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Setup of an Hanbury-Brown-Twiss experiment and characterization of semiconducter nanocrystals

Report of the internship in M1
presented by

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The internship was carried out at the
Laboratoire Kastler-Brossel, Paris
under supervision of
Quentin Glorieux
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Contents

1 Introduction

This report presents my internship in the Kastler-Brossel laboratory (LKB) from April to July 2015. The LKB is a fundamental physics research facility ~~funded~~ hosted by CNRS, the École Normale Supérieure (ENS), the Pierre and Marie Curie University (UPMC) and the Collège de France.
I worked in the quantum optics group under supervision of Quentin Glorieux. This group works on miniaturized optical devices, generally called nanophotonics. Such devices may be useful to further push quantum communication. CITATION NEEDED
In one experiment the group investigates the coupling of optical fibers to semiconductor nanocrystals. It may be possible to emit single fluorescence photons of the crystals directly into optical fibers. This is especially interesting because the nanocrystals (NC) are easy to produce and emit fluorescence photons in a small range of wavelengths, which can be controlled through varying the crystal geometry. Why the used nanocrystals have these admirable properties is shortly explained in the following.

2 Theoretical background

The used semiconductor nanocrystals consist of a spherical CdSe-crystal whose diameter is in the order ~~of some~~ nanometers~~.~~ This sphere is embedded in a elongated (20-70 nm) CdS-rod. Such structures are therefore called dot-in-rods and can be created by seeded growth [Carbone et al., 2007].
Through the different poten~~t~~ials in the two different regions, a~~n~~ light induced electron-hole pair is confined. This confinement leads to quantization of states and can be compared to a particle in a box [Rogach, 2008]. The stronger the confinement, the lager gets the separation of the states. So small dots in large rods will emit blue light if the electron-hole pair recombines and big dots in small rods will emit red light. Therefore the emission spectrum can be controlled by changing the crystal geometry.
Thanks to several non-radiative relaxation processes including interaction with phonons and Auger processes [Kambhampati, 2011] the nanocrystals can be excited by ultraviolet or blue light and then emit red light. That qualifies them for fluorescence experiments. During my internship I performed such a fluorescence experiment which is explained in the next part.

3 Definition of task

This part first presents the experimental setup and the characteristics of semiconductor nanocrystals that can be determined with it. Afterwards the problems with this setup and my t[illegible]are explained.

3.1 Experimental setup

To study the photon emission of the used nanocrystals and test if the are really single photon emitters a Hanbury-Brown-Twiss (HBT) setup can be used, such as the one built at LKB by [illegible]anceau, 2014] and depicted in Figure 1.

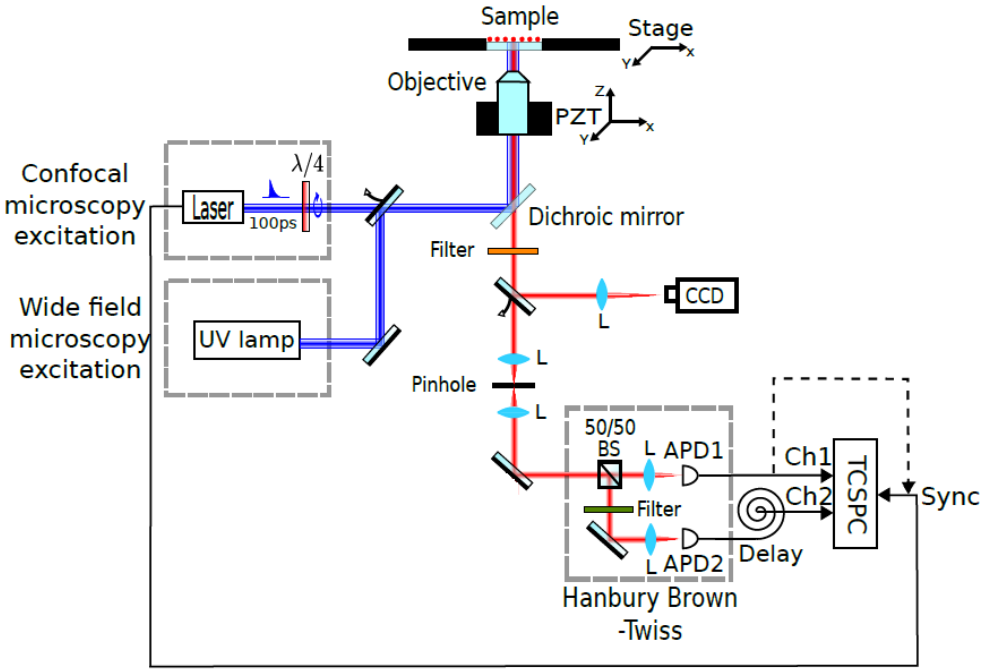

Figure 1: Experimental setup used to characterize the nanocrystal photon emission.

