Chapter 5

Luminescence spectroscopy of single CdSe/ZnS quantum dots: Reversible properties

5.1 Introduction .................................................................................................. 112
5.2 Materials and Methods ................................................................................. 114
  5.2.1 Quantum dot synthesis ......................................................................... 114
  5.2.2 Sample preparation .............................................................................. 114
  5.2.3 Surface modification ............................................................................ 115
  5.2.4 Experimental setup ............................................................................... 115
5.3 Multi-state model of optically generated excitons....................................... 116
  5.3.1 Energy states in quantum dots ............................................................. 116
  5.3.2 State-density distribution and ionization of single quantum dots ...... 120
5.4 Results and Discussion ................................................................................ 124
  5.4.1 Random diffusion ................................................................................. 126
  5.4.2 Intensity fluctuations ............................................................................ 127
  5.4.3 Influence of oxygen on the emission count rate .................................. 128
  5.4.4 Blanking ................................................................................................ 132
5.5 Conclusion ................................................................................................... 133
5.1 Introduction

One of the unique properties of semiconductor quantum dots (QDs) is the change in the electronic structure as a function of particle size \(^1-^3\). Size effects start to influence the absorption and emission spectra for CdSe particles smaller than \(\sim 15\) nm in diameter. Due to the confinement of electrons and holes in the nanometer-sized crystallites the energy level scheme resembles that of an atom, with many discrete energy levels. The separation between energy levels increases as the particle size decreases and results in a blue shift in the (optical) absorption and emission spectra of the quantum dots. This implies that the optical properties of the QDs are tunable by adjusting their size. For CdSe the relation between the energy of the lowest energy absorption transition and the particle size is well known \(^1-^3\). In a recent paper by Mikulec et al. \(^4\) the wavelength of the (exciton) emission maximum of CdSe QDs has been reported for a large range of particle sizes. The data are reproduced in figure 5-1A and the associated photon energy of the exciton emission is shown in figure 5-1B.

The QDs have some advantageous properties for the use as luminescent labels in biological systems \(^6-^8\). Compared to organic dyes, they have broad a excitation spectrum, a narrow, symmetric emission spectrum and they are more photo-stable. Due to the broad excitation spectrum QDs can be excited far away from the emission wavelengths and differently sized quantum dots can be excited using one excitation wavelength.

About five years ago it has been demonstrated that it is possible to measure emission spectra for a single quantum dot \(^9\). Figure 5-2 shows some single QD emission spectra. For comparison, the emission spectrum of an organic dye (tetramethylrhodamine, TMR) is shown in the same figure. The narrow, symmetric emission spectra in combination

\[\text{Figure 5-1. (A) CdSe exciton emission wavelength maximum as function of the QD size. The data are reproduced from Mikulec et al.}^4\text{. (B) The corresponding energy at the emission maximum (in eV) plotted as a function of the QD size. As a comparison the horizontal line denotes the bandgap of bulk CdSe at 300 K (1.74 eV})^5\text{.}\]
The study of the luminescence of single semiconductor quantum dots has revealed many interesting properties and processes that cannot be observed for an ensemble of many quantum dots. Some of the properties and processes are reversible while others are irreversible. Reversible phenomena of fundamental interest like spectral diffusion and blinking (on/off behavior) are important for potential applications of single quantum dots as labels in biological systems. Most studies on spectral diffusion and blinking have been performed at cryogenic temperatures. Random spectral diffusion at low temperatures has been related to ionization of quantum dots due to Auger processes. As a result of the ionization and subsequent recombination processes, the charge distribution around the dot changes, resulting in spectral (Stark) shift of the emission. In a recent study convincing evidence has been presented for this mechanism. A clear relation between blinking (explained by photo-ionization) and the occurrence of a spectral jump has been established in that study. At room temperature less information is available on spectral diffusion and blinking of single quantum dots.

Next to the random spectral diffusion at room temperature, a systematic blue shift has been reported as well. The blue shift is irreversible and has been attributed to photo-oxidation of the CdSe in the quantum dot. The photobleaching behavior of QDs is another irreversible process that we investigated.

In this chapter the reversible changes in the luminescence of single quantum dots under continuous illumination will be discussed. Properties and processes that will be addressed in are the blinking behavior of the quantum dots and the spectral diffusion of the luminescence. Furthermore, the fluctuations in the light output are addressed and the influence of oxygen on the light output. To explain the observed behavior a model is outlined in which relaxation to various states of the quantum dot are included after optical generation of an electron-hole pair.

