking order [28, 39, 41], where the unit cell of one layer is rotated by 60° in relation to the unit cell above [41]. That means a nitrogen atom in

one layer is positioned on top of a boron atom of another layer. AB stacking (boron on top of boron, nitrogen on nitrogen) has been observed but is less common [42].

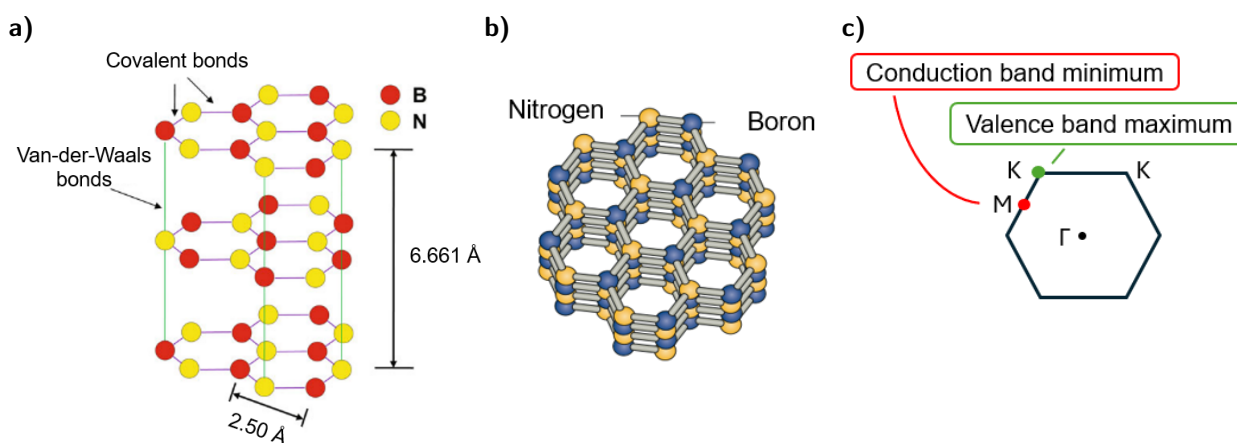


Figure 2.11: a) Sketch of the structure of hexagonal boron-nitride in AA' configuration. It consists of boron and nitrogen atoms arrayed in a planar lattice bound by covalent bonds. Several planes are bound by weak van-der-Waals forces (adapted from [39]). b) Sketch of hBN from top. The hexagonal shape and the resulting 'honeycomb' structure as well as the AA' stacking order can be seen (taken from [40]). c) shows the Brillouin zone for a hexagonal lattice with the most important symmetry points.

2.5.1.1 Orbital hybridization

The hexagonal symmetry and the semiconductor characteristics of hBN are a consequence of sp^2 hybridization. This is a concept of valence band theory, in which atomic orbitals are mixed to form new, hybrid orbitals to form chemical bonds.

Boron has five electrons: two are in $1s$ states and three are valence electrons occupying the $2s$ and $2p$ orbitals ($1s^2 2s^2 2p^1$). For nitrogen, the electronic configuration is $1s^2 2s^2 2p^3$ and has five valence electrons in the $2s$ and $2p$ orbitals (see Fig. 2.12a).

The $1s$ electrons are called core electrons and do not participate in atomic bonding. However, when the atoms bind to each other, the $2s$ and $2p$ orbitals can mix to form hybridized orbitals [43]. There are different types of hybrid orbitals, but the one responsible for the 2D, honeycomb lattice of hBN is sp^2 hybridization. This process is shown in the top part of Fig. 2.12b. The $2s$ orbital together with the p_x and p_y orbitals mix to form three new sp^2 orbitals. They have a slightly lower energy than the remaining p_z orbital. The lower part of Fig. 2.12b shows the resulting 3D orbital configuration of the atom: the three sp^2 orbitals are arranged in the x-y plane 120° from each other. Each atom has three neighbors and where the orbitals overlap, they form strong covalent σ -bonds, resulting in the honeycomb lattice.

The remaining p_z orbital is oriented along the z-axis, perpendicular to the hexagonal lattice plane. The p_z electrons form partially delocalized π electron states which collectively form valence and conduction energy bands [43]. This leads to $\pi - \pi$ interaction, which is a particular

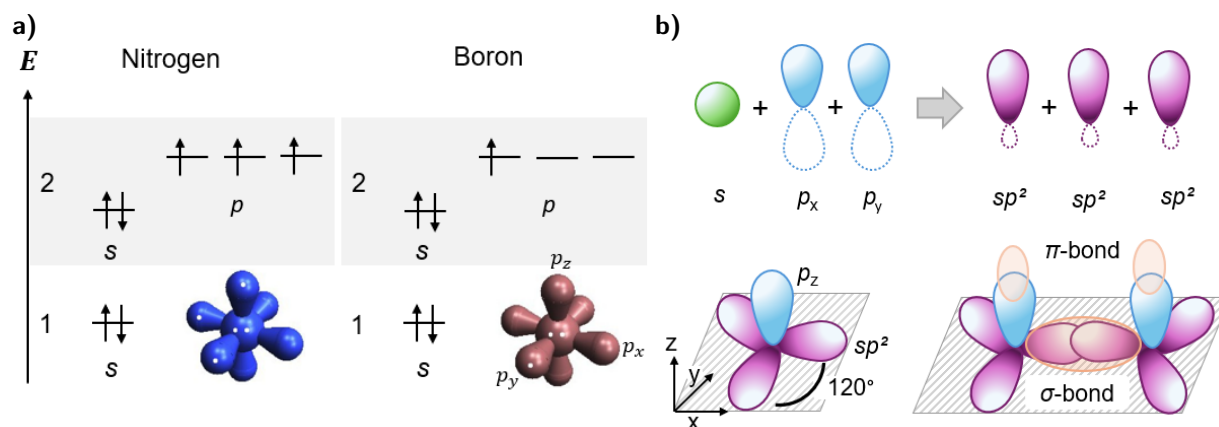


Figure 2.12: a) Electronic configuration of boron and nitrogen. The numbers one and two specify the electron shell, s and p the orbitals in the respective shell. The 3D-orbitals are shown as an inlay containing the corresponding number of electrons in white (orbital inlays taken from [44]). b) shows the sp^2 hybridization process. On top are the s (green) and p (blue) orbitals that hybridize to three sp^2 (purple) orbitals. The shading represents positive values of the wave function, which corresponds to bonding states. The resulting 3D orbital configuration is shown below that: the three sp^2 orbitals are arranged along an x-y-plane with 120° angles between them and the remaining p orbital perpendicular in z direction. When the sp^2 orbitals of two of these atoms overlap, they form a covalent σ -bond, while the remaining p orbitals can have out-of-plane interactions with the layers above or below (forming π -bonds).

type of dispersion force from van der Waals forces [45], resulting in the stacking of individual layers.

The AA' stacking order is energetically favorable, because the electron-rich nitrogen atom of one layer is positioned exactly above the electron-deficient boron atom of the adjacent layer [46]. This structure gives rise to the semiconductor properties: The valence band is made of the highest energy filled electronic states primarily derived from the nitrogen p_z orbitals, while the conduction band is made of unoccupied states above the valence band mainly derived from the boron p_z orbitals [42]. The energy difference between the highest occupied level and the lowest unoccupied level is called the Fermi energy [43]. If the Fermi energy falls in an energy gap between valence (highest occupied) and conduction (lowest unoccupied) band, then the material will be semiconducting or insulating, depending on the width of the bandgap. The different electronegativity of boron and nitrogen atoms causes polarization.

2.5.1.2 Bandgap

As explained in Section 2.1.1.2, the smallest symmetrical unit in a crystal lattice is called the Brillouin zone, the center of which is denoted with Γ . The most important points of symmetry (critical points) in a hexagonal Brillouin zone are the corners of the hexagon (K) and the mid-points on the edges between the corners (M) (see Fig. 2.11c). These symmetries determine whether a material has a direct or indirect bandgap. A direct bandgap means transition at the same point in the crystal (from K to K, M to M or Γ to Γ), whereas transitions between the

different critical points indicate an indirect bandgap.

Efforts to determine the band structure and bandgap energies of hBN have yielded values between 4.5 to 7.25 eV [23, 39, 40, 47, 48]. These discrepancies have been attributed to interlayer interactions and the number of individual layers [28, 42, 49]. Monolayer hBN is a direct bandgap semiconductor material with bandgap energy of 6.5 eV. As the number of layers increase, the bandgap becomes indirect with an energy around 6 eV. This indirect bandgap depends once again on the number of layers, interlayer interaction, and stacking order (see Fig. 2.13). Because of the wide bandgap, hBN is classified as an insulator.

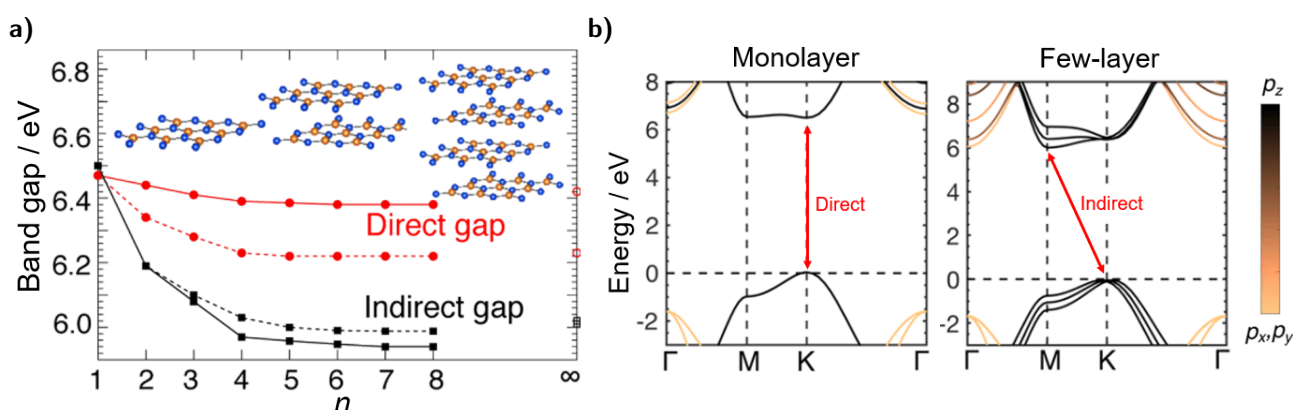


Figure 2.13: Bandgap of hBN based on the number of layers. **a)** shows the bandgap energies (y-axis) for n number of layers (x-axis) (taken from [42]). The dashed line represents the rarer AB stacking order, the solid line the more common AA' stacking. **b)** displays the band structure for monolayer hBN (left) and few-layer hBN (right) (adapted from [42]), where the y-axis displays the energy and the x-axis denotes the different symmetry (critical) points of the crystal. The color of each band indicates the p_z and $p_{x,y}$ character or the states as according to the color bar.

Fig. 2.13a shows the calculated results of the evolution of the direct and indirect bandgaps of hBN for an increasing amount of layers. The black data assumes an indirect bandgap (K-M) and the red data a direct one (K-K). The solid lines show the trend for hBN in AA' stacking order and the dashed line for the less common AB stacking order. For monolayer hBN, the direct gap assumption has slightly lower energy than the calculation with an indirect gap, but all subsequently added layers show much lower energy with the assumption of an indirect gap with AA' stacking order [42].

Fig. 2.13b shows the band structure with the critical points for monolayer and few layer hBN. Again, it can be seen that the valence band maximum and conduction band minimum for the monolayer hBN occur at the same critical point (K), whereas few-layer hBN has its valence band maximum at K and conduction band minimum at M, indicating an indirect bandgap (also seen in the Brillouin zone in Fig. 2.11c) [42, 49].

2.5.2 Optically active defects

Lately, hBN has risen to prominence because of its single photon emitter capacity. Single-photon emission in hBN monolayers has first been discovered in 2016 [47], where it was theorized to exist because of its large bandgap - much larger than that of other 2D-materials [50]. There are several advantages of hBN over other established room-temperature single-photon sources like defects in diamond, but mostly, the advantages stem from the 2D-nature of the material. Light from point-defects in diamond often suffer from the bulky dielectric environment and light ends up trapped, leading to reduced efficiency of emission. In the case of hBN, this challenge can be overcome due to significantly reduced dielectric thickness down to a single atomic layer. This leads to higher brightness, because emitters are closer to the surface; the same property can also be exploited for easy coupling to waveguides and integration to on-chip photonics [51]. Furthermore, cited advantages include the inherent hBN properties already discussed in previous sections like stability under high pressure and a strong response to applied strain or electric fields.

Luminescent point defects in hBN act as single-photon emitters and can be described as an artificial atom having ground and excited states within the host bandgap [28]. Since the bandgap is very wide, different defects can cause emission in a large range of the electromagnetic spectrum and emission in UV, visible and near-IR range have been reported [6, 28, 52]. Multiple methods can be used to prepare thin film hBN down to a single atomic layer such as exfoliation of synthesized bulk crystal, chemical vapor deposition (CVD) or metal organic vapor phase epitaxy (MOVPE) [51]. The characteristics of the emission differ depending on the host materials, i. e. monolayer, thin film, bulk crystals or nanoflakes [6, 53]. This work focuses on emission in exfoliation-based nanoflakes which is one of the most studied platforms for hBN emission.

2.5.2.1 Theoretical investigation

Theoretical investigations of defects use calculation methods to gauge possible defects in hBN, their structural properties and stability as well as their electronic and magnetic properties. These calculations based on quantum mechanical considerations usually need approximations to reduce their complexity and the most important one is the Born-Oppenheimer approximation. It is based on the fact that electrons move much faster than nuclei because the proton or neutron mass is roughly 1870 times that of an electron. Thus, when viewed from the perspective of the nuclear coordinates, electronic motions occur as if the nuclei were fixed in place [54] and their motions are independent of each other. Methods for further approximations are incorporated into models based on density functional theory (DFT), Hartree-Fock (HF) and post-HF methods [52].

Defects in hBN can be native or impurity-based and Fig. 2.14 shows the hBN lattice with proposed defects of both kinds.

Native or intrinsic defects often form during growth and commonly include vacancies and anti-

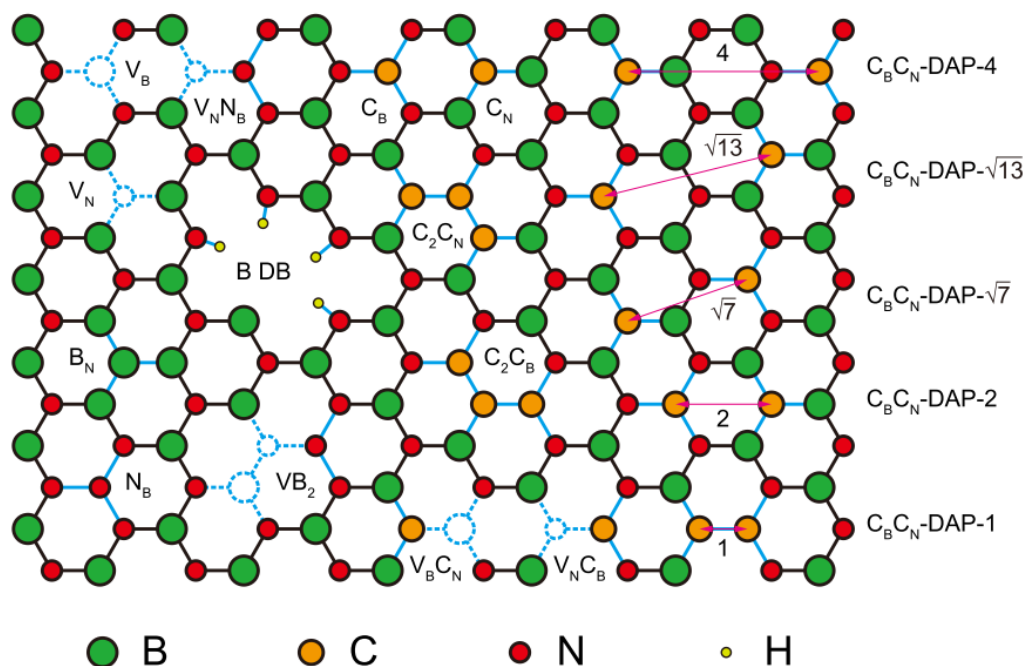


Figure 2.14: Atomic lattice of hBN (B - boron, C - carbon, N - nitrogen, H - hydrogen) with some defects including vacancies (V_B , V_N), anti-site defects (N_B , B_N), carbon defects (C_B , C_N), boron dangling bonds (B DB), donor-acceptor pair (DAP) and combinations of these (taken from [52]).

site defects. The simplest vacancy are monovacancies, where either a boron atom (V_B) or a nitrogen atom (V_N) is missing from the lattice. Anti-site defects are faults in the alternating lattice structure, e. g. a boron replaces a nitrogen atom (B_N) or the vice versa (N_B). When monovacancies and anti-site defects occur next to each other, they form new defects ($V_N N_B$) with other properties.

Another native defect that has been proposed is based on dangling bonds (DB) [55], which form by two missing boron and one missing nitrogen atom. This creates a void with four dangling nitrogen bonds and one primary boron DB. The DB approach takes into account out-of-plane displacement and occurs at surfaces, interfaces and grain boundaries.

Fig. 2.14 also shows impurity-based defects with carbon being the most common impurity in hBN. Impurities can be introduced during growth and processing (e.g., oxygen (O), carbon (C), silicon (Si) and sulfur (S)) or artificially implanted through post-processing (e.g., molybdenum (Mo), thallium (Ti) and cerium (Ce))[52]. Additionally, defects with the same structure can exhibit differences based on their charge state according to their local environments.

Carbon-related defects are under much debate in combination with the experimental data and range from monomers (C_B , C_N) to carbon dimers or trimers (e. g. $C_B C_N$, $C_N C_B$, $C_2 C_N$) to complex donor-acceptor pairs (DAP), where impurities can be further removed from another through the crystal lattice. The DAPs are labeled according to their separation in the ideal lattice, with '1' being the dimer [56].

There are many more calculations based on other impurities or with out-of-plane geometries,

however observed characteristics of defects in experiments have not corresponded perfectly with theoretical calculations except in the case of the V_B^- defect.

Since the defects in the hBN lattice are plentiful, they also cover a broad range of characteristics, with emission wavelengths from UV to near-IR. The next sections will cover the most prevalent emission, their characteristics and probable defects attributable to the emission.

2.5.2.2 Ultra-violet

The wide bandgap of 5.8 eV to 6 eV corresponds to a wavelength of ~ 210 nm and therefore theoretically supports emission in the deep UV range. In fact, photoluminescence in the UV range has already been observed in 1981 [57] during the investigation of hBN powder with poor quality compared to the high-purity crystals currently available. They discovered emission from the zero-phonon line at 4.095 eV (around 300 nm). Later, crystals of higher purity were found to exhibit cathodoluminescence, in which light is emitted after being excited by electrons, essentially being the opposite of the photoelectric effect [58].

This effect proved emission in the deep UV range with the peak emission intensity at 5.765 eV (215 nm). More emission ranges in UV were identified by Museur et al. in 2008, when they noticed that the emission range largely depends on the excitation energy. This way, they were able to find emission between 3 eV and 6 eV (413 nm to 205 nm). They tentatively attribute the emission to a carbon defect with possible involvement of a C_N impurity [59].

So far, the UV emission has been an ensemble property; the first isolated emitter in the UV range was shown in 2016 [60]. Fig. 2.15a shows the second-order correlation measurement and spectrum for this UV-emitting single-photon emitter, which they measured utilizing cathodoluminescence at 150 K. They, too, point to a C_N defect as a source for this emission.

In the same year, Vuong et al. did an investigation of the temperature-dependent light-matter interaction for ensembles [61]. They propose that deep-UV emission (> 4.8 eV) arises from stacking faults, while ~ 4 eV emission originates from a V_N -defect bound to a carbon or an oxygen atom (Fig. 2.15c). The temperature dependent spectra showed a significant broadening of the zero phonon line (ZPL) and phonon side band (PSB) with increasing temperature (see Fig. 2.15b). They also conclude that the phonon side band includes both in-plane and out-of-plane phonon interactions [61].

The nature of this defect is not conclusively known, but the $C_B C_N$ has been identified as a possible match. Theoretical investigations [62, 63] have shown ZPL and PSB energies close to the experimentally determined ones and other factors are in agreement as well, such as the Huang-Rhys (HR) factor, which characterizes electron-phonon coupling. The spectrum and defect geometry are depicted in Fig. 2.15d. Other proposed defects include the 4C and 6C defect, in which a whole or partial BN hexagon is replaced with carbon atoms [64]. Simulated spectra of these impurities are very similar to the $C_B C_N$ defect, which highlights the difficulty to unequivocally identify the nature of these defects.

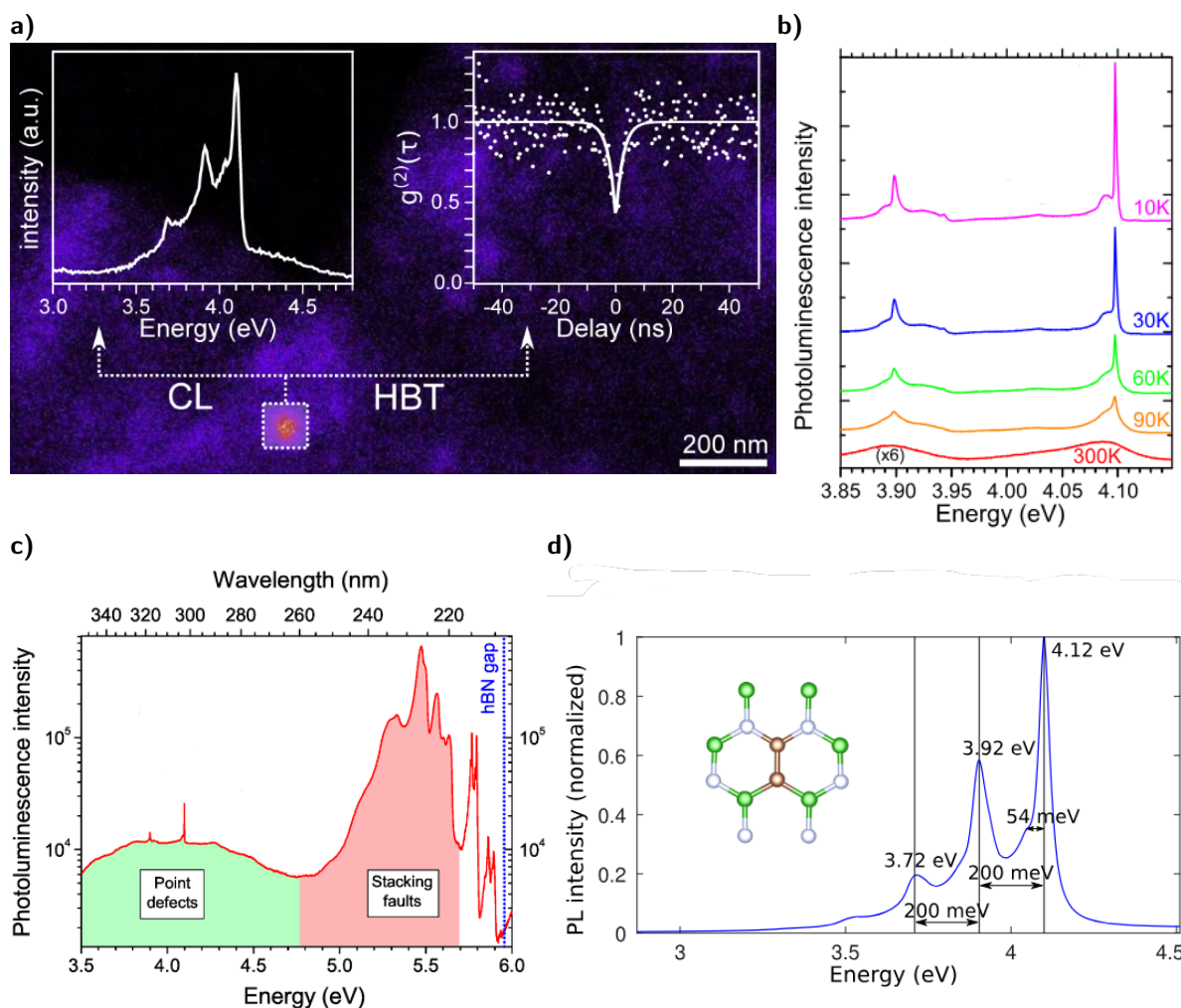


Figure 2.15: UV emission from point-defects in hBN. **a)** Cathodoluminescence (CL) intensity map (purple background) with the spectrum and second-order correlation measurement overlaid (from [60]). **b)** Temperature dependent spectrum measurements of the 4.1 eV color center with an excitation energy of 4.6 eV (from [61]). **c)** Photoluminescence spectrum of bulk hBN at 10 K with an excitation energy of 6.3 eV. The bandgap energy of 5.95 eV is indicated by a blue dotted line. The red-shaded area is attributed to stacking faults, the green area to point-defects (from [61]). **d)** Simulated PL spectrum of the $C_B C_N$ defect, the vertical lines indicate the energy of the measured peaks. The defect geometry is shown as an inset (BN lattice as green and gray, C-atoms in brown) (taken from [63]).

2.5.2.3 Near-infrared

The negatively charged boron vacancy (V_B^-) defect, consisting of a missing boron atom replaced by an extra electron in the hBN lattice, is currently the only understood spin defect (defect possessing an isolated electron spin). It is created with ion beam (e. g. xenon, helium, argon) or neutron or electron irradiation, however ion irradiation is the most convenient and widely used method [52]. The ions knock boron atoms out of the hBN lattice and leave behind ensembles of V_B^- defects [65, 66]. The photoluminescence (PL) spectrum at room temperature shows a wide emission centered at ~ 820 nm (see Fig. 2.16a). The amount of defects - and consequently

for ensemble defects also the brightness - depends on the fluence of the irradiation beam and the influence of the Xe-fluence on the count rate is shown in Fig. 2.16b. Under cryogenic temperatures, the emission remains mostly unchanged (Fig. 2.16c) and the full width at half maximum (FWHM) of the spectrum narrows only slightly by a few nanometers [52, 66].

The atomic structure was determined by Gottscholl et al in 2020 [67] after they successfully performed optically detected magnetic resonance (ODMR) at room temperature. Fig. 2.16d shows a simplified V_B^- energy-level diagram. It consists of a triplet ground state and triplet excited state with a metastable singlet state (see section 2.5.3). Spin-optical properties arise due to the spin-dependent inter-system crossing and pumping with a microwave frequency that is resonant with the energy difference between ground and excited state sub-levels, leading to a decrease or increase in fluorescence intensity.

A resulting ODMR spectrum of V_B^- at room temperature is shown in Fig. 2.16d. This property makes this defect promising for sensing applications, however the defect has not been isolated (no single-photon emission) and its quantum efficiency is low (0.3%) [52, 68]. This is due to the long lifetime of the metastable state, which also limits their sensitivity as sensor.

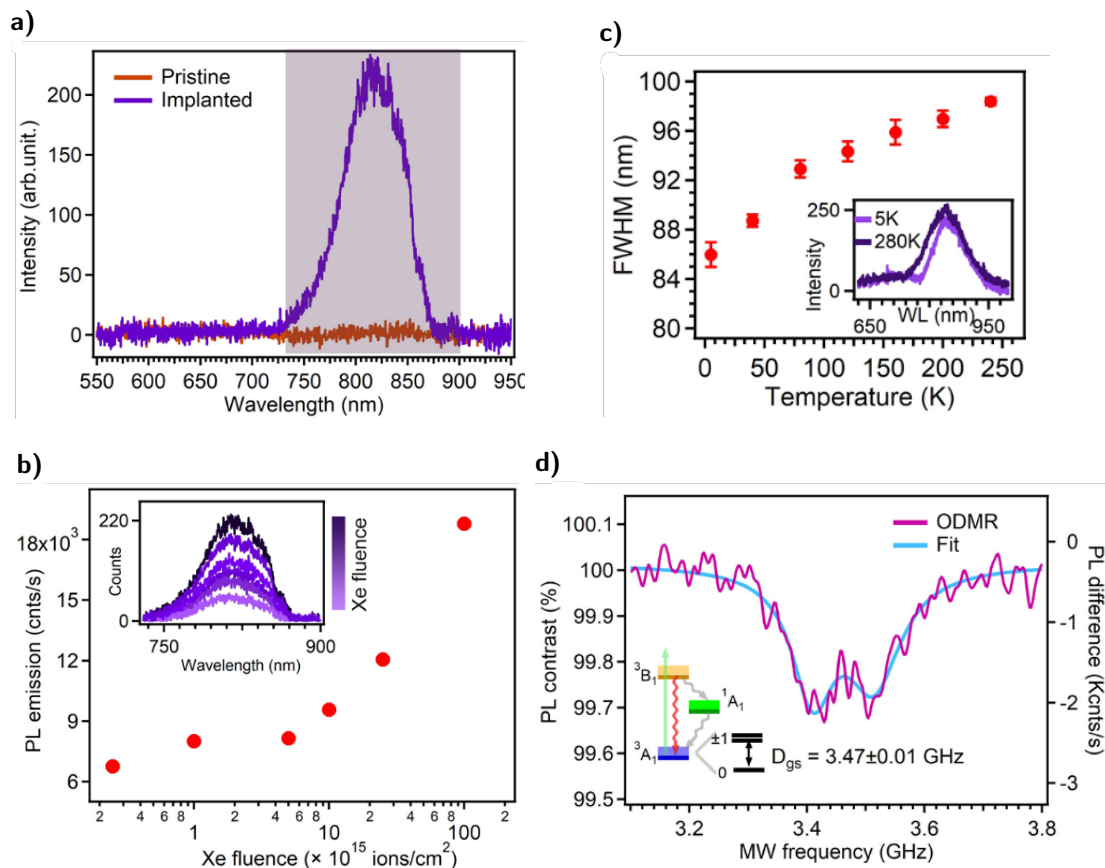


Figure 2.16: Characteristics of V_B^- defect. **a)** Shows the photoluminescence spectra of pristine hBN (orange) and the V_B^- defect (purple). **b)** shows the PL emission under different fluences of a Xe^+ beam. With higher fluences, the defect becomes more pronounced and emission is higher. **c)** shows the PL spectrum for the same defect at different temperatures, while **d)** displays the ODMR spectrum of the V_B^- defect (taken from [66]).

2.5.2.4 Visible

By far, the most studied emission in hBN is in the visible range. Reports of emission range between 500 nm and 760 nm, but most commonly, the ZPL is located around 580 nm [6, 26, 53, 65, 69, 70]. The line shape of the emission spectra has been shown to depend heavily on the number of layers, with emission from defects in monolayer hBN much broader than emission from hBN with several layers (see Fig. 2.17a) [47].

In multilayer hBN, emission spectra exhibit large shifts in the wavelength, but the general line shape is similar as shown in Fig. 2.17b. Generally, the zero-phonon line is a prominent peak with a less intense phonon-side band red-shifted by 150 meV to 160 meV [71]. Fig. 2.17c shows the distribution of the ZPL within one sample, ranging between 540 and 740 nm.

Under cryogenic temperatures, the ZPL and PSB become narrower (see Fig. 2.17d), but the FWHM does not seem to be uniform between different emitters [47, 69].

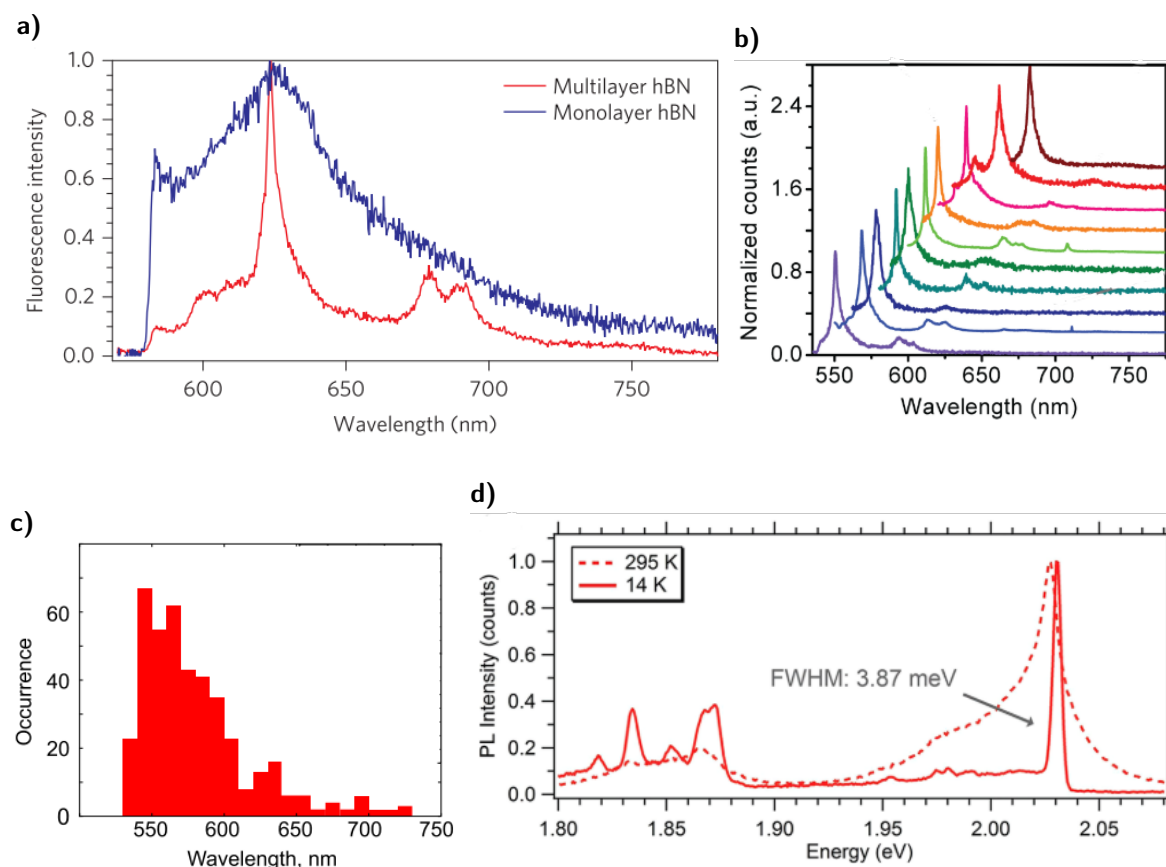


Figure 2.17: **a)** Comparison between the spectrum of visible emission in monolayer hBN and multilayer hBN (taken from [47]). **b)** Spectra in the visible range for different emitters, showing the same lineshape over a wide range in the visible spectrum (adapted from [71]). **c)** Histogram of the different ZPL positions in a sample (adapted from [70]). **d)** Spectrum of an emitter at room temperature (295 K) and 14 K (taken from [69]).

These differences in ZPL position have been attributed to strain, variations in the dielectric environment, surface oxidation, amount of monolayers or different underlying defects [53, 69, 70],

but since the point-defect responsible for this emitter has not been identified, the reason has not been conclusively been determined.

It seems to exist natively in CVD grown hBN but it is also claimed to be created by high temperature annealing and ion irradiation. Creation of luminescent defect centers is often attributed to annealing in argon [71–73], but also in other atmospheres such as oxygen or nitrogen [72, 74]. However, in [75] emitters were created by electron radiation and subsequently annealed in argon at 850 °C, which quenched the previously measured emission.

Another contested characteristic is their stability; emission intensity is often reported to fluctuate (blinking) or vanish (bleaching). [71] found emitters bleach and blink, but only when excited with a blue laser (405 nm), while stable under green excitation (532 nm). This is however contradictory with other reports, since 532 nm is the most common excitation wavelength for this emitter and yet reports of instability are plentiful. [73] found that their untreated reference samples exhibit blinking and bleaching, but after ion implantation the emitters are mostly optically stable. [65] claimed emission of this wavelength range is unstable under continuous laser irradiation, while [76] found intensity fluctuations under both cw and pulsed excitation. [72] investigated the photostability of an hBN monolayer and compared it to the stability of this layer encased by one more "empty" hBN layer and one "sandwiched" between two empty hBN layers. They found that each additional layer protects the emitters from photobleaching, but does not eliminate the process completely. They conclude that availability of oxygen from the atmosphere (monolayer), the substrate (second layer) and from impurities within the crystal lattice (three layers) leads to photochemical reactions and bleach or dim emission. However, when [51] investigated the photostability in various hBN samples, they found that the substrate material does not affect the bleaching, but acknowledge that oxygen trapped between the hBN layer and substrate could lead to bleaching.

In another paper, a sample was annealed at 500 °C in hydrogen, oxygen and ammonia and found that the emission remains unchanged in both oxidizing and reducing environments [69]. However, they note that each annealing step also created new emitters and quenched others. Since formation of defects depends on the annealing temperature, they conclude that a vacancy must be involved and that the charge state is neutral because the hydrogen environment would have changed that charge state and eliminated emission.

When first discovered in 2016, the emission was attributed to $N_B V_N$ based on concurrence of experimental with simulated data [47]. However, while the difference in ZPL can be partially attributed to strain, the magnitude of strain needed to account for the entire observed range of ZPL positions is high [69] and simulation of the $N_B V_N$ defect is not in perfect accordance with the experimental data.

[74] ascribes fluorescence to $V_N C_B$ and experimental proof of involvement of carbon followed: Mendelson et al. grew hBN samples with different carbon concentrations and showed that the carbon content scales directly with the density of emitters. A high amount of carbon produced ensemble fluorescence, while a low amount produced isolated emitters [26]. Additionally, they

Table 2.1: Literature review (non-exhaustive) of visible single-photon emission in hBN. Compared characteristics are the substrate used, the hBN host material, the method of obtaining that material, the treatments on the sample, the zero-phonon line (ZPL) emission, the emitter stability and the corresponding paper.

Substrate	Host	Method	Treatment	ZPL / nm	Stability	Source
SiO ₂ /Si	Few layer	CVD	450 °C air, 850 °C Ar	550-590	Bleaching Blinking	[72]
SiO ₂	Multilayer	CVD, wet transfer cleaner	air 350 °C - 750 °C, UV	560	-	[7]
SiO ₂	Few layer	LPCVD	Applied voltage	580 ± 10	Stable	[53]
SiO ₂	Nanoflakes	Dropcast	850 °C Ar	500 - 680	Bleaching (405 nm), Stable (532 nm)	[71]
SiO ₂ /Si	Flakes	Exfoliated	850 °C Ar, ion implantation, laser ablation, electron irradiation	~ 600	Blinking, bleaching (ref), stable (ion imp.)	[73]
SiO ₂ /Si	Flakes	Exfoliated	oxygen irradiation, 850 °C N	570 - 620	-	[74]
SiO ₂	Mono- & Multilayer	Exfoliated	850 °C Ar	623	Stable (multil.), Blinking, bleaching (monol.)	[47]
SiO ₂	Nanoflakes	Dropcast	Electron irr. or 850 °C and 500 °C in H ₂ O/NH ₃	590 or 708	Stable	[69]
Glass	Monolayer	CVD	-	575 ± 15	Blinking	[70]
Quartz	Nanoflakes	Dropcast	850 °C air	567 - 701	Blinking	[76]
SiO ₂ /Si	Flakes	Exfoliated	Electron irradiation	575	Stable	[75]

used multispecies ion implantation on a variety of different samples and found that only carbon implantation created visible range SPEs. As before, the density of SPEs corresponds directly to the ion implantation dose. They also found that an ensemble of this emitter displays an ODMR signal at ~ 0.7 GHz.