The NCs are deposited on a microscope, with an oil immersion objective with an numerical aperture of 1.4. To do so, they get diluted in chloroform to a density of 10^{-13} Some μl of this liquid are placed on the microscope cover slips, where the chloroform evaporates and only the nanocrystals stay back.
In the *wide field mode*, the nanocrystals are excited by an mercury UV-lamp. The emitted light passes a dichroic mirror and a filter and is registered by a CCD camera. This mode allows to have an overview over a larger area of the p[illegible], so a well-suited, e.g. single NC and not a cluster, can be examined in the *confocal mode*. In this mode the NC is excited by a pulsed laser. The emitted photons pass a beam splitter (BS) and are ob[illegible]ed by one of two avalanche photo-diodes (APD). A time correlated single photon counting (TCSPC) device makes it possible to measure the exact arrival time of the detected photons. Every event is marked with three informations: the channel (APD) on which the photon was detected, the time in comparison to

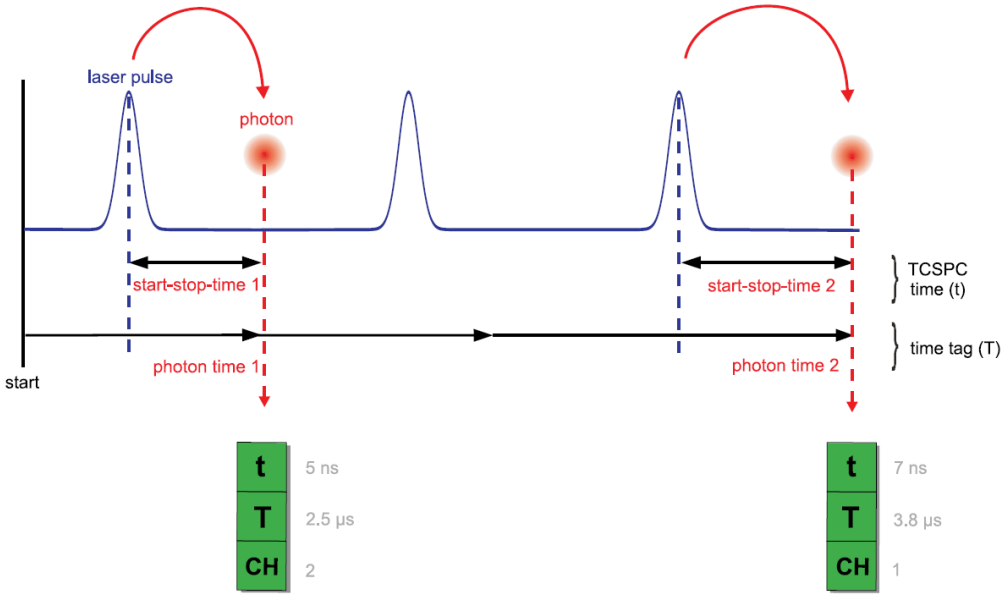

Figure 2: TCSPC principle. Each event is labeled with the information on which APD it was detected (channel), the time elapsed since the measurement started (macrotime) and since the last synchronization e.g. laser pulse (microtime). Figure adapted from [Wahl, 2014].

the start of the acquisition, called macrotime and the time in comparison to the last laser pulse, called microtime. These informations are visualized in Figure 2.

With these informations for every photon detection it is possible to conclude on several characteristics of the nanocrystals such as their blinking, photoluminescence decay and their photon antibunching. These characteristics are explained in the next part as well as their calculation.

3.2 Characteristics of nanocrystals

3.2.1 Blinking

Nanocrystals show blinking behaviour, e.g. periods of emission intermittency. There are two different states observed: a *bright state* with high photon emission rates and a *dark state* with low or no emission at all. The intermittency follows a power-law that is valid over several orders of magnitude in both probability density and in intermittence time. This blinking still poses problems for theory although progress has been made [Frantsuzov et al., 2008].

In the experiment blinking of the nanocrystal is noticeable as periods with high and periods with low count rates. This can be visualized by binning the macrotime and calculating for each bin the number of photons detected. A histogram of this count-rate over macrotime plot should show two distinct peaks.

