Lab 3: Experimental Observation of Single-Emitter Fluorescence  
Lab 4: The Hanbury Brown & Twiss setup and Photon Anti-bunching

Laboratory Report  
Mehul Malik and Pengke Li  
October 22nd, 2007

Abstract: Fluorescence from single-emitter DiI dye molecules, CdSe and PdSe Quantum dots is observed using an EM-CCD camera and in more detail using a confocal microscope with avalanche photodiodes. Single-emitter “blinking” effects are observed clearly and images displaying single-emitter behavior are recorded. An attempt is made to observe photon anti-bunching effects using two APDs in a Hanbury Brown and Twiss setup. Preliminary correlation data is recorded which shows prospective anti-bunching effects.

I. Introduction

The perpetual question – what is a photon? – has intrigued physicists ever since the 17th century. The atomist Pierre Gassendi proposed a particle theory of light as early as 1660. Towards the late 1600s, Christian Huygens and Robert Hooke separately published alternate wave theories of light. Newton took on where Gassendi had left off and further studied and promoted the corpuscular nature of light in the 1700s. The wave nature of light was experimentally demonstrated by Thomas Young in 1803 with his famous double slit interference experiment. Further work by the likes of Poisson and Foucault in the mid 1800s led to the widespread acceptance of the wave theory of light. It wasn’t until the late 19th century that science reverted back to Newton’s corpuscular description of light, when Einstein proposed the famous photoelectric effect. This led to the beginnings of Quantum Theory, when Max Planck described light as consisting of
With the growth in popularity over the last century of the Quantum theory of light, many efforts have been made to experimentally realize this fundamental building block of quantum mechanics – the single photon. Easily describable in theory, the single photon can be thought of as a small quantum of energy, so miniscule that it has been extremely hard to create and observe one experimentally under laboratory conditions. Attempts made in the past to observe single photon emission have included heavily attenuating laser pulses or exciting single atoms at extremely low temperatures, none of which have yielded an efficient single photon source (SPS) capable of producing single photons “on demand.” The primary problem with these techniques has been that photons, being bosons, do not obey the Pauli Exclusion Principle, and tend to bunch together. Thus, it is exceptionally hard to separate out two photons “bunched” together in the same quantum state.

The experiment described in this report is a new and unique way of realizing single photon emission at room temperature with anti-bunching using the technique of confocal fluorescence microscopy. The anti-bunching properties of the sources used are experimentally observed using a Hanbury Brown and Twiss (HBT) setup.

II. Theory

The state of the photons is expressible through their second-order coherence function, $g^{(2)}(\tau)$, which is a measure of temporal coherence between two consecutive photons and is written as a function of time delay between measurements, $\tau$:

$$g^{(2)}(\tau) = \frac{\langle I_T(t+\tau)I_R(t) \rangle}{\langle I_T(t+\tau) \rangle \langle I_R(t) \rangle}$$

Here, the T and R subscripts denote the transmitted and reflected arm respectively in the Hanbury Brown and Twiss setup shown in figure 1 below. This was first suggested as an alternative to the first-order coherence function involving fields in stead of intensities. The HBT setup used in our experiment is described in more detail in the next section.
Fig. 1. The incident (I) beam is split into transmitted (T) and reflected (R) beams at a 50/50 beamsplitter. Detections at T and R are examined to see where or not they occur simultaneously.

Of particular interest in our experiment is the case of simultaneous measurements, which corresponds to the temporal coherence at zero time delay between the two paths:

\[ g^{(2)}(0) = \frac{\langle I_T(t)I_R(t) \rangle}{\langle I_T(t) \rangle \langle I_R(t) \rangle} = \frac{\langle I(t) \rangle^2}{\langle I(t) \rangle^2} \]

According to the Cauchy-Schwartz inequality, \[ \langle I(t) \rangle^2 \geq \langle I(t) \rangle \]. This leads to the condition for all kinds of chaotic light: \( 1 \leq g^{(2)}(0) < \infty \). It is instructive to express the intensity in the coherence function in terms of field operators. This in turn is expressed in terms of creation, annihilation and number operators as follows:

\[ g^{(2)}(\tau) = \frac{\langle \hat{E}^{(-)}(t)\hat{E}^{(-)}(t+\tau)\hat{E}^{(+)}(t+\tau)\hat{E}^{(+)}(t) \rangle}{\langle \hat{E}^{(-)}(t)\hat{E}^{(+)}(t) \rangle \langle \hat{E}^{(-)}(t+\tau)\hat{E}^{(+)}(t+\tau) \rangle} \]

\[ = \frac{\langle \hat{a}^+\hat{a}^+\hat{a}\hat{a} \rangle}{\langle \hat{a}^+\hat{a} \rangle^2} = \frac{\langle \hat{n}(\hat{n}-1) \rangle}{\langle \hat{n} \rangle^2} \]

\[ = 1 + \frac{\langle (\Delta \hat{n})^2 \rangle - \langle \hat{n} \rangle}{\langle \hat{n} \rangle^2} \]