In their theoretical analysis, they focused on the ZPL energy of 2.1 eV, a lifetime of 2-6 ns and high quantum efficiency as properties to select a model and dismissed $V_N C_B$, instead focusing on $V_B C_N^-$. However, this defect simulation has a lower predicted energy than their experimental data.

In 2022, Stern et al. demonstrated ODMR spectra from SPEs, with $\sim 5\%$ of their emitters showing a measurable ODMR signal (see Fig. 2.18b). They similarly attribute the emission to a carbon related defect with a strong candidate being a carbon trimer identified by [63], because of the overlap in the spectrum as well as theorized ODMR signal at room-temperature. The simulated spectrum of the carbon trimer $C_2 C_N$ is shown in Fig. 2.18c together with experimental data. These spectra are similar to the spectrum of the SPE which exhibited an ODMR signal as shown in Fig. 2.18a.

It is also possible that difference in strain and local environment are not sufficient to explain the range of ZPL position and instead, different defects produce very similar spectral lineshape. [77] proposes that emission between 540 and 720 nm is attributable to four classes of emitters instead of one.

Table 2.1 gives a literature overview and demonstrates the differences in fabrication, treatment and recorded behavior between different samples. It is important to note that this overview

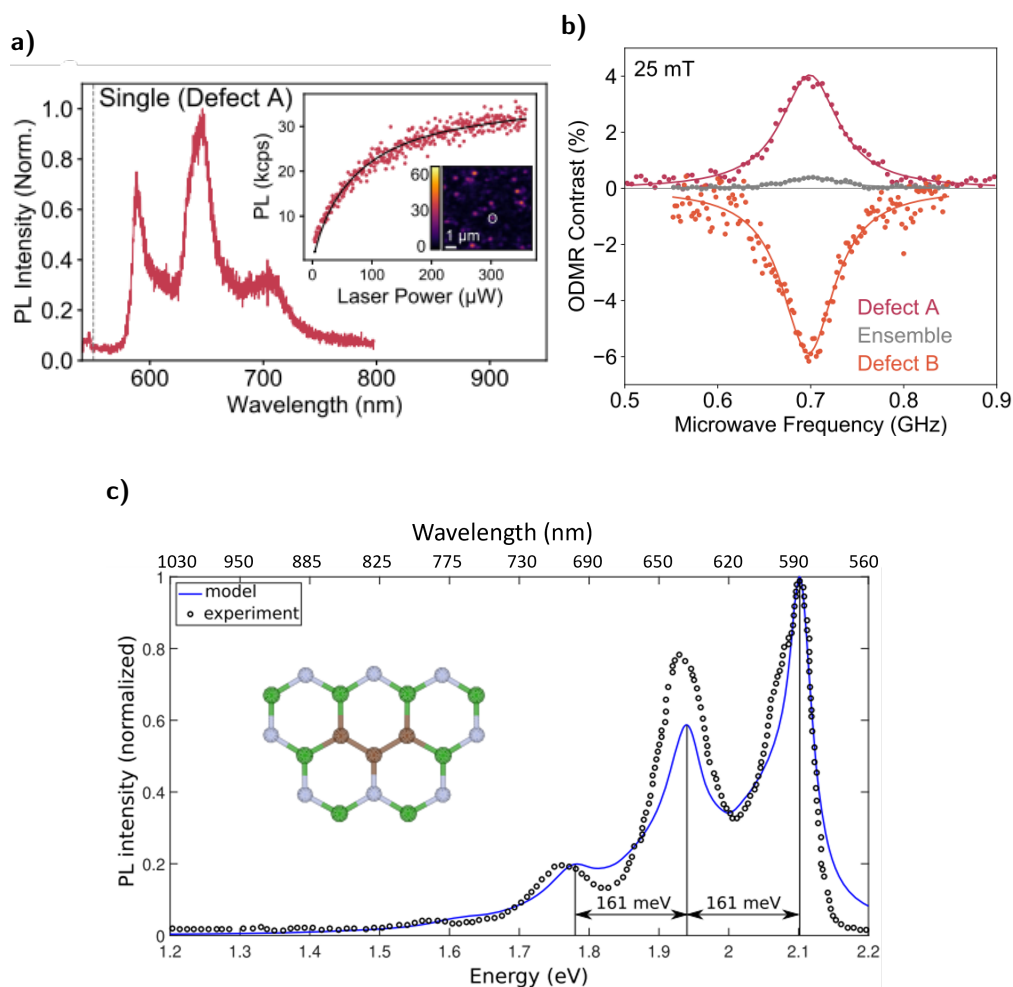


Figure 2.18: a) Normalized spectrum of an SPE that exhibits ODMR signal. b) Room-temperature saturated ODMR of single defects in comparison to ensemble with an applied magnetic field of 25 mT (taken from [78]). c) Calculated spectrum for a C_2C_N defect together with an experimental spectrum. The inlay shows the defect structure, with boron green, nitrogen gray and carbon in brown (adapted from [63]).

is not exhaustive as there are many more publications and is just meant as an illustration of the difficulty pinpointing the nature of this defect. The emitters studied in this thesis are expected to be comparable to those reported by [71] in Table 2.1, as the hBN material and sample preparation procedures were similar. They have been theorized to originate from a carbon defect – either in connection with vacancies, as carbon clusters or even more advanced complexes [79].

Since emission from this defect is the most common, has a narrow ZPL, shows high brightness and seems to be spin-active, it is of great interest for possible applications in sensing, metrology and applications where the 2D-nature of the defect can be exploited, such as coupling to waveguides or lensed fibers [28].

2.5.3 Photodynamics of hBN point-defects

We already discussed the basic principles of excitation and emission in section 2.1.1, where we looked at a two-level system. However, most emitters are more complicated than this and point defects in hBN are no exception. In this work, we will assume a three-level system for the defect in the visible range as this is the most common approximation in literature [28, 47, 51, 78], although four-level systems have been suggested [76]. Therefore, this section gives an overview of a three-level energy system and how it relates to the second-order correlation function.

2.5.3.1 Three-level system

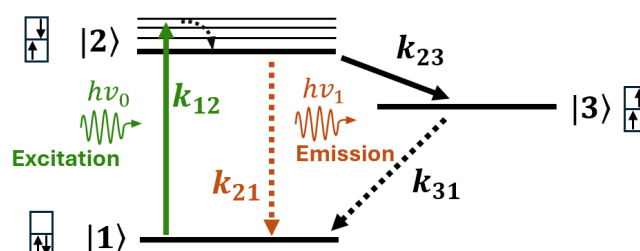


Figure 2.19: Jablonski diagram for a 3-level energy system with transition rates. The solid black lines denote the ground state $|1\rangle$, excited state $|2\rangle$ and a metastable state $|3\rangle$ with their spin states indicated next to them with small up and down arrows. The large arrows between the states denote transitions from one state to another with their respective transition rates k_{xy} indicating the transition direction.

Fig. 2.19 shows the Jablonski diagram for a 3-level energy system with corresponding transition rates. The system in the ground state $|1\rangle$ can be excited to a higher, excited state $|2\rangle$ by absorption of a photon with the energy $h\nu_0$. The rate at which the system is excited from $|1\rangle$ to $|2\rangle$ is denoted as k_{12} and is proportional to the excitation laser power [80].

The system then instantly relaxes non-radiatively to the lowest vibrational modes of $|2\rangle$, from where it can decay radiatively to $|1\rangle$ by emitting a photon with a lower energy $h\nu_1$ (fluorescence). This process is described by the decay rate k_{21} . However, a 3-level system also includes another pathway via an intermediate meta-stable state $|3\rangle$.

Electrons in the ground state $|1\rangle$ are normally paired in bonds with their spins opposite to each other, which means the spins cancel each other out and their spin quantum number $S_{|1\rangle} = 0$. When the system is excited, one unpaired electron remains in the lower orbital while another unpaired electron is excited to a higher orbital. In the excited state $|2\rangle$, the spins are still oriented anti-parallel and $S_{|2\rangle} = 0$. States with $S = 0$ are known as singlet states, because their spin multiplicity $m_s = (2S + 1) = 1$.

However, the spin of the excited electron can also be oriented parallel to the ground state electron so that $S_{|3\rangle} = 1$. Therefore, the multiplicity $m_s = 3$, giving rise to a triplet state. In Fig. 2.19, the spins of the electrons are indicated by the small arrows in the boxes representing orbitals next to the state.

Even though this case is the most common one, triplet ground states with two electron of parallel spin exist and are not uncommon in crystals with defect centers or dopant ions. In fact, they are of particular interest for sensing applications especially in regards to magnetic field applications [81].

Since photons do not carry spin, they can only excite transitions between states of the same spin, i. e. from $|1\rangle$ to $|2\rangle$; transitions are therefore dominated by singlet-singlet interactions $|1\rangle \rightleftharpoons |2\rangle$. These transitions occur on time scales in the nanosecond regime [17].

Transitions to and from a triplet state occurs on much larger time scales due to spin selection rules, which is what the term "metastable" refers to. Relaxation from the singlet state $|2\rangle$ to the triplet state $|3\rangle$ is non-radiative; the process is called inter-system crossing (ISC). The decay process between the different spin states occurs at a much slower rate (k_{23}) and is mediated by the spin-orbit coupling. Therefore, $k_{23} \ll k_{21}$ [80]. Relaxation from $|3\rangle$ to $|1\rangle$ occurs under emission of a photon (phosphorescence) on a much larger time scale up to milliseconds (k_{31}).

To obtain the rate at which photons are emitted by this system, it is important to know the population p_i of each state, where $i = \{1, 2, 3\}$ - dropping the $|\rangle$ notation for simplicity. Population - or more accurately the probability that a state is occupied - is an ensemble property, so that in this context it either refers to several identical quantum emitters or alternatively one emitter observed many times. The system has to be in one of the three states at all times, therefore

$$p_1 + p_2 + p_3 = 1. \quad (2.22)$$

By using the transition rates between states, we can describe the change of the populations with

$$\dot{p}_1 = -k_{12}p_1 + k_{21}p_2 + k_{31}p_3, \quad (2.23)$$

$$\dot{p}_2 = k_{12}p_1 - (k_{21} + k_{23})p_2, \quad (2.24)$$

$$\dot{p}_3 = k_{23}p_2 - k_{31}p_3 \quad (2.25)$$

The decay rate k_{21} can be further divided into a radiative and non-radiative contribution $k_{21} = k_r + k_{nr}$ [19, 82].

For a steady state analysis of Eq. 2.23 - 2.25 we assume that that populations are constant in time and their derivatives zero. The photon emission rate R can then be described by

$$R = p_2 k_r, \quad (2.26)$$

which means the photon emission rate is the population of the excited singlet state multiplied by the radiative decay rate. This definition can explain the saturation behavior of fluorescence; i.e. with increasing excitation power, the photon emission rate R tends towards a finite value

[19, 82].

However, to gain insight into the statistical properties of light, we need to look at how the population of levels depends on time τ .

2.5.3.2 Derivation of $g^{(2)}(\tau)$ for a three-level system

In sections 2.2 and 2.4 we discussed the characteristics of non-classical light and showed how the nature of photon statistics causes bunching and anti-bunching behavior.

Anti-bunching means that photons are emitted one after another separated by a specific and characteristic time. After a photon has been emitted, the atom has to be excited again before it is capable of emitting another photon. The time between photon emission is therefore determined by the excitation rate k_{12} and by the time the system remains in the excited state before relaxation.

Since we expect non-classical light and want to describe the photodynamics of such a system, we will start with the definition of the $g^{(2)}(\tau)$ given in Eq. 2.18 and rewrite it in terms of the probability of finding photons:

$$g^{(2)}(\tau) = \frac{P(t, t + \tau)}{P(t)P(t + \tau)}. \quad (2.27)$$

$P(t, t + \tau)$ describes the probability of recording a photon after a time τ , provided that a photon was recorded at time t [19]. This can be re-written in terms of conditional probabilities with a relation from probability theory for events A and B :

$$P(A | B) = \frac{P(A \cap B)}{P(B)}, \quad (2.28)$$

where $P(A | B)$ is the conditional probability of A given B . Therefore, we can write Eq. 2.27 as [82]:

$$g^{(2)}(\tau) = \frac{P(t + \tau | t)}{P(t)}. \quad (2.29)$$

The conditional probability $P(t + \tau | t)$ therefore expresses that a photon is recorded after a time delay τ , given that another photon was recorded at time t . This probability to emit a second photon is therefore ruled by the population dynamics of the excited state $p_2(\tau)$ and therefore must include the radiative decay rate k_r . The probability to detect this photon further has to take into account the detection efficiency η and we can write [19]:

$$P(t + \tau | t) = P(\tau | 0) = \eta k_r p_2(\tau) \quad (2.30)$$

The probability that a photon is recorded at any given time t is proportional to the steady-state probability $p_2(\infty)$ of the system to be in an excited state. Therefore, it can be described as $P(t) = \eta k_r p_2(\infty)$. We can then re-write Eq. 2.29 as

$$g^{(2)}(\tau) = \frac{\eta k_r p_2(\tau)}{\eta k_r p_2(\infty)} = \frac{p_2(\tau)}{p_2(\infty)} \quad (2.31)$$

$p_2(\tau)$ can be obtained by solving the rate equations of Eq. 2.23 - 2.25 with the initial conditions that at $\tau = 0$ the system is in the ground state so that $p_1(0) = 1$, $p_2(0) = 0$. By combining Eq. 2.22, 2.23 and 2.23 we obtain the following equations:

$$\begin{aligned} \dot{p}_1 &= -(k_{12} + k_{31})p_1 + (k_{21} - k_{31})p_2 + k_{31} \\ \dot{p}_2 &= k_{12}p_1 - (k_{21} + k_{23})p_2. \end{aligned} \quad (2.32)$$

This system of differential equations can be written in matrix form in the following [19]:

$$\dot{\mathbf{p}}(\tau) = \mathbf{M} \cdot \mathbf{p}(\tau) + \mathbf{J} = \begin{pmatrix} -(k_{12} + k_{31}) & k_{21} - k_{31} \\ k_{12} & -(k_{21} + k_{23}) \end{pmatrix} \cdot \mathbf{p}(\tau) + \begin{pmatrix} k_{31} \\ 0 \end{pmatrix},$$

where $\mathbf{p}(\tau)$ and $\dot{\mathbf{p}}(\tau)$ describe the vectors containing the populations p_1 and p_2 or their derivatives, respectively.

Such a matrix equation can be solved by defining a new vector $\mathbf{q}$ which is related to $\mathbf{p}$ by the equation $\mathbf{p}(\tau) = e^{\mathbf{M}\tau} \cdot \mathbf{q}$. With a Laplace transformation, Heaviside expansion and the condition $p_1(0) = 1$, we can obtain a solution for $p_2(\tau)$ from which - with Eq. 2.31 - we can express the $g^{(2)}(\tau)$ -function as [19, 82]:

$$g^{(2)}(\tau) = 1 - (1 + A) \cdot e^{-\lambda_1 \tau} + A \cdot e^{-\lambda_2 \tau} \quad (2.33)$$

with

$$A = \frac{k_{12}k_{23}}{k_{31}(k_{12} + k_{21})}, \quad \lambda_1 = k_{12} + k_{21}, \quad \lambda_2 = k_{31} + \frac{k_{12}k_{23}}{k_{12} + k_{21}}. \quad (2.34)$$

These are simplified expressions based on the assumption that decay processes between different spins take a much longer time, therefore $k_{21} \geq k_{12} \gg k_{23} \geq k_{31}$.

The kinetics between ground and excited states (states $|1\rangle$ and $|2\rangle$) are characterized by the first term and describe the anti-bunching with λ_1 as the anti-bunching decay rate. The second term describes the population and lifetime of the metastable state, which corresponds to the bunching behavior of the system, λ_2 is thus the decay rate for the bunching effect. The inverse of the decay rates $\lambda_{1,2}$ therefore describe the lifetimes $\tau_{1,2}$ for the anti-bunching and bunching behaviors, respectively. A is the photon bunching amplitude.

Eq. 2.33 is the basis for fitting the experimental data, which will be described in detail in section 3.

2.6 Confocal microscopy

The previous sections explained single-photon emission from optically active defects in crystal lattices such as single-photon emitters in hBN, but when speaking of a single-photon source (SPS), we cannot just consider the emission characteristics without examining how the light is collected. For this purpose, this section will provide an overview of confocal microscopy.

The first confocal microscope was developed by Minsky in the mid fifties to investigate neural networks in brain tissue [83]. A lack of computing power reduced the feasibility of this first confocal microscope, but by the end of the sixties, Egger and Petrán were able to observe brain cells by using a mechanical scanning device, the Nipkow disk [84].

A scanning technique is essential for confocal microscopy. The big advantage of confocal microscopy in contrast to conventional microscopy is the reduction of background noise outside the confocal plane. This is achieved by using a small pinhole which cuts off signals outside the focus and therefore increases the resolution. However, this means that only one small spot at a time can be imaged, which is why scanning is necessary to get a larger picture.

Scanning is performed by either moving the sample [83] or moving the excitation light [84].

2.6.1 Working principle

Fig. 2.20 shows the working principle of a confocal microscope. The excitation light (green) of a point light source (e. g. a laser) is reflected at a dichroic mirror, directed onto a lens or objective and therefore focused on the sample. The sample is excited and emits light (red), which is collected by the same objective, passes through the dichroic mirror and is focused on the tiny hole of the pinhole. This pinhole realizes spatial filtering and stops emission light from outside the plane of focus from being detected (yellow).

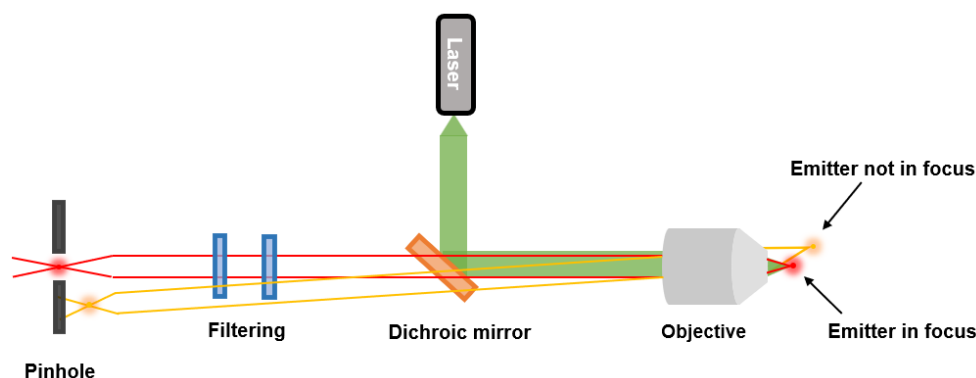


Figure 2.20: Sketch of the working principle of confocal microscopy. The excitation light (green) of a laser is reflected at a dichroic mirror and with the help of a microscope objective it is focused into a single spot on the sample. The emission light of this spot passes through the dichroic mirror, passes spectral filtering and is detected. A pinhole before the detection realizes spatial filtering and stops emission light from outside the plane of focus from reaching the detector (yellow emission).

2.6.2 Resolution and point-spread function

The resolution of a confocal microscope is limited by diffraction as first described by Ernst Abbe in [85]. When a point-shaped object is imaged using an optical system, the image will be a blurred point due to diffraction. The intensity distribution of that image is called the point-spread function (PSF). Under the approximation of a paraxial system (i. e. one with small numerical aperture), the PSF can be described with the bessel function J_1 [86].

The numerical aperture NA of an objective is defined as

$$\text{NA} = n \sin \alpha. \quad (2.35)$$

The angle α is half of the opening angle of the objective and n the refractive index of the medium. By using the NA, we can use the reduced variables ζ and ρ to describe the PSF along the optical axis z (or radial direction r). λ is the wavelength of light.

$$\rho(r) = \frac{2\pi}{\lambda} \cdot \text{NA} \cdot r \quad (2.36)$$

$$\zeta(z) = \frac{2\pi}{n\lambda} (\text{NA})^2 z \quad (2.37)$$

At the focal plane ($\zeta = 0$), the PSF is rotation symmetric and corresponds to an airy disc:

$$\text{PSF}(0, \rho) = 2J_1^2(\rho)/\rho^2 \quad (2.38)$$

where J_1 is the first-order Bessel function, which arises from a mathematical analysis of diffraction patterns with circular symmetry. This describes the airy disks: a pattern with a bright round disc in the center surrounded by concentric circles with decreasing intensity. Along the optical axis ($\rho = 0$), the PSF can be described by

$$\text{PSF}(\zeta, 0) = \left(\frac{\sin(\zeta/4)}{\zeta/4} \right)^2. \quad (2.39)$$

Fig. 2.21a shows $\text{PSF}(\zeta, \rho)$ for a paraxial approximation. The PSF is a diffraction pattern due to the circular aperture and is a measure of resolution - two points viewed by a microscope can only be separated if they are far enough apart for their PSF to be distinct [86].

In the case of confocal operation, excitation and emission occur at the same spot. Both the illuminated and the observed volume can therefore be described by the three-dimensional PSF and if the same optics are used for illumination and observation, we can write:

$$\text{PSF}_{\text{conf}}(\zeta, \rho) = \text{PSF}_{\text{Exc}}(\zeta, \rho) \cdot \text{PSF}_{\text{Em}}(\zeta, \rho). \quad (2.40)$$

The resulting three-dimensional PSF for confocal operation is shown in Fig. 2.21b. The difference between the confocal and regular PSF becomes immediately apparent: The confocal PSF is narrower which leads to higher resolution and the side maxima are much less pronounced.

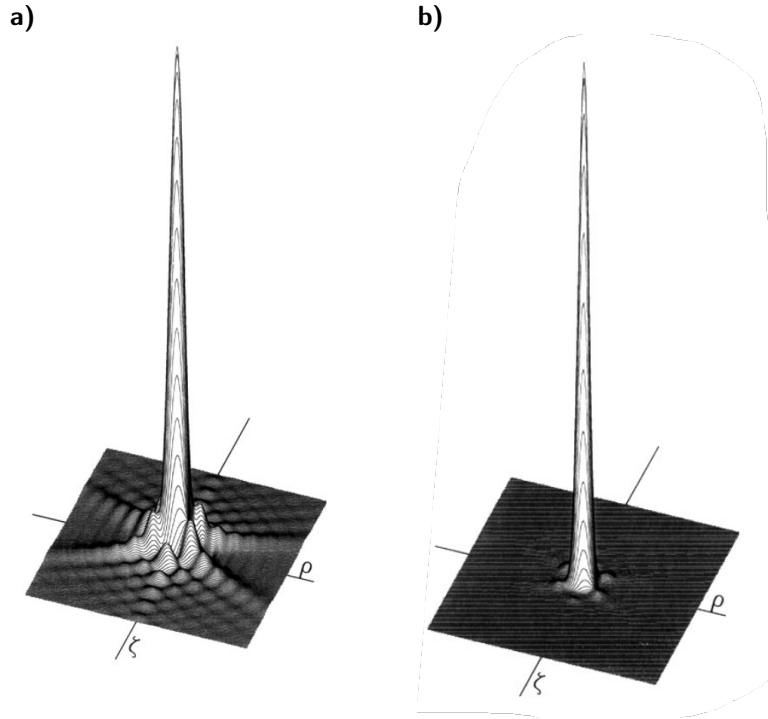


Figure 2.21: Point-spread function for regular or confocal case. **a)** $\text{PSF}(\zeta, \rho)$ **b)** Confocal case, product of two identical PSF (taken from [86]).

The Rayleigh criterion is often used to describe the resolution of a microscope: Two spots are still separable from each other if the center of the airy disk of the first coincides with the first dark circle of the airy pattern of the second. The radius of an airy disk and therefore its lateral resolution limit [85] of a conventional microscope is

$$r_{\text{airy}} = 0.61 \frac{\lambda}{\text{NA}}. \quad (2.41)$$

For a confocal microscope the resolution improves by a factor of $\sqrt{2}$:

$$r_{\text{conf}} = \frac{0.61}{\sqrt{2}} \frac{\lambda}{\text{NA}}. \quad (2.42)$$

Along the optical axis, the resolution improves from $2\lambda n/(\text{NA})^2$ for a conventional microscope to $1.5\lambda n/(\text{NA})^2$ for a confocal one [19]. However, it is important to note that the size of the confocal pinhole has a big influence on the axial resolution. A smaller pinhole filters more stray light which increases the resolution. This leads to the conclusion that we could just choose the smallest pinhole available; however, the reduced noise comes at the cost of also reduced emission signal, so that the signal-to-noise ratio does not increase. The optimal radius of the pinhole is therefore usually on the order of the Airy disk radius, so that only the center of the PSF reaches the detector [19, 86].

3 Experimental Methods

3.1 Sample preparation

The hBN samples used in this work are made from commercially available nanoflakes from the company Graphene supermarket ("Pristine hBN nanoflakes in ethanol / water solution", BN-100ML, Graphene supermarket as part of Graphene labs). hBN samples from this manufacturer are commonly used across literature [7, 51, 69, 71, 76], because they are inexpensive, readily accessible, and require no additional processing such as exfoliation – however, as of 2025, they ceased operations.

The nanoflakes have a lateral size of 50 nm to 200 nm with a thickness of 1 to 5 monolayers and a concentration of 5.4 mg/L according to the datasheet (see Appendix). Fig. 3.1 shows a schematic of the sample preparation protocol developed and implemented in this work.

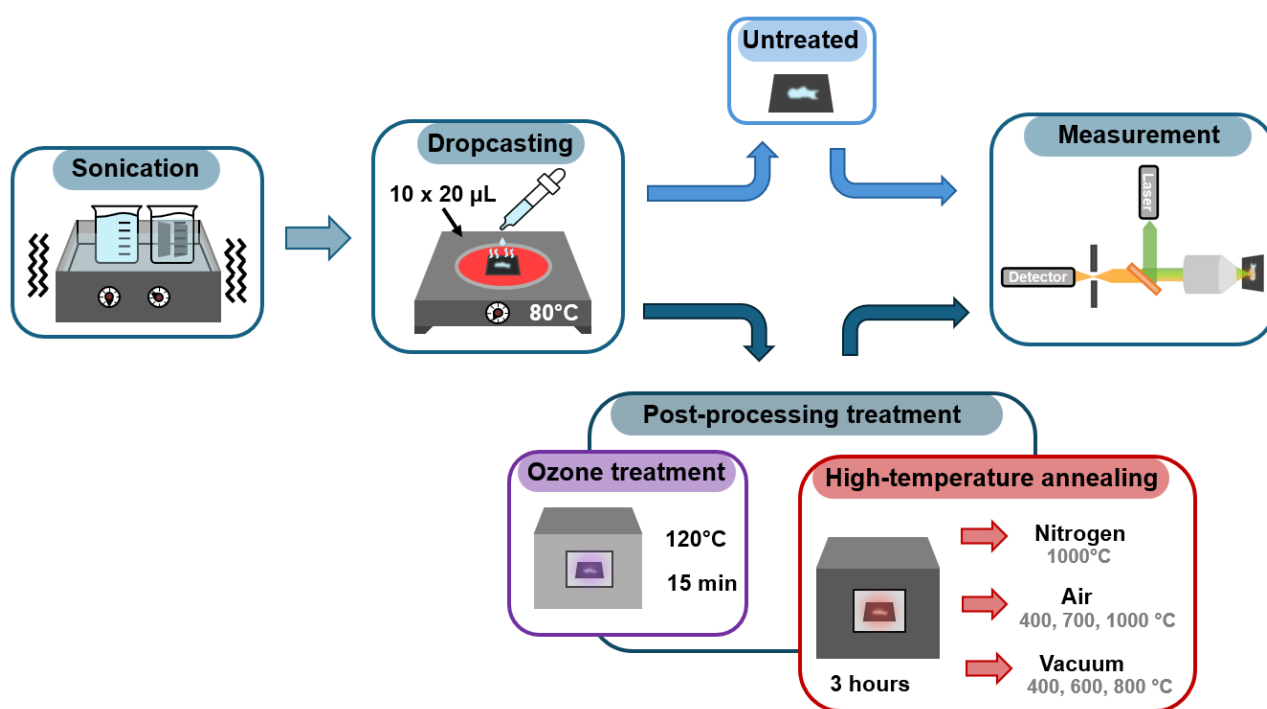


Figure 3.1: Schematic diagram showing the sample preparation. First, the hBN solution and the cover slides or wafers are sonicated. The silicon wafer is then placed on a hot plate and ten 20 µL are dropcast onto the heated slide. The untreated sample is done after this step, otherwise a post-processing treatment (PPT) is applied. Different PPTs consist of ozone treatment or high temperature annealing conducted under various atmospheres and temperatures.

First, the hBN flakes are sonicated for ten minutes in an ultra sonic bath (TI-H-10, Elma Schmidbauer GmbH) and the sample cover slides are cleaned for sample preparation. Slides are either made of borosilicate glass (24 x 24 mm, Epredia) or silicon (Square CZ-Si wafer (25 x 25 mm) with a thickness of $500 \pm 25 \mu\text{m}$, p-type (Boron) from the company MicroChemicals GmbH). The cleaning procedure for the sample cover slides of either material is identical. They

are first cleaned with extra pure acetone (D0490, Honeywell), then rinsed with distilled water and subsequently sonicated in 5 % Hellmanex® III solution (Hellma® Analytics). After that, they are rinsed with ethanol (S 99 % VG 1 %, SAV Liquid Production GmbH), then distilled water and subsequently dried using compressed air.

The slides are placed on a hot plate (D-6010, neoLab Migge GmbH) with a temperature of 85 °C to accelerate the drying process of the dropcast solution. Using a microliter pipette, between one and twelve 20 µL drops are dropcast onto the heated sample slides.

Samples are either characterized after this step or alternatively, a post-processing treatment (PPT) is applied. Based on common treatments mentioned in literature (see section 2.5.2.4), high temperature annealing and ozone treatment are chosen to investigate whether they improve the creation of single-photon emitters, as well as their photon flux stability and single-photon purity.

The ozone treatment is carried out for 15 min at a temperature of 120 °C. Thermal annealing is applied for three hours on each sample and different temperatures and atmospheres are tested: nitrogen at 1000 °C, vacuum at 400 °C, 600 °C, and 800 °C, and air at 400 °C, 700 °C and 1000 °C, respectively. Argon is most commonly chosen as an inert atmosphere for annealing (see Table 2.1), however nitrogen provides an equally unreactive environment and is therefore an adequate substitute. The temperatures for the sample preparation are chosen based on device availability (high-temperature ovens and ozone cleaner) and their capabilities.

Fig. 3.2 shows the temperature profile for annealing at 400 °C in air, serving as both the actual progression and a representative example for the other annealing conditions. The sample is heated at 13 K/min to rapidly reach the target temperature, maintained there for 3 h, and subsequently cooled down slowly.

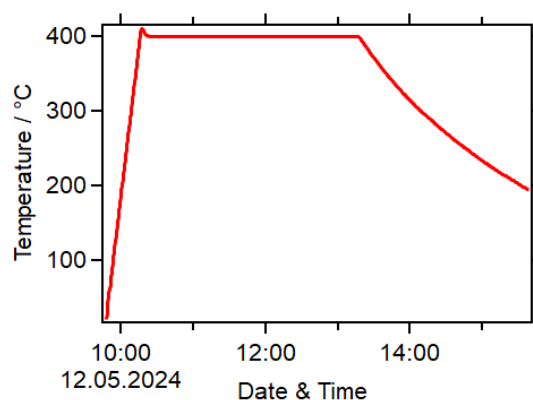


Figure 3.2: Progression of the temperature during the annealing process with a heating rate of 13K/min. The sample is allowed to cool down passively after the annealing step with no controlled cooling rate.

A light microscope image of such a prepared sample is shown in Fig. 3.3. The light microscope (Panthera C2, Trinocular, Motic) is a transmission microscope; for imaging the samples on Si wafers, a goosehead illuminator (KL1500 compact, Schott AG) is used to illuminate the

sample from above. Fig. 3.3a shows an image of the sample with four times magnification: the dropcasting process leaves behind lines of dense hBN flakes and the concentration of flakes over the sample is uneven. The ten times magnification in Fig. 3.3b shows the difference between a high density area and a low density area with a sharp transition.

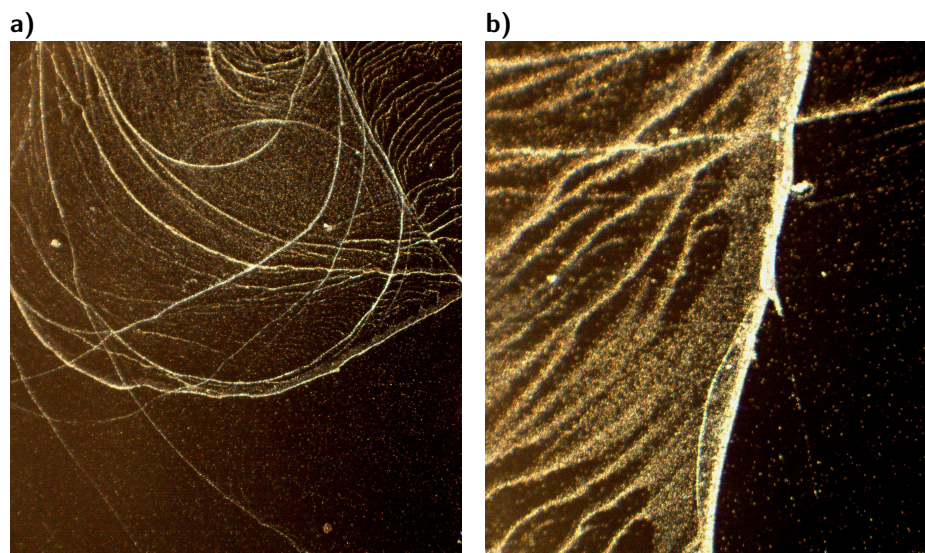


Figure 3.3: Images of an hBN sample (hBN15) with a light microscope under **a)** four times magnification or **b)** ten times magnification. Areas with a high flake concentration are visible as bright lines ('dropcast lines'), while areas with a low flake concentration show the single flakes as small bright dots standing out from of the dark background of the Si wafer.

The prepared samples are numbered for their identification; a table of sample names, their substrate, concentration and PPT is attached in the Appendix.

3.2 Confocal microscope setup

The characterization of the samples is carried out with a confocal microscope. The general working principle was explained in Section 2.6, whereas this section will describe the specific setup used for this work.

Fig. 3.4 shows a simplified sketch and Fig. 3.5 shows photographs of the setup. A 532 nm continuous wave laser (Ventus 532, Novanta Photonics) is used to excite the sample. A neutral density filter wheel (NDC-100C-4M, Thorlabs Inc.) is used to select the desired excitation power. Afterwards, a laser line filter (532 nm MaxLine® (LL01-532-12.5), Semrock) is used to remove possible side-band wavelengths of the laser. Two plano-convex lenses are used to widen the beam, which is reflected by a dichroic beamsplitter (FF560-FDi01-25x36, Semrock) onto a silver mirror (PF10-03-P01, Thorlabs Inc.).

So far, the beam path has stayed horizontal, i. e. parallel to the optical table. The mirror reflects the beam into the vertical, where it is collected by a microscope objective. For samples on cover glass, an oil immersion objective (CFI Plan Apochromat Lambda, MRD31905 100x

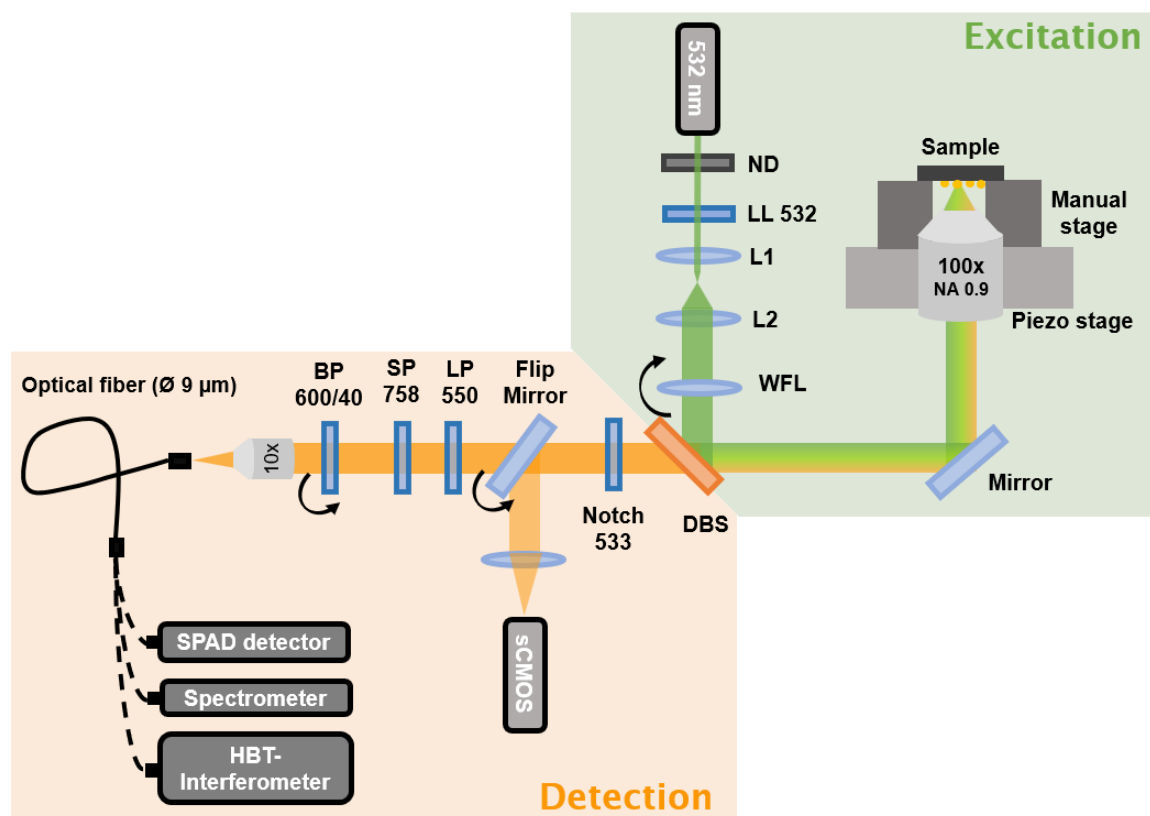


Figure 3.4: Sketch of the confocal setup used for the characterization of the single-photon emitters. The light from a 532 nm excitation laser passes through a neutral density filter (ND), a laser line filter (LL) and two lenses, which are used to broaden the excitation beam. It is focused by a microscope objective, which also collects the emission light. The emission light then passes through a dichroic beam splitter (DBS) and is spectrally filtered by a notch filter at 533 nm, a 550 nm long pass filter (LP), a 758 nm short pass filter and a 600 nm band pass filter (BP) with 40 nm bandwidth. Then the filtered emission light is coupled into a fiber, which is connected to either a single SPAD detector, an HBT interferometer or a spectrometer. Alternatively, a wide-field lens (WFL) and a mirror can be placed in the beam path to excite a large area of the sample and thus obtain its emitted microphotoluminescence, which is captured by an sCMOS camera.