3.2.2 Photoluminescence decay

The excited state of the nanocrystal that relaxes and emits the observed photon, has a specific lifetime. This lifetime can be calculated by performing a histogram over the microtimes. Since the probability for the excited state to decay, stays constant, the histogram should show an exponential decay. But the bright and the dark state have different lifetimes so a double exponential should be observed.
This experiment limits the repetition rate of the laser. The time between two pulses must be several times larger than the lifetime, so that the registered photon definitely has its origin in the actual and not in the previous laser pulse.

3.2.3 Photon antibunching

The above properties could also be performed using only one APD. The second one is needed to observe photon antibunching. Antibunching means that the nanocrystal does not emit photons randomly or in groups (bunched) but only one photon at a time. In the setup used, this photon can then be detected *either* on APD1 *or* on APD2. When performing a histogram over the time delays of events between different APDs, one should observe no photons for zero time delay. On the other side, time delays belonging to one, two or several laser pulses should be detected very often, as shown in Figure 3.
If one examines a cluster of NCs, several photons can be emitted at the same time and therefore zero time delay will also be observed. Thus this experiment enables to test whether the investigated object is a single photon emitter or not.

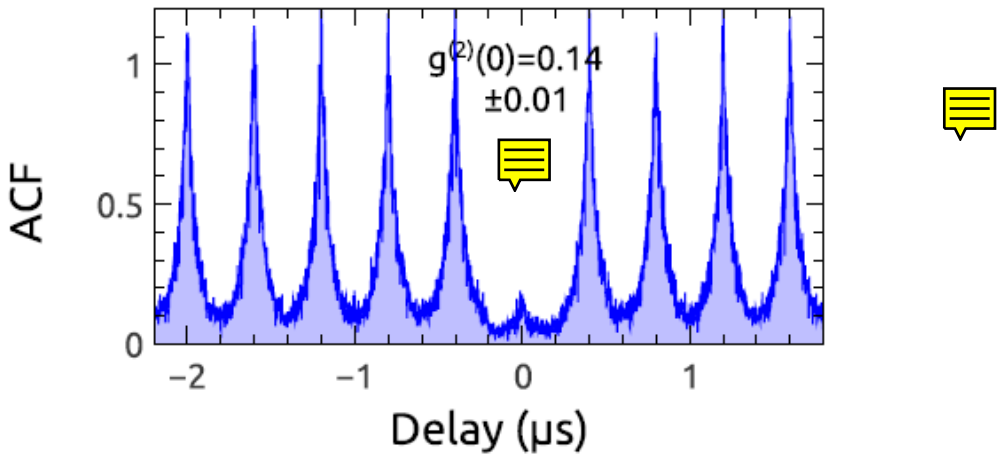

Figure 3: Shown is the autocorrelation function over the delay time. Antibunching causes the peak at zero delay to be significantly smaller than the peaks at multiple of the laser repetition. Figure from [Manceau et al., 2014].

3.3 Problems with the setup

The setup was built by Mathieu Manceau in the course of his PhD thesis and enabled to determine blinking statistics, lifetime, and further examine photon antibunching

of different types of nanocrystals, as showed in [Manceau, 2014].
Unfortunately Mathieu Manceau left the group and over the following time different people worked on it, causing several changes and leaving the experiment inoperative. My task was to provide a fully properly functioning experiment. The realized work done to achieve this aim and the encountered problems are described hereafter.

4 Realized work

~~In this part some of the problems I had to think of and steps I had to take to get an operative experiment are described.~~

4.1 Data extraction

The TCSPC device used is the PicoHarp300 with a PHR 800 router to provide different channels. This device returns binary files, from which the needed information has to be extracted. ~~Here the main program used before is outdated and does not work any more. But parts of it could still be used to~~ extract the microtime and channel number of an registered photon event. The macrotime is calculated by counting the synchronization pulses since the start of the measurement and dividing their number by the laser frequency.
The resolution of this times depends on the considered measurement time, but can be up to 4 ps by properly chosen parameters. The acquisition parameters like resolution and acquisition time can also be extracted.

4.2 Dead time

After detection of a photon, the APD cannot detect another one, during the so called *dead time*, some tens of nanoseconds. If two photons would hit an APD shortly after each other, only the first one would be detected, as depicted in Figure 4. This would lead to a *pile-up*, an overweighting of short detection times in the lifetime-histograms. To avoid such a pile up, one has to make sure to have single photon statistics, e.g. almost never more than one photon per laser-pulse. When dead-times of the TCSPC device are also considered, one should not have a count rate of higher than 5 percent of the laser repetition rate. Here we use pulse repetition rates of 2.5 MHz so the count rate should not be higher than 125 kHz.