Chapter 6 will deal with the irreversible processes, i.e. the blue shift and photobleaching, and the total light output of the QDs before they are photobleached will be discussed.
5.2 Materials and Methods

5.2.1 Quantum dot synthesis

The ZnS-capped CdSe nanoparticles were synthesized using a similar method as was described by Hines and Guyot-Sionnest. The synthesis was performed in a glove box under dry nitrogen. Stock solutions of Cd²⁺, Zn²⁺, S²⁻ and Se²⁻ in trioctylphosphine (TOP) were prepared. For the Cd²⁺/TOP stock solution 1.6 g (0.011 mol) dimethylcadmium was dissolved in 15.5 ml TOP. The Zn²⁺/TOP stock solution was prepared by dissolving 1.23 g (0.01 mol) diethylzinc in 9.0 ml TOP. 1.3 g Se (0.016 mol) was dissolved in 16.0 ml TOP and 2.0 ml (0.01 mol) hexamethyldisilathiane was dissolved in 8.0 ml TOP to obtain the Se²⁻/TOP and S²⁻/TOP stock solutions, respectively. Cd²⁺/Se²⁻/TOP and Zn²⁺/S²⁻/TOP stock solutions were freshly prepared for every synthesis. The Cd²⁺/Se²⁻/TOP stock solution was prepared by mixing 0.4 ml Cd²⁺/TOP with 0.4 ml Se²⁻/TOP and further dilution with 2.0 ml TOP. Addition of 1.6 ml S²⁻/TOP and 1.12 ml Zn²⁺/TOP to 8.28 ml TOP gave the Zn²⁺/S²⁻/TOP stock solution.

The synthesis was performed in trioctylphosphine oxide (TOPO, 25 g). TOPO was heated to 300 °C and after half an hour, the temperature was raised further to 370 °C. The heater was then removed and when the temperature had decreased to 360 °C, 1.4 ml Cd²⁺/Se²⁻/TOP stock solution was injected rapidly (0.13 mmol Cd²⁺, 0.20 mmol Se²⁻). The reaction mixture was allowed to cool down to 300 °C and at this temperature 5.5 or 13.73 ml of the Zn²⁺/S²⁻/TOP stock solution was added in five portions at approximately 20 s intervals for batch 1 and 2 respectively. The larger amount of Zn²⁺/S²⁻/TOP of batch 2 leads to the formation of a thicker ZnS capping layer. Based on the added amount of Zn²⁺/S²⁻/TOP, the average capping thickness would be 4 and 7 monolayers for batch 1 and 2 respectively. After the injection of Zn²⁺/S²⁻/TOP the reaction mixture was allowed to cool down to 100 °C and was kept at this temperature for one hour. The nanocrystals were precipitated by adding anhydrous methanol. The precipitate was collected by centrifuging (2500 × g, 5 min), washed three times with anhydrous methanol and then dispersed in doubly distilled chloroform. The maximum emission wavelength in solution of both quantum dot batches was around 600 nm, corresponding to an average diameter of 5 nm of the quantum dots. The polydispersity in the two batches was about 50%, as was deduced from the rather broad emission spectrum of an ensemble measurement on QDs in solution.

5.2.2 Sample preparation

The microscope samples were prepared on cover glasses in a glove box under nitrogen, using two methods. In the first method a small droplet of (diluted) QD solution was deposited and spread out on a cover glass. The samples were allowed to dry in nitrogen ambient overnight. The final density of QDs on the glass slide was estimated from two-dimensional scans using the microscope. The density of QDs was observed to be
~10^{-1} \mu m^{-2}. The samples that were prepared by this method showed a considerable fraction of colocalized QDs, as observed by the spectral analysis of the measurements. Measurements that showed more than one QD in the detection volume were expelled from further analysis. In the second method the QDs were deposited on the cover glass by spin coating, to reduce colocalization. Now, the density of QDs was ~10^{-2} \mu m^{-2}. The cover glass was placed on a closed flow-chamber. To prevent oxygen from entering the cell during the measurement under nitrogen there was a continuous flow of nitrogen gas through the holder. For the measurements in air, the sample was flushed thoroughly with ambient air and the sample was left for at least 15 minutes to reach a complete surrounding of the QDs by the ambient air.

5.2.3 Surface modification

The surface of the QD is very important with respect to the luminescence quantum yield. Surface defects are reported as the main sources for non-radiative recombination of an exciton. To improve the luminescence quantum yield of the QDs they are capped with a semiconductor material that has a limited lattice mismatch with respect to the QD core material, but that has a larger bandgap$^{11,17}$. The capping reduces the surface defects and with that the number of non-radiative (surface related) recombination pathways. By these means the quantum yield for photon emission is improved and reported up to 50% at room temperature$^{16-18}$.

When CdSe QDs are capped with a ZnS shell, the QDs are not water-soluble anymore. For use as markers in biological samples however the QDs are required to be water-soluble. In that case an extra modification step is needed to make the QDs water-soluble. One possibility is to overcoat the QDs with a silica layer$^6$. Other approaches use molecules with a sulphydryl (i.e. mercapto) on one end and a carboxylic acid$^7$ or hydroxyl group$^{19}$ on the other. The molecules are coupled to the QD using the sulphydryl group, while the other group provides the water-solubility and furthermore enables specific coupling of proteins to the QD. It should be noted that these QDs in water might not have the same high luminescence quantum yield as the QDs in a dry atmosphere.

The CdSe QDs that were applied here were coated with a ZnS capping with a thickness of 4 or 7 monolayers as described in § 5.2.1. No additional modification has been carried out and the QDs are consequently not water-soluble.

5.2.4 Experimental setup

Fast spectral imaging was performed employing a confocal laser-scanning microscope (