Oil A, Nikon) with 100x magnification and a numerical aperture of 1.45 is used. Since Si-wafers are opaque, the oil immersion objective has to be replaced by air objective (100x magnification, NA = 0.95, MPLAPON100X M Plan Apochromat, Olympus) for samples on these wafers. The vertical orientation is chosen so that the sample is placed horizontally on top of the objective; thereby the immersion oil will not drip and can spread homogeneously between objective and cover glass.

Before the excitation beam is collected by the objective, its optical power can be measured with a power meter (S170C, Thorlabs) that can be flipped into the beam path.

For focusing the beam onto the sample with the immersion oil objective lens, Immersol 518 F oil (by Zeiss) is used. This immersion oil has been chosen for its low auto-fluorescence. The focused laser light then excites the sample mounted above the objective.

As described in section 2.6, a confocal microscope requires scanning of a sample to obtain the

complete fluorescence image of a specific area of the sample, since only one spot is illuminated at a time. This scanning procedure is carried out with a piezo actuator translation stage (P563.3CD, PI (Physik Instrumente) L.P.), on which the sample is mounted. The stage has a travel range of 300 μm in x, y and z directions and a resolution of 0.5 nm to 2 nm (travel range depends on closed-loop or open-loop operation). This stage is controlled by a digital piezo controller (E-725.3CD, PI (Physik Instrumente) L.P.) to position the stage precisely. Therefore, positioning of the sample relative to the objective is limited to a 300 μm by 300 μm square. To circumvent this limitation, a manual translation stage (built in-house) is mounted on top of the piezo stage and can be used for rough, manual positioning (travel range 1.5 cm with a resolution of 1 μm).

The fluorescence of the sample is collected by the same objective. It is then reflected by the silver mirror and passes through the dichroic beamsplitter. Behind the dichroic mirror, a notch filter (NF533-17, Thorlabs Inc.) is used to eliminate possible reflections of the excitation beam. The light then passes through a 550 nm long pass filter (FELH0550, Thorlabs Inc.) to further suppress the excitation beam and a 758 nm short pass filter (F39-758, Semrock) to cut off background noise outside the desired emission band. A 600/40 nm bandpass filter can be flipped into the beam path. The filtered emission light is then coupled into a single-mode fiber ($\varnothing 9 \mu\text{m}$, SMF-28e+, Corning) by a 10x magnification objective (10X EO HR Infinity Corrected Objective, Edmund Optics). The single-mode fiber is either connected to a SPAD detector (SPCM-AQRH-16-FC, Excelitas Technologies), to a beamsplitter (TM50R5F1A, Thorlabs Inc.) for a Hanbury-Brown & Twiss interferometer or to a spectrometer.

In this work, two Excelitas detectors (SPCM-AQRH-16-FC) are used to count the photons emitted by the sample. The dark count rate of the detectors, according to the data sheet, should not exceed 25 counts/s and the corresponding efficiency in a wavelength range of 550 nm to 700 nm should be between 60 % to 70 %.

3.2.1 Camera image with wide-field illumination

Instead of coupling the emission light into a fiber for confocal scans or other measurements, a camera can be used to obtain a live image of the fluorescence emitted by the sample. For this, a wide field lens ($f = 500 \text{ mm}$, LA1380, Thorlabs Inc.) can be flipped into the excitation beam path, which ensures a wide-field ("broad") illumination of the sample instead of excitation in a focused spot.

The fluorescence of the sample is collected by the objective, passes through the dichroic mirror and is then diverted to a sCMOS camera (Orca Flash 4.0, Hamamatsu) by a mirror that can be flipped into the beam path. A lens tube with a 10x magnification lens ($f = 250 \text{ mm}$, 88-925, Edmund Optics) is mounted in front of the camera to focus the light.

With the wide-field illumination, a bigger area of the sample can be illuminated and analyzed in comparison with confocal excitation. An example of the camera image with the wide field

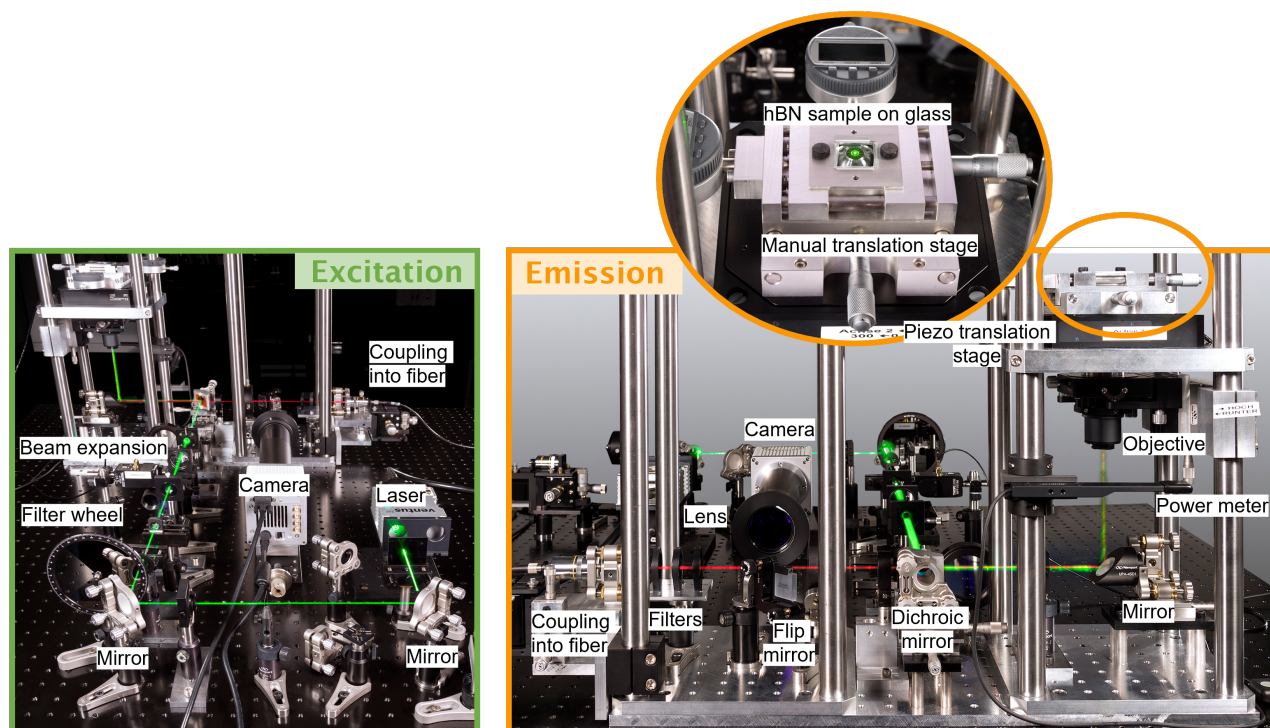


Figure 3.5: Pictures of the room-temperature confocal setup. The excitation pathway is shown on the left, where the laser beam (green) is reflected by two mirrors before passing through the filter wheel. The beam is expanded before being reflected by the dichroic mirror. This can be seen in the picture on the right, which shows the emission pathway. The excitation beam is reflected by the dichroic mirror and another mirror before being collected by the objective. An hBN sample on glass is shown on top as an inset, where the focused laser spot can be seen. The emission light (red) is then collected, passes through the dichroic mirror and optical filters. Finally, the emission is coupled into a single-mode fiber. A flip mirror is used optionally to capture the image of the fluorescence emitted using wide-field excitation of the sample on the camera.

lens is shown in Fig. 3.6. The image was taken with the wide-field configuration at an optical excitation power of $150\ \mu\text{W}$. The emission of the hBN defects can be seen as bright dots.

To determine the scale of the area visible in the camera, the camera image is compared with a scan. A diamond sample with a prominent X-marker on the edge of the crystal is positioned in the field of view in the camera (see Fig. 3.7a) and then a scan of the area is taken (see Fig. 3.7b). The photoluminescence scan shows the x and y position of the piezo translation stage in micrometers (more detail on the PL scans in Section 3.3.1).

The marker is fully visible both in the image displayed by the camera (wide-field mode) and in the scanned image (confocal mode). The scan provides the dimensions of the marker ($30\ \mu\text{m}$ by $30\ \mu\text{m}$). Given that the marker fills the complete camera image, it can be concluded that the area on the sample visible with the camera is likewise $30\ \mu\text{m}$ by $30\ \mu\text{m}$.

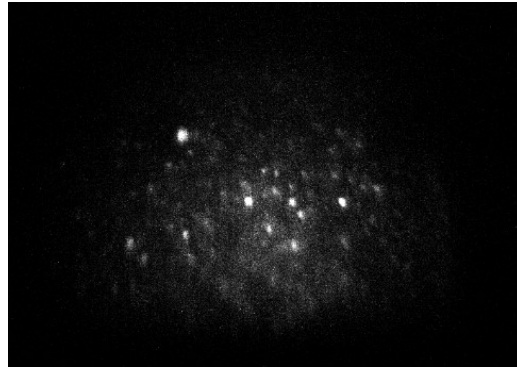


Figure 3.6: Camera image of an hBN sample (hBN04) in wide-field illumination at an optical excitation power of $150\ \mu\text{W}$. The diameter corresponds to approximately $30\ \mu\text{m}$. The bright dots correspond to the fluorescence emitted by the sample.

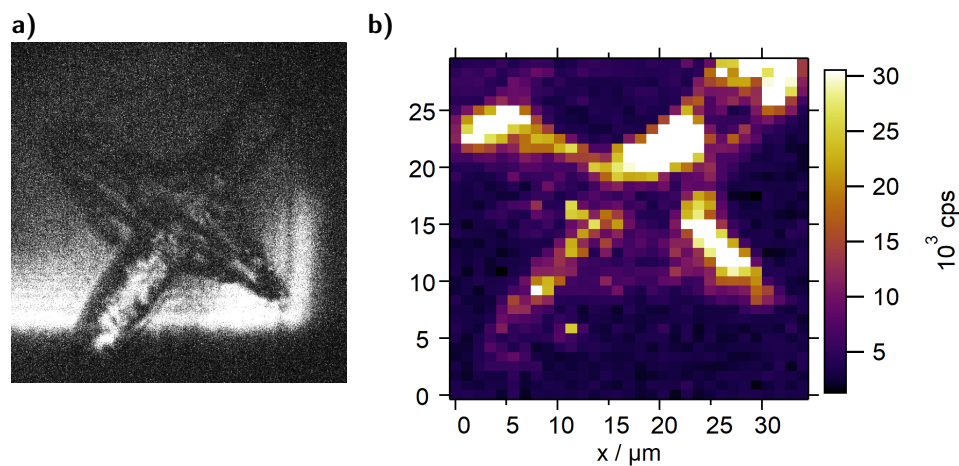


Figure 3.7: Comparison of sCMOS camera image and photoluminescence scan. **a)** shows the X-marker on an SnV-diamond sample positioned on the edge of the crystal. **b)** shows a photoluminescence scan of the same area. The x and y axis show the micrometer position of the piezo translation stage and the color bar on the right indicates the count rate, which has been limited to $30 \cdot 10^3 \frac{\text{counts}}{\text{s}}$ for better contrast.

3.2.2 Laser power characterization

As mentioned, the laser excitation power can be selected by rotating an ND filter wheel in the excitation beam path. To automate this process, the ND filter wheel is mounted on a rotation stage (RS-120, Physik Instrumente). The rotation stage is controlled with a controller (C-863, PI) via their software PIMikroMove (PI) or in an integrated LabVIEW program (see section 3.3.6 for details). With this, the LabVIEW script can measure the saturation characteristic of the emitters automatically (see section 3.3.2). The ND filter wheel has a coated area ($\sim 270^\circ$) in which the attenuation of the laser beam can be adjusted continuously, while the remaining 90° are uncoated. To know which angle of the rotation stage corresponds to which power, the excitation power is measured below the objective for every angle in 1° steps. A graph of the resulting power/angle dependency is shown in Fig. 3.8. The ND filter wheel is roughly aligned

so that $0^\circ - 270^\circ$ corresponds to the coated, attenuating region, and $270^\circ - 360^\circ$ to the uncoated, fully transmitting region.

In this work, most measurement are carried out at $102\ \mu\text{W}$ excitation power at an angle of 86° . If the reference position of the stage is lost and has to be reset, the power/angle dependency measurement has to be repeated.

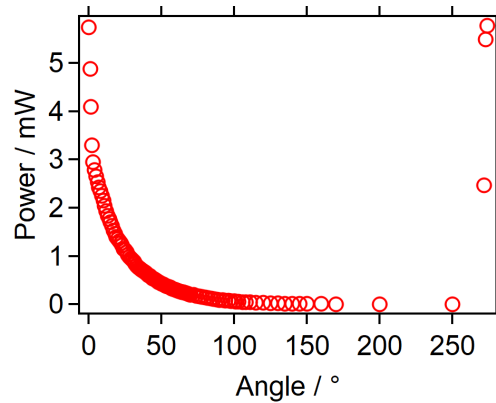


Figure 3.8: Graph of the optical excitation power dependence on the rotation stage angle. The x-axis shows the angle of the rotation stage (i. e. ND filter wheel) and the y-axis the corresponding laser power measured in front of the microscope objective.

3.2.3 Spectrometer

To investigate the emission spectrum of the emitters, the output fiber is connected to a liquid nitrogen cooled spectrometer (iHR320, HORIBA Ltd., Kyoto).

Fig. 3.9 shows a sketch of the spectrometer that illustrates its working principle. The output single-mode fiber of the confocal setup is connected to the multi-mode fiber of the entrance slit (bottom left) through which the light enters and hits a collimating mirror (top left). The collimated beam is diffracted by a grating (bottom middle) into its different wavelengths and then focused by another mirror (top right) onto the focal plane of the camera (bottom right). A liquid nitrogen-cooled CCD camera (Type CCD30-11; Model CCD-1024x256-bidd-3ls) is used to detect the light.

There are three different gratings available, which are mounted on a rotating turret. The gratings have different resolutions. In this work, the third grating is used because it has the lowest resolution and therefore covers the largest range (part number 510-49). It has 150 grooves / mm with a blaze wavelength of 500 nm (covering >500 nm). The other gratings show higher resolution but a smaller spectral range (40 nm to 80 nm). Emission of the hBN point-defects typically cover ~ 100 nm with no fine structures to be resolved, which is why these finer gratings are not necessary.

The spectrometer is calibrated by using different reference light sources (Hg/Ar pen lamp (LSP035) by Lot-QuantumDesign GmbH and a 638 nm laser (MCLS1-638) by Thorlabs), which are fixed in front of the spectrometer fiber. Then the spectrum is measured with the spectrome-

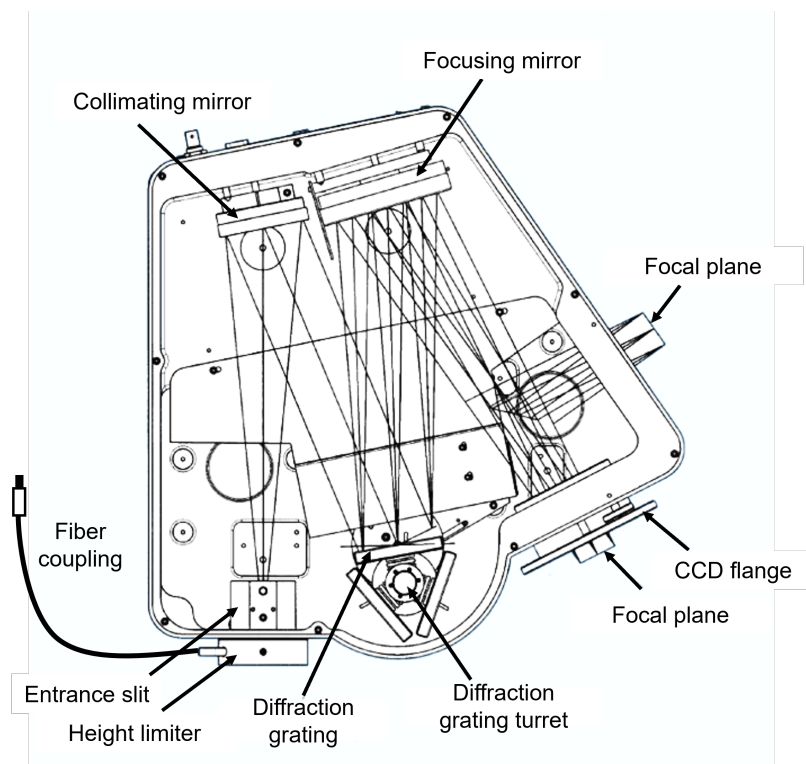


Figure 3.9: Sketch of the iHR320 spectrometer. Emission light enters via a fiber at the entrance slit (bottom left), which is collimated by an off-axis parabolic mirror (top left), and subsequently directed onto the selected diffraction grating (bottom middle) mounted on a turret. The grating separates the light into its different wavelengths, which are then focused by a second off-axis mirror onto a CCD camera (bottom right) (adapted from [87]).

ter and compared to the reference spectrum of the light source. The peak positions are adjusted to the correct wavelengths according to the reference spectrum. This is repeated for all gratings. It is important to note that this procedure only calibrates the wavelength positions, not the intensity of the peaks.

3.2.3.1 Spectrum correction

The CCD camera of the spectrometer converts incoming photons into electrons with a wavelength-dependent efficiency. The manufacturer-specified quantum efficiency in the range of 300 nm - 1100 nm is shown in Fig. 3.10a. Within the spectral range relevant to hBN emission, the efficiency increases from below 90 % at 500 nm to approximately 95 % at 750 nm, indicating an inhomogeneous spectral response. In addition, the spectrometer's optical components and the selected grating introduce further wavelength dependent effects. Consequently, the measured intensity does not directly represent the true optical emission but rather the product of the actual spectrum and the spectrometer's wavelength-dependent sensitivity, $R(\lambda)$.

To determine $R(\lambda)$, a calibrated quartz halogen lamp (OSRAM XENOPHOT Airfield-Lamp HLX 64361, 6.6 A, 150 W) with a known relative emission spectrum is measured using the spectrometer. A corresponding background measurement is acquired and subsequently subtracted

from the measured lamp spectrum. Fig. 3.10b shows the resulting background-corrected spectrum (I_{meas}) alongside the reference spectrum I_{ref} , normalized to their wavelength-dependent irradiance within the range of 540–760 nm. This is the range limited by the optical setup and corresponds to the spectral region relevant for hBN emission.

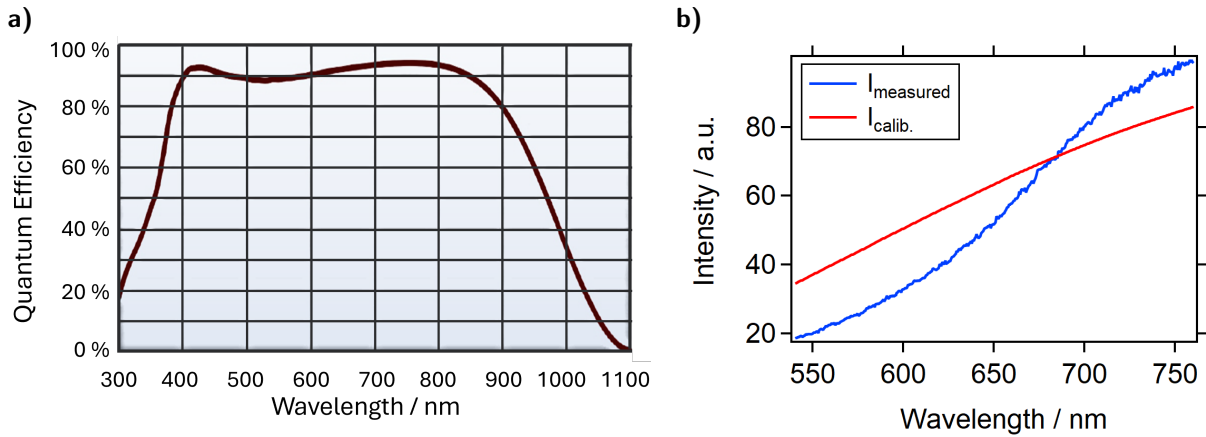


Figure 3.10: **a)** Quantum efficiency of the spectrometer’s CCD camera according to the manufacturer (adapted from [88]). **b)** Measured spectrum of a calibrated halogen lamp (blue) in comparison with the reference spectrum (red).

When comparing Fig. 3.10a and Fig. 3.10b, it can be seen that the measured spectrum (blue curve in Fig. 3.10b) deviates from the reference (red) proportionally to the detector sensitivity between 550 and 750 nm in Fig. 3.10a: the spectrometer underestimates intensities between 540 and 650 nm and overestimates those at longer wavelengths in comparison to the reference spectrum. The wavelength-dependent sensitivity is therefore obtained by dividing the measured lamp spectrum by the known reference spectrum,

$$R(\lambda) = \frac{I_{\text{meas}}(\lambda)}{I_{\text{ref}}(\lambda)}, \quad (3.1)$$

where the reference data points are interpolated to match the wavelength spacing of the measured spectrum.

To correct a measured spectrum, the recorded intensity is divided by the obtained wavelength-dependent sensitivity function:

$$I_{\text{corr}}(\lambda) = \frac{I_{\text{meas}}(\lambda)}{R(\lambda)}. \quad (3.2)$$

This correction yields a spectrum that more accurately represents the true emission intensity, independent of the instrument’s spectral response. The validity of the correction procedure is verified by applying it to the measured lamp spectrum, which, after division by $R(\lambda)$, reproduces the reference spectrum. All emission spectra are corrected in this manner prior to further analysis to avoid introducing systematic bias.

The effect of the correction procedure is demonstrated in Fig. 3.11. The uncorrected (measured) spectrum is shown in blue, while the corrected spectrum is displayed in red. After correction,

the relative intensity of the ZPL increases noticeably, highlighting the importance of the spectral calibration - particularly for quantitative analyses such as determining the full width at half maximum (FWHM) or calculating the Debye–Waller factor (see Section 4.2.5).

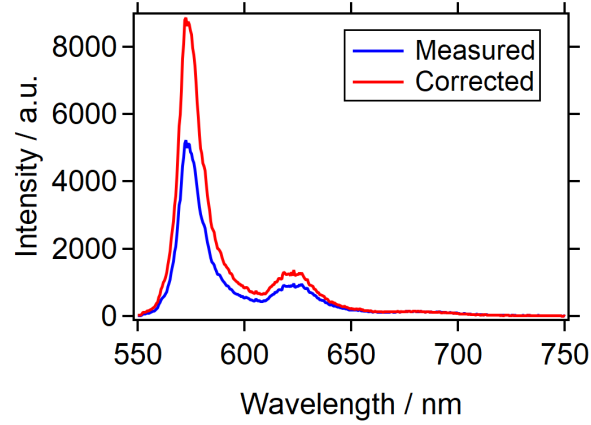


Figure 3.11: Spectrum of an hBN emitter before (blue) and after (red) correction with the wavelength-dependent sensitivity function (emitter E73, hBN08).

3.2.4 Transmission

The efficiency of the measurements is affected by the optical losses in the setup. Therefore, the setup transmission is measured and improved where necessary. The measurement procedure is outlined in Fig. 3.12. A 4-channel fiber coupled laser source (638 nm, MCLS1-638, Thorlabs) needs to be connected to the output single mode fiber, but since the multi mode laser fiber and the output single mode fiber of the setup (SM fiber 1) have different core diameters, losses occur due to this mismatch. Therefore, the same type of single mode fiber as SM fiber 1 is connected in between (SM fiber 2). This way, the losses between SM fiber 1 and SM fiber 2 are minimized and the transmission for SM fiber 1 can be more accurately measured.

After being coupled into the fiber, the red laser light propagates through the optical path in the opposite direction to the sample emission. The optical power is measured for a time interval of 30 s before and after each component and the average is determined by the power meter (PM100D, Thorlabs). For each component, this measurement is repeated ten times. The average of these ten measurements is calculated for before and after each component and the ratio is calculated to obtain the transmission T . Furthermore, the standard deviation σ is calculated and used to calculate the relative uncertainty:

$$\sigma_{\text{rel}} = \sqrt{\left(\frac{\sigma}{T}\right)_{\text{before}}^2 + \left(\frac{\sigma}{T}\right)_{\text{after}}^2}. \quad (3.3)$$

"Before" and "after" refers to the standard deviation of the ten power measurement before and after a component. The uncertainty for the total transmission is calculated from these relative uncertainties with

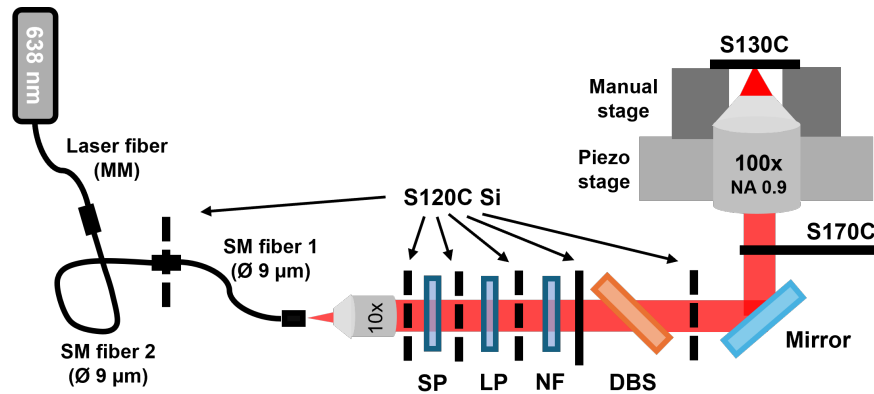


Figure 3.12: Sketch presenting the transmission measurements of the setup. A red laser (638 nm) with a multimode (MM) laser fiber is connected to an single mode fiber (SM fiber 2, diameter = 9 µm) which is connected to the outcoupling setup fiber of the same diameter (SM fiber 1). The red laser light is then guided through each relevant component (fiber coupling objective, short pass filter (SP), long pass filter (LP), notch filter (NF), dichroic beam splitter (DBS), mirror and objective). The power is measured before and after each component by a photodiode. Most of the components are measured with a S120C Si photodiode (black dashed lines indicate the positions), but in front of the objective, the fixed S130C photodiode is used, while a S170C photodiode is mounted at the sample position.

$$\sigma_{\text{total}}^2 = \sum \sigma_{\text{rel}}^2. \quad (3.4)$$

The transmission measurements are performed using different Thorlabs photodiodes. A Si photodiode (S120C) is employed for most positions along the beam path and mounted sequentially behind each optical component, as indicated by the dashed or solid black lines in Fig. 3.12. The optical power below the microscope objective is measured using a fixed S130C photodiode, while a S170C photodiode is used to determine the power at the sample position behind the objective. The latter features a sensor area comparable in size to the sample slides and can be securely mounted on the sample holder.

To correct for differences in detector sensitivity, all photodiodes are cross-calibrated by mounting each at the same position and measuring the optical power following the same procedure used for the transmission measurements. The S130C measures $(99.92 \pm 0.6) \%$ of the optical power compared to the S120C, while the S170C measures $(100.73 \pm 0.99) \%$ relative to the S130C. The transmission values and associated uncertainties for the relevant optical components (mirror and microscope objective) are adjusted accordingly. As a result, these elements exhibit higher uncertainties than the other components in the optical path.

The determined transmission values are shown in Table 3.1 together with the optical component, their part number and the transmission according to the manufacturer. Manufacturer information on the transmission of the objective used for coupling the emission into the fiber and also the fiber itself is not available.

Initially, biggest loss was introduced by the air objective with only 60 % transmission, even though according to the manufacturer, the transmission in this wavelength range should be

Table 3.1: Transmission data of the confocal setup. The first column lists the specific components assessed that influence the transmission of emission light, with the second column providing the part numbers. The next two columns display the transmission values for each component. Included are the manufacturer's transmission values for the emission wavelength and the transmission measured using a power sensor. The last column lists the calculated uncertainties for each measured transmission value.

Optical component		Transmission ($\lambda = 638$ nm)		
Description	Product number	Manufac.	Measured	Uncertainty
Air Objective	Zeiss EC Epiplan-Neofluar 100x/0,9 Pol M27	92.00 %	87.05 %	1.03 %
Mirror	Thorlabs (PF10-03-P01 Protected Silver)	96.00 %	99.12 %	0.43 %
Dichroic mirror (DBS)	Semrock (FF560-Di01-25x36)	97.40 %	95.70 %	0.07 %
Notch Filter (NF)	Thorlabs (NF533-17)	> 98.00 %	98.90 %	0.06 %
Short pass filter (SP)	Semrock (F39-758)	> 98.00 %	98.89 %	0.07 %
Long pass filter (LP)	Thorlabs (FELH0550)	> 95.00 %	95.89 %	0.07 %
Objective 10x	Edmund Optics (#43-907)		88.40 %	0.08 %
SM fiber	Corning (SMF-28e+)			
Total		Multiplied:	68.46 %	1.13 %

approximately 92 %. This discrepancy was likely introduced through the broad laser beam, so that not all laser light is collected by the objective. A pinhole has been used to narrow the beam to account for this, which yields a transmission of 87.05 % thereby reducing the discrepancy significantly. However, the air objective remains the largest contributor to the loss of the system.

The total transmission can be determined by measurement or by multiplying the transmission of each component. Measuring the power at the start (before the fiber) and at the end (after the objective) is not directly possible, because the pinhole in front of the objective limits the beam, therefore the power is greatly reduced. Opening the pinhole, however, will lead to less collected light by the objective. Therefore, the transmission before the objective can be compared instead. The transmission obtained by measuring the power before the SM fiber 1 and below the objective is (76.46 ± 0.44) %, where the uncertainty is calculated using Eq. 3.3.

The transmission obtained by multiplying the individual transmission values instead uses the uncertainty propagation from Eq. 3.4 and gives a value of (78.64 ± 0.46) % (below the objective). For the total transmission, including the independently measured transmission for the objective, the total system transmission reduces to (68.46 ± 1.13) %.

According to manufacturer specifications, the transmission of the employed optical components is expected to vary only weakly over the hBN emission range (550–700 nm). While a slight decrease in transmission efficiency may occur at wavelengths above ~ 650 nm, and a minor increase below ~ 600 nm, these variations are small compared to the overall uncertainty. Therefore, the total transmission efficiency of (68.46 ± 1.13) %, determined at 638 nm, is taken as a good

approximation for the hBN emission spectral range.

3.3 Measurement procedures

This section will describe the different measurement methods needed to characterize the different parameters of hBN samples that describe their photon emission performance.

3.3.1 Photoluminescence scans

The first step in characterizing the samples is to carry out photoluminescence scans. For this purpose, the sample is placed on top of the piezo nanopositioning stage, which moves the sample relative to the objective while collecting the counts at each position.

The piezo stage used in this setup has a travel range of 300 μm in x, y and z direction with a resolution of 2 nm. It is controlled via an open-loop piezo controller that is connected to a data acquisition (DAQ) card through the analog input channels. The piezo controller is set up for analog control with a jupyter script (see Appendix, 9.3.2).

When operating a piezo stage in open-loop mode, the actual position is not fed back or compared to the commanded position. It is therefore essential to operate below the mechanical resonance frequencies of the stage. Near resonance, the motion can become strongly amplified, distorted and ultimately damage the stage [89]. At higher driving frequencies, the stage cannot reliably follow the input signal due to its limited mechanical bandwidth, leading to phase lag and a distorted scan image. The resonance frequencies themselves depend on the mechanical load. For the present setup, which includes a manual translation stage mounted on top, the manufacturer specifies resonance frequencies of 93 Hz in the x- and y-directions and 148 Hz in the z-direction. Accordingly, the stage should be operated at frequencies below these values to ensure stable and accurate positioning.

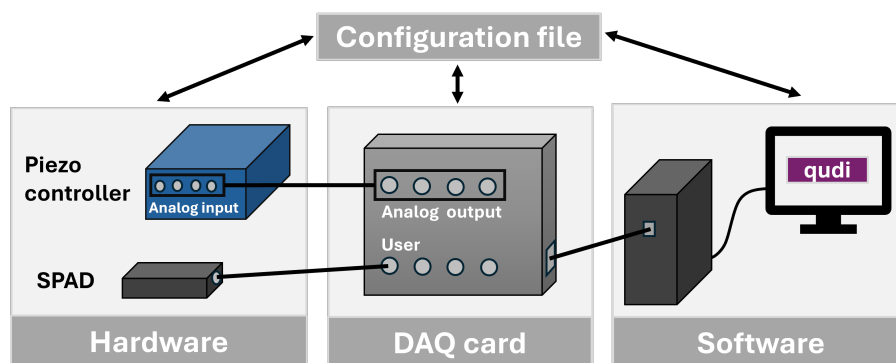


Figure 3.13: Block diagram of the setup for qudi. The necessary hardware (piezo controller and SPAD detector) are connected with BNC cables to the data acquisition card (DAQ card). The DAQ card is connected to the PC. A configuration file communicates between the elements by defining hardware parameters, input and output channels of the DAQ card and the desired software modules.

The scans are performed using the software qudi, a python-based program designed for experiment control [90]. The program requires a configuration file that establishes the connections between the hardware, the DAQ card and the software. This is demonstrated in Fig. 3.13.

The hardware (SPAD detector and piezo controller) is connected via BNC cables to the DAQ card, which is in turn connected to the computer. A configuration file communicates between these elements by defining hardware parameters such as travel range and piezo frequency, setting up the connected channels (analog output for the piezo controller, specific user channel for the count rate of the SPAD) and connecting these parameters to the desired software elements (configuration file in Appendix).

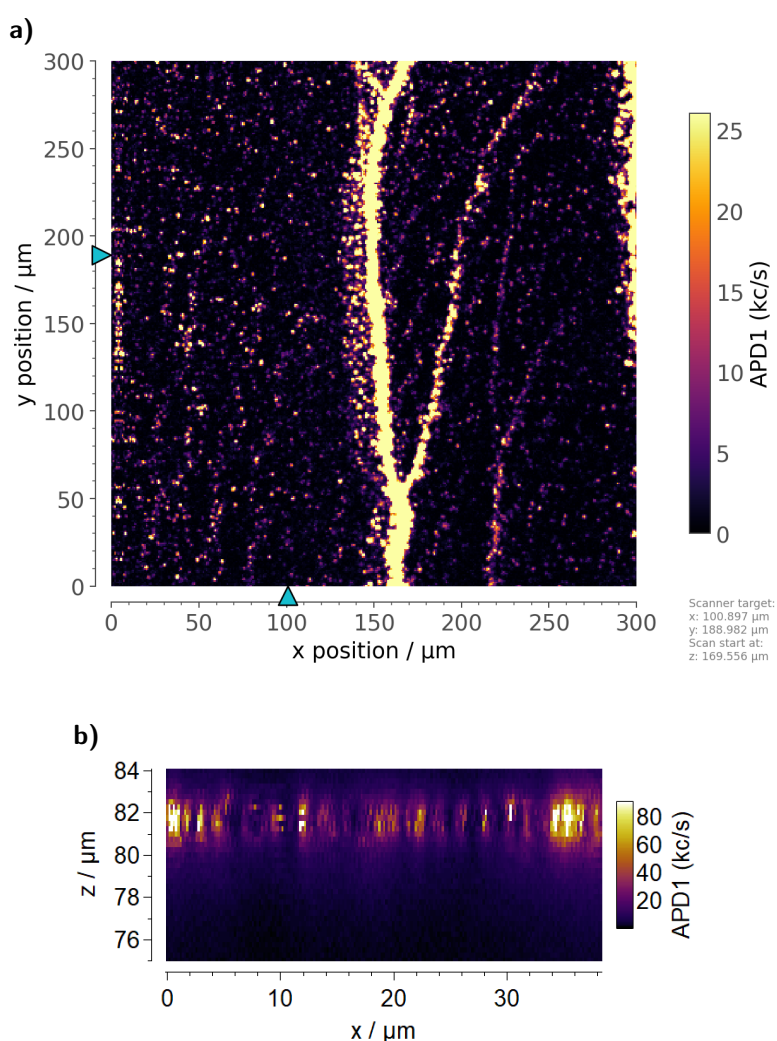


Figure 3.14: Example of photoluminescence scans of hBN samples. The x and y axis show the piezo position and the color bar on the side shows the corresponding counts at each point of the scan (in $1 \cdot 10^3 \frac{\text{counts}}{\text{s}}$). The maximum count value on the color scale is adjusted in both scans to achieve better contrast. **a)** shows a full range xy-scan (300 μm by 300 μm) of sample hBN15 with a resolution of 350 by 350 pixels corresponding to a step size of 0.85 μm. **b)** shows a 2-dimensional focus scan, with a step size of 0.2 μm in x direction, and 0.375 μm in z direction. The focus plane can be seen at approximately 82 μm, where the emitters exhibit the highest count rate.

The full 300 μm by 300 μm range is scanned in approximately 15 min with a large step size of 1 μm , which is used for an estimation of emitter density and rough positioning on the sample. An example of a full range scan is shown in Fig. 3.14a.

The x and y-axes show the piezo translation stage position of the 2D-image while a color scale represents the count rate in kcounts/s. High-density dropcast-lines are visible in the middle, while other areas have a lower emitter density with space between individual emitters, similar to the light microscope images in Fig. 3.3.

After the full range scan, higher-resolution scans of smaller areas with the desired emitter density are performed. A step size of 0.2 μm is generally sufficient to adequately resolve the hBN emitters while still maintaining a high scanning speed. Here, it is important to note that in qudi, the step size is not set directly. Instead, the resolution is selected by the number of pixels for the scan. In that case, a 300 μm by 300 μm scan with a resolution of 300 by 300 pixels corresponds to a step size of 1 μm . To select an emitter for further evaluation, a crosshair can be moved to the desired position; however, due to the open-loop operation mode, the crosshair position is slightly offset to the left (approx. 1 μm).