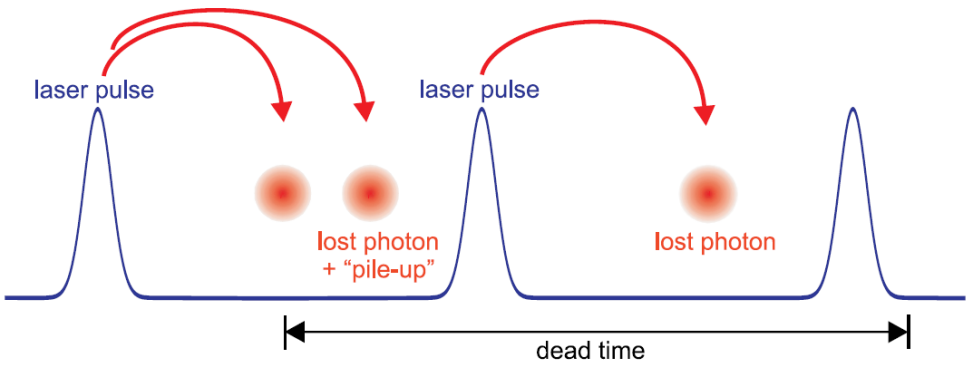

Figure 4: The dead time of the detection system leads to a pile-up if count rates are bigger than 5 percent of the pulse rate. Figure adapted from [Wahl, 2014].

4.3 Optical and electronic instruments

The experimental setup at the beginning of my internship had some deviations to the one shown in Figure 1. The instruments were not well aligned, the APD mountings had a backlash, a lens after the pinhole and the filter in the HBT was missing. The latter is needed to avoid crosstalk between the APDs, that means, low energy photons created on one APD are registered at the other one.
In addition the electronic connections were disorderly and enabled crosstalk and new switches were produced to easily switch between ~~an labview program~~ to directly observe the APD count rates and the TCSPC device. These defects were corrected, everything was clearly labeled and unnecessary parts were removed.
To obtain reasonable results one has to choose the thresholds at the TCSPC device wisely, because no photon event should be missed but noise should not be taken into account. Since the APD output signals are the same for every detection event, constant fraction discriminators are not necessary and constant trigger values are sufficient.
Nevertheless not all problems could be solved: The microscope uses mirrors on a rail, to send the light either to the CCD, the eyepiece or the APDs. Here exists a backlash, so that one either has to work with bigger pinholes or realign the pinhole after every change of observation piece. The latter is a drawback because the nanocrystals are not always stable over time periods of several minutes under excitation with the laser. Another problem are impurities somewhere within the microscope, which are not in the focal plane, but still reduce the signal-to-noise ratio.

4.4 Fluorescence obstacles

A major problem on the way to single photon observation were obstacles, that emitted green light. The nanocrystals observed should emit light in a small range between 620 and 660 nm. (SHOW SPECTRUM?) The green obstacles were encountered in a ~~big~~ range of sizes: Very large pieces and also small dots that could easily be mistaken for NCs. To fix this problem a first unsuccessful try was to use an old NC sample. Then I changed the dilution of the NCs from chloroform to toluene which still did not solve the problem. It is possible that the liquid attacks the plastic pipette tips and storage containers so a glass syringe and glass containers were used. Still the obstacles were present, although their number was slightly reduced. Than i observed, that the acetone used, to clean the syringe and the microscope cover slips, shows fluorescence as already mentioned by [A. Lozano and Hanson, 1992]. Cleaning with toluene instead led a strong reduction of these green spots.
Nevertheless there was still a strong fluorescence background observed. This background showed strong bleaching by laser excitation. This made it very hard to optimize the position of the laser spot on a nanocrystal, since the signal strength always increased when changing the spot position. With a better filter that replaced the one after the dichroic mirror, this problem could be reduced. This filter has to be adapted for every different type of nanocrystals observed. Still one should always take a background measurement and reduction to correctly perform lifetime measurements.