When the photons are in a thermal state; i.e. their state is an incoherent mixture; there will be a high probability of obtaining photons in both the T and R arms of the setup simultaneously. This will correspond to \( \langle (\Delta \hat{n})^2 \rangle = \langle \hat{n} \rangle + \langle \hat{n} \rangle^2 \), and a \( g^{(2)} \) value of 2. When the
photons are in a classical or coherent state (a quantum mechanical state with classical expectation values), the statistics are Poissonian and the variance equals the mean, i.e. 
\[ \langle (\Delta \hat{n})^2 \rangle = \langle \hat{n} \rangle . \] Thus, for coherent light, \( g^{(2)} \) has a value of unity.

\[
g^{(2)}_{\text{thermal}}(0) = 2 \]
\[
g^{(2)}_{\text{classical}}(0) = 1
\]

However, for non-classical states, such as the single photon state, the statistics are sub-Poissonian and thus we get the condition: 
\[ \langle (\Delta \hat{n})^2 \rangle < \langle \hat{n} \rangle . \] The coherence function will then violate the classical condition and yield values lower than unity. This is what we hope to achieve, at least qualitatively, using the Hanbury Brown and Twiss setup in our experiment.

\[
g^{(2)}_{\text{non-classical}}(0) \leq 1
\]
\[
g^{(2)}_{\text{non-classical}}(0) \leq g^{(2)}_{\text{non-classical}}(r)
\]

**III. Experiment**

The different single photon sources used in this experiment include DiI dye molecules in Toluene solvent, CdSe quantum dots in Toluene solvent and in a Cholesteric Liquid Crystal (CLC) host, and never before studied PdSe quantum dots in different CLC hosts. As is later verified in the experiment, the use of a CLC host increases the fluorescence lifetime of the quantum dots and allows for greater efficiency. A sample is prepared on a microscope slide and fluorescence is first observed using a cooled EM-CCD camera. An area with many single emitters is brought into focus on the sample and the system is switched over to the confocal microscope setup. The confocal microscope used in this experiment allows us to limit light collection from a single molecule. This is done by focusing light through an oil immersion objective which allows for greater resolution and a wider collection angle. The sample is then scanned through the objective focus using a precision nano-drive controlled from a computer running the LabVIEW software. The samples used in this experiment fluoresce at a wavelength greater than the excitation wavelength of 532 nm, and the fluorescent light is directed using a dichroic mirror towards the Hanbury Brown and Twiss (HBT) setup.
The HBT setup consists of a 50/50 non-polarizing beamsplitter leading to two APDs aligned in perpendicular directions. As explained in the previous section, the HBT setup is used to measure the second-order coherence function for two photons arriving at the APDs with a time delay \( \tau \). In this case, the second-order coherence function is proportional to the coincidence counts. In order to verify anti-bunching, we must be able to observe non-classical values of \( g^{(2)} \) (i.e. \( g^{(2)} \leq 1 \)) for a time delay of zero, which corresponds to photons arriving at the two APDs simultaneously \((g^{(2)}(0))\). This is done by having one APD send a “start” signal and the other a “stop” signal. In this manner, a histogram of time delays between two consecutive events is made using the TimeHarp 200 PCI card. If anti-bunching occurs, the histogram will show a dip at zero time delay.

The two kinds of quantum dots used have very different fluorescent lifetimes. The CdSe quantum dots have much shorter lifetimes on the scale of a few nanoseconds whereas the PdSe quantum dots fluoresce for several microseconds. Thus, as is seen later in the report, it is much easier to observe anti-bunching with the PdSe quantum dots than with the CdSe quantum dots.
IV. Data

Single-emitters of three types are imaged using the cooled CCD-EM camera and the APDs in conjunction with the confocal microscope. The first sample imaged is a solution of DiI dye molecules of molarity roughly equal to $1 \times 10^{-9}$ M. The second sample imaged is a solution of CdSe quantum dots in Toluene solvent and in CLC hosts. Finally, PbSe quantum dots are imaged in a CLC host as well. Samples of CCD images for all three samples are shown in figures 3, 4 and 5. A video showing stark blinking effects of the CdSe quantum dots was also made at the time of observation and is attached to this report as an .avi file.
Both quantum dot samples were also imaged using the confocal microscope and the APDs. Due to focal misalignment (i.e. only in the z-axis), one APD gave much lower counts than the other. While this had an effect on the images obtained from the two APDs, it did not severely affect the second-order coherence function and the histogram. This problem was later rectified and later data shows images of equal brightness from both APDs. When an area with many single emitters was identified, a smaller scan was made using the piezo-electric transducer that scans the sample through the objective focus. Stark blinking effects in a 3x3 micron scan of CdSe quantum dots are seen in figure 7.