The optimal focus for different emitters may vary due to the different orientation of the flakes. To determine the focus plane, scans in the z-direction can be carried out. Focus scans can be performed either as a one-dimensional scan with a fixed x-y position, or as a two-dimensional scan. An example of a 2D-focus scan is shown in Fig. 3.14b, where the y-position of the piezo translation stage is fixed while x and z directions are being scanned. The focus lies generally at the position where the emitters exhibit the highest count rate. With the 2D-scan, the average focus position of the emitters can be selected, and individual emitters can be focused on using a one-dimensional z-scan.

Before using qudi, Agilent Vee (Keysight Technologies) was used for scans with a program written in the working group. This method of taking scans does not use the DAQ card and instead uses the digital controller directly. Furthermore, the count rate in Agilent Vee is taken by using frequency counters (53220A, Keysight Technologies). This process is significantly slower and was therefore later changed to qudi. Differences in functionality are limited to how the scan speed and piezo step size are set.

3.3.2 Saturation measurements

To measure the saturation behavior of an emitter, the excitation power is continuously increased while the count rate is measured for each excitation power. Excitation powers between 10 μW and 4 mW are selected and set with the ND filter wheel on the rotation stage. The emitter is measured for 60 s at each specific power and the average count rate is recorded. This process is repeated for background noise close to the emitter.

This can be done manually with PIMikroMove and TimeTagger Lab software to record the count rate or with a LabView code developed in this work. In this code, the corresponding

angles for the desired excitation powers are set and then the count rate at each angle is measured for one minute and saved.

For the analysis, the background signal is subtracted from the emitter signal to remove the background contribution. The resulting count rate is plotted against the excitation power (P). The resulting curve shows the saturation behavior (intensity I) of the emitter and is modeled with the equation:

$$I = \frac{N_{sat}}{1 + \frac{P_{sat}}{P}} + m \cdot P \quad (3.5)$$

where N_{sat} is the count rate at saturation, P_{sat} is the saturation power and m is a factor to describe the linear portion of a possible remaining background contribution [76]. Since the background at the emitter position cannot be measured directly, the nearby background is used as an estimate. The background signal at the emitter position might deviate, thereby introducing a linear contribution that is not attributed for by the background correction.

3.3.3 Second-order correlation measurement

To measure the second order correlation function, the output single-mode fiber is connected to a beamsplitter and subsequently to two SPAD detectors (SPAD 1 and SPAD 2). The detectors are connected to a TimeTagger (TimeTagger 20, Swabian Instruments GmbH) with BNC cables, but the signal of SPAD 1 is split with a T-junction, with one side going to the DAQ card (for scans) and the other to the TimeTagger. This creates a reflection at the TimeTagger possibly due to impedance mismatch: the count rate at the TimeTagger is double the amount of the count rate the DAQ card records.

When the DAQ card measures 10 kcounts/s, the TimeTagger registers 20 kcounts/s. Separate BNC connections confirm the correct rate is 10 kcounts/s. Since an impedance-matching transformer suppresses the signal at one device, the TimeTagger trigger level is adjusted accordingly to match the correct signals: 1 V for SPAD 1 and 0.5 V for SPAD 2.

The correlation measurement is taken in either TimeTagger Lab or in the self-written LabVIEW code. The count rate is taken simultaneously. Generally, the parameters for the $g^{(2)}(\tau)$ measurements are 400 bins with a resolution of 200 ps and for the count rate measurement 1000 points with an integration time of 100 ms.

In Fig. 3.15a, the raw data of such a correlation measurement is shown. The x-axis shows the time delay and the y-axis the coincidence events. The time delay is recorded in picoseconds by the time tagger that correlates the signal from both detectors. The anti-bunching dip does not lie directly at zero time delay. This shift in the time delay can be caused by different length optical fibers or BNC cables which introduce a signal delay.

First, the signal is corrected so that the anti-bunching dip coincides with zero time delay. After that, the coincidences are normalized with

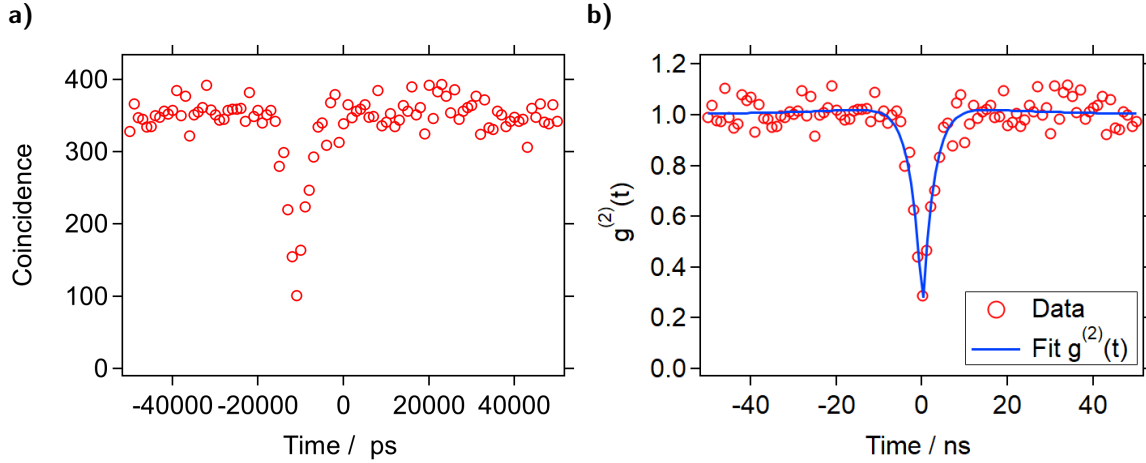


Figure 3.15: Example of the data analysis for the second-order correlation measurement for emitter E79 in untreated hBN (hBN06) at 100 μW . **a)** shows the raw data where the x-axis is the time delay in picoseconds and the y-axis the absolute coincidence count. **b)** shows the normalized and fitted data, where the x-axis shows the time delay in nanoseconds and the y-axis is normalized to show the $g^{(2)}(0)$ value.

$$g^{(2)}(\tau) = \frac{N_c}{R_1 \cdot R_2 \cdot \Delta\tau \cdot T}, \quad (3.6)$$

where N_c represents the coincidence counts, $\Delta\tau$ is the bin width, T is the acquisition time and R_1 and R_2 are the average count rates at both detectors, which are the measured count rates divided by the exposure time [91]. Afterwards, the normalized data can be fitted with the fit function for a three-level system (see Eq. 2.33):

$$g^{(2)}(\tau) = 1 + c_2 \cdot \exp(-|\tau - \tau_{off}| \cdot t_2) + c_3 \cdot \exp(-|\tau - \tau_{off}| \cdot t_3). \quad (3.7)$$

c_2 and c_3 are the amplitudes and t_2 and t_3 the decay rates of the photon anti-bunching and bunching, respectively. τ_{off} accounts for a possible offset in the delay τ . The first term therefore describes the anti-bunching and the second term the bunching behavior of the data. Detailed information on the individual terms and how they relate to the kinetics of the emitter energy system are described in detail in section 2.5.3.2.

The normalized and fitted measurement can be seen in Fig. 3.15b, where the anti-bunching dip is shifted to be at $\tau = 0$. The coincidences are normalized and then fitted with Eq. 3.7.

3.3.4 Statistical recording of data

For an analysis of stability and what effect the different post-processing treatments have on the hBN samples, a statistical analysis of the emitters is performed. For this, first a PL scan is carried out (see Section 3.3.1) which is then used to identify and document emitters. Next, an emitter is selected to measure the count rate and $g^{(2)}(\tau)$ simultaneously for 100 s. The data is saved, analyzed using a Spyder script (see Appendix, 9.3.3) and then the emitter is documented

in the PL map with a number and the $g^{(2)}(0)$ value.

Based on the count rate fluctuation, the emitters are also color-coded: white/red for a stable emitter, yellow for an emitter that bleached, pink for an emitter with high count rate fluctuations ('blinking') and green if it entered a dark state (see Fig. 3.16).

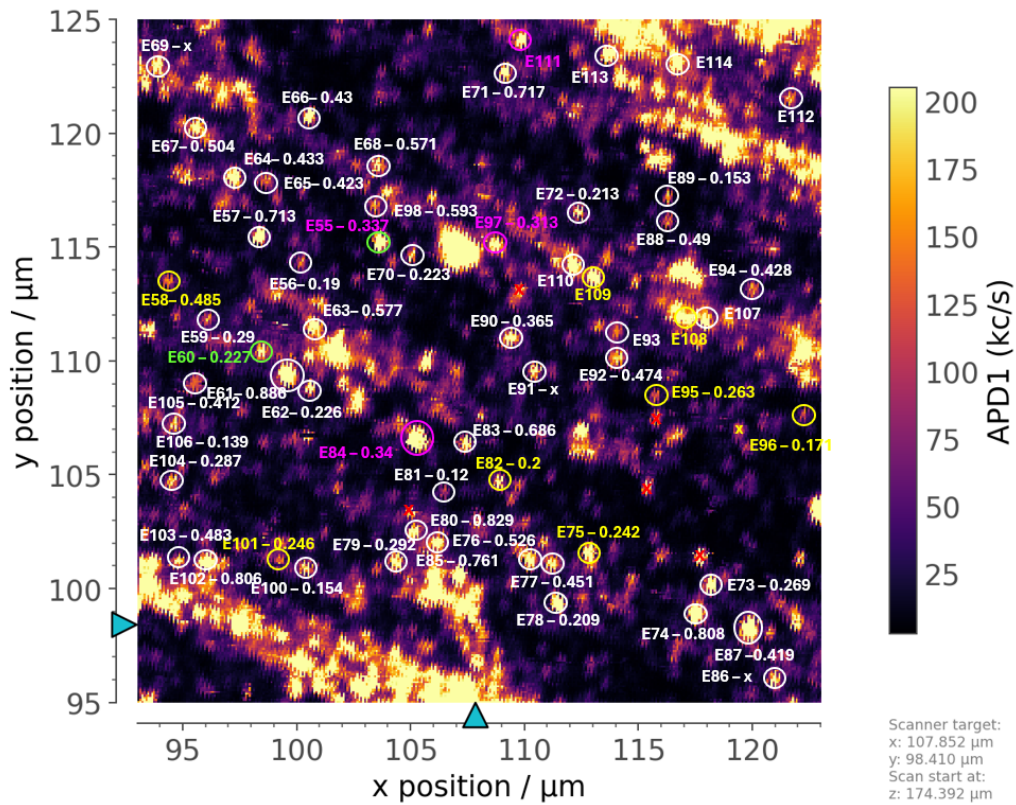


Figure 3.16: Example of a photoluminescence map with recorded emitters of sample hBN06 at 100 μ W. The measured emitters are denoted as E- (with the corresponding emitter number) followed by the measured $g^{(2)}(0)$ value. Emitters that did not show any anti-bunching ($g^{(2)}(0) = 1$) are listed as x. The emitters are color coded as follows: white - stable, yellow - bleached, pink - blinking and green - dark state. The x and y axis show the piezo position and the color bar on the side shows the corresponding counts at each point of the scan (in kcounts/s). The maximum counts are adjusted in the color bar to allow for better contrast.

These color-coded emitters are counted per sample and used to obtain the statistical data about emitter stability (section 4.2.4). When an emitter shows several behaviors, it is sorted into one of the categories with the priority being bleaching > dark state > blinking. Therefore, if an emitter showed blinking and then bleached within the 100 s observation window, it is recorded as bleaching.

Emitters that do not show any anti-bunching are marked with an x and contribute to the statistic of the amount of single-photon emitters present in the sample, but are not included in the stability statistics.

3.3.5 Relative calibration

After the characterization of the emitters, the same setup can be used for an application-based measurement: a relative calibration of two single-photon detectors. This calibration determines the wavelength-dependent detection efficiency of one detector relative to the other. This relative approach relies on the ratio of detected count rates and therefore does not require the traceable standard needed for absolute radiometric calibrations.

The relatively narrow and stable emission from the characterized single-photon emitters provides a suitable light source for this purpose, while the room-temperature operation enables a straightforward comparison of the detector responses across the visible spectral range.

To ensure spectral confinement, the emission is filtered to the emitter's ZPL using a 600/40 nm bandpass filter (FBH600-40, Thorlabs) before being coupled into the single-mode output fiber. The fiber output is then connected to a 50/50 fiber-based beamsplitter in order to apply the fiber-exchange technique [92], as illustrated in Fig. 3.17. Fibers A and B are connected via FC/PC couplers to SPAD 1 and SPAD 2, respectively. Each detector is connected to a counter (threshold: 1 V, impedance: 50 Ω) (Agilent 53220A/Keysight 53220A), synchronized by an external trigger operating at 0.5 Hz.

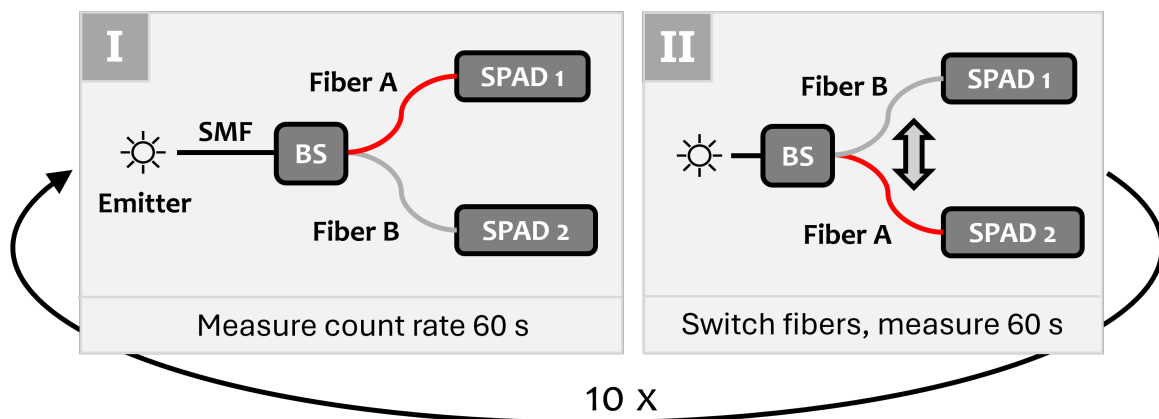


Figure 3.17: Sketch demonstrating the working principle of the relative calibration using the fiber exchange technique. The emission light from the output single-mode fiber is connect to a 50/50 beamsplitter, the ends of which are connected to two SPAD detectors. After simultaneously measuring the count rates at both detectors, fibers A and B of the beamsplitter are switched from one detector to the other and the measurement is repeated. This process is repeated a total of ten times.

The electrical signals from the detectors are integrated over a period of one second and the emission is measured for one minute (counts/s). Afterwards, the fibers are switched, so fiber A is connected to SPAD 2 and fiber B to SPAD 1 and the measurement is repeated. This is done to account for the splitting ratio of the beamsplitter. This pair of measurements is repeated ten times (i. e. a total of twenty 60s measurement intervals).

After these measurements, a shutter is used to block the laser, after which the dark counts are measured with the same measurement procedure. The count-rate measurements are subse-

quently dark-count corrected for each detector with $\dot{N} = \dot{N}_{measured} - \dot{N}_{dark}$.

The ratio of detection efficiencies r between the two SPAD detectors is determined with

$$r = r' \cdot f_{sr}, \quad r' = \sqrt{\frac{\dot{N}_{1,A}}{\dot{N}_{2,B}} \cdot \frac{\dot{N}_{1,B}}{\dot{N}_{2,A}}}. \quad (3.8)$$

Here, $\dot{N}_{x,y}$ denotes the background-corrected count rate (in counts per second) of detector $x \in \{1, 2\}$ when connected to fiber $y \in \{A, B\}$. The factor f_{sr} is a correction factor that accounts for the splitting ratio of the beam splitter which can be influenced by coupling instabilities and repeatability errors between measurements. If the splitting ratio is constant, $f_{sr} = 1$.

To estimate the uncertainty for relative detection efficiency, a weighted mean and its corresponding relative uncertainty are calculated as follows. First, for each measurement, the count rate ratio of SPAD 1 and SPAD 2 is calculated. From these ratios, the mean value $\bar{\mu}$ and the standard error of the mean (SEM) are determined. The relative uncertainty for each ratio is then given by

$$\sigma_{1,2} = \frac{\text{SEM}}{\bar{\mu}}.$$

Since r' combines two independent measurement pairs, the relative uncertainties are combined according to

$$\sigma = \frac{1}{2} \sqrt{\sigma_1^2 + \sigma_2^2}.$$

The corresponding absolute uncertainty for a measurement pair is $\epsilon = \sigma \cdot \bar{r}'$.

The weighted mean $\bar{x}$ of all ratios is calculated using $w_i = \epsilon_i^{-2}$ as the weighting factor. The external consistency, also referred to as the Birge ratio [93, 94], is then obtained with

$$BR = \frac{1}{n-1} \frac{\sum_{i=1}^n w_i (\bar{r}'_i - \bar{x})^2}{\sum_{i=1}^n w_i}, \quad n = 10 \quad (3.9)$$

Dividing the Birge ratio by the weighted mean yields a relative type A uncertainty for the calibration. This value is then combined with the type B uncertainty, represented here by the SEM of the beam-splitter ratio. The total combined relative uncertainty u is used to calculate the expanded uncertainty U of the calibration, given by

$$U = 2 \cdot (u \cdot \bar{x}).$$

where the coverage factor of 2 corresponds to a confidence level of approximately 95 % [95].

3.3.6 Software

Confocal scans are taken by qudi-core (Version 1.5.1, Ulm-IQO, Ulm) with Python 3.9.13. Before this, Agilent VEE Pro (Version 9.3.15222.1, Keysight Technologies, Santa Rosa) was used for the PL scans. The sCMOS camera is used with Tokupic 3.0.0 (Hamamatsu, Hamamatsu

City). Measurements of count rate or second order correlation are taken either with TimeTagger Lab (Version 2.17.4, Swabian Instruments GmbH) or with a self written LabVIEW code (LabVIEW 2024 Q1 (64-bit) 24.1f0, National Instruments). The PI piezo actuator translation stage for sample positioning and the rotation stage for filter wheel rotation are either used through one of the aforementioned programs or otherwise manually controlled with PIMikro-Move (Version 2.36.1.0, Physik Instrumente GmbH).

Data analysis is carried out with Spyder (Version 6.0.7, Open-source), Igor Pro (first version 6.3.7.2, then version 9.0.5.1, WaveMetrics Inc.) and MATLAB (R2018a version 9.4.0.813654, MathWorks). The codes for data analysis are included in the Appendix.

Additional used software include FiberChekPRO 2.4.1.6892 (VIAVI Solutions Inc., Chandler) for inspecting fiber ends with a digital fiber scope and MoticImages (Version 3.1.1.132b, Motic China Group Co.) to record images with the light microscope.

4 Results and discussion

In this chapter, the characterization results of the untreated hexagonal boron nitride (hBN) samples are presented and discussed first, followed by the results obtained after the post-processing treatments described in Section 3.1. The analysis includes a comparison between untreated and post-processed (PPT) samples, highlighting the effects of the different treatments on the properties of the emitters. In addition, a relative calibration measurement is demonstrated as a potential application of an hBN-based single-photon source (SPS). Parts of the data presented in this chapter have been published in [96] and [97].

4.1 Untreated hBN samples

4.1.1 Count rate & single-photon purity

The characterization begins with a photoluminescence scan (described in Section 3.3.1), from which individual emitters are identified and selected for further characterization. Subsequently, the raw count rate and single-photon purity are measured simultaneously, since the count rate during the correlation measurement is required for proper normalization (see Section 3.3.3, Eq. 3.6).

Two representative emitters are shown over the following sections to illustrate some of the typical behavior observed during the measurements (without bandpass filter). Fig. 4.1 presents the count rate and $g^{(2)}(\tau)$ of two emitters from different substrates. These examples represent the variation in stability and brightness that is characteristic of visible hBN defects.

Fig. 4.1 shows the count rate and $g^{(2)}(\tau)$ for two emitters from different samples: E79 on a Si wafer (hBN06, Fig. 4.1a-b) and E20 on a glass slide (hBN03, Fig. 4.1c-d). The data for E79 was acquired at an excitation power $P = 40 \mu\text{W}$, while E20 was excited at $P = 50 \mu\text{W}$.

Emitter E79 exhibits a stable count rate of approximately 60 kcounts/s with $g^{(2)}(0) = 0.33$. In contrast, E20 displays pronounced intensity fluctuations, with the total count rate varying between 60 kcounts/s and 200 kcounts/s and a simultaneously measured $g^{(2)}(0) = 0.31$. The data is not background-corrected.

Fluctuations such as those observed for E20 commonly occur in hBN defects (see section 2.5.2.4). In cases where such fluctuations are very strong, their characterization cannot be performed. In this case, E20 bleached before $g^{(2)}(\tau)$ could be measured as a function of excitation power. By contrast, E79 remained stable even at higher excitation powers for several hours before bleaching. Fig. 4.2a shows the count rate for E79 under 4 mW excitation, exceeding 2.1 Mcounts/s while remaining largely stable.

Fig. 4.2b and c illustrate the evolution of the second-order correlation of emitter E79 with the excitation power. In general, the $g^{(2)}(0)$ value degrades at higher excitation powers due to two primary effects. First, the background noise increases linearly while the emitter count rate

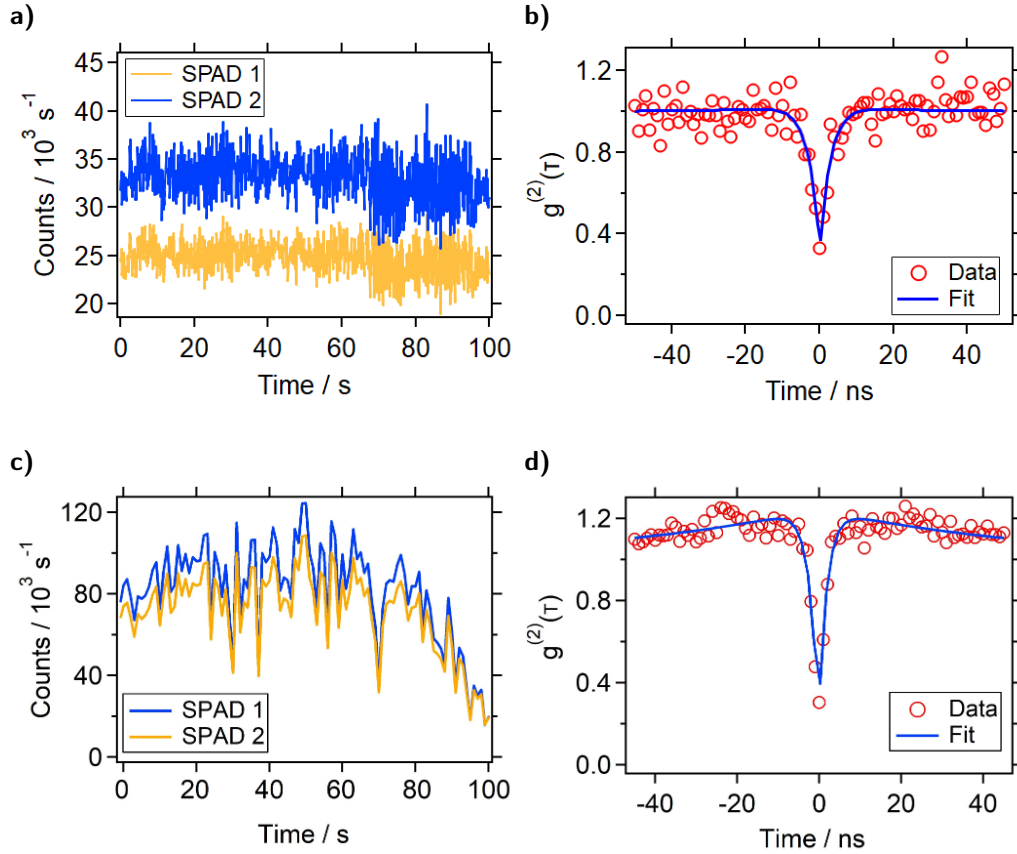


Figure 4.1: Count rate and second-order correlation for two selected emitters. **a)** Count rate for an emitter (E79, hBN06) on a Si wafer at excitation power $P = 40 \mu\text{W}$. The x-axis shows the time and the y-axis displays the counts per second. **b)** Corresponding second-order correlation for the same emitter. The x-axis shows the time delay in ns and the y-axis the corresponding $g^{(2)}(\tau)$ value. **c)** Count rate for an emitter (E20, hBN03) on a glass slide at excitation power $P = 50 \mu\text{W}$. **d)** Corresponding $g^{(2)}(\tau)$ for the same emitter.

saturates. Second, the emitter's photodynamics become more pronounced at higher excitation powers (detailed in Section 2.5.3.2), which can be seen in Fig. 4.2c. This graph shows the fitted $g^{(2)}(\tau)$ functions for different excitation powers. With increasing optical power, photon bunching becomes more prominent, indicating a greater population of the metastable state, which in turn reduces single-photon purity. The strongest bunching is observed at 4 mW, where $g^{(2)}(0) > 0.5$, thereby exceeding the single-photon threshold.

At the lowest excitation powers (20 μW and 40 μW), the single-photon purity is likewise reduced – this time due to a larger relative contribution from background noise at low emitter count rates. The lowest measured $g^{(2)}(0)$ values are found at $P = 0.1 \text{ mW}$ and 0.2 mW , where $g^{(2)}(0) = 0.25$. Based on these results, an excitation power of $P = 100 \mu\text{W}$ was selected as the standard for cross-sample comparison of emitters.

To assess the overall single-photon purity of untreated hBN emitters, both the count rate and second-order correlation function are measured for a total of 577 emitters across six different samples. The resulting distribution of $g^{(2)}(0)$ values is summarized in Table 4.1. The data is

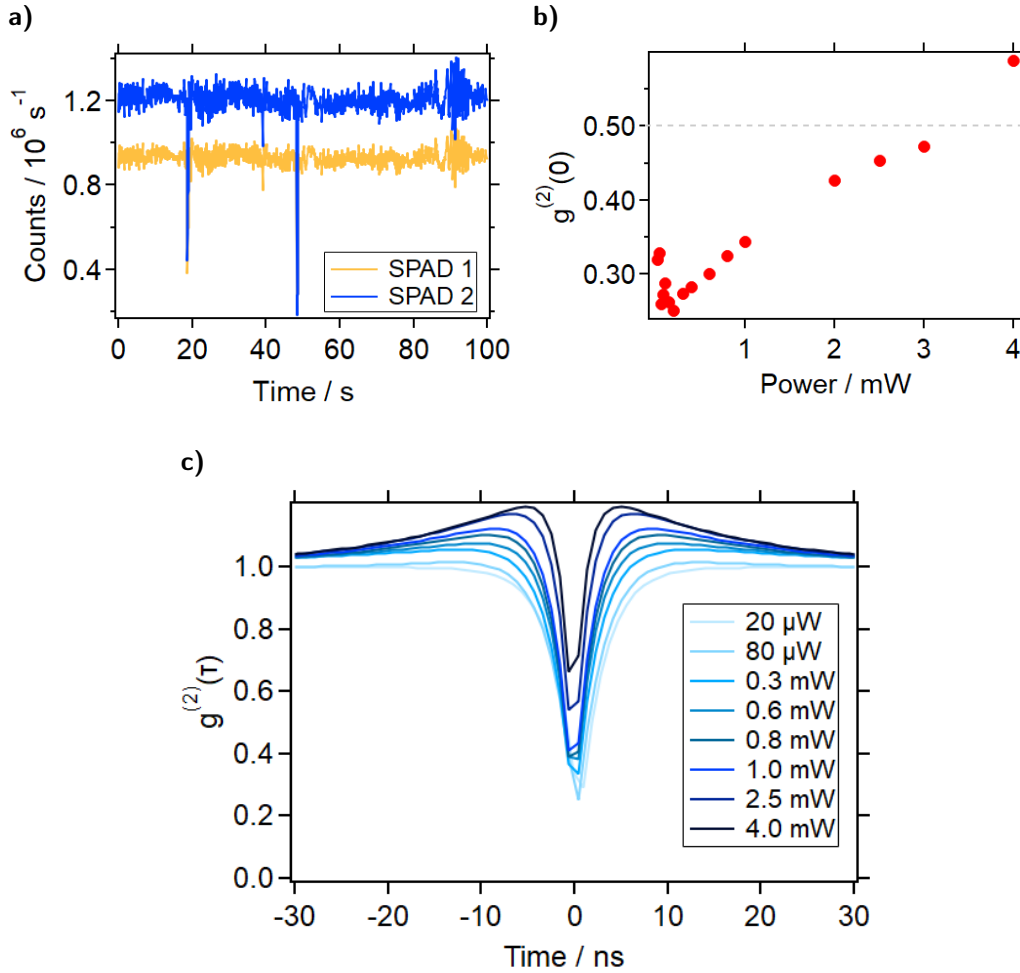


Figure 4.2: Power-dependent second-order correlation for emitter E79, hBN06 as well as the count rate at 4 mW. **a)** Count-rate for E79 at 4 mW excitation power. The emission is bright and mostly stable. **b)** $g^{(2)}(0)$ value plotted against the excitation power. As the power increases, the $g^{(2)}(0)$ value increases. A gray dashed line marks $g^{(2)}(0) = 0.5$. **c)** Fit functions of the $g^{(2)}(\tau)$ measurements at different excitation power. With increasing excitation power, the bunching gets more pronounced.

not corrected for background noise.

Among the measured emitters, 89 show no antibunching ($g^{(2)}(0) = 1$), corresponding to 15.4 % of the total. They could originate from contamination of either by-products during fabrication or dust. The remaining 488 emitters exhibit antibunching and are denoted as “quantum emitters”, representing 84.6 % of the total. Of these, approximately 60 % have $g^{(2)}(0) \geq 0.5$ and are classified as non-single-photon emitters (non-SPEs). As discussed in section 2.4, all emitters with $g^{(2)}(0) < 0.5$ are considered single-photon emitters (SPEs), leaving 40 % of quantum emitters in this category, with an average $g^{(2)}(0) = 0.37 \pm 0.08$. This means that roughly one third of all detected emission in untreated samples comes from from SPEs. The lowest observed $g^{(2)}(0)$ is 0.15.

The normalized histogram of $g^{(2)}(0)$ values for all quantum emitters is shown in Fig. 4.3, with the mean $g^{(2)}(0)$ value marked by a vertical orange line. The average single-photon purity of

Table 4.1: Amount of measured emitters, the percentage that are quantum emitters, further divided into single-photon emitters (SPEs) and non-single-photon emitters (non-SPEs), as well as their mean $g^{(2)}(0)$ value and its corresponding standard deviation σ .

	N	%	Mean $g^{(2)}(0)$	σ
Measured emitters	577			
Quantum emitters	488	84.6 %	0.56	± 0.2
Non-SPEs	291	59.6 % (50.43 % of total)	0.69	± 0.14
SPEs	197	40.4 % (34.1 % of total)	0.36 (min. 0.15)	± 0.08

untreated quantum emitters is $g^{(2)}(0) = 0.555 \pm 0.197$. In a normal distribution, approximately 68 % of values lie within one standard deviation of the mean; here, 66.9 % of $g^{(2)}(0)$ values fall within $0.358 < g^{(2)}(0) < 0.752$ (1σ), while 97.9 % lie within two standard deviations. The distribution exhibits fewer low- $g^{(2)}(0)$ tails, likely due to background contributions, which explains why the minimum observed value is $g^{(2)}(0) = 0.15$. A Kolmogorov–Smirnov test confirms that the distribution can be considered approximately normal [98].

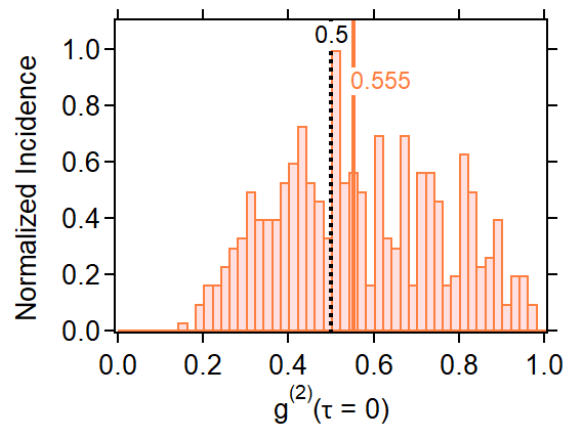


Figure 4.3: Histogram and average of $g^{(2)}(0)$ values for all measured untreated emitters. The x-axis shows the $g^{(2)}(0)$ values (bin width = 0.02), the y-axis shows the normalized incidence for each bin. The average $g^{(2)}(0) = 0.55$ and is indicated by the solid orange line.

The count rates of the SPEs are shown in Fig. 4.4a as a scatter plot, where the y-axis represents the count rate. The x-axis is unlabeled and serves only to distribute the data points horizontally for better visibility. To accurately represent the emitters' average brightness, only the “on” periods of emission are considered in the mean count rate calculation, excluding any “off” times caused by blinking, dark states or bleaching.

Count rates range from 123 kcounts/s to 903.3 kcounts/s, with an arithmetic mean of (325.4 ± 202.6) kcounts/s. The large standard deviation reflects the strong variability between emitters. Calculating the *geometric mean* and associated standard deviation (as opposed to the arithmetic mean) provides a more accurate representation of the distribution, because the geometric mean

indicates a central tendency in the data.

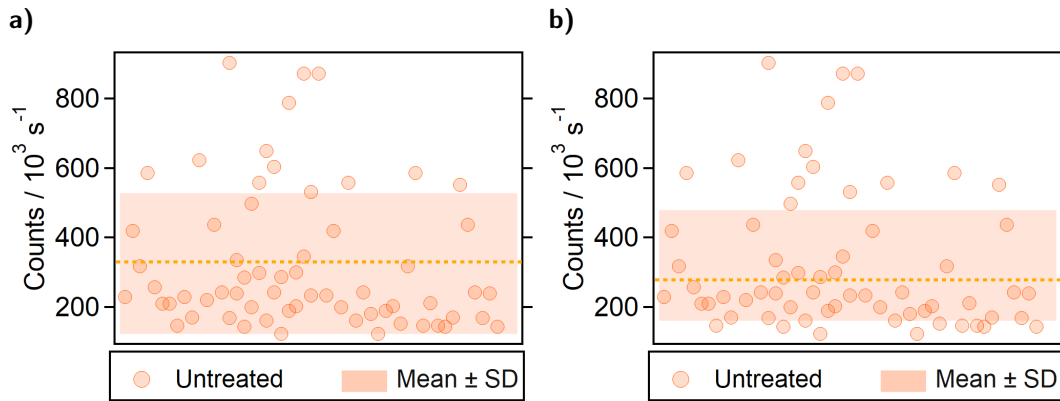


Figure 4.4: Scatter plot of the average count rate for SPEs in the sample. The y-axis shows the count rate while the x-axis is unlabeled, serving only to distribute data points horizontally for clarity, with each point in the plot corresponding to the average count rate for a single-photon emitter. The mean count rate value is represented by a dashed line surrounded by $\pm$ standard deviation. **a)** uses the arithmetic mean and standard deviation while **b)** uses the geometric mean and standard deviation, calculated in log space and back-transformed into linear space, giving rise to asymmetric bounds.

For this, the count rate data (x) is log-transformed ($x' = \log_{10}(x)$), and the arithmetic mean μ' and standard deviation σ' are calculated in log space. These values are subsequently transformed back to linear space using $\mu_x = 10^{\mu'}$ and $\mu \pm \sigma = 10^{\mu' \pm \sigma'}$.

When plotted in linear units, the resulting standard deviation appears asymmetric around the mean, as shown in Fig. 4.4b. The geometric mean corresponds to an average count rate of 277.7 kcounts/s, with asymmetric bounds of 160.9 kcounts/s (lower) and 479.5 kcounts/s (upper). This asymmetry reflects the underlying distribution observed in the scatter plot, in which the bulk of emitters exhibits lower count rates with several high-value outliers.

4.1.2 Spectral properties of hBN

After measuring the count rate and second-order correlation, the next step is to record the emission spectrum. For this purpose, one output fiber of the beamsplitter is connected to the spectrometer's input, while the other remains attached to a SPAD detector to monitor the emitter position and signal stability during the measurement.

Fig. 4.5a shows the spectra for several different hBN emitters from one sample. They are consistent with the most commonly reported emission characteristics of hBN single-photon emitters [6, 26, 28], where the zero-phonon line (ZPL) typically appears between 550 nm and 620 nm, accompanied by a red-shifted phonon sideband (PSB), 160 meV lower in energy. This corresponding to approximately 45 nm at 575 nm. The PSB originates from coupling between the electronic transition and lattice vibrations, as discussed in section 2.1.1.2.

In contrast, Fig. 4.5b displays two atypical spectra. Emitter E64 (red) shows an additional smaller peak preceding the expected ZPL, while emitter E08 (purple) exhibits two comparable

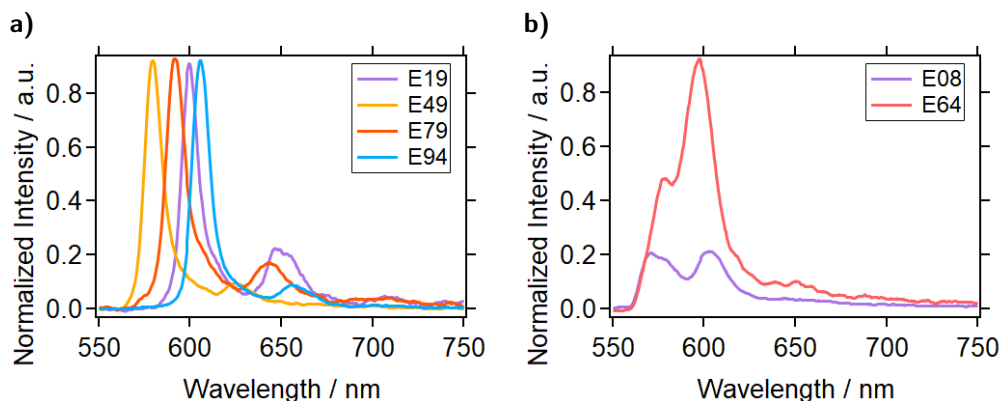


Figure 4.5: Emission spectra of several emitters from untreated samples. The x-axis shows the wavelength and the y-axis the intensity. **a)** Spectra of emitters with the characteristic hBN lineshape. The ZPL with high intensity is located at different wavelengths for each of the emitters, followed by the PSB. **b)** Emission of two emitters that do not look like the characteristic hBN spectrum.

peaks without a clearly defined ZPL. These deviations from the usual lineshape are most likely caused by the optical filters used in the setup. Specifically, the dichroic mirror and long-pass filter introduce a cutoff around 550 nm, which prevents the detection of shorter-wavelength emission. Since literature reports ZPL positions ranging from 530 nm to 700 nm [6], it is plausible that for these two emitters, the true ZPL lies below the filter cutoff, leaving only the PSB fully visible while the ZPL is cut off.