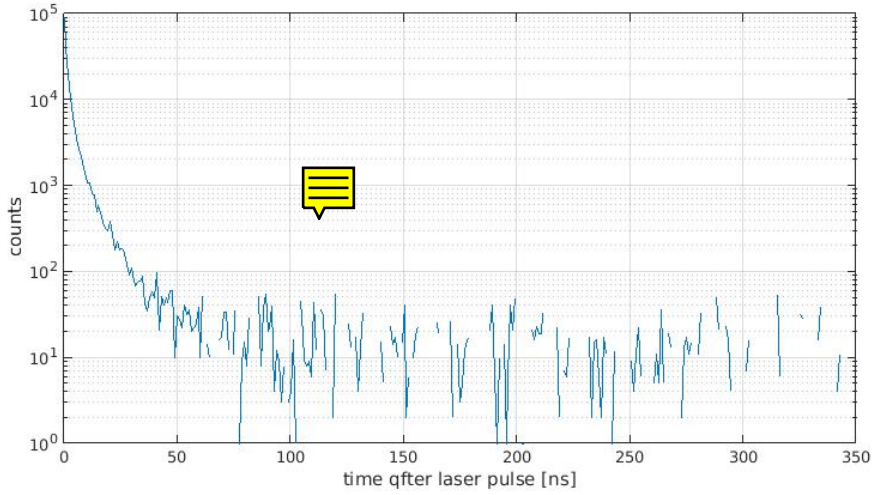

Figure 5: The deployed curves show the background-subtracted decay of a nanocrystal after the laser pulse on a log-scale, where negative values have been ignored. This decay curve has does not fit a double exponential.

4.5 Non-exponential decay

After ensuring proper conditions without significant obstacles, lifetime measurements could be performed. Therefore at first several nanocrystals were observed in the wide field mode with the ~~CCD~~. If blinking is visible in this mode, the spot might be a single crystal, whereas a non-blinking spot is a cluster of several nanocrystals. Thus a blinking spot was chosen and examined in the confocal mode.
But the results did not show double exponential behavior as seen in Figure 5. The fitting procedure is not possible here and the decay times are far smaller than expected and already observed. Up to now the reason for this behavior remains unclear. A possible explanation is a strong background which is then bleaching out, so that it's reaction to the laser pulse is lower, when the background measurement is taken. Only one out of ten NCs shows a clear double exponential decay as shown in Figure 6. Observing several of these measurements made it possible to build an average over the decay times. The results of single measurements and the calculated average are shown in Table 1, in comparison to observations by [Manceau et al., 2014]. The difference between these results will be discussed in section 5.

4.6 Photon correlation

To test if the observed spot is a single nanocrystal and a single photon emitter, one has to observe photon antibunching as explained in subsubsection 3.2.3. To do so, the signal of one of the APD1 can be used as the synchronization signal, so the microtime of APD2 becomes the delay time between the two photon events. Such measurements have successfully been performed and single photon emitters have

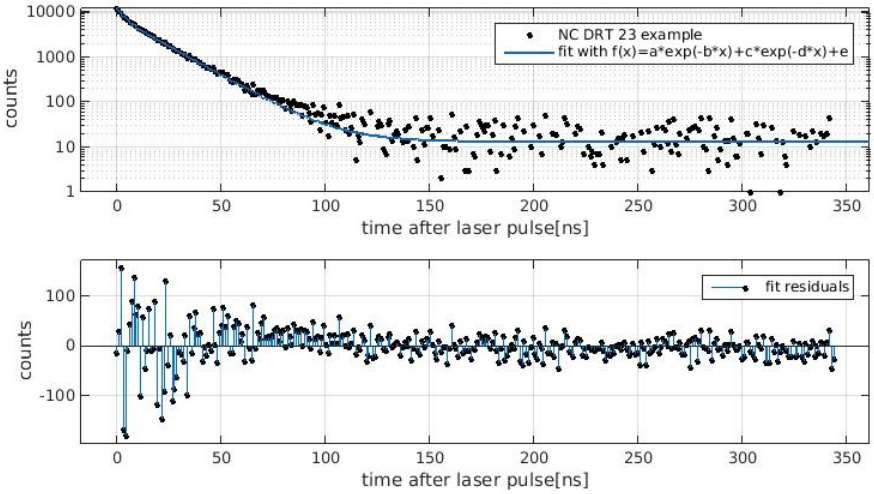

Figure 6: Shown is the decay of NC4 on a log scale with a double exponential fit (top) and the fit residuals (bottom).

description	t_1	t_2
single NC1	21.4(8)	1.79(6)
single NC2	19.3(2)	1.55(5)
single NC3	24.0(1)	1.64(2)
single NC4	16.6(2)	3.22(2)
average	20.3(2)	2.05(2)
Manceau2014 DRb	28	2.6

Table 1: Deployed are the two lifetimes with fitting error obtained for four different NCs of DRT23, the average out of these four measurements and the results of [Manceau et al., 2014].