![Figure 6](from: 091301_CdSe_qd.ppt)

Fig. 6. Confocal microscope image of CdSe quantum dots (40 x 40 microns)
From: 091301_CdSe_qd.ppt

![Figure 7](from: 091301_CdSe_qd.ppt)

Fig. 7. Confocal microscope image of CdSe quantum dots showing blinking (3 x 3 microns)
From: 091301_CdSe_qd.ppt

![Figure 8](from: 100201_PbSe_CLC2.ppt)

Fig. 8. Confocal microscope image of PbSe quantum dots in CLC host (40 x 40 microns)
From: 100201_PbSe_CLC2.ppt
Data was recorded to observe photon anti-bunching using the TimeHarp 200 PCI card. The plot in figure 11 shows a histogram of coincident photon counts versus time delay between them. The peaks correspond to the laser repetition rate. Since the CdSe quantum dots have a very short fluorescence lifetime, they only fluoresce for a short time after each laser pulse. If anti-bunching is observed, then we would expect the peak corresponding to the zero time delay pulse (approximately \( t = 87 \) ns) to be much smaller than the other peaks, which are thermal in nature. This would indicate that the coherence function for simultaneous intensity measurements (i.e. \( \tau = 0 \)) has non-classical values. In our data for CdSe quantum dots, we cannot see clear evidence for anti-bunching. However, the histogram for fluorescence from PdSe quantum dots in a CLC host (figure 12) suggests anti-bunching as the coherence function for \( \tau = 0 \) is clearly less than that for \( \tau > 0 \). If enough time delay could be introduced, we could shift the zero time delay point.
far enough and a clear dip would be observed. However, due to lab limitations, this is not practical at this time. More experiments need to be carried out to confirm that this dip is truly from anti-bunching and is not an artifact of the PbSe quantum dots. A CLC host is used in order to make a photonic band gap cavity, which optimally should increase fluorescence while decreasing the fluorescence lifetime.

![CdSe in Toluene Solvent](image1)

**Fig. 11.** Averaged histogram of Photon Counts v/s time delay between consecutive fluorescence events from CdSe quantum dots: 092704_qd_phbg_5x5.xls

![PbSe in CLC host](image2)

**Fig. 12.** Averaged histogram of Photon Counts v/s time delay between consecutive fluorescence events from PbSe quantum dots in CLC host showing anti-bunching: 092704_qd_phbg_5x5.xls
The fluorescence lifetime is measured for DiI dye in four different media: toluene solvent, CLC1, CLC2 and CLC5 hosts. Data is obtained using the same setup but by sending the “start” signal from fluorescence detection from either APD and the “stop” signal from the laser pulse. This seemingly inverse method is used because the laser repetition rate greatly exceeds the maximum conversion rate of the TimeHarp circuit. In this manner, we are actually measuring the time delay between fluorescence and the next laser pulse but this data can be manipulated to show fluorescence decay as the laser pulses are of a periodic nature. One of the fluorescence measurements (for DiI dye in CLC1 host) is plotted below in figure 13.

An exponential fit of the following form is made in MATLAB to all four sets of data:

\[ F(t) = F_b + F_0 e^{-t/\tau_0} \]

\( F_b \) is a constant background and \( \tau_0 \) is the time decay constant and is a measure of the fluorescence lifetime. The six measured values are listed in table 1. Three repeated measurements of DiI dye molecules are made in Toluene solvent, and then measurements
are made in three different liquid crystal hosts. We find that the fluorescence lifetime of the DiI dye molecules is increased slightly by immersion in cholesteric liquid crystals hosts. All three hosts yield similar values, thus confirming our measurements.

<table>
<thead>
<tr>
<th>Host Medium</th>
<th>Fluorescence Lifetime (ns)</th>
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<tbody>
<tr>
<td>Toluene Solvent</td>
<td>2.165</td>
</tr>
<tr>
<td></td>
<td>2.169</td>
</tr>
<tr>
<td></td>
<td>2.186</td>
</tr>
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<td>CLC1</td>
<td>3.493</td>
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<tr>
<td>CLC2</td>
<td>3.574</td>
</tr>
<tr>
<td>CLC5</td>
<td>3.566</td>
</tr>
</tbody>
</table>

Table 1. Fluorescence lifetimes of DiI dye molecules in different host media

V. Summary

Confocal microscopy was used to observe and detect single photon emitters and a Hanbury Brown and Twiss setup was used to measure the second-order coherence function of two photons arriving with a certain time delay between them. Three kinds of sources were imaged: DiI dye molecules, CdSe quantum dots and PdSe quantum dots. Both quantum dots were studied using the HBT setup and the second-order coherence function was measured. Possible anti-bunching was observed from the PdSe quantum dots in a CLC host. This anti-bunching behavior needs to be confirmed through further experiment. The fluorescence lifetime of DiI dye molecules is measured in different host mediums and it is observed that the lifetime is increased slightly in a cholesteric liquid crystal host. The impact of this on the anti-bunching characteristics of quantum dots is another topic that needs further study.