Across all measured emitters, the average ZPL position is (2.109 ± 0.049) eV with a mean full width at half maximum (FWHM) of (46.9 ± 16.6) meV. According to Eq. 2.1, this corresponds to an average wavelength of (587.9 ± 27.3) nm, in agreement with previously reported values summarized in Table 2.1.

This confirms that the optical setup and spectral calibration accurately capture the emission properties of hBN single-photon emitters. A more in-depth analysis of the hBN spectra is presented in Section 4.2.5, which includes the spectra of untreated and PPT samples.

4.1.3 Saturation

To evaluate the emission behavior of the investigated emitters with respect to the optical excitation power, their emission is measured with a SPAD (count/s) for one minute at different excitation powers. The procedure is repeated for the background signal, which is then subtracted from the emitter counts and the resulting background-corrected saturation is fitted as detailed in Section 3.3.2.

Fig. 4.6 shows the saturation behavior for the same two example emitters as in Section 4.1.1. The measured power-dependent count rate of emitter E79 (red circles) and the count rate for the background signal measured in close proximity to the emitter (blue circles) is shown in Fig. 4.6a. The background increases linearly while the emitter counts first increase steeply and

then saturate. To obtain the emitter counts without the contribution of the linear background, the background signal is subtracted from the measured emitter count rate, yielding the corrected emitter counts (filled red circles). The corrected counts are then fitted with Eq. 3.5 (red line). The fit yields values of $N_{\text{sat}} = (1836 \pm 165)$ kcounts/s and $P_{\text{sat}} = (1202.3 \pm 25.8)$ μW . Fig. 4.6b shows the saturation for E20. Only the background-corrected counts are plotted for simplicity.

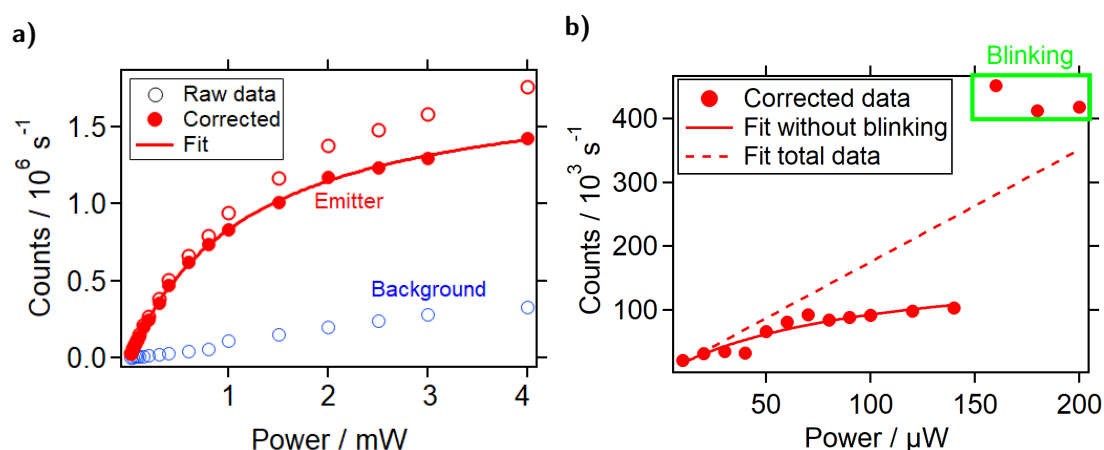


Figure 4.6: Count rate as a function of the excitation power. **a)** Raw counts for E79 (red) and background counts (blue) are plotted as empty circles, while the corrected counts without the background contribution are filled circles. The corrected counts are fitted using Eq. 3.5. **b)** The background corrected counts for E20 are plotted together with two fit functions. One plots the saturation of the complete data (dashed line), the other fit only uses the data without the blinking points.

The emitter already showed count rate fluctuations during the first characterization step as shown in Fig. 4.1c. Initially, it appeared to reach saturation rather rapidly during the measurement process, approaching 110 kcounts/s at 150 μW . However, at 160 μW the measured emitter count rate unexpectedly quadrupled to 450 kcounts/s and remained at the same level for the two subsequent measurements. This is marked in Fig. 4.6b in green with the notation "blinking". The attempt to re-characterize the emitter at this high-emission level failed, as the emitter bleached before the lower power measurements could be repeated.

Two fit functions are plotted in the graph. A failed attempt at fitting the complete data set (dashed red line) yields $N_{\text{sat}} = (7.17 \pm 11.4) \cdot 10^9$ counts/s and $P_{\text{sat}} = (4.09 \pm 6.42)$ W and a fitting error from Igor Pro (see section 3.3.6 for softwares). The resulting fit looks linear and the fit parameters are obviously unreasonable. Therefore, the blinking data is removed for a second fit (solid red line), which then yields $N_{\text{sat}} = (182.3 \pm 35.4)$ kcounts/s and $P_{\text{sat}} = 95.9 \pm 35$ μW . The second fit does not return an error and seems to describe the emitter behavior before it started blinking more accurately. However, the lack of further saturation data makes it impossible to determine the values conclusively.

This measurement highlights one of the main challenges encountered throughout the characterization of the emitters in these hBN nanoflakes. Strong fluctuations in the count rate and

frequent bleaching events at high excitation powers make reliable measurements difficult and limit the number of emitters that can be fully characterized. Consequently, the saturation measurement of only 13 emitters could be completed. The corresponding fit results are summarized in Fig. 4.7, where the obtained saturation count rate N_{sat} is plotted as a function of the determined saturation power P_{sat} .

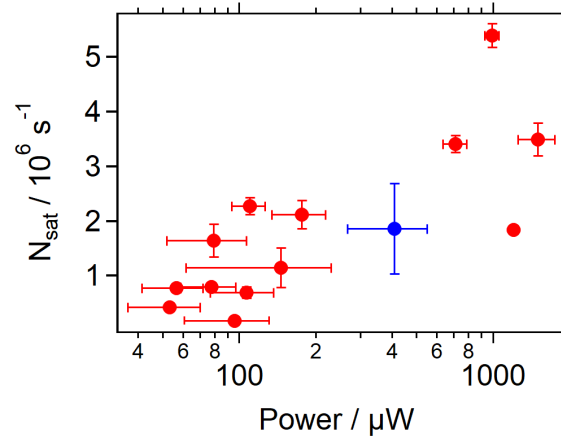


Figure 4.7: Saturation counts as a function of their respective saturation power. The x-axis displays the power on a logarithmic scale to space out the points to make it easier to read, while the saturation count rate in Mcounts/s is plotted on the y-axis. The error bars show the errors obtained from the fit. The blue point represents the average saturation count rate and power.

The excitation power is shown on a logarithmic scale to improve the visibility of the data distribution. The emitters exhibit a wide range of saturation behaviors: some saturate quickly at relatively low powers and moderate count rates, while others reach high saturation intensities. Direct measurements reveal count rates up to 4.5 Mcounts/s, with fitted values exceeding 5 Mcounts/s. Most emitters, however, saturate between approximately 700 kcounts/s and 2.5 Mcounts/s at excitation powers of 60 μW to 200 μW .

The mean value, shown in blue, corresponds to $N_{\text{sat}} = (1861.5 \pm 826.1)$ kcounts/s at $P_{\text{sat}} = (408.4 \pm 141.7)$ μW . Here, the error bars represent the propagated fitting errors rather than the statistical spread of the data.

In the literature, saturation count rates exceeding 7 Mcounts/s are reported for the same type of hBN-defect (based on the emission spectrum) [99]. Such high values can result from several factors, including variations in collection efficiency, background suppression, host material quality, fitting methodology, and emitter stability.

When compared to other room-temperature single-photon emitters, the observed hBN emitters lie at the upper end of the brightness range. Their saturation behavior is comparable to that of SiV^- centers in diamond, which are reported to reach 3-4.8 Mcounts/s [3, 100]. In contrast, SnV^- and NV^- centers typically exhibit lower saturation count rates, ranging between roughly 150 kcounts/s and 1 Mcounts/s [3, 101]. These results show the potential of hBN point-defects as a bright room-temperature single-photon source. However, their stability concerning the

frequent bleaching and emission fluctuations currently pose a major challenge for their reliable implementation, as discussed in more detail in the following section.

4.1.4 Stability

Almost all investigated hBN emitters show temporal fluctuations in the photon emission - with measured count rate fluctuations ("blinking") of at least 15 kcounts/s and up to > 300 kcounts/s. Whether or not a blinking emitter is considered unstable depends on the severity and interval of the blinking.

The measured count rate corresponding to the photon emission of E79 in Fig. 4.2a exhibits fluctuations of 141 kcounts/s (SPAD 2) around an average count rate of 1.2 Mcounts/s, yielding a ± 5.9 % deviation from the mean. The stability measurements are used to investigate the reliability of the emitter measurement and its characterization. The successful characterization of E79 shows that not all blinking is obstructive. A threshold is therefore established to define acceptable count rate fluctuations. Consequently, if blinking is continuous and within ± 10 % of the average count rate, the emitter is considered stable for the remainder of this work, as fluctuations below this threshold did not hinder characterization.

Permanent photobleaching is also observed in most of the investigated emitters. After an unpredictable time period (ranging from seconds to hours) under constant illumination, the emitter will bleach or enter a dark state. In several cases, it was observed that an emitter considered to be bleached recovered after a dark state lasting several hours.

Therefore, in addition to characterizing the count rate and $g^{(2)}(0)$, the stability of each of the 488 quantum emitters is recorded. During the first 100 s of measurement, it is recorded whether the emitter exhibited blinking over the established threshold of ± 10 %, entered a dark state or bleached. The emitters are recorded and sorted into a category as described in Section 3.3.4. A count rate trace for an emitter (E109, hBN06) demonstrating all three of the unpredictable behaviors is shown in Fig. 4.8a.

This emitter shows severe short-term blinking in the range of 100 kcounts/s (± 62 % from the mean), then briefly enters a dark state before emitting irregularly again. It bleaches after 70 s and is therefore recorded in the category "bleaching" according to the priority of bleaching $>$ dark state $>$ blinking.

The result of the stability characterization is illustrated in a histogram in Fig. 4.8b. Of the 488 quantum emitters, 110 (22.5 %) exhibit one of the three identified unstable behaviors. The most prevalent occurrence is bleaching (9.2 %), followed by blinking (7.2 %), whereas the transition into a dark state is the least common (6.1 %). Given that the recovery duration of dark states ranges from seconds to hours, it is plausible that some emitters categorized as "bleaching" within the 100-second measurement period may actually have transitioned into a dark state rather than having undergone permanent photobleaching.

It should be stressed again that most emitters eventually undergo bleaching after prolonged

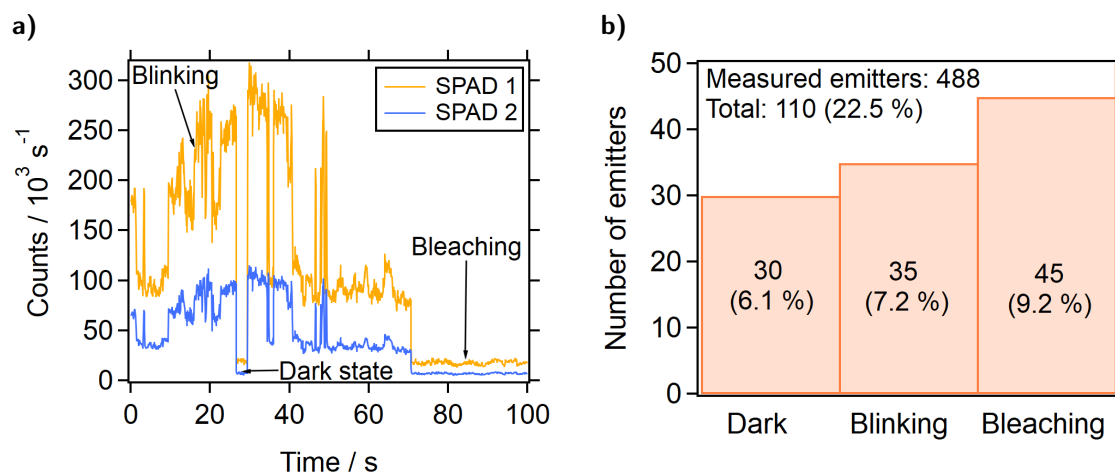


Figure 4.8: Unpredictable behavior of hBN emitters over time. **a)** Photon emission over time of an unstable emitter. The emitter shows severe blinking, then enters a short-term dark state before it eventually bleaches. The x-axis shows the time over a 100 s measurement period and the y-axis the count rate. **b)** Histogram of all unstable emitters sorted into the categories dark state, blinking and bleaching.

continuous excitation; however, such occurrences are not recorded in this statistical analysis as it exclusively pertains to measurements obtained during the initial 100 seconds. Furthermore, increased excitation power leads to faster bleaching and exacerbates irregular behavior.

In order to assess the likelihood of finding an emitter with high single-photon purity and without unpredictable emission behavior, it is first necessary to understand how the stability of SPEs differs from that of non-SPEs. Accordingly, the stability data in Fig. 4.8b can be separated into these two categories. The result are depicted in Table 4.2.

Table 4.2: Number of irregular emission events recorded for single-photon emitters (SPE) in comparison to non-SPEs. The first and second columns indicate the type of emitter and the total number, respectively. The three subsequent columns illustrate the number of emitters exhibiting one of the three unstable behaviors, both in absolute numbers and as a percentage of the total. The final column provides the sum of these values.

	Total	Dark	Blinking	Bleaching	Sum
Non-SPE	291	14	22	22	58
		4.8 %	7.6 %	7.6 %	19.9 %
SPE	197	16	13	23	52
		8.1 %	6.6 %	11.7 %	26.4 %

While 22.5 % of all quantum emitters exhibit irregular emission behavior, separating it into SPEs and non-SPEs shows that SPEs are more likely to display at least one of the three behaviors (26.4 %), with bleaching remaining the most frequent (11.7 %). While blinking is more common than entering a dark state across quantum emitters, this trend is reversed for SPEs where more enter a dark state (8.1 %) than show blinking (6.6 %). In contrast, non-SPEs are

less prone to instability overall (19.9 %), with blinking and bleaching occurring at similar rates (7.6 %), while entering a dark state is less frequent (4.8 %).

This result is consistent with expectations, since non-SPEs often consist of clusters of several SPEs. If one SPE in a cluster enters a dark state, the other SPEs still emit light – therefore, the cluster appears to be blinking.

Considering the proportion of SPEs in a sample (34.1 % of the total) and their stability, this indicates that only 25.1 % of emitters in an untreated sample are single photon emitters with a relatively stable photon emission.

Untreated hBN SPEs exhibit high photon emission, good single-photon purity, and narrow ZPLs - properties that are highly desirable at room-temperature operation. However, as demonstrated, their emission is often unstable. Since a stable and reliable performance of the photon emission is essential for applications such as in quantum radiometry, sensing, and communication, strategies to improve stability are required. In the following section, post-processing treatments are explored as a route to achieve such stability.

4.2 Samples with post-processing treatments

The photon flux instability of hBN emission shown in the last section is a characteristic commonly described in literature (see Table 2.1). The typical methods described to improve the stability include high-temperature annealing, protecting hBN from the oxygen, ion implantation, or different excitation wavelengths. To investigate how PPTs such as ozone treatment and high-temperature annealing influence the characteristics of the nano-flake samples, they are treated in different atmospheres and temperatures (chosen based on literature and device availability, see section 3.1) before being characterized.

This section first describes the feasibility assessment of the chosen treatments and then compares the characterization results of treated and untreated samples.

4.2.1 Feasibility of the treatments

The post-processing treatments used in this work were selected based on methods reported in the literature for enhancing emitter formation, single-photon purity, and stability, and are implemented using the experimental capabilities available in this study.

However, due to the various substrate and different structural forms of hBN (e.g. monolayers, nanoflakes, bulk crystals, etc.) used in the treatments reported in the literature, their effectiveness and feasibility may deviate when applied to the samples prepared in this work. For example, high-temperature annealing is not suitable for samples on glass slides due to their low softening temperature which is why all post-processing treatments are carried out on Si wafer samples.

This section discusses several PPTs that proved infeasible for these samples, while the results of the feasible treatments are shown in later sections.

4.2.1.1 Air annealing

After high-temperature annealing in air, two samples exhibited noticeable visual changes: those annealed at 700 °C and 1000 °C. Fig. 4.9 shows photos of the three air annealed samples.

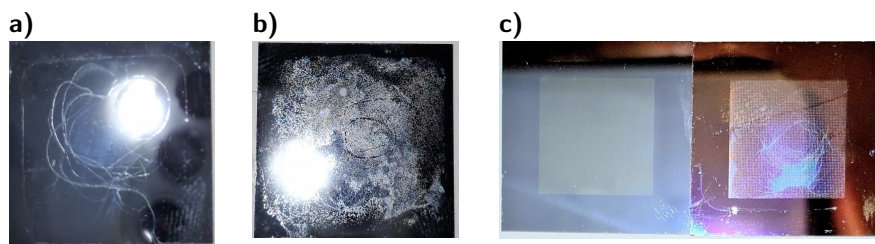


Figure 4.9: Pictures of the three air-annealed samples at different temperatures. **a)** hBN29: sample annealed at 400°C in air. The Si wafer looks the same as before the annealing. Here, the dropcast lines of the hBN solution can be observed. **b)** hBN09: sample annealed at 700°C in air. The surface looks tarnished and the dropcast lines are not clearly visible. **c)** Empty slide (left) and hBN19 (right, annealed in air at 1000°C). Both slides have a grid structure on top, however, hBN19 has a red tarnish to it that is absent in the empty slide as well as the other samples after air annealing. The dropcast lines appear to have a blue tinge to them.

Fig. 4.9a displays the sample annealed at 400°C (hBN29). It shows a reflective Si wafer, with faint dropcast lines visible and looks identical to untreated samples. Fig. 4.9b is a photo of the sample annealed at 700 °C (hBN09). Here, the edges of the wafer are reflective, while the rest of the sample surface looks tarnished and rough. The dropcast lines cannot be seen.

Fig. 4.9c shows two Si wafers with a grid made of 5 nm chromium (Cr) and 40 nm gold (Au). The wafer on the left is an empty slide without hBN nano-flakes, while the right one shows the sample annealed at 1000 °C in air. The annealed Si wafer appears more orange in color and although the hBN dropcast lines can be observed, they seem to have a bluish tint.

Further investigation under the light microscope shows that the sample annealed at 700 °C exhibits star-shaped structures on the surface (see Fig. 4.10a).

The nanoflakes are obscured by these structures, however, where the growth is less dense, the nanoflakes can still be seen. Star- or snowflake-like patterns are common during crystal growth, where dendrites form at nucleation points [102]. Nuclei can be the flakes themselves or contaminations on the surface. It is likely that organic impurities oxidize (or carbonize depending on the impurity) and form crystalline dendrites during cooling.

Since dendritic growth obscures the flakes, attempts to characterize individual emitters did not yield any results (see Fig. 4.10b). Emitters can still be found in areas with less dense dendritic growth but the background emission is elevated (~ 45 kcounts/s) compared to untreated samples (~ 5 kcounts/s), while the emitter count rate remains low (~ 10 kcounts/s). Consequently, the background is approximately four times higher than the emitter signal, and thus

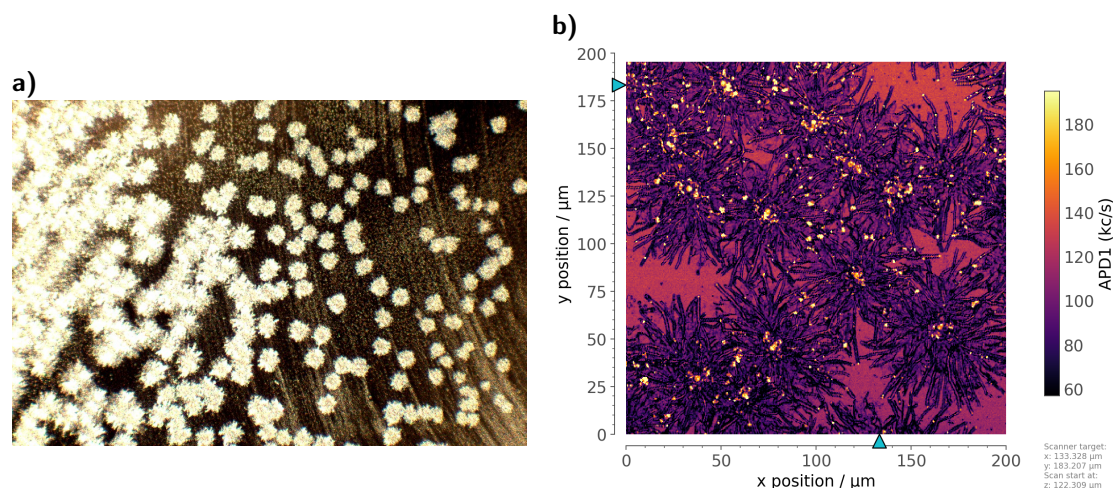


Figure 4.10: a) Image of hBN09, sample annealed at 700°C in air. The image was taken with a light microscope at 10x magnification. Star-like formations can be seen on the surface of the sample, obscuring the nano-flakes below. b) Photoluminescence scan of the sample. The star-like patterns can be seen clearly without other emission from emitters being visible in the empty areas between stars.

dominates the detected emission. No antibunching was observed from the emitters. Therefore, high-temperature annealing at 700 °C in air is deemed unsuitable for these samples.

The second visually distinct sample is the one annealed at 1000 °C in air. Fig. 4.11a shows a PL scan of the sample prior to annealing. The grid is visible through a higher background and flakes dropcast on top of the grid therefore appear brighter than emitters within the cell. A label can be seen at the bottom (X197 Y199).

In contrast, Fig. 4.11b shows a scan of one grid square after annealing. The marker (X138 Y183) remains visible, but the surface has developed uneven structures with large dark patches and small islands along the grid lines. Faint emitters can still be discerned within the cell.

The effect of hole and island formation has been studied by [103], who found that high-temperature annealing of gold thin films on silicon wafers promotes thermally accelerated diffusion. This process minimizes the system's surface free energy, leading to the formation of nano-islands and holes.

Consequently, the observed effects can be attributed to the presence of the gold grid. However, based on the results from annealing in air at 700 °C, it is unlikely that the process would be suitable even in the absence of the gold structures. At 1000 °C, oxidation would proceed even more rapidly; therefore, this annealing step was not repeated on another sample.

Therefore, the only air-annealed sample suitable for characterization is the one annealed at 400°C.

4.2.1.2 Vacuum annealing

Unlike the air-annealed samples, those annealed in vacuum show no immediate visual changes. Under the light microscope, they appear identical to their state prior to annealing. However, PL

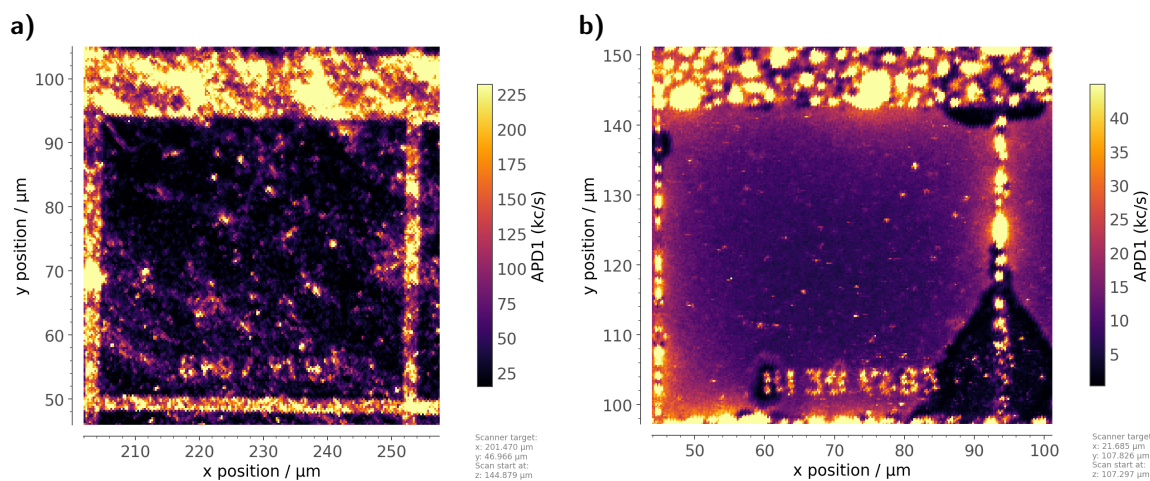


Figure 4.11: Comparison of photoluminescence scans before and after annealing in air at a temperature of 1000°C. The x and y axes show the x and y positions of the piezo translation stage, respectively. The color bar on the left indicates the count rate in kcounts/s. **a)** PL scan before annealing. The grid is visible through a higher background contribution. Flakes dropcast on top of the grid therefore seem brighter than emitters in the cell. A label can be seen at the bottom (X197 Y199). **b)** Scan after annealing. A marker can still be identified (X138 Y183), but the surface has developed uneven formations with large dark areas and small islands along the grid lines. Faint emitters can be distinguished in the cell.

scans of vacuum-annealed samples show bright (> 500 kcounts/s) and dense emission without the normally characteristic varying emitter density or dropcast lines. A PL map of sample hBN26 (400 °C, vacuum) is shown in Fig. 4.12a. The count rate maximum for the color bar is set to 225 kcounts/s to optimize the contrast.

The characterization of individual emitters shows a continuous decline in the count rate. This contrasts with the typical behavior exhibited by the hBN emitters detailed in section 4.2.4, which is characterized by sudden and abrupt blinking, transitions between on and off states, or bleaching. Scanning a previously scanned area for a second time reveals a substantial reduction in overall emission. No emitter demonstrates antibunching.

A spectrum of one emitter is displayed in Fig. 4.12b. The emission is broad with (550 nm to 800 nm) and steady, lacking the characteristic features of hBN point-defects. All three samples exhibit the same behavior. In order to eliminate the possibility of an error occurring during the annealing process, the procedure is repeated in a different vacuum oven. As previously, the sample exhibits dense emission with a broad spectrum and continuous bleaching, confirming the phenomenon is reproducible and not the result of an error.

The sample is cleaned to ascertain whether the substrate or the hBN reacted under vacuum, consequently leading to this broad emission. Cleaning is carried out first with Hellmanex® in a sonic bath, then the sample is wiped with ethanol, sonicated in ethanol and finally cleaned with distilled water. A PL map (Fig. 4.13a) of the cleaned sample shows remaining low-intensity emission (~ 10 kcounts/s). Its spectrum exhibits a lineshape more characteristic of hBN point-defects, with a ZPL (possibly cut-off by the dichroic mirror) and the expected PSB

(see Fig. 4.13b).

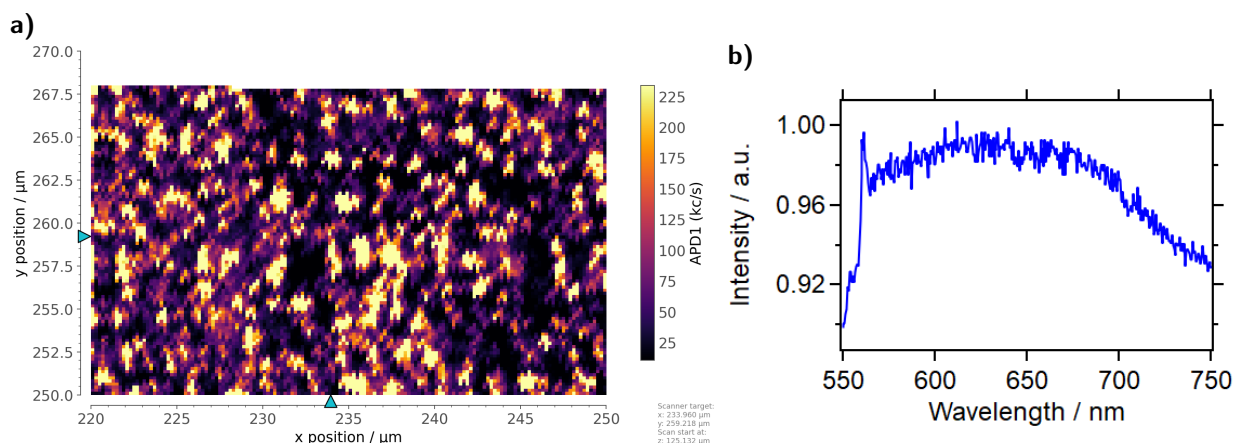


Figure 4.12: a) Photoluminescence scan of a vacuum-annealed sample. Emission is bright and dense without the normally characteristic varying emitter density or dropcast lines. b) The spectrum of a selected vacuum-annealed emitter shows a broad, steady emission without the usual hBN characteristics.

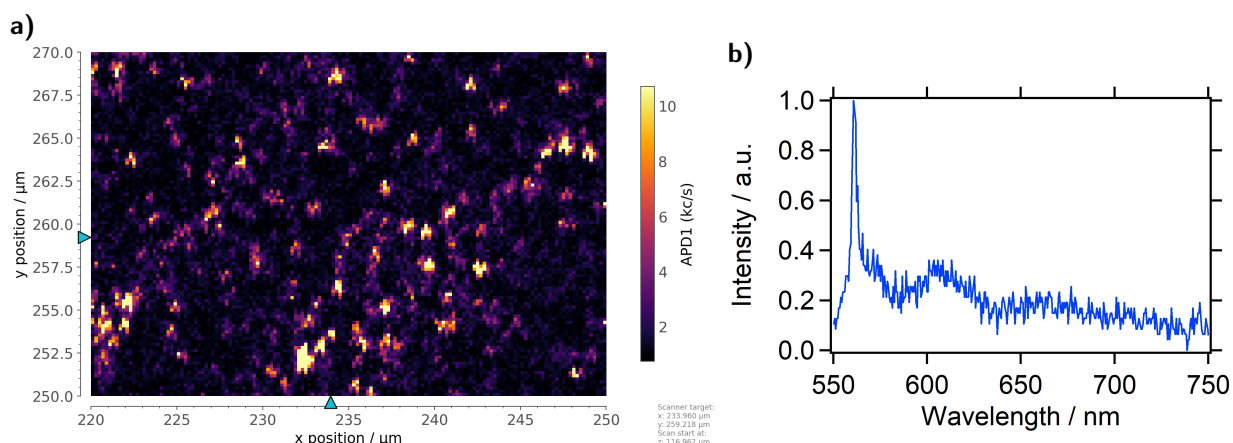


Figure 4.13: a) PL scan of the vacuum annealed sample after cleaning it. Emission is less dense and bright. b) Spectrum of an emitter in the cleaned sample. The broad emission is not seen, instead the spectrum resembles the typical spectral shape of the hBN emission.

Since the broadband, dense emission is removable by cleaning, it suggests that the effect is not intrinsic to Si wafer or the hBN lattice. Instead, it is more likely that the hBN nano-flake solution contains residual organic contaminants which partially carbonize during the annealing, creating a bright, broad photoluminescent layer on top of flakes. This finding is consistent with the effects previously observed during air annealing. Consequently, vacuum annealing is determined to be unsuitable as a PPT of hBN samples when prepared according to the methodology as detailed in Section 3.1.

Based on the results outlined above, the post-processing treatments determined to be successful include high-temperature annealing in air at 400 °C, annealing in nitrogen at 1000 °C, and ozone exposure at 120 °C, which will be discussed in detail in the following sections.

4.2.2 Single-photon purity

The successfully treated PPT samples are characterized using the same protocol as the untreated samples (see Section 4.1) to ensure that the probed characteristics can be compared directly between samples. Table 4.3 shows how many of the measured emitters are quantum emitters, further divided into amount of non-SPEs and SPEs. For each of these categories, the corresponding average $g^{(2)}(0)$ value and its standard deviation is depicted. The untreated sample results are shown alongside the results for the ozone treatment, the samples annealed in nitrogen at 1000 °C (N₂ 1000 °C) and the sample annealed in air at 400 °C.

Table 4.3: Comparison of the amount of quantum emitters (QE) in different PPT samples. QEs are then further divided into SPEs and non-SPEs. The corresponding $g^{(2)}(0)$ value is shown with its standard deviation. The lowest measured $g^{(2)}(0)$ value for each sample is shown in the last row.

	Untreated	Ozone	N ₂ 1000°C	Air 400°C
Amount QE	84.6 %	97.6 %	100 %	95.9 %
$g^{(2)}(0)$	0.56 ± 0.20	0.35 ± 0.18	0.29 ± 0.17	0.29 ± 0.15
Non-SPE	59.6 %	20.2 %	16.2 %	6.9 %
$g^{(2)}(0)$	0.69 ± 0.14	0.65 ± 0.08	0.60 ± 0.09	0.66 ± 0.15
SPE	40.4 %	79.8 %	83.9 %	93.1 %
$g^{(2)}(0)$	0.36 ± 0.08	0.27 ± 0.12	0.23 ± 0.11	0.27 ± 0.11
Min. $g^{(2)}(0)$ value	0.154	0.027	0.063	0.036

The percentage of quantum emitters increased in all the PPT samples. While roughly 85 % of emission in untreated samples originated from quantum emitters, > 95 % of emission comes from quantum emitters in the PPT samples. In the nitrogen annealed sample, all measured emitters exhibit antibunching. As the uncorrelated emission is attributed to surface contamination, the successful PPTs likely removed a substantial amount of these residues, while the unsuccessful treatments may have interacted with them instead.

Of the quantum emitters in untreated samples, only 40 % can be classified as SPEs. The PPTs significantly increase the amount of measured SPEs; the ozone treated sample demonstrates single-photon emission from roughly 80 % of quantum emitters, while the highest amount of SPEs is found in the air annealed sample with 93 %.

In general, all PPT samples demonstrate a clear enhancement in the single-photon purity in comparison to the untreated samples. The untreated samples display a mean $g^{(2)}(0)$ of 0.56 ± 0.20 , whereas the ozone treated sample shows the highest mean $g^{(2)}(0)$ of the PPT samples with 0.35 ± 0.18 .

Table 4.1 also presents the lowest $g^{(2)}(0)$ value measured for each treatment condition. The data for the minimum $g^{(2)}(\tau)$ measurements is plotted in Fig. 4.14. All PPT samples exhibit emitters with $g^{(2)}(0) < 0.1$, while the lowest $g^{(2)}(0)$ for untreated samples only reaches 0.154 (0.13 for the fit). The lowest value is displayed by an emitter in an ozone treated sample (E122,

hBN06) with $g^{(2)}(0)=0.027$ (compared to 0.068 for the fit).

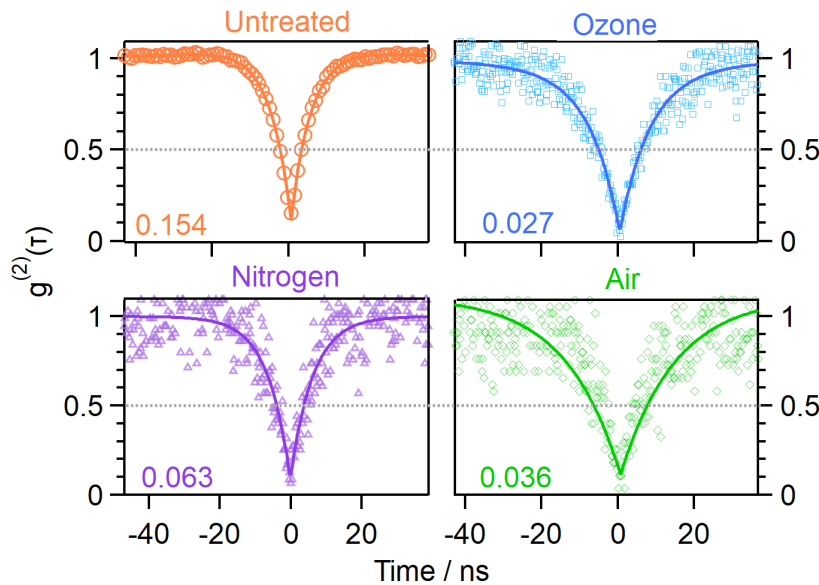


Figure 4.14: Second order correlation for emitters with the lowest measured $g^{(2)}(0)$ in each sample (upper left: untreated, upper right: ozone, lower left: annealed in nitrogen at 1000 °C, lower right: annealed in air at 400 °C). The x-axis shows the time delay, and the y-axis shows the normalized coincidence. The grey dashed line indicates the value 0.5.

Discrepancies between the raw data and the fit can be attributed to several parameters. Since the measurements are not corrected for background noise, the fit parameters may not be entirely consistent with the measured data and can raise or lower the fitted $g^{(2)}(0)$ value. Furthermore, the three-level system to model the $g^{(2)}(\tau)$ for hBN point-defects might not accurately describe the photodynamics of the emitters as proposed by [76].

Since the nature of the emission of hBN defects in this wavelength range is unclear, it is possible that different defects cause the emission and therefore different fit models might be required to accurately fit each emitter. Since this is not done in this work, discrepancies between values from the data and the fit are expected.

The distribution of the $g^{(2)}(0)$ values is shown in Fig. 4.15a–c, where all measured emitters are plotted as normalized histograms (bin width of 0.02) for each treatment condition and compared to the histogram of the untreated samples (orange for untreated, blue for ozone, purple for nitrogen, and green for air). The mean $g^{(2)}(0)$ -value for each treatment is indicated by a solid vertical line, while the single-photon threshold at $g^{(2)}(0) = 0.5$ is marked by a dashed black line.

Emitters with $g^{(2)}(0) < 0.2$ are rare in the untreated samples but appear more frequently in the PPT samples. Conversely, emitters with $g^{(2)}(0) > 0.8$ – indicating several emitters – are common in the untreated samples but much less prevalent in the treated ones. Overall, all PPT samples exhibit a clear shift of the $g^{(2)}(0)$ distribution toward lower values, demonstrating an

improvement in single-photon purity across treatments.

Fig. 4.15d shows the mean $g^{(2)}(0)$ values with their standard deviations as error bars for each treatment. All PPT samples exhibit an average $g^{(2)}(0)$ value within the single-photon regime, whereas the mean of the untreated samples does not.