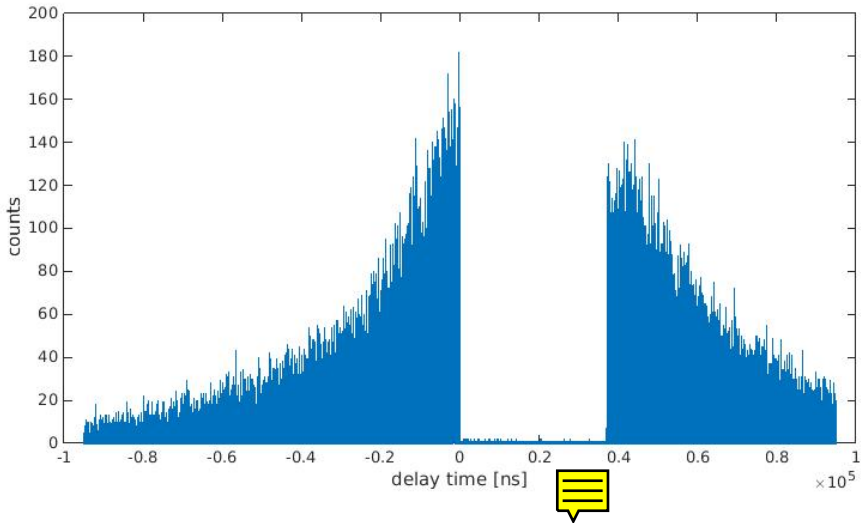

Figure 7: Histogram over the delay time. Very few photons are detected for a region of about 72 μs if APD1 encounters the first photon event.

been observed.
This method however has a drawback: Only positive delays are taken into account, that means only events where APD1 registers the first photon and APD2 the second photon. If APD2 registers the first photon of a pair, this so called negative delay is not taken into account. To avoid that, and to enable post-selection of detection times, e.g. times of emission in bright or dark state, another approach is used.
One takes a measurement with the laser pulse as synchronization signal, so every event carries the information at which channel it was registered, macro- and micro-time (as time to the last laser pulse). After the measurement, consecutive photons, which arrive on different channels are selected. *Consecutive* means here, up to five events in between. The delay between these photons in absolute time is calculated and can be plotted as a histogram which now shows both positive and negative delays. The central peak corresponds to zero delay. Its height compared to the other peaks gives the degree of second-order coherence $g^2(0)$.
Up to now such measurements can be performed, but obtained results show a gap and almost no detection for the case when APD1 encounters the first photon, as shown in Figure 7. Direct observation of the APD output signal with an oscilloscope displays that the signal of APD1 is a rectangle with a width of about 72 μs which corresponds to the width of the detection gap, wheres APD2 shows a signal width of only 60 ns.
This problem still has to be further investigated in the upcoming weeks.

5 Conclusion

During my internship I brought into action a Hanbury-Brown-Twiss setup, which can now be used to perform lifetime measurements of nanocrystals, as well as measurements of $g^2(0)$. The lifetime measurements are well fitted by a double exponential model. The obtained results differ signifi[illegible]ly from previous measurements, which can be explained by the age of the sample. The sample examined here is already over a year old and thus only partly comparable to the one used by [Manceau et al., 2014]. Increasing the number of observed NCs would be helpful, but was not possible in the limited extent of this internship. Nevertheless the results show that measuring decay times with this HBT setup can successfully be performed.
The $g^2(0)$ measurements allows to testify if an examined object is a single photon emitter, which is useful for the group at LKB, because they want to couple single NCs to nanofibers. Here some progress still has to not only take events into account, where APD2 detects the first photon, but also the ones where APD1 detects the first photon.
~~In the course of the internship many small technical problems were solved. A lot of the arising questions could have easily been answered with some experience with the setup. To prevent future experimenters from asking the same questions and spending an unnecessary large amount of time on their solutions, a simple manual of the experiment will be written.~~

Acknowledgements

I want to specially thank Quentin Glorieux for his advice during the internship that very often helped me to overcome practical difficulties. Furthermore I want to thank Anjani and Clement for having an open ear for my experimental and theoretical problems and the rest of the quantum optics group for creating such a nice working climate.

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