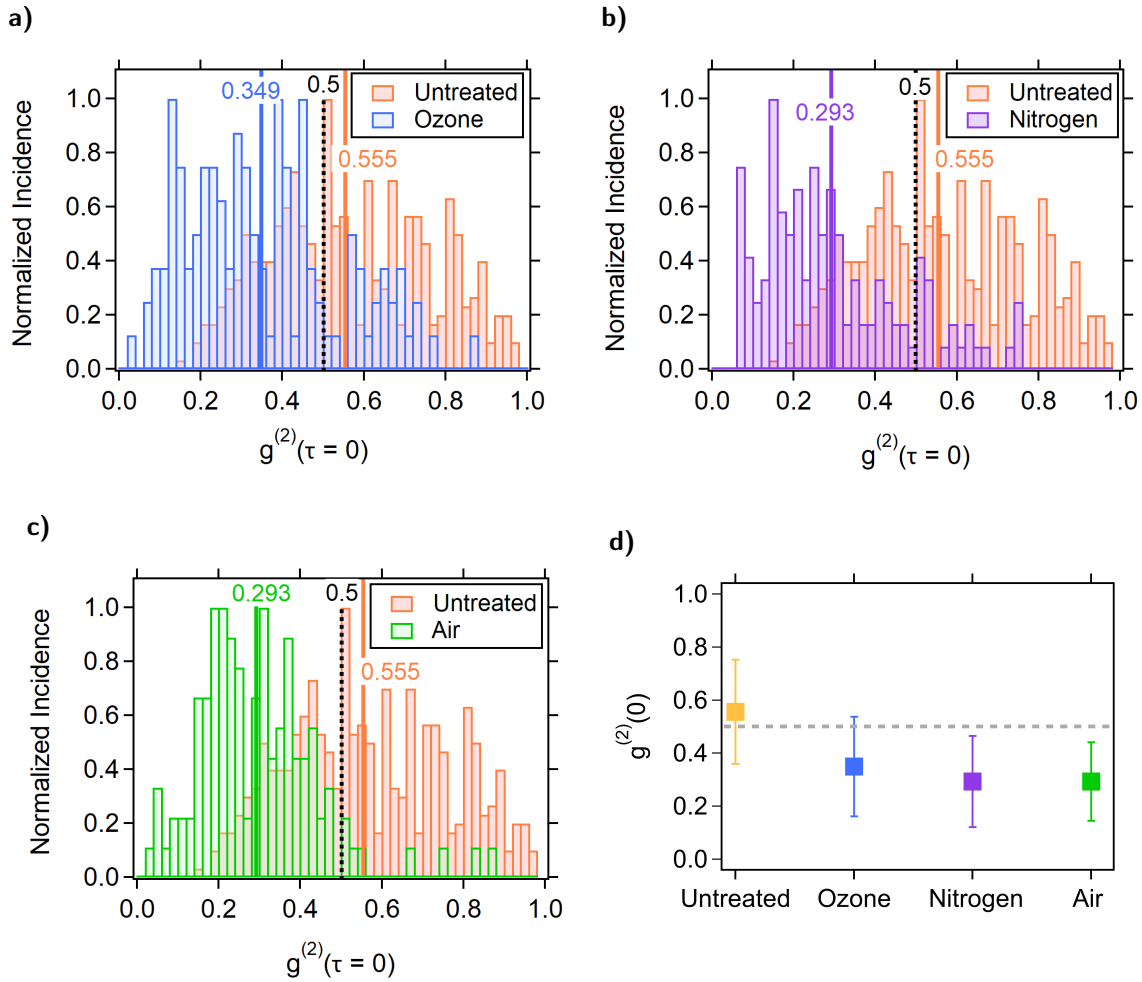


Figure 4.15: Comparison of the single-photon purity between the untreated samples and the PPT samples. **a) - c)** show the normalized histograms of the measured $g^{(2)}(0)$ values for the different samples. The x-axis displays the $g^{(2)}(0)$ value (bin width 0.02) and the y-axis indicates the normalized incidence. The mean value for each sample is represented by a solid vertical line, while 0.5 is marked with a black dashed line. The untreated sample (orange) is plotted as a comparison with each of the PPT samples: **a)** ozone (blue), **b)** annealed in nitrogen at 1000 °C (purple) and **c)** annealed in air (green) at 400 °C. **d)** shows the average $g^{(2)}(0)$ value with its standard deviation (error bar). The gray dashed line indicates the value 0.5.

This improvement may be due to the removal of surface contaminants and the associated background emission, the formation of new SPEs [72, 74], or the quenching of existing ones [69], thereby reducing emitter clusters. Each of these mechanisms will be revisited and evaluated in the relevant sections below.

The selected measurement region on each sample may also influence the apparent number of

SPEs, as densely populated areas can lead to higher background signals and increased emitter overlap. To minimize this effect, regions with lower emitter densities were prioritized during data acquisition. Nevertheless, this approach cannot completely exclude the possibility of signal contributions from nearby or overlapping emitters.

Another consideration is the number of emitters analyzed per sample. For the untreated samples, a total of 577 emitters were measured, whereas each PPT condition includes between 120 and 140 emitters. As a result, the statistical robustness of the PPT datasets is somewhat lower than that of the untreated reference. Despite this, a consistent trend is observed across all PPT samples, showing a clear improvement in single-photon purity compared to the untreated hBN samples.

To assess whether the PPTs induce the formation of new emitters, a sample with a gold grid is first scanned, then subjected to ozone treatment, and subsequently scanned again in the same area using the markers for orientation. Ozone treatment was chosen for this test because high-temperature annealing can damage the gold grid (see Section 4.2.1). While annealing temperatures are below the gold melting point (1000°C), gold starts reacting with Si at lower temperatures ($\sim 370^{\circ}\text{C}$) [104]. Ozone cleaning offers a faster and safer alternative for the before-and-after comparison.

Fig. 4.16 shows the PL scans before (a) and after (b) ozone treatment. The two scans appear nearly identical: no systematic quenching or creation of new emitters is observed. Minor variations in brightness can be attributed to short-term intensity fluctuations rather than the treatment itself. From this comparison, it can be concluded that no new emitters are created – at least in the case of ozone treatment.

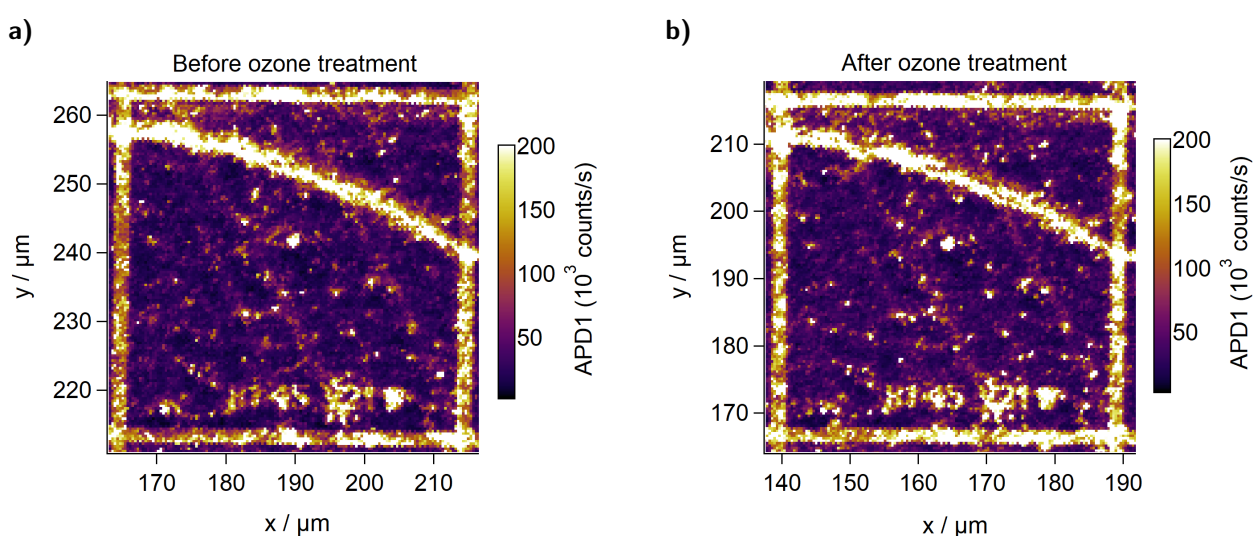


Figure 4.16: PL scan of the same area of a sample (hBN17) **c)** before and **c)** after ozone treatment. The color bar is adjusted for the best contrast. The scans appear nearly identical—no quenching or creation of emitters can be observed.

4.2.3 Count rate

To evaluate the effect of the treatments on the count rates, the average count rate per emitter over the 100 s measurement period is calculated, excluding intervals without emission (dark states and bleaching). The corresponding results are shown as scatter plots in Fig. 4.17a–c.

Each plot shows the count rates for SPEs of the untreated samples in comparison to each PPT. The y-axis represents the average count rates for individual emitters, while the x-axis distinguishes emitters with no explicit labels or categorical assignments. Since the average count rates span several orders of magnitude, their distribution is more appropriately represented on a logarithmic scale. The same applies to the calculation of the mean and standard deviation, as shown for the untreated data in Section 4.1.1.

The mean count rate for each PPT is depicted as a horizontal line, however the standard deviation is omitted in the scatter plot to avoid overlap. Instead, Fig. 4.17d compares the mean count rate values between the PPT samples and the untreated samples with the standard deviation as error bars. The standard deviation is asymmetric due to the back-transformation into linear space.

The air-annealed sample exhibits the most pronounced difference from the untreated samples, with most emitters skewed toward lower count rates. Emitters in the nitrogen-annealed sample display the largest range of count rates (based on the scatter plot, not the standard deviation), whereas those in the ozone-treated sample appear most similar to the untreated sample. The highest average count rate is observed for an emitter in the nitrogen-annealed sample with 1.43 Mcounts/s, while the lowest average count rate of 22.9 kcounts/s is found in the same sample.

The scatter plots in Fig. 4.17 display the count rates of the SPEs for each PPT, covering a wide range from low to high values. To examine how the count rates relates to single-photon purity, Fig. 4.18 shows the average count rate (y-axis) for each quantum emitter in the nitrogen-annealed sample as a function of its respective $g^{(2)}(0)$ value (x-axis). The geometric mean count rate is represented by a dashed horizontal line and the single-photon threshold of $g^{(2)}(0) = 0.5$ is marked by a vertical line.

Most emitters with below-average count rates (< 137.8 kcounts/s) exhibit single-photon behavior, while only a few non-SPEs show similarly low photon emission. Emitters with $g^{(2)}(0) < 0.1$ generally show count rates below 120 kcounts/s, with two exceptions. The emitter with the highest count rate (1.42 Mcounts/s) exhibits $g^{(2)}(0)$ value of 0.46.

Generally, high count rates do not necessarily correlate with reduced single-photon purity; however, lower count rates are more frequently associated with SPEs. This trend is expected, as clusters of emitters contribute cumulatively to the total count rate, leading to higher overall intensities and correspondingly higher $g^{(2)}(0)$ values.

Overall, the mean count rates for each PPT are substantially lower than those of the untreated emitters. Nevertheless, individual emitters with very high count rates (exceeding 800 kcounts/s)

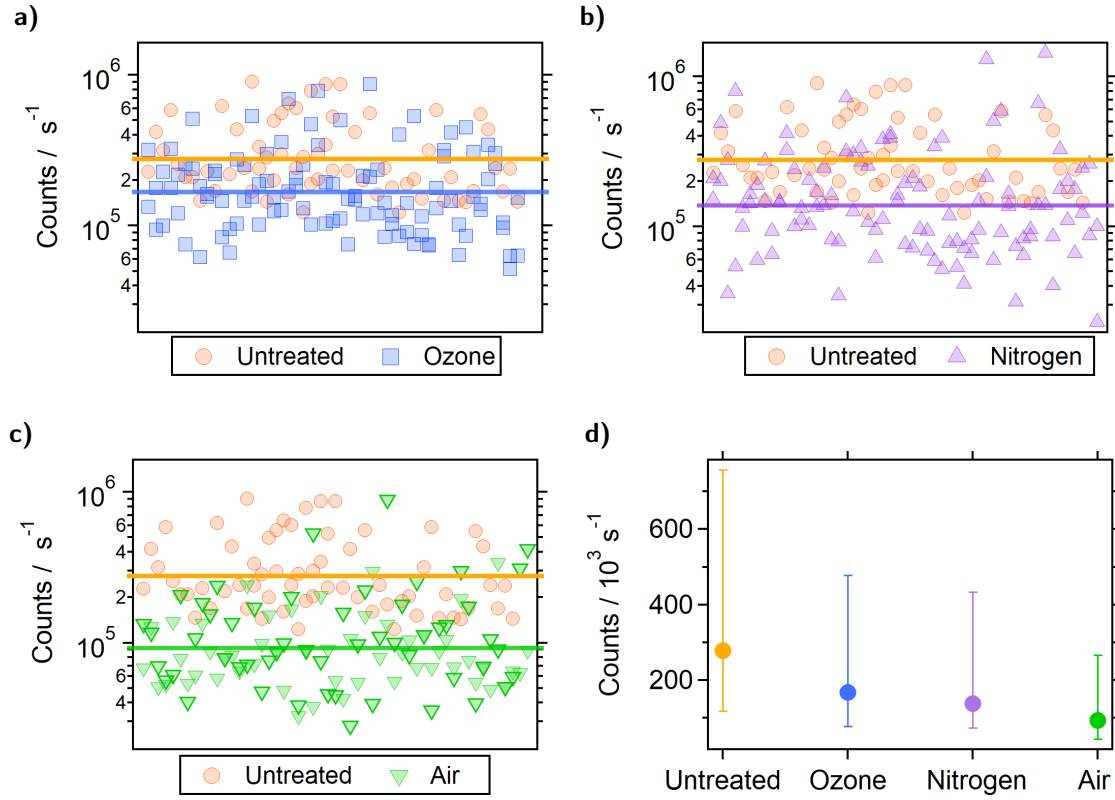


Figure 4.17: Count rate comparison between untreated and PPT samples. **a - c)** depict the scatter plots of the average count rate for SPEs in the sample. The y-axis shows the count rate on a logarithmic scale while the x-axis is unlabeled, serving only to distribute data points horizontally for clarity, with each point in the plot corresponding to a single-photon emitter. The geometric mean is represented with a horizontal line. Each plot shows the untreated sample values (orange) compared with **a)** ozone (blue), **b)** annealed 1000°C in nitrogen (purple), and **c)** annealed in air (green). **d)** shows the mean count rate with its standard deviation calculated in log space and back-transformed into linear space for each PPT.

are present in all samples.

This supports the hypothesis that a background contribution is removed by the PPT, resulting in a shift of the bulk of the emitters to lower photon emission levels. This is also consistent with the higher single-photon purity.

To estimate the influence of background emission on the measured lower $g^{(2)}(0)$ values, the combined second-order correlation function of two emission sources, a and b , must be considered. The corresponding expression is given by

$$g_{a,b}^{(2)}(0) = \frac{g_a^{(2)}(0) \cdot \langle \hat{n}_a \rangle^2 + g_b^{(2)}(0) \cdot \langle \hat{n}_b \rangle^2 + 2 \cdot \langle \hat{n}_a \hat{n}_b \rangle + 2 \cdot \langle \hat{n}_b \hat{n}_a \rangle}{\langle \hat{n}_a + \hat{n}_b \rangle^2}. \quad (4.1)$$

If b is a Poissonian source independent of a , then $\langle \hat{n}_a \hat{n}_b \rangle = \langle \hat{n}_a \rangle \langle \hat{n}_b \rangle$. With a variable $r = \langle \hat{n}_a \rangle / \langle \hat{n}_b \rangle$, this simplifies to [91, 105]:

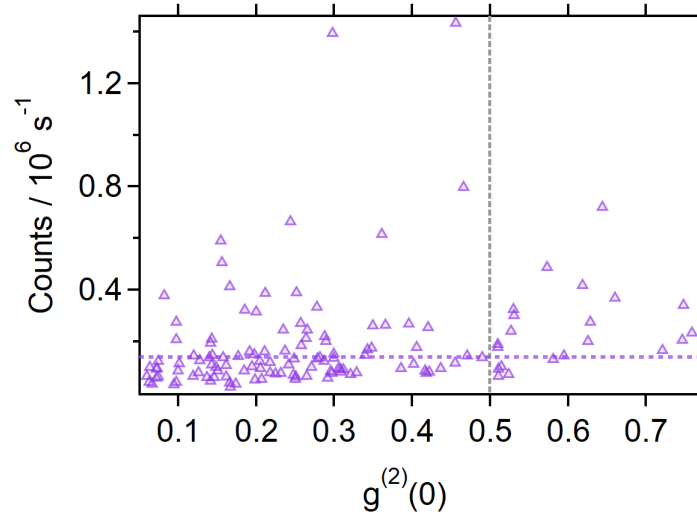


Figure 4.18: Plot of the count rate as a function of the corresponding $g^{(2)}(0)$ value for each emitter for the nitrogen annealed sample. The average count rate is indicated with a purple horizontal line and $g^{(2)}(0)=0.5$ is marked by a gray vertical line.

$$g_{a,b}^{(2)}(0) = \frac{g_a^{(2)}(0) \cdot r^2 + 2r + 1}{(r + 1)^2}. \quad (4.2)$$

When source b is considered as an uncorrelated background contribution, $g_{a,b}^{(2)}(0)$ corresponds to the measured value including background emission, while $g_a^{(2)}(0)$ represents the background-corrected value. Rearranging Eq. 4.2 yields

$$g_a^{(2)}(0) = \left(1 + \frac{\langle \hat{n}_b \rangle}{\langle \hat{n}_a \rangle}\right)^2 \left(g_{a,b}^{(2)}(0) - 1\right) + 1. \quad (4.3)$$

Assuming that the PPT treatments reduce the background emission and thereby improve the single-photon purity, $g_{a,b}^{(2)}(0)$ can be considered as the average $g^{(2)}(0)$ value of the untreated samples (0.555), whereas $g_a^{(2)}(0)$ corresponds to the average value obtained after the PPTs (0.349 - 0.293). Using this relation together with the average count rate n_{ab} of the untreated samples (277 kcps), the required background contribution n_b can be determined with $n_a = n_{ab} - n_b$ to estimate how much background emission must be removed to account for the observed improvement in single-photon purity. The results together with the average values needed for comparison are shown in Table 4.4.

For the ozone-treated samples, a reduction of the background contribution by 48.1 kcounts/s would be sufficient to explain the observed improvement in single-photon purity. However, the difference in average count rates between the untreated and ozone-treated samples is 110.1 kcounts/s, exceeding the calculated background contribution by a factor of 2.29. The discrepancy is the most pronounced for the air-annealed samples, where the measured reduction in emission intensity ($\Delta N = 184.2$ kcounts/s) exceeds the calculated background contribution ($n_b = 57.4$ kcounts/s) by a factor of 3.21. These results suggest that, although the reduction of

Table 4.4: Calculated background contribution required to explain the improvement in $g^{(2)}(0)$ for each PPT. $\bar{N}_{\text{tot}}$ denotes the average total count rate for each treatment, while ΔN represents the difference between the average count rate of the treated and untreated samples. The fourth column lists the average $g^{(2)}(0)$ values, and the final column gives the calculated background contribution n_b required to account for the observed improvement in single-photon purity relative to the untreated samples.

	$\bar{N}_{\text{tot}}/\text{kcounts}\cdot\text{s}^{-1}$	$\Delta N/\text{kcounts}\cdot\text{s}^{-1}$	$g^{(2)}(0)$	$n_b/\text{kcounts}\cdot\text{s}^{-1}$
Untreated	277.7		0.555	
Ozone	167.6	110.1	0.349	48.1
Nitrogen	137.8	139.9	0.293	57.4
Air	93.6	184.2	0.293	57.4

background emission likely plays a significant role in the improved single-photon purity, additional mechanisms must contribute to the reduced emission intensity observed after the PPTs. Possible contributions include changes in the local emitter environment, enhanced non-radiative decay channels, or increased spectral instability. How the stability of the emitters is affected by the treatment will be discussed in the following section.

4.2.4 Stability

While the single-photon purity improved after the treatments and the average count rate decreased, the primary goal is to investigate the influence of the PPTs on emitter stability. Fig. 4.19 shows the histograms of irregular emission events for the different treatments in comparison with the untreated samples. In the untreated samples, 22.5 % of emitters exhibited irregular emission behavior. This amount increased to 25 % for the ozone-treated samples, 32 % for the nitrogen-annealed samples, and 52.5 % for the air-annealed samples. Hence, none of the PPTs improved the stability of the hBN emitters; instead, annealing in air appears to have made them considerably more likely to exhibit unstable behavior.

Protecting emitters from oxygen-rich environments during measurement has been reported to reduce photobleaching [72]. Therefore, exposure of hBN to oxygen during annealing could have introduced additional oxygen-related impurities, increasing the likelihood of photochemical reactions during characterization. The reduced stability observed in the nitrogen-annealed sample may, however, be attributable to statistical variation due to the smaller sample size.

To further distinguish how stability differs between SPEs and non-SPEs, Table 4.5 summarizes the stability statistics for each sample in regards to single-photon behavior. In the untreated, nitrogen-annealed, and air-annealed samples, SPEs exhibit higher rates of instability than non-SPEs, whereas the opposite trend is observed for the ozone-treated sample.

However, because the number of measured non-SPEs in the PPT samples is small, the absolute amount of emitters with irregular behavior has a disproportionate influence on the results. The same can be observed for the annealed samples. Only one non-SPE in the air-annealed

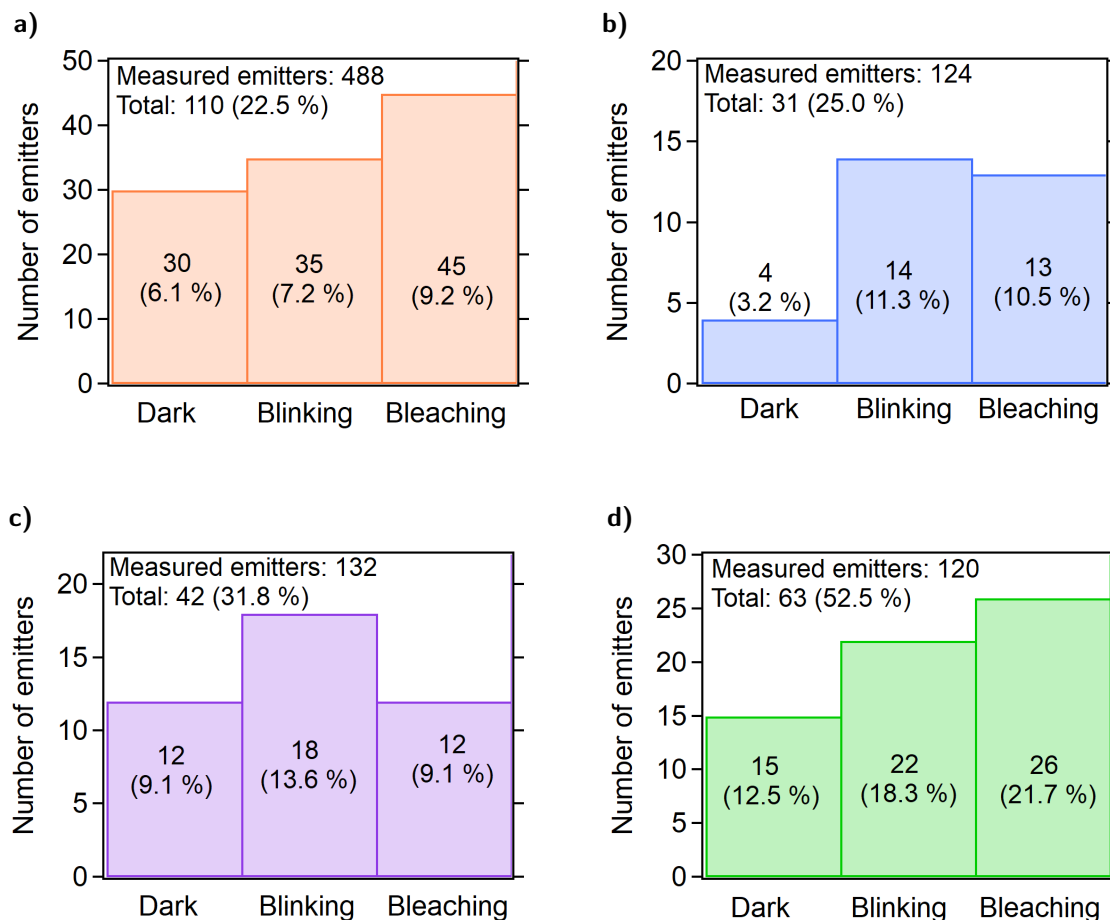


Figure 4.19: Histogram of irregular photoemission events during the first 100 s of recording. The x-axis shows the recorded behaviour (i.e. blinking, bleaching, or entering a dark state) and the y-axis shows the number of quantum emitters for samples **a)** untreated **b)** ozone treatment **c)** annealed at 1000°C, nitrogen **d)** annealed at 400°C, air. The number of measured emitters and the number of total irregular emission events are displayed in the upper left corner.

shows irregular behavior (blinking), which corresponds to 8.3 % of non-SPEs in the sample showing irregular behavior. It is therefore unlikely that the ozone-treated sample truly behaves differently from the others; the apparent deviation is likely an artifact of limited sampling statistics rather than an intrinsic difference between treatments.

Using the information from Table 4.3 and Table 4.5, the likelihood of finding a relatively stable SPE ($N_{\text{SPE,stable}}$) for each sample can be determined with

$$N_{\text{SPE,stable}} = N_{\text{QE}} \cdot N_{\text{SPE}} \cdot (1 - N_{\text{SPE,unst.}}). \quad (4.4)$$

N_{QE} is the amount of quantum emitters in a sample (in percentage), of which N_{SPE} emitters are SPEs (Table 4.3). $N_{\text{SPE,unst.}}$ is the total amount of unstable SPEs (sum, in percentage) in the last column of Table 4.5. In the untreated samples, only 25.1 % of the emission can be attributed to stable SPEs. This fraction increases to 38 % in the air-annealed sample, to 54.1 %

Table 4.5: Number of irregular emission events recorded for single-photon emitters (SPE) in comparison to non-SPEs for all treatment condition. The first column indicates the PPT, while the second and third column indicate the type of emitter and the total number, respectively. The three subsequent columns illustrate the number of emitters exhibiting one of the three unstable behaviors, both in absolute numbers and as a percentage of the total. The final column provides the sum of these values.

		Total	Dark	Blinking	Bleaching	Sum
Untreated	Non-SPE	291	14 4.8 %	22 7.6 %	22 7.6 %	58 19.9 %
	SPE	197	16 8.1 %	13 6.6 %	23 11.7 %	52 26.4 %
Nitrogen	Non-SPE	22	0 0 %	2 9.1 %	1 4.6 %	3 13.6 %
	SPE	110	12 10.9 %	15 13.6 %	12 10.9 %	39 35.5 %
Ozone	Non-SPE	25	1 4.0 %	6 24.0 %	1 4.0 %	8 32.0 %
	SPE	99	3 3.0 %	8 8.1 %	12 12.1 %	23 23.2 %
Air	Non-SPE	12	0 0 %	1 8.3 %	0 0 %	1 8.3 %
	SPE	108	15 13.9 %	21 19.4 %	26 24.1 %	62 57.4 %

for the nitrogen-annealed samples, and 59.9 % for the ozone-treated sample. Thus, although the stability of the emitters stayed similar or even declined, the reduction of surface contamination and the improvement in single-photon purity ensure a higher proportion of stable SPEs overall. In the PPT samples, stable SPEs are therefore more likely to be found than in the untreated samples. However, this improvement applies only to short-term stability: during prolonged measurements, particularly under higher excitation power, emitters generally still bleach after unpredictable time intervals.

The two-dimensional structure of hBN leaves defects more exposed to surface adsorbates and charge states compared to bulk systems such as diamond, which can contribute to spectral instability and variability among emitters. Oxygen is another potential source of instability since oxygen atoms are very mobile in detaching and attaching to defect sites causing photochemical reactions which can lead to blinking, dimming or bleaching [72, 106]. Oxygen impurities can occur natively in the crystal lattice and made mobile by high laser powers. Porous top (or bottom) layers can also provide an entry point for oxygen from the air or the substrate [72]. Protecting the hBN from oxygen-rich environments during measurement could therefore potentially increase emitter stability. Substrate engineering with lower charge trap densities can

provide another potential avenue to enhanced stability by further encapsulation [71].

4.2.5 Spectra

4.2.5.1 Zero-phonon line position

The spectral shape of the emitters is generally consistent across all samples, characterized by a distinct zero-phonon line (ZPL) and phonon sidebands (PSB) approximately (164.0 ± 10.2) meV red-shifted from the ZPL. Fig. 4.20a shows representative emission spectra from four emitters, each taken from a different sample (orange = untreated, green = air-annealed, blue = ozone-treated, purple = nitrogen-annealed). These emitters are selected to illustrate that the overall lineshape remains consistent, even though the ZPL position varies. This variation in ZPL position does not appear to be correlated with the applied PPT. After converting the wavelength to energy units and aligning the spectra such that the ZPL of each emitter is located at 0 eV (subplot in Fig. 4.20a), the phonon sidebands appear at approximately the same energy separation (ΔE) in all spectra.

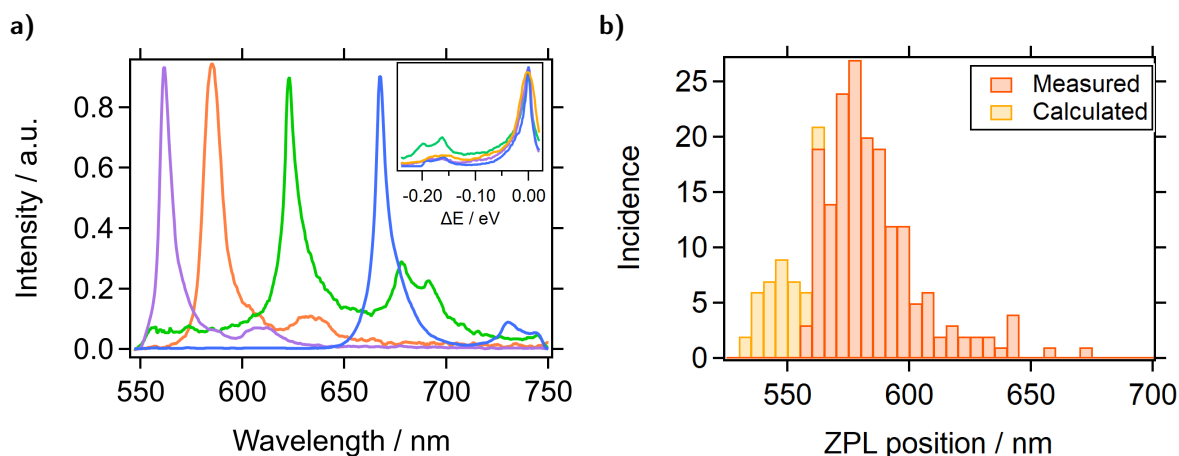


Figure 4.20: a) Spectra of different emitters with the characteristic line shape. The x-axis shows the wavelength and the y-axis the normalized intensity. The inset shows the spectra converted to energy units (eV) and shifted, so that the ZPL lie on top of each other. b) Histogram of ZPL positions with a bin width of 5 nm. The x-axis shows the wavelength bins, the y-axis the incidence. The experimentally determined ZPL positions are represented in orange while the additional ZPL positions obtained from extrapolation from the PSB position are added in yellow.

Experimentally, the ZPL positions span a range of 555 nm to 670 nm. However, because the dichroic mirror and long-pass filter block emission below 550 nm, it is likely that ZPLs at shorter wavelengths are present but not detected. In fact, ZPL positions around 540 nm are reported frequently in literature [23, 70, 77, 99]. As discussed in Section 4.1.2, some emitters display unusual spectral features, such as less intense peaks at shorter wavelengths than the apparent ZPL. These spectra likely correspond to emitters whose actual ZPLs lie below the

detection cutoff of the setup. For such cases, the separation between ZPL and PSB can be used to estimate the ZPL position from the PSB peak. To obtain these estimated positions, spectra are converted to energy units (eV), the PSB position is identified, and the mean energy separation of 164 meV is added. The resulting energies are then converted back to wavelength (nm).

All experimentally determined and calculated ZPL positions are plotted as a histogram in Fig. 4.20b, where the x-axis denotes the ZPL wavelength and the y-axis the frequency of occurrence. Experimentally measured ZPLs are shown in orange, while the estimated positions are shown in yellow. The average ZPL wavelength - including the calculated data - is $\lambda = (579.9 \pm 30.2)$ nm.

The wide span of ZPL positions has been attributed to the same emitter species experiencing strain, differences in the dielectric environment or amount of monolayers, or different defect species with similar spectral properties [53, 69, 70].

4.2.5.2 Full width at half maximum

High-temperature annealing of hBN point-defects is reported in the literature to narrow the zero-phonon line (ZPL) of the emission spectrum [7]. To examine whether this effect occurs in the self-prepared samples, the ZPLs are fitted with a Lorentzian function to obtain the full width at half maximum (FWHM). Prior to fitting, the spectra are converted from wavelength to energy (in eV), as a fixed difference in nanometers does not correspond to a constant energy difference across the varying ZPL positions. Although the ZPL is more accurately described by an asymmetric Lorentzian, the symmetric Lorentzian model provides a sufficiently accurate approximation for determining the FWHM.

Fig. 4.21 presents representative spectra of two emitters from the nitrogen-annealed sample with fitted ZPLs: one exhibiting a high-intensity ZPL (Fig. 4.21a, E40) and another showing lower overall intensity (Fig. 4.21b, E84). The spectra are shown in blue, with the Lorentzian fits overlaid in red. The FWHM is indicated by two red arrows around each respective peak; the values are (18.45 ± 0.47) meV for E40 and (39.79 ± 2.51) meV for E84. Although both emitters display ZPLs within the same energy range (2–2.1 eV), the FWHM of E40 is smaller – likely due to its higher emission intensity which results in a lower relative background contribution, better resolution and a more accurate fit.

Fig. 4.22 shows the FWHM as a function of the average ZPL position for all samples. The mean FWHM is (45.0 ± 2.2) meV, while the average ZPL position is 2.11 eV (corresponding to 587.6 nm). This average excludes emitters with cut-off ZPLs, as their linewidths cannot be determined.

The untreated and ozone-treated samples exhibit linewidths and ZPL positions close to the overall mean. In contrast, the nitrogen-annealed sample contains a higher proportion of high-energy emitters with correspondingly narrower linewidths (≈ 38 meV), while the air-annealed sample displays broader emission (≈ 55 meV) and a shift toward lower photon energies.

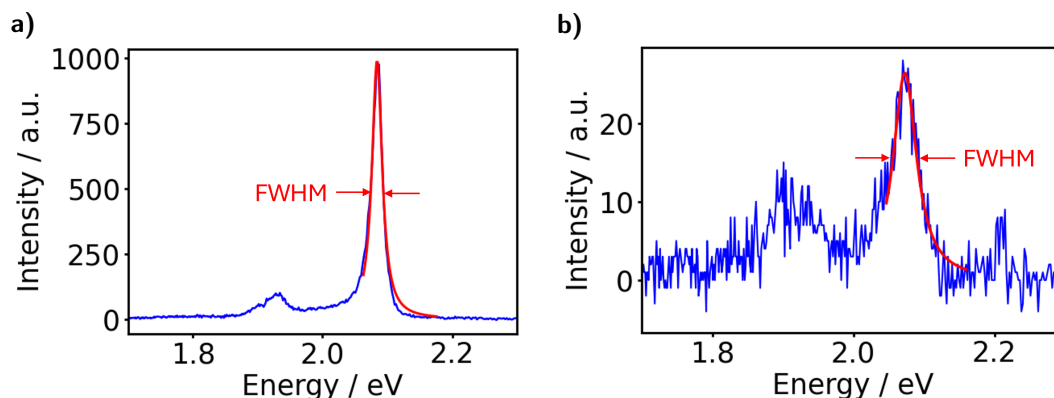


Figure 4.21: Spectra (blue) of two emitters of the nitrogen annealed sample (hBN08) with a Lorentzian fit (red) of the ZPL. The FWHM is indicated with red arrows around the peak. **a)** shows the spectrum of E40 and exhibits a bright and narrow ZPL. **b)** shows the spectrum of E84 from the same sample, but the emission is substantially less bright. The ZPL is much less pronounced in comparison to the PSB.

Although some individual emitters may exhibit narrower ZPLs after treatment, the overall dataset does not reveal a consistent linewidth-narrowing trend following the post-processing treatments. Despite the substantial spread in ZPL energies across all samples, a weak linear correlation is apparent: emitters with lower photon energies tend to show broader ZPLs.

This correlation likely arises from the intrinsic nature of the underlying defects. Lower-energy emitters are generally associated with deeper defect levels and stronger lattice relaxation, leading to enhanced electron–phonon coupling and thus broader ZPLs. In contrast, higher-energy emitters typically exhibit weaker phonon coupling and reduced lattice distortion, resulting in narrower linewidths [26, 66]. [51] similarly reported that emitters with linewidths > 100 meV are associated with higher instability – consistent with the findings of this work, where the air-annealed sample shows both the broadest linewidths and the greatest degree of photoinstability.

However, the considerably broader linewidth in the air-annealed sample may be linked to the reduced count rates observed in the treated samples overall: emitters with lower emission intensity tend to exhibit broader ZPLs (as illustrated in Fig. 4.21b) and lower energy ZPL positions often display lower overall intensity. Given that the air-annealed sample shows the lowest average count rate, the broader linewidths could be a consequence of reduced emission intensity: a lower signal-to-noise ratio of dim emitters can lead to an apparent broadening of the fitted linewidth (fitting an emitter with poor SNR leads to fits becoming less constrained). However, the reduced intensity, especially at lower energy ZPLs may also reflect intrinsic differences in the emitter environment, such as enhanced spectral diffusion or non-radiative decay processes.

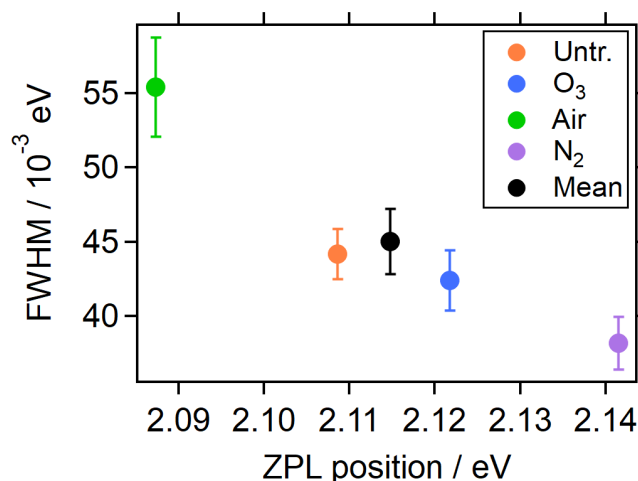


Figure 4.22: Average ZPL linewidth (FWHM) as a function of the mean ZPL position for each PPT (untreated = orange, ozone = blue, air = green, nitrogen = purple) and the overall mean (black). The FWHM is displayed on the y-axis in meV and the ZPL position on the x-axis in eV.

4.2.5.3 Debye-Waller factor

The amount of electron–phonon coupling determines the fraction of the emission into the ZPL compared to the total emission. This is described by the Debye-Waller factor, which is generally a key figure of merit for solid-state SPEs, because it determines the spectral bandwidth and therefore, how spectrally pure and coherent photon emission is. For applications in quantum communication, indistinguishable photons are required [3] and therefore, broad or intense sidebands are detrimental in quantum optical systems since they reduce the probability of zero-phonon transitions.

The Debye-Waller factor is defined as the amount of photons emitted into the ZPL divided by the total amount of photons emitted [100, 107]:

$$\alpha = \frac{\int d\lambda I_{\text{ZPL}}}{\int d\lambda I_{\text{total}}}. \quad (4.5)$$

Experimentally, the Debye–Waller factor can be estimated by integrating the area under the corrected emission spectrum (see Section 3.2.3.1) and comparing it to the contribution from the ZPL. However, accurately separating ZPL and PSB is often challenging, particularly when they lie close to each other and consequently overlap. In most cases, the ZPL area can be approximated by integrating under the Lorentzian fit of the ZPL peak. However, because the ZPL is often slightly asymmetric, this approach can underestimate α . Conversely, when the PSB extends into the ZPL region, the calculated value may be overestimated due to overlap between the two spectral features.

This effect is illustrated for two representative emitters in Fig. 4.23. The first emitter (Fig. 4.23a), from an untreated sample (hBN01, E54), shows a dominant ZPL (blue-shaded area) with a relatively weak PSB contribution (total area in red), resulting in a Debye–Waller factor of

$\alpha_{E54} = 78.7\%$. In contrast, the emitter shown in Fig. 4.23b, from the air-annealed sample (hBN29, E44), exhibits a much smaller contrast between ZPL and PSB. The significant spectral overlap likely leads to an overestimated Debye–Waller factor of $\alpha_{E44} = 38.5\%$.

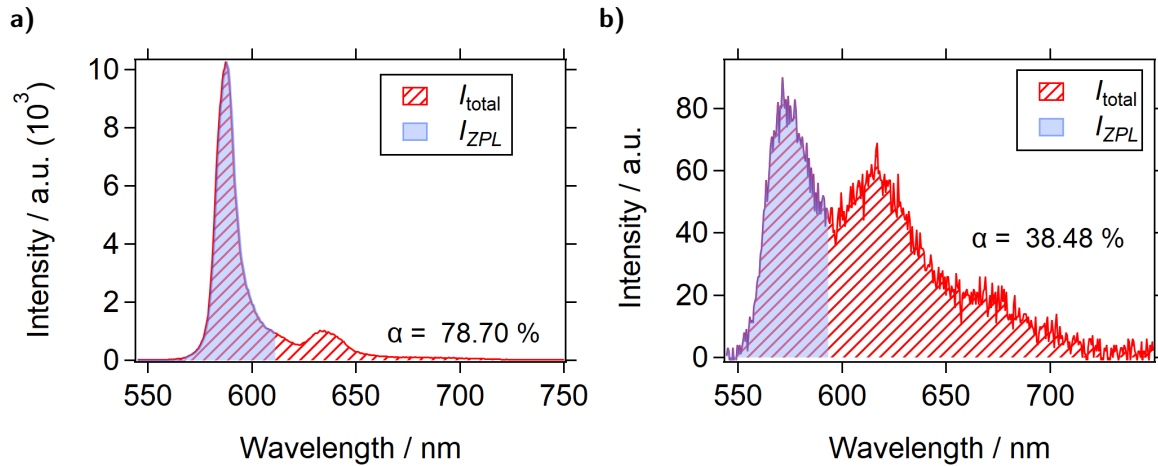


Figure 4.23: Emission spectra of two emitters with the ZPL shaded in blue and the total shaded red. The areas under the curve are used in the calculation of the Debye–Waller factor α . **a)** Spectrum of an emitter in an untreated sample. The ZPL is very prominent and fitted with a Lorentzian, while the PSB is less pronounced. 78.7 % of photons are emitted into the ZPL according to the Debye–Waller calculation. **b)** Spectrum of an emitter in the air-annealed sample. The ZPL and PSBs are less distinct and the corresponding DW factor is 38.5 %.

Because the emission characteristics of individual emitters vary significantly, the Debye–Waller factor α also fluctuates strongly, ranging from a minimum of 31.4 % to a maximum of 85.8 %. For several emitters, the ZPL lies outside the detectable spectral range due to setup limitations, making their α values indeterminable. The average Debye–Waller factor across all evaluated emitters is $(64.0 \pm 11.4)\%$.

Fig. 4.24 presents a histogram of the calculated Debye–Waller factors, where the x-axis indicates α values between 0.2 and 1, and the y-axis shows their incidence. Most emitters exhibit Debye–Waller factors between 50 % and 80 %, which approximately overlaps with one standard deviation to either side of the mean value (marked with a red vertical line).

The average α values for the different samples show little variation, ranging from 59.7 % (air-annealed) to 67.3 % (untreated), as summarized in Table 4.6. The untreated, ozone-treated, and nitrogen-annealed samples display similar mean values, while the air-annealed sample shows a slightly reduced average, however the deviation within the samples is bigger than the deviations between samples. No clear correlation between ZPL position and the Debye–Waller factor is observed.

Based on similar published studies of room-temperature emitters, hBN point-defects exhibit comparatively high DW factors, typically ranging between 50 % and 80 % [3, 6, 47], consistent with the results obtained in this work. These values are significantly higher than those of other solid-state emitters operating at room temperature, such as NV-centers in diamond ($\alpha \approx$

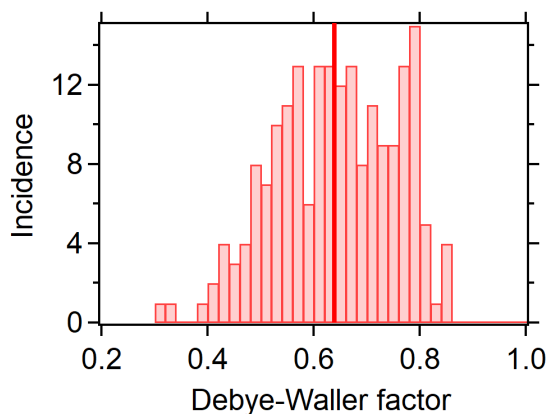


Figure 4.24: Histogram of the Debye-Waller factors for all measured SPEs obtained from their corrected spectrum. The x-axis shows the DW factor between 0.2 and 1.0, while the y-axis displays the incidence. The mean value is indicated by a vertical red line.

Table 4.6: Mean Debye-Waller factor α and corresponding standard deviation σ for SPEs in samples with each treatment condition (untreated, ozone, nitrogen and air).

Sample	α	σ
Untreated	67.3 %	10.8 %
Ozone	62.5 %	9.0 %
Nitrogen	64.2 %	12.3 %
Air	59.7 %	12.1 %

3 – 5 %) or molecular emitters ($\alpha < 10$ %) [24, 100]. Even SiV and SnV centers in diamond, which can achieve DW factors around 70 %, generally require cryogenic temperatures to sustain such performance [108].

A high DW factor together with room-temperature operation and a two-dimensional crystal structure makes hBN a promising platform for integrated quantum photonics. However, the spectral instability seen in hBN emitters throughout this work and in literature remain a key challenge limiting their practical application.

4.2.6 Lifetime

The fluorescence lifetime τ_f describes the average time an emitter spends in its excited singlet state before emission occurs. This process is driven by the decay rate k_{21} as previously introduced in Section 2.5.3. The decay rate consists of the radiative (k_r) and non-radiative decay rates (k_{nr}) and relate to the lifetime via

$$\tau_f = \frac{1}{k_r + k_{nr}}. \quad (4.6)$$

To obtain the fluorescence lifetime experimentally, typically a short light pulse is used to excite the sample. The lifetime is then described by the decrease in excited emitters with time. The fluorescence lifetime can then be determined by measuring the time it takes the fluorescence

intensity to reach $1/e$ of its original value I_0 at $t = 0$ (optical excitation with a pulse). For a single emitter, the experiment is repeated several times and the results are plotted as a histogram [54].

In the absence of a pulsed laser, information about the lifetime can instead be extracted from the second-order correlation measurement. Eq. 3.7 and Eq. 2.33 (see Sections 2.5.3.2 and 3.3.3) describe the three-level energy system of the hBN point-defects and the fit function for the experimental $g^{(2)}(\tau)$ data. The antibunching decay rate is denoted t_2 in the fit function and λ_1 in the theoretical derivation of the $g^{(2)}(\tau)$ function.

To obtain an approximation of the lifetime, the $g^{(2)}(0)$ data is recorded at a range of low powers, each of which are fitted and the value for t_2 is extracted. They are subsequently plotted as a function of the respective power and through a linear fit, the decay rate at zero power, $t_{2,P=0}$, is extrapolated. The excited state lifetime is then calculated with $\tau_f = 1/t_{2,P=0}$ [109–112].

An example of this procedure is shown in Fig. 4.25. The second-order correlation of an emitter (E07) in the ozone-treated sample (hBN06) is measured at different excitation powers.

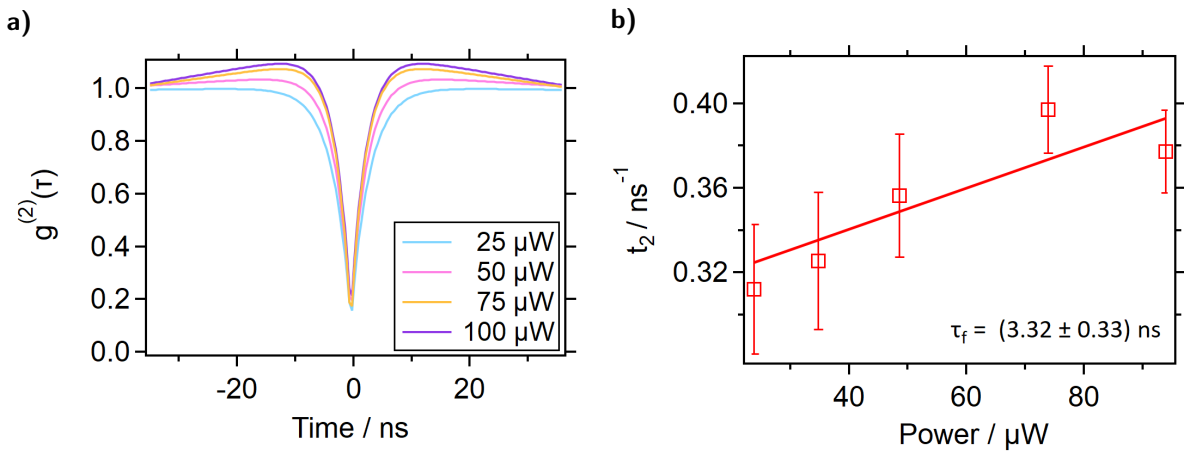


Figure 4.25: **a)** Fit functions of the $g^{(2)}(\tau)$ measurements at different excitation powers for an emitter (E07) in an ozone-treated sample. The data points are omitted for clarity, as the overlap in the scatter plots would obscure the underlying trends. **b)** The extracted decay rates t_2 of the fit functions are plotted as a function of the excitation power. The values are fitted and the intersection point with the y-axis is used to calculate the excited state lifetime τ_f of the emitter.

The fits for each of these measurements are displayed in Fig. 4.25a. The decay rate t_2 is extracted from these fits and plotted as a function of the excitation power in Fig. 4.25b. The error bars represent the calculated error factor from the $g^{(2)}(\tau)$ fit. The values are fitted with a linear function and the intersection with the y-axis is extrapolated and used to calculate the lifetime. The lifetime for this emitter is calculated to be $\tau_f = (3.32 \pm 0.33) \text{ ns}$. The error is obtained through the error propagation of the fitting errors for each $g^{(2)}(\tau)$ measurement with the error for the linear fit.

While this way of extrapolating the lifetime from the $g^{(2)}(\tau)$ measurements is not as accurate

as the usual time-correlated single-photon counting (TCSPC) approach using a pulsed laser, it can be assumed to be accurate enough to provide an estimate and confirm the lifetime values reported in literature. The lifetime of the hBN point-defects in the visible range is often reported between 2 and 6 ns [26].

The obtained lifetimes of individual emitters vary significantly. This is illustrated in Fig. 4.26, where the second-order correlation fit functions for six different emitters are displayed. The interpolated lifetimes range from 1.6 ns to 18.7 ns, with each value shown in the same color as its corresponding fit. As expected from the fit function, emitters with longer lifetimes exhibit broader antibunching dips. This reflects the underlying photodynamics of point defects: an emitter that remains in the excited state longer before emitting a photon produces a slower recovery of the correlation function to $g^{(2)}(\tau) = 1$. Conversely, emitters that emit photons more rapidly display narrower dips, as their correlation functions return to one more quickly.

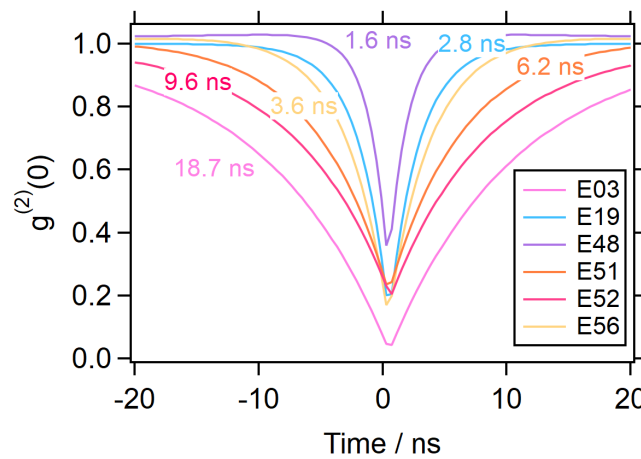


Figure 4.26: Comparison of $g^{(2)}(0)$ shape in connection to the calculated lifetime. Fit functions for different emitters in the nitrogen-annealed sample at low excitation power $P = 20 \mu\text{W}$. For each emitter, the extrapolated lifetime is denoted in the same color as the corresponding fit. The data points are omitted for clarity, as the overlap in the scatter plots would obscure the underlying trends.

Because the emitters are prone to photobleaching under continuous-wave excitation, determining their lifetimes in this way is challenging. In many cases, multiple $g^{(2)}(\tau)$ measurements per emitter cannot be completed before bleaching occurs, as was similarly noted during the saturation measurements in Section 4.1.3. By extrapolating the lifetimes from 20 emitters – each characterized at five excitation powers – an average lifetime of (6.05 ± 3.92) ns is obtained. The reported uncertainty represents the combined fitting errors from all emitters.

The obtained average is slightly higher than the typically reported range of 2-6 ns for visible hBN defects, which may arise from several factors: limited sampling (20 emitters), potential inaccuracies in extrapolating the lifetime from the fitting model, and genuinely longer lifetimes for certain defect types, as previously reported in the literature [69].

The lifetime of the emitter is related to the spectral linewidth of the ZPL by the Heisenberg un-

certainty principle. For defects in dielectric materials, the measured linewidths are generally far from being lifetime-limited. Nevertheless, calculating the lifetime-limited linewidth illustrates the influence of the surrounding lattice on the observed spectral broadening. In the ideal case, where no additional broadening mechanisms are present, the linewidth is determined solely by the finite lifetime of the excited state through

$$\Delta E \Delta t \gtrsim \hbar. \quad (4.7)$$

The shape of the zero-phonon line roughly follows a Lorentzian lineshape with a width determined by the excited-state lifetime. Therefore, when setting $\Delta t = \tau_f$, it follows that

$$\Delta E \gtrsim \frac{\hbar}{\tau_f}. \quad (4.8)$$

Without the influence of the lattice, the natural line width (FWHM) of an emitter is therefore given by the inverse lifetime. However, the lattice reduces the lifetime of the excited state by introducing non-radiative decay mechanisms (phonons) [16, 54].

The presented emitter E07 in Fig. 4.25 exhibits a ZPL linewidth of $\Delta E_{\text{ZPL,measured}} = (30.1 \pm 1.1) \text{ meV}$. The lifetime-limited linewidth - calculated using Eq. 4.8 - yields $\Delta E_{\text{ZPL,minimum}} \approx 0.2 \cdot 10^{-3} \text{ meV}$. The experimentally determined linewidth is therefore orders of magnitude broader than the linewidth limit (10^{-5}).

Above absolute zero temperature, thermal motions will introduce random disturbances to the local environment. These perturbations shift the energy of the electronic transition, introducing a temperature dependent broadening of the line width [54]. A factor of more than 10^{-5} , that arises as a consequence of fast dephasing, is usual at room-temperature [24].

4.3 Relative calibration

Narrow-band, room-temperature emitters are of particular interest for the purpose of calibrating single-photon detectors, because they can serve as a convenient quasi-monochromatic photon source to test the spectral response and relative sensitivity of detectors under ambient conditions. The following section therefore explores the use of hBN point-defects for a room-temperature relative calibration of two SPAD detectors.

Emitter E102 (hBN06) is selected for the relative calibration because of its ZPL position and high single-photon purity while also maintaining good temporal stability. The ZPL position is relevant because a 600 nm bandpass filter with 40 nm bandwidth is used to isolate its ZPL emission. The resulting filtered spectrum can be seen in Fig. 4.27a. The measurement is carried out at an excitation power of 100 μW and the corresponding $g^{(2)}(0)$ and count rate trace of the filtered emitter are shown in Fig. 4.27b and Fig. 4.27c. The emitter has a count rate of approximately 300 kcounts/s and a measured $g^{(2)}(0)$ of 0.224. Using Eq. 4.3, the estimated

background-corrected value yields $g_{corr}^{(2)}(0) = 0.205$. This emitter did not bleach even after many hours of continuous excitation.

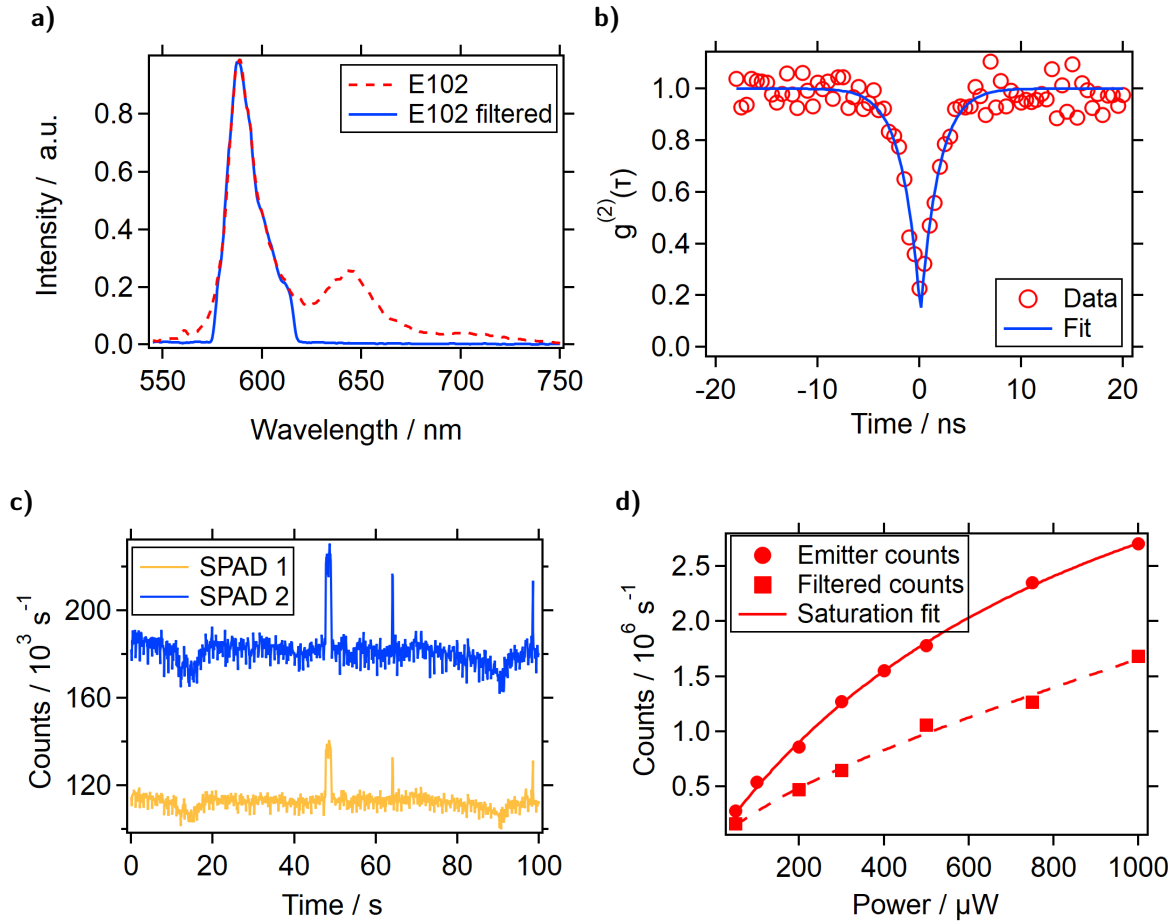


Figure 4.27: Characterization of the single-photon emitter E102 for a relative calibration. **a)** Photoluminescence spectrum with and **b)** Second-order correlation measurement at 100 μW excitation power and with bandpass filter and **c)** Count rate over time and **d)** Saturation measured with and without bandpass filter.

The relative calibration of the SPAD detectors is carried out using the fiber-exchange calibration technique described in Section 3.3.5. Two identical SPAD detectors (SPCM-AQRH-16-FC, Excelitas) are connected to the setup via a multimode fiber-based beamsplitter.

The detection efficiency ratio, including its expanded uncertainty, is determined according to Eq. 3.8, yielding a value of $r_{\text{E102,filtered}} = 1.038 \pm 0.022$. This represents the weighted mean with the expanded uncertainty of the ten measurement pairs. The results for each measurement pair with their type A uncertainty and the weighted mean with the expanded uncertainty are displayed in Fig. 4.28.

Since detectors of identical type are compared, a ratio close to one is expected. The type A uncertainties for individual measurement pairs range between 0.6 % and 0.12 %, which arise from statistical variations. Evaluating the external consistency (Birge ratio) results in a combined type A uncertainty of 0.24 %.

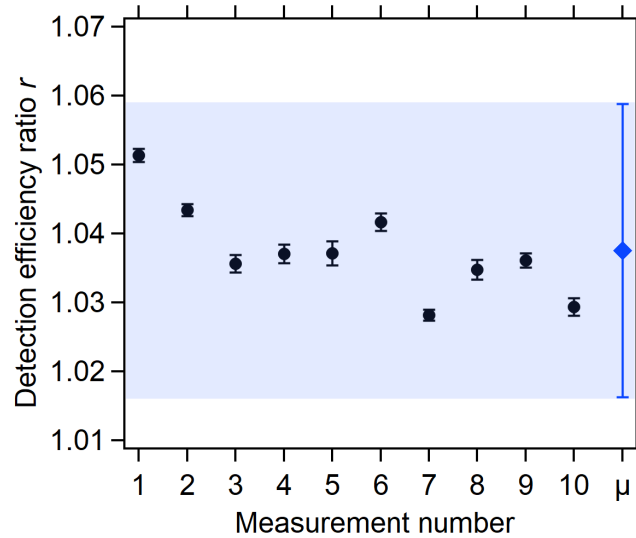


Figure 4.28: Ratio of detection efficiencies for the ten measurement pairs with their type A uncertainties as error bars (black circles). The resulting weighted mean with the total expanded uncertainty is plotted in blue, with the area of the expanded uncertainty shaded.

Ideally, the ratio of detection efficiencies would remain constant if the beamsplitter ratio is perfectly stable and all measurements are performed consistently. However, the spread between the ten measurement pairs indicates an additional contribution to the overall uncertainty from fluctuations in the beamsplitter ratio.

The photon flux varied on average by 2 % relative to its mean value, caused by blinking as seen in the count rate trace in Fig. 4.27c. While such fluctuations do not directly affect the relative calibration, they can lead to an overestimation of the splitting-ratio uncertainty, which is estimated to be approximately 1 %. This uncertainty therefore likely arises from coupling losses and emitter blinking. In particular, variations in coupling efficiency can occur due to slight misalignments in the FC/PC fiber connectors – rotating the fibers during attachment can change the amount of light transmitted by each BS fiber, thereby altering the effective splitting ratio. A smaller overall uncertainty could therefore be achieved by using a more stable emitter and by employing a more robust fiber-coupling.

Other sources of systematic uncertainty can arise from wavelength-dependent variations in the detector efficiencies. Since the emission from hBN point-defects is relatively broad and not strictly monochromatic (limited to approximately 40 nm by the bandpass filter), the detection efficiency can vary across this spectral range. This effect is not included in the current uncertainty budget and could be reduced by employing a narrower filter. However, this would significantly decrease the overall count rate, which, while not critical for a relative calibration, would limit other measurements.

An absolute calibration using a traceable standard was attempted as well. Such a procedure requires high photon fluxes to ensure a detectable signal on the reference detector. A low-noise photodiode (Femtowatt Photoreceiver with Si photodiode, FWPR-20-Si, FEMTO) was used as the reference detector. Since this detector outputs a voltage signal, emitters with count rates

exceeding 1 Mcounts/s are required to produce a measurable voltage above the background noise. Furthermore, measurements should be repeated at several voltage levels, therefore an emitter with even higher count rates ideally up to 3 Mcounts/s is needed.

However, this calibration proved challenging. Although emitters with 1 – 3 Mcounts/s are not uncommon, the use of the bandpass filter reduces the signal by up to 60 %. Moreover, achieving adequately high count rates typically requires higher excitation powers, which in turn leads to increased instabilities such as blinking and bleaching.

In total, 22 calibration attempts were made, all of which failed due to emitter instability. This highlights the intrinsic challenge of using hBN point-defects for long-duration measurements where emission stability is critical. While these emitters are exceptionally bright and spectrally pure for room-temperature SPEs, their short-term stability is limited and their long-term stability essentially absent under the described conditions.

In addition to these limitations, another contribution to the uncertainty in detector calibrations arises from the $g^{(2)}(0)$ value, which in this case exceeds the threshold typically required for metrology-grade single-photon sources ($g^{(2)}(0) < 0.1$) [113]. The associated multiphoton probability introduces a systematic uncertainty in the calibration procedure, which is difficult to quantify in the case of CW excitation.

Taken together, these observations, along with the trend that higher single-photon purity is associated with reduced count rates and the comparatively broad emission spectrum of hBN emitters (FWHM ~ 25 nm), indicate fundamental limitations for their use in metrological detector calibration.

Consequently, the combination of a purity–brightness trade-off, spectral broadening, and limited long-term stability introduces additional systematic uncertainties that prevent their application as traceable primary calibration standards.

4.4 Identification of the hBN point defect

The exact nature of the point defect responsible for the observed emission remains unknown; however, several studies provide compelling evidence that it is associated with carbon-related impurities [26]. Possible defect configurations giving rise to visible emission have already been discussed in Section 2.5.2. In this section, the experimental findings presented are placed in the context of some of these proposed defect models.

Density functional theory (DFT) simulations are needed for identification of the point defects responsible for the emission in the hBN lattice. One approach is to consult the hBN defect database, which compiles DFT-calculated properties for over 200 defect configurations [114].

Generally, DFT calculations are limited by its approximations, especially since the database primarily considers unstrained defect configurations. Calculated transition energies can therefore deviate from experimentally observed values, since strain, local dielectric environment, and uncertain charge states influence the optical properties of the defects and complicate direct

comparison with experiments. To account for these limitations and use the database effectively, the authors include a procedure for identifying likely defect candidates based on multiple experimentally observed parameters.

Using this procedure with the experimental parameters obtained in this work – specifically the ZPL position, excited-state lifetime, and Debye–Waller factor – and applying filters for carbon-based impurities within a multilayer host material, several plausible defect candidates can be identified. These are summarized in Fig. 4.29.

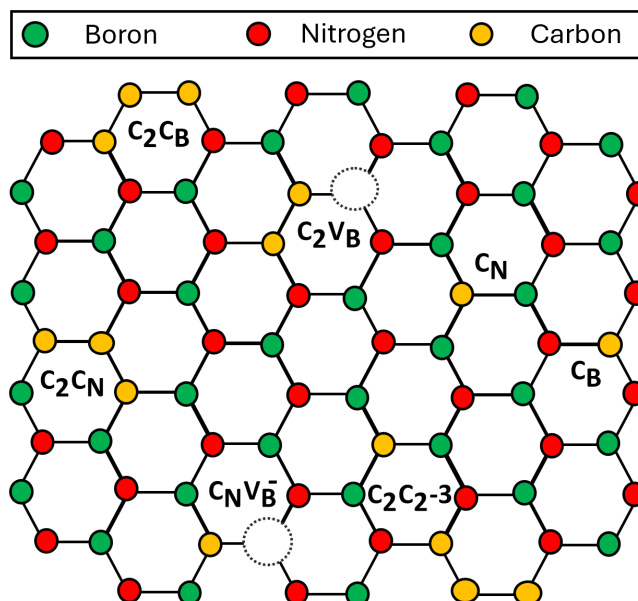


Figure 4.29: Point defect candidates possibly responsible for the emission observed in this work. The hBN lattice consists of boron (green) and nitrogen (red) atoms, with carbon impurities (yellow) highlighted as the most likely sources of the observed emission. The defect structures and corresponding parameters are selected based on density functional theory (DFT) calculations from the hBN defect database [114].

The selection includes several defect types that appear compatible at first glance; however, some exhibit properties inconsistent with the experimental results. For instance, the C_N and C_B defects show calculated lifetimes that are significantly longer than the few-nanosecond regime observed, while others such as C_2C_N and C_2C_B display ZPL positions that deviate considerably from the measured range. Nevertheless, since the ZPL energy can be affected by factors such as local strain, charge environment, and stacking configuration, these defects cannot be entirely ruled out, even though their predicted ZPLs (around 500 nm and 770 nm, respectively) and lifetimes (approximately an order of magnitude larger than measured) lie outside the experimental range.

More promising candidates are C_2C_2-3 , C_2V_B , and $C_NV_B^-$, all of which exhibit ZPL positions within the experimentally observed range and lifetimes between 10 ns and 30 ns. The corresponding calculated properties for these defects are summarized in Fig. 4.29. Notably, the $C_NV_B^-$ defect displays a relatively low Debye–Waller factor compared to the experimentally determined values, although this discrepancy may arise from linewidth broadening effects that

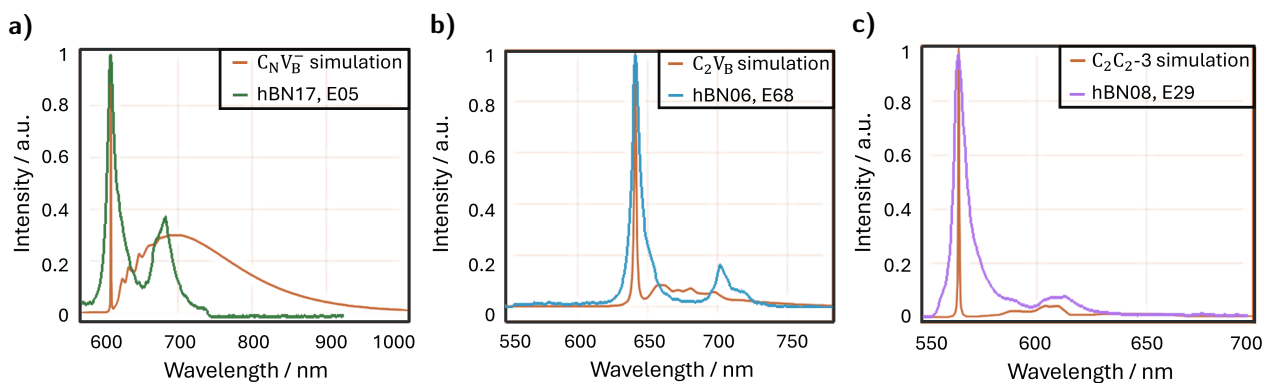


Figure 4.30: Simulated emission spectra of three carbon-based defects in hBN, obtained from density functional theory (DFT) calculations in the hBN defect database [114] in comparison with measured spectra from emitters with the same ZPL position. The defects shown are: **a)** $C_N V_B^-$, **b)** $C_2 V_B$, and **c)** $C_2 C_2 - 3$ (taken on 05.11.2025).

are not fully captured in the DFT models.

Table 4.7: Overview of three possible defect candidates, their simulated ZPL positions, lifetimes, and Debye–Waller factors obtained from the hBN defect database [114]. The rows below the possible defects lists individual emitters of the ozone treated sample (hBN06) and their corresponding measured values for comparison with the simulated defect properties. The last row lists the experimentally determined mean values from this work.

Defect	ZPL position	Lifetime	DW factor
$C_N V_B^-$	608 nm	35 ns	0.03
$C_2 V_B$	641 nm	14 ns	0.41
$C_2 C_2 - 3$	564 nm	17 ns	0.33
E10	577 nm	13.2 ns	0.63
E08	631 nm	16.9 ns	0.58
E12	590 nm	5.8 ns	0.75
E13	667 nm	3.7 ns	0.78
E07	565 nm	3.3 ns	0.58
Average (exp.)	580 nm	6 ns	0.64

To further verify these observations, the simulated emission spectra of the three candidate defects are shown in Fig. 4.30, together with experimental data of an emitter with the same ZPL position. The $C_N V_B^-$ defect exhibits a broad projected phonon sideband, which is inconsistent with the typical emission lineshape observed for hBN SPEs (see Fig. 4.30a). The experimental data exhibits a much smaller phonon side band than can be seen in the simulation. In contrast, the remaining two defects show narrower ZPLs and weaker PSBs that more closely resemble the experimental spectra (Fig. 4.30b-c). Notably, the PSB of the $C_2 C_2 - 3$ defect appears red-shifted by approximately the same amount as the experimental data, further supporting its suitability as a potential candidate.

It is possible that multiple defect species contribute to the observed emission in the prepared samples, which could account for the wide range in optical characteristics measured during

this work. Moreover, the hBN defect database does not fully capture experimental variability, as effects such as stacking order, layer number (beyond monolayer and bulk), local lattice strain and changes in the environment are not considered in the simulations. These factors can significantly influence the electronic structure and optical response of the defects. Nevertheless, among the evaluated candidates, C_2V_B and $C_2C_2 - 3$ emerge as the most plausible origins of the emission observed in this study.

Note that simulated data in the database is updated continuously when improved simulation data is available. The data presented was accessed on 05.11.2025 and values and spectra might differ from the ones presented when accessed at another time.

5 Conclusion and Outlook

Point defects in hexagonal boron nitride (hBN) continue to emerge as a highly promising platform for room-temperature single-photon emission. The easily prepared nanoflakes used in this work offer a fast and accessible route to identifying bright single-photon emitters (SPEs) with good single-photon purity. Post-processing treatments (PPTs) such as high-temperature annealing or ozone cleaning proved effective in enhancing the number of observable SPEs, primarily by removing background fluorescence and improving the single-photon purity. Across all samples, PPTs reduced the average $g^{(2)}(0)$ from 0.56 in untreated hBN to values between 0.29 and 0.35. The purest emitter identified in this study reached a minimum $g^{(2)}(0) = 0.027$, found in the ozone-treated sample.

Despite these improvements, emitter stability remains a significant challenge. More than 25 % of detected SPEs exhibit intensity fluctuations, short-term dark states, or photobleaching within the first 100 s of observation. Over longer timescales, nearly all emitters bleach under continuous-wave excitation. Although PPTs do not directly improve the stability of individual emitters, they substantially increase the probability of encountering a stable one: from roughly 25% in untreated samples to 38% after annealing in air, 54% after annealing in nitrogen, and 60% after ozone treatment due to more available SPEs in the samples.

Several photophysical characteristics of the emitters stand out. The Debye–Waller factor reaches an average value of $(64.0 \pm 11.4) \%$, with individual emitters spanning 30–85%. These values are far higher than those of NV centers ($\sim 3\%$) and more comparable to SiV centers, underlining the potential of hBN defects for applications requiring strong ZPL contributions. The emitters exhibit high brightness under room-temperature operation, with average count rates of 100–300 kcounts/s at 100 μ W excitation power, depending on treatment. The brightest emitter, in the nitrogen-annealed sample, reached 1.4 Mcounts/s; after accounting for detector efficiency and setup transmission, this corresponds to a photon flux exceeding 3 Mphotons/s, while emitters at saturation exhibit even higher photon fluxes (> 4.5 M photons/s).

The ZPLs show an average FWHM of 45 meV (approximately 25 nm) centered around 2.2 eV (587.6 nm), with a wide range of ZPL positions. Lifetime measurements yield an average excited-state lifetime of approximately 6 ns. Combining this information (lifetime, Debye–Waller factor, and ZPL position) with entries from the hBN Defects Database while filtering for carbon-related defects, several possible candidate defects emerge. Among these, the carbon cluster defect $C_2C_2 - 3$ and the vacancy-complex C_2V_B are the best matches to the experimentally measured properties. However, there are many complex structures not included in the database that deserve exploring more - specifically donor-acceptor pairs comprised of multiple defects forming donor and acceptor levels within the band gap [79, 115].

An additional outcome of this work is the demonstration that these emitters can serve as a reference source for the *relative* calibration of SPAD detectors. However, due to the instability of most defects under continuous excitations – especially at the high excitation powers needed

to reach the necessary count rate – improved emitter stability will be crucial before *absolute* calibration becomes feasible.

Overall, this thesis demonstrates that hBN nanoflakes are straightforward and convenient to use, but the photostability of individual emitters remains the primary limitation – particularly for applications requiring long-term measurements. Literature suggests that oxygen exposure contributes to the instability of hBN defects [72, 106], which aligns with the bleaching behavior observed here. Encapsulation in oxygen-poor environments or measurements in inert atmospheres could help verify this hypothesis for the platform at hand.

Another proposed mechanism for the observed instabilities is based on charge dynamics in the vicinity of the defect, which may induce spectral diffusion due to a shift in optical transition energies or photo-induced transitions between different defect charge states. This can modify the emission intensity, lead to temporarily optically inactive configurations or move emission outside of the detected range [53, 79, 116, 117].

Low-temperature experiments could provide deeper insight into phonon coupling, strain environments, and intrinsic linewidths. It would also enable more precise lifetime estimations from ZPL linewidth measurements and could help distinguish between competing defect candidates. With improved methods for stabilization, defect engineering, and controlled sample environments, hBN has the potential to become a leading platform for scalable, room-temperature quantum photonics.

6 References

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9 Appendix

9.1 Acknowledgement

Copyrighted material has been reproduced after obtaining permission from the publishers. This concerns figures in the theoretical background (section 2) taken from publications which have not been published as open access. Furthermore, I acknowledge project funding from the EMPIR project 20IND205 QADeT and the EPM project 23NRM04 NoQTeS.

9.2 hBN samples

9.2.1 Samples

Table 9.1: Table of self-made samples used for this work. Included are the sample name, the substrate, the concentration and the PPT applied.

Sample name	Substrate	Concentration	PPT
hBN01	Glass	10 x 20 μ L	
hBN02	Glass	1 x 20 μ L	
hBN03	Glass	5 x 20 μ L	
hBN05	Glass	10 x 20 μ L	
hBN06	Silicon	10 x 20 μ L	Ozone
hBN08	Silicon	10 x 20 μ L	Nitrogen 1000 °C
hBN09	Silicon	8 x 20 μ L	Air 700 °C
hBN10	Glass	5 x 20 μ L	
hBN12	Glass	12 x 20 μ L	
hBN13	Silicon	12 x 20 μ L	Ozone
hBN14	Silicon	10 x 20 μ L	Nitrogen, 1000 °C
hBN15	Silicon	10 x 20 μ L	Ozone
hBN16	Silicon	12 x 20 μ L	
hBN17	Silicon, grid	10 x 20 μ L	Ozone
hBN19	Silicon, grid	10 x 20 μ L	Air, 1000 °C
hBN26	Silicon	10 x 20 μ L	Vacuum, 400 °C
hBN27	Silicon	10 x 20 μ L	Vacuum, 600 °C
hBN28	Silicon	10 x 20 μ L	Vacuum, 800 °C
hBN29	Silicon	13 x 20 μ L	Air, 400 °C
hBN32	Silicon	10 x 20 μ L	Vacuum, 400 °C

9.2.2 Sample preparation protocol

1. Fill a small Petri dish with acetone under the exhaust hood and label it (acetone).
2. Place the silicone wafers in the acetone and leave it to soak a couple of minutes.

3. Fill the sonic bath with water to the indicated line (can be seen by the residue left on the walls of the sonic bath). Make sure the red lever in the back is turned so that the water does not flow out again.
4. Turn the knob in the front to 'degas' for one minute, then set it to continuous operation.
5. Shake the hBN solution for 1-2 min using the lab dancer (blue conical device). When pressing in the middle, it will vibrate. Afterwards, place the hBN solution in the sonic bath.
6. Fill a beaker with 5% Hellmanex solution.
7. Use tweezers remove the Si wafers from the acetone and rinse them with distilled water. Leave the Petri dish with acetone under the exhaust hood to evaporate.
8. Place the cleaned wafers into the Hellmanex solution and add the beaker to the sonic bath.
9. Prepare the hot plate by placing it under the exhaust and turning it on. Adjust the temperature to 85°C by turning the temperature knob and set the temperature by pressing the knob. Place three glass microscope slides on top of the hot plate with 1-2 mm distance between them. They will prevent the wafers from sticking to the surface.
10. Prepare the microliter pipette by adjusting it to 20 μ L and placing the correct size tip box next to it. Microliter pipettes have different pressure points for taking and releasing liquid and discarding the tips (look up how to use if unfamiliar).
11. Remove the beaker with the wafers from the sonic bath and rinse them with ethanol, then distilled water.
12. Dry them using compressed air. The outlet is at the wall with a rubber tube attached to it. Turn the knob at the side until compressed air is coming out. Control the pressure of the compressed air by pinching the end of the rubber tube. When drying the wafers, make sure to grab them tightly with tweezers at the side of the wafer, then clean the shiny side with the compressed air so that no water stains can be seen on the surface.
13. Place the wafers on the microscope slides on the hot plate, making sure to be able to lift them in the gap between the microscope slides.
14. Remove the hBN solution from the sonic bath, turn it off and place the solution opened next to all other components.
15. Drop 20 μ L drops after each other on each wafer. Wait until they dry and repeat placing 20 μ L drops all over the wafer, making sure to let them dry between each drop.

16. When done, place the samples in the coin style wafer shippers (round boxes) and label each box with a sample number, the concentration of hBN (e.g. hBN21, 5 x 20 μ L) and the date.
17. Unplug the hot plate, let the water drain out of the sonic bath and put all solutions back in the cabinet. Place Parafilm around the lid of the hBN solution bottle. Parafilm is a waxy sealing film that can be stretched and prevents evaporation. The Hellmanex beaker can be rinsed with water.

9.2.3 Datasheet

The datasheet for the commercial hBN nanoflakes (from the now out-of-service Graphene Supermarket website) is attached, starting on the next page.

Description

Boron Nitride (BN) Pristine Flakes in Solution, 100 ML

BN Pristine Flakes are nanoscale crystals dispersed in ethanol/water solution. Solution of nano-BN has a white translucent color, in contrast to the milky suspension of micro-sized BN flakes.

Properties:

Lateral Size: 50-200 nm

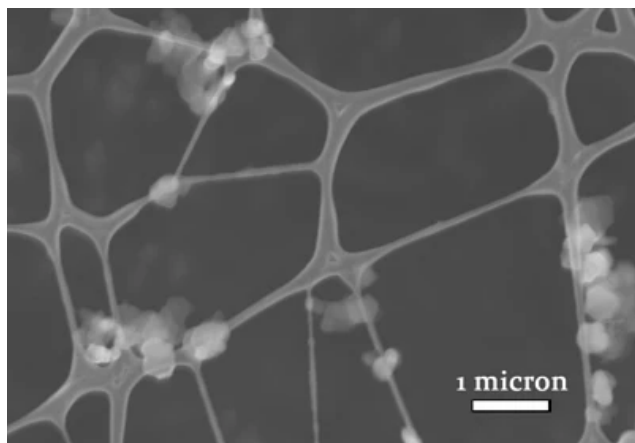
Thickness: 1-5 Monolayers

Purity in Dry Phase: >99%

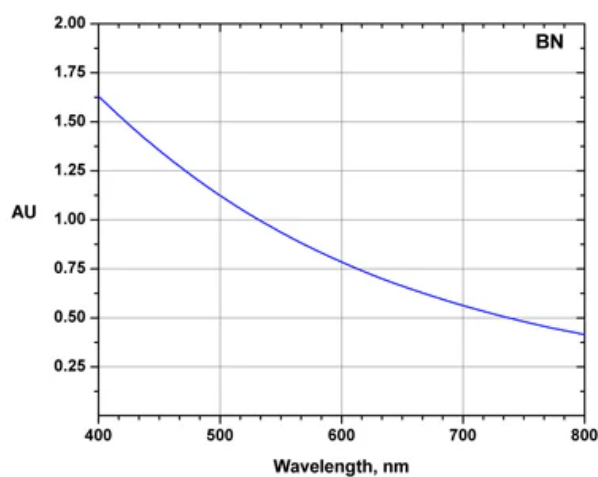
Solution Concentration: 5.4 mg/L

Solution is stable under ambient conditions

SEM IMAGE OF A BN FLAKE

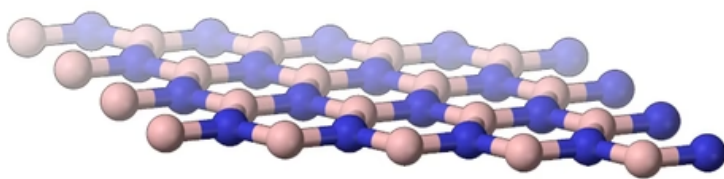


UV-VISIBLE ABSORPTION SPECTRUM



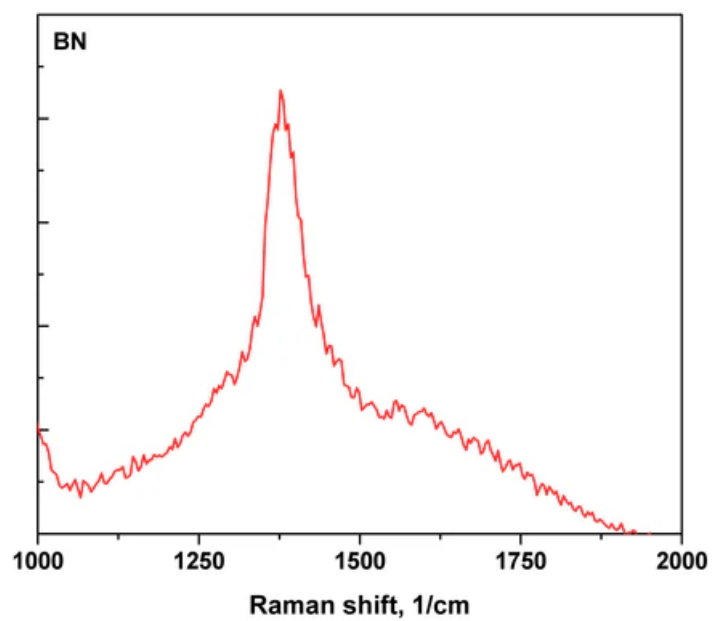
Boron nitride is a chemical compound with chemical formula BN, consisting of equal numbers of boron and nitrogen atoms. BN is isoelectronic to a similarly structured carbon lattice and thus exists in various crystalline forms. The hexagonal form corresponding to graphite is the most stable and softest among BN polymorphs, and is therefore used as a lubricant and an additive to cosmetic products.

DEPICTION OF BN MOLECULAR STRUCTURE



Preparation Method: Solution-based Exfoliation

BN RAMAN SPECTRUM



Applications

Dielectric Layer in Transistors

Hybrid Materials

BN Research

Inks

Thin Insulating Films

Protective Coatings

Deep Ultraviolet (DUV) Emitters

9.3 Codes

9.3.1 Qudi: Configuration file

```
1
2  # The recommended path for user specific files is C:\Users\<user_name>\
  qudi\config
3
4  global:
5      # list of modules to load when starting
6      startup_modules: []
7
8      # Module server configuration for accessing qudi GUI/logic/hardware
  modules from remote clients
9      remote_modules_server:
10         address: 'localhost'
11         port: 12345
12
13     # Server port for serving the active qudi module namespace locally (
  localhost).
14     # Used by e.g. the Qudi jupyter kernel.
15     namespace_server_port: 18861
16
17
18     force_remote_calls_by_value: True
19
20     # Qss stylesheet for controlling the appearance of the GUIs.
21     stylesheet: 'qdark.qss'
22
23     # Default root directory for measurement data storage. All eventual
  data sub-directories should
24     # be contained within this directory. This is not enforced, just
  convention.
25     # The fallback directory is <user home>/qudi/Data/
26     # default_data_dir: C:\Users\neverhorst\qudi\Data
27
28     #C:\Users\mess413\qudi\Data
29
30     # Save data to daily data sub-directories by default
31     daily_data_dirs: True
32
33  gui:
34      time_series_gui:
35          module.Class: 'time_series.time_series_gui.TimeSeriesGui'
36          options:
```

```

37         use_antialias: True # optional, set to False if you
    encounter performance issues
38     connect:
39         _time_series_logic_con: time_series_reader_logic
40
41     scanner_gui:
42         module.Class: 'scanning.scannergui.ScannerGui'
43     options:
44         image_axes_padding: 0.02
45         default_position_unit_prefix: null # optional, use unit
    prefix characters, e.g. 'u' or 'n'
46         optimizer_plot_dimensions: [2,1]
47     connect:
48         scanning_logic: scanning_probe_logic
49         data_logic: scanning_data_logic
50         optimize_logic: scanning_optimize_logic
51
52     poi_manager_gui:
53         module.Class: 'poimanager.poimanagergui.PoiManagerGui'
54     options:
55         data_scan_axes: xy #optional, default: xy
56     connect:
57         poi_manager_logic: 'poi_manager_logic'
58
59     odmr_gui:
60         module.Class: 'odmr.odmrgui.OdmrGui'
61     connect:
62         odmr_logic: 'odmr_logic'
63
64
65     task_runner_gui:
66         module.Class: 'taskrunner.task_runner_gui.TaskRunnerGui'
67     connect:
68         task_runner: 'task_runner_logic'
69
70     logic:
71         time_series_reader_logic:
72             module.Class: 'time_series_reader_logic.TimeSeriesReaderLogic'
73         options:
74             max_frame_rate: 20 # optional (default: 20Hz)
75             channel_buffer_size: 1048576 # optional (default: 1MSample)
76             max_raw_data_bytes: 1073741824 # optional (default: 1GB)
77             calc_digital_freq: True # optional (True by default)
78         connect:
79             streamer: ni_instreamer
80
81     scanning_probe_logic:

```

```

82     module.Class: 'scanning_probe_logic.ScanningProbeLogic'
83     options:
84         max_history_length: 20
85         max_scan_update_interval: 2
86         position_update_interval: 1
87     connect:
88         scanner: ni_scanner
89
90     scanning_data_logic:
91         module.Class: 'scanning_data_logic.ScanningDataLogic'
92         options:
93             max_history_length: 20
94         connect:
95             scan_logic: scanning_probe_logic
96
97     scanning_optimize_logic:
98         module.Class: 'scanning_optimize_logic.ScanningOptimizeLogic'
99         connect:
100             scan_logic: scanning_probe_logic
101
102
103     poi_manager_logic:
104         module.Class: 'poi_manager_logic.PoiManagerLogic'
105         connect:
106             scanning_logic: 'scanning_probe_logic'
107             optimize_logic: 'scanning_optimize_logic'
108             data_logic: 'scanning_data_logic'
109
110
111     odmr_logic:
112         module.Class: 'odmr_logic.OdmrLogic'
113         connect:
114             microwave: mw_source_smiq
115             data_scanner: ni_finite_sampling_input
116
117
118     task_runner_logic:
119         module.Class: 'taskrunner.TaskRunnerLogic'
120         options:
121             module_tasks: {}
122
123     hardware:
124
125         ni_scanner:
126             module.Class: 'interfuse.ni_scanning_probe_interfuse.
NiScanningProbeInterfuse'
127             connect:

```

```

128         scan_hardware: 'ni_io'
129         analog_output: 'ni_ao'
130     options:
131         ni_channel_mapping:
132             x: 'ao0'
133             y: 'ao1'
134             z: 'ao2'
135             #a: 'ao3'
136             APD1: 'PFI8'
137             #APD2: 'PFI9'
138             #AI0: 'ai0'
139             #APD3: 'PFI10'
140         position_ranges: # in m
141             x: [0, 300e-6]
142             y: [0, 300e-6]
143             z: [0, 300e-6]
144         frequency_ranges:
145             x: [1, 5000]
146             y: [1, 5000] #these voltages have to be adjusted to
147             z: [1, 1000] # for that you have to look up the
148             specifications, mine should be around 150 Hz
149         resolution_ranges:
150             x: [1, 10000]
151             y: [1, 10000]
152             z: [1, 10000]
153         input_channel_units:
154             APD1: 'c/s'
155             #AI0: 'V'
156             #APD2: 'c/s'
157             #APD3: 'c/s'
158         backwards_line_resolution: 50 # optional
159         maximum_move_velocity: 400e-6 #m/s
160
161     ni_io:
162         module.Class: 'ni_x_series.ni_x_series_finite_sampling_io.
163         NIXSeriesFiniteSamplingIO'
164     options:
165         device_name: 'Dev1'
166         input_channel_units: # optional
167             PFI8: 'c/s'
168             #PFI9: 'c/s'
169             #PFI10: 'c/s'
170             #ai0: 'V'
171             #ai1: 'V'
172         output_channel_units:
173             'ao0': 'V'
174             'ao1': 'V'

```

```

172         'ao2': 'V'
173     adc_voltage_ranges:
174         #ai0: [-10, 10] # optional
175         #ai1: [-10, 10] # optional
176     output_voltage_ranges:
177         ao0: [-10, 10]
178         ao1: [-10, 10]
179         ao2: [-10, 10]
180
181     frame_size_limits: [1, 1e9] # optional #TODO actual HW
182     constraint?
183     output_mode: 'JUMP_LIST' # 'JUMP_LIST' # optional, must be
184     name of SamplingOutputMode
185     read_write_timeout: 10 # optional
186     #sample_clock_output: '/Dev1/PFI11' # optional
187
188     ni_ao:
189         module.Class: 'ni_x_series.ni_x_series_analog_output.
190         NIXSeriesAnalogOutput'
191         options:
192             device_name: 'Dev1'
193             channels:
194                 ao0:
195                     limits: [-10.0, 10.0]
196                     keep_value: True
197                 ao1:
198                     limits: [-10.0, 10.0]
199                     keep_value: True
200                 ao2:
201                     limits: [-10.0, 10.0]
202                     keep_value: True
203                 ao3:
204                     limits: [-10.0, 10.0]
205                     keep_value: True
206
207     ni_instreamer:
208         module.Class: 'ni_x_series.ni_x_series_in_streamer.
209         NIXSeriesInStreamer'
210         options:
211             device_name: 'Dev1'
212             digital_sources: # optional
213                 - 'PFI8'
214                 #- 'PFI9'
215             #analog_sources: # optional
216             # - 'ai0'
217             # - 'ai1'
218             # external_sample_clock_source: 'PFI0' # optional

```

```

215         # external_sample_clock_frequency: 1000 # optional
216         adc_voltage_range: [-10, 10] # optional
217         max_channel_samples_buffer: 10000000 # optional
218         read_write_timeout: 10 # optional
219
220     mw_source_smiq:
221         module.Class: 'microwave.mw_source_smiq.MicrowaveSmiq'
222         options:
223             visa_address: 'GPIB0::13::INSTR'
224             comm_timeout: 100 # in milliseconds
225
226     ni_finite_sampling_input:
227         module.Class: 'ni_x_series.ni_x_series_finite_sampling_input
.NIXSeriesFiniteSamplingInput'
228         options:
229             device_name: 'Dev1'
230             #digital_sources: # optional
231             #- 'PFI8'
232             digital_channel_units: # optional
233                 'PFI8': 'c/s'
234             analog_channel_units: # optional
235                 'ai0': 'V'
236                 'ai1': 'V'
237
238     microwave_dummy:
239         module.Class: 'dummy.microwave_dummy.MicrowaveDummy'
240
241

```

9.3.2 Jupyter: Digital control of piezo controller

```

1     # PI provides Python compatibilty, PIPython, installed from Github
2     from pipython import GCSDevice
3     from pipython import GCS30Commands as cmd
4     pi_inst=GCSDevice()
5
6     # find out which devices are connected
7     devices = pi_inst.EnumerateUSB(mask='')
8
9     # make and show list of connected devices
10    for i, device in enumerate(devices):
11        print('{} - {}'.format(i, device))
12        pi_inst.ConnectUSB("1234567")
13
14    # Activating servo mode for each axis
15    pi_inst.SV0(1,1)

```

```

16 pi_inst.SV0(2,1)
17 pi_inst.SV0(3,1)
18 pi_inst.qSV0()
19
20 '''
21 Piezo Controller is now connected and servo control activated.
22 Now the sensors have to be adjusted and for this, gain and offset have
to be configured.
23 For this, we need advanced control rights:'''
24 pi_inst.CCL(1,'advanced')
25
26 # Checking the MaxScaledValue (qTMX) and MinScaledValue (qTMN)
27 pi_inst.qTMN(), pi_inst.qTMX()
28 MinScaledValue = 0
29 MaxScaledValue = 300
30
31 # Normalized Value refers to the voltage, the voltage range is -10 to 10
V and is converted into values between -100 and 100
32 MinNormValue = -100
33 MaxNormValue = 100
34
35 #Calculation from p. 84 of the E-725 Handbook
36 GAIN = (MaxScaledValue - MinScaledValue) / (MaxNormValue - MinNormValue)
37 OFFSET = MaxScaledValue - GAIN * MaxNormValue
38 print('GAIN: %.2f' %GAIN)
39 print('OFFSET: %.2f' %OFFSET)
40
41 # Adjust the offset and gain
42 print("Offset",'\\t\\t', 'Gain')
43 for i in range(4,7):
44     pi_inst.SPA(i, 0x02000200, 150) # Offset
45     pi_inst.SPA(i, 0x02000300, 1.5) # Gain
46     print(pi_inst.qSPA(i, 0x02000200),pi_inst.qSPA(i, 0x02000300) )
47
48 # Control analog lines
49 for i in range(1,4):
50     print(pi_inst.qSPA(i, 0x06000500))
51
52 #Adjust analog lines
53 pi_inst.SPA(1, 0x06000500,4)
54 pi_inst.SPA(2, 0x06000500,5)
55 pi_inst.SPA(3, 0x06000500,6)
56
57 pi_inst.close
58
59 print('DONE')
60

```

9.3.3 Spyder: Count rate & Second-order correlation

```

1  import numpy as np
2  import pandas as pd
3  #import seaborn as sns
4  from scipy.optimize import curve_fit
5  from scipy.optimize import minimize
6  from scipy import stats
7  import matplotlib.pyplot as plt
8  import sympy as sp
9  from sympy import *
10
11  #Set directory and the settings of the measurements
12  directory = '../06-2024/20240709/'
13  Emitter = 'E122'
14  #angles = 104, 94, 86, 76, 70
15  #Powers = 50, 73, 102, 155, 197
16  Power = 102
17  AcquisitionTime = 100
18  sample = 'hBN06'
19
20  binname = 200
21  binwidth = binname*10**(-12)
22  Nbins = 400
23  ExposureTime = 1
24
25
26  file_counts = directory + sample + '_' + Emitter + '_counts_' + str(
Power) + 'uW' + '.txt'
27  file_g2 = sample + '_' + Emitter + '_g2_' + str(Power) + 'uW' + '_bin'+
str(binname)+'ps_time'+str(AcquisitionTime)+'s.txt'
28
29  pathResults = directory + 'Graphs//'
30  pathg2 = directory
31
32
33  ##### Load the counts #####
34  Counts1, Counts2 = np.loadtxt(file_counts, dtype=np.float64 ,delimiter
= '\t', unpack=True, usecols=(1,2), skiprows=1)
35
36
37
38
39  ##### Load the g2 data #####
40
41
42  Time_ps = np.loadtxt(file_counts, dtype=np.float64 ,delimiter = '\t',

```



```

unpack=True, usecols=(0),skiprows=1)
43     Time = Time_ps*10**(-12)
44     xdataps, Coincidences = np.loadtxt(pathg2 + file_g2 , dtype=np.float64
, unpack=True, usecols=(0,1),skiprows=1)
45     xdata = xdataps/1000
46
47
48
49     ##### Laser calibration #####
50     Plaser= [6.04,5.40,4.71,4.10,3.6,2.6,2.02,1.52,1.,0.5]
51     Psample= [2.8,2.64,2.25,1.83,1.36,1.15,0.89,0.67,0.44,0.22]
52
53     def lin_fit (x,m,q):
54         y = m*x + q
55         return y
56
57     poptP, pcovP = curve_fit(lin_fit,Plaser,Psample)
58     m,q = poptP
59
60     #This gives power on sample from the power measured underneath objective
61     P = 0.47656*Power
62
63
64     # Plot the counts
65
66     CountTrace, (ax5) = plt.subplots(nrows=1, ncols=1, figsize=(10, 7))
67     fontsize = 30
68     for tick in ax5.xaxis.get_major_ticks():
69         tick.label1.set_fontsize(fontsize)
70     for tick in ax5.yaxis.get_major_ticks():
71         tick.label1.set_fontsize(fontsize)
72     ax5.set_title(Emitter + ' Counts', fontsize = fontsize)
73     plt.plot(Time,Counts1/1000,c='b',label = 'SPAD1')
74     plt.plot(Time,Counts2/1000,c='r',label = 'SPAD2')
75     ax5.set_ylabel('kcps', fontsize=fontsize)
76     ax5.set_xlabel('t / s', fontsize=fontsize)
77     ax5.tick_params(axis='x', labels=fontsize)
78     ax5.tick_params(axis='y', labels=fontsize)
79     ax5.legend(fontsize=fontsize)
80     plt.savefig(pathResults + Emitter + '_' + str(round(P, 2)) + '
uW_CountTrace.png')
81
82     ##### Normalize the g2 data #####
83     errCoincidences = np.sqrt(Coincidences)
84
85     Rate1 = np.mean(Counts1)/ExposureTime
86     Rate2 = np.mean(Counts2)/ExposureTime

```

```

87     errRate1 = np.std(Counts1)
88     errRate2 = np.std(Counts2)
89
90     CoincNorm = Coincidences/(Rate1*Rate2*binwidth*AcquisitionTime)
91     errCoincNorm = np.sqrt((errCoincidences/(Rate1*Rate2*binwidth*
AcquisitionTime))**2+((Coincidences*errRate1)/((Rate1**2)*Rate2*binwidth*
AcquisitionTime))**2+((Coincidences*errRate2)/((Rate2**2)*Rate1*binwidth*
AcquisitionTime))**2)
92
93
94     ##### find minimum and move curve to 0 #####
95
96     def find_index_minimum(x_data, y_data):
97         g0 = np.min(y_data)
98         x_min = tuple([np.where(y_data == g0)])
99         x_value_center_in_0 = x_data[x_min]
100         return float(x_value_center_in_0[0])
101
102     x0 = find_index_minimum(xdata, CoincNorm2)
103     g2min = np.min(CoincNorm2)
104
105
106     ##### fit the g2 curve #####
107
108     def g2_fit(x,c2, c3, xoff, t2, t3,I):
109         g2 = I*(1-c2*np.exp(-abs(x-xoff)*t2)+ c3*np.exp(-abs(x-xoff)*t3))
110         return g2
111
112     popt, pcov = curve_fit(g2_fit,xdata,CoincNorm2,p0=(0.,0.,x0
,0.2,0.003,1.),maxfev=20000)
113     c2, c3, xoff, t2, t3,I = popt
114     errors = np.sqrt(np.diag(pcov))
115     y_fit=g2_fit(xdata,c2, c3, xoff, t2, t3,I)
116
117     ##### print the t2 value and its error #####
118     print('Power \t t2 \t t2_error')
119     print(str(round(P, 5))+'\t' "{: .4f} \t { :.4f}".format(t2,errors[3]))
120     print(Rate1+Rate2)
121
122
123     ##### plot g2 data #####
124
125     g2Graph, (ax5) = plt.subplots(nrows=1, ncols=1, figsize=(10, 7))
126     for tick in ax5.xaxis.get_major_ticks():
127         tick.label1.set_fontsize(fontsize)
128     for tick in ax5.yaxis.get_major_ticks():
129         tick.label1.set_fontsize(fontsize)

```

```

130
131     ax5.set_title(Emitter + ' fit g\u00B2(t)', fontsize = fontsize)
132
133     ax5.scatter(xdata-x0, CoincNorm2,color='b',label='Power on sample = ' +
134     str(round(P,2))+'\uW')
135
136     ax5.plot(xdata-x0, y_fit,color='r',label='fit' )
137
138     ax5.set_ylabel('g\u00B2(t)', fontsize=fontsize)
139     ax5.set_xlabel('t / ns', fontsize=fontsize)
140     #plt.ylim((0,2))
141     plt.xlim((xdata[0]-x0-1,xdata[-1]-x0+1))
142     ax5.axhline(y=0.5, xmin=0.0, xmax=xdata[-1], color='r', alpha =0.5)
143     ax5.axhline(y=0, xmin=0.0, xmax=xdata[-1], color='k')
144     ax5.tick_params(axis='x', labels=fontsize)
145     ax5.tick_params(axis='y', labels=fontsize)
146     ax5.legend(fontsize=18)
147     plt.text(-3,0.03,'g2 = ' + str(round(g2min, 3)), fontsize = 25)
148     plt.savefig(pathResults + Emitter + '_' + str(round(P, 2)) + '\uW_g2.png')

```

9.3.4 Spyder: Spectrum with Lorentzian fit

```

1
2     import numpy as np
3     import pandas as pd
4     from scipy.optimize import curve_fit
5     from scipy.optimize import minimize
6     from scipy import stats
7     import matplotlib.pyplot as plt
8     import math
9     import sympy as sp
10    from sympy import *
11
12
13
14    directory = '../spectra/untreated/'
15    pathSpectra = directory + '590 - 650 nm/' + '#+ 'spectra/'
16    pathGraphs = directory + 'Graphs/'
17    fileName = 'cut_corr_hBN06_100muW_5s_E102'
18
19    #Emitter = 'E120'
20    Wavelength , Intensity = np.loadtxt(pathSpectra + fileName + '.dat',
21    dtype=np.float64 ,delimiter = '\t', unpack=True, usecols=(0,1),skiprows
22    =1)
23
24    Int_corr = Intensity #- IntensityBkg #790 #

```

```

23
24 xData = []
25
26 ##### FIT #####
27 inv_wavelength=1/Wavelength * 10**9;
28 energy_ev = (2.99792458*10**8)*(6.62606896*10**(-34))
/(1.60217649*10**(-19))*inv_wavelength;
29
30 max_y = np.max(Int_corr)
31 max_x = energy_ev[np.argmax(Int_corr)]
32 print("Maximum =", max_x)
33
34 lim_max = max_x + .1
35 lim_min = max_x - .02
36 # Create a mask for the region of interest
37 mask = (energy_ev > lim_min) & (energy_ev < lim_max)
38
39 # Apply mask
40 xData = energy_ev[mask]
41 yData = Int_corr[mask]
42
43 ##### Fit a lorentzian #####
44 def lorentzian( x, x0, a, gam ):
45     return a * (gam/2) / ( (gam/2)**2 + ( x - x0 )**2) #gamma is the
FWHM
46
47
48 params,cov2=curve_fit(lorentzian,xData,yData, p0=(2.0,100,0.06), maxfev
= 10000) #p0=(580., 300., 1.)
49 ZPL, A, G = params
50 errorPeaks = np.sqrt(np.diag(cov2))
51 Int_fit = lorentzian(xData, *params )
52
53
54 #####
55
56 print('Lorentzian curve_fit for '+fileName)
57 print('ZPL = {:.f} +- {:.f}'.format(params[0], errorPeaks[0]))
58 print('A = {:.f} +- {:.f}'.format(params[1], errorPeaks[1]))
59 print('Gamma = {:.f} \t {:.f}'.format(params[2], errorPeaks[2]))
60 print('ZPL, FWHM, err = {:.f}\t{:.f}\t{:.f}'.format(params[0], params[2],
errorPeaks[2]))
61
62
63
64 ##### PLOT #####
65

```

```

66     Spectrum, (ax5) = plt.subplots(nrows=1, ncols=1, figsize=(7, 5))    #set
the figure size
67     fontsize = 25
68     for tick in ax5.xaxis.get_major_ticks():
69         tick.label1.set_fontsize(fontsize)
70     for tick in ax5.yaxis.get_major_ticks():
71         tick.label1.set_fontsize(fontsize)
72     fontsize = 25
73     ax5.set_title('Spectrum of ' + fileName, fontsize=fontsize)
74
75     # Plot the SPECTRUM
76     ax5.plot(energy_ev, Int_corr, c='b', linewidth=1.8) #, label = fileName )
77
78     # Plot the FIT
79     ax5.plot(xData, Int_fit, c = 'r', linewidth=2.2)
80
81     # change axis to spines
82     for axis in ['top', 'bottom', 'left', 'right']:
83         ax5.spines[axis].set_linewidth(2)
84
85     # increase tick width
86     ax5.tick_params(width=2)
87
88
89     ax5.set_ylabel('Intensity / a.u.', fontsize=fontsize)
90     ax5.set_xlabel('Energy / eV', fontsize=fontsize)
91     ax5.set_xlim(1.7, 2.3)
92     #ax5.set_ylim(0, 250)
93     ax5.tick_params(axis='x', labelsize=fontsize)
94     ax5.tick_params(axis='y', labelsize=fontsize)
95
96
97     plt.text(600, max_y/2, 'Max. energy = ' + str(round(max_x)) + " eV",
98     fontsize = 25)
99
100     plt.show()
101     plt.savefig(pathGraphs + 'Corrected_Spectrum_' + fileName + '
102     _energy_Fit_100uW' + '.png')
103

```

9.3.5 Matlab: Spectrum correction, DW-factor calculation

```

1         % The path for correction file
2     cd ('...\spectra\')

```

```

3
4 correction_file=load('Spectrum_correction_540-760nm.txt');
5
6 % The files path
7 cd('...\2023\08-2023\230815')
8
9 % The spectrum files stem name
10 Spectrum_filePattern = 'hBN06_100muW*.dat'; %28_100uW_E%
11
12 % Looking at the data files with the name pattern
13 Spectrum_fileList = dir(Spectrum_filePattern); % Get a list of files
    matching the pattern
14
15 % Loading the background data
16 background_data = textread('hBN28_100uW_flake-bg.dat', '%f', 'headerlines',1)
    ;
17
18
19 % Background intensity - every 2nd element is taken, as no separation
    between columns
20 bg_intensity = background_data(2:2:end);
21
22
23 % Allocating the max_intensity vector
24 max_intensity = zeros( length(Spectrum_fileList), 1 );
25 ZPL = zeros( length(Spectrum_fileList), 1 );
26 ZPL_area = zeros( length(Spectrum_fileList), 1 );
27 all_area = zeros( length(Spectrum_fileList), 1 );
28 DW_factor = zeros( length(Spectrum_fileList), 1 );
29 filenames = strings(length(Spectrum_fileList), 1 );
30
31
32 lambda_min = 540;
33 lambda_max = 760;
34 % loop for all the files
35 for i = 1:numel(Spectrum_fileList)
36
37     Spectrum_fileName = Spectrum_fileList(i).name; % Get the name of each
    file
38
39     % Data importing
40     Spectrum_data= textread(Spectrum_fileName, '%f', 'headerlines',1);
41
42     %%%%%% Process the data as needed %%%%%%
43
44     wavelength = Spectrum_data(1:2:end);
45     intensity = Spectrum_data(2:2:end);

```

```

46
47     % subtracting background
48     intensity_corr = intensity - 795;%bg_intensity;%
49
50
51
52     %%%%%%%%% cut data to between 540 and 760 nm, calibrate & save
53     %%%%%%%%%
54
55     % --- Cut to desired wavelength window
56     mask_cut = (wavelength >= lambda_min) & (wavelength <= lambda_max);
57
58     % Handle cases where some files might not reach the exact limits
59     if sum(mask_cut) < 10 % arbitrary threshold
60         warning('File %s has too narrow a range, skipping.',
61             Spectrum_fileName);
62         continue
63     end
64
65     %%%%%%%%% cut data that I work with from now on %%%%%%%%%
66     wavelength_cut = wavelength(mask_cut);
67     intensity_cut = intensity_corr(mask_cut);
68
69     % correct spectrum with the calibration file, USE THIS NOW %
70     calibrated_intensity = intensity_cut ./ correction_file;
71
72     % --- Save new file with '_cut' added ---
73     [~, name, ext] = fileparts(Spectrum_fileName);
74     newFileName = sprintf('cut_corr_%s%s', name, ext);
75
76     % Combine into a 2-column matrix for saving
77     corr_data = [wavelength_cut calibrated_intensity];
78
79     % Save as text file with tab delimiter and header
80     fid = fopen(newFileName, 'w');
81     fprintf(fid, 'Wavelength (nm)\tIntensity\n');
82     fclose(fid);
83     dlmwrite(newFileName, corr_data, '-append', 'delimiter', '\t', '
84     precision', 6);
85
86     %%%%%%%%% Calculate Debye waller, normalize or change to eV
87     %%%%%%%%%
88     %find the maximum intensity and the corresponding wavelength
89     max_intensity(i) = max(calibrated_intensity);

```

```

89 [maxYValue, indexAtMaxY] = max(calibrated_intensity);
90 ZPL(i) = wavelength_cut(indexAtMaxY(1));
91
92
93 % calculate debye waller factor
94
95 mask_zpl = wavelength_cut >= ZPL(i)-20 & wavelength_cut <= ZPL(i)+20; %
    define area for under the ZPL, ZPL maximum +- 22 nm
96 ZPL_area(i) = trapz(wavelength_cut(mask_zpl), calibrated_intensity(
    mask_zpl)); % get area of ZPL
97
98 mask_total = wavelength_cut >= 550 & wavelength_cut <= 750; % define
    area for the total area
99 all_area(i)=trapz(wavelength_cut(mask_total), calibrated_intensity(
    mask_total)); %get total area
100
101 DW_factor(i)=ZPL_area(i)/all_area(i); % divide areas to get DW factor
102
103
104 % put filename into a string array to save it as well
105 filenames(i) = string(Spectrum_fileName);
106
107
108
109 % converting to energy units
110 %inv_wavelength=1./wavelength_cut * 10^9;
111 %energy_ev = (2.99792458*10^8)*(6.62606896*10^(-34))
    /(1.60217649*10^(-19))*inv_wavelength;
112
113 % normalizing data
114 %norm_intensity = (calibrated_intensity) / max(calibrated_intensity);
115
116
117
118 %%%%%%%%%%%%% Plot all %%%%%%%%%%%%%
119 plot(wavelength_cut,calibrated_intensity)%norm_intensity)
120 hold on
121 %plot(wavelength_cut,intensity_cut) %compare before and after
    calibration
122
123 % Fill ZPL region
124 area(wavelength_cut(mask_zpl), calibrated_intensity(mask_zpl), '
    FaceColor', 'r', 'FaceAlpha', 0.3, 'EdgeColor', 'none')
125
126 % Fill the total integrated area
127 %area(wavelength_cut(mask_total), calibrated_intensity(mask_total), '
    FaceColor', 'b', 'FaceAlpha', 0.2, 'EdgeColor', 'none')

```



```
128
129
130     axis tight
131     xlabel('Wavelength / nm')
132     %xlabel('Energy / eV')
133     ylabel('Intensity')
134     set(gcf,'color','w')
135     set(gca,'LineWidth',2,'FontSize',20);
136     title('Spectrum')
137     %ylim([0 1])
138     %ylim([700 3000])
139     %xlim([1.6 2.3])
140     xlim([547 750])
141
142     hold on
143
144 end
145
146
147
148 hold off
149
150
151 T = table(filenames, ZPL, ZPL_area, all_area, DW_factor, 'VariableNames', {'
    Emitters', 'ZPL_pos', 'ZPL_area', 'all_area', 'DW_factor'});
152
153 writetable(T, 'DW-factor-spectra.txt', 'Delimiter', '\t') %save data
154
155
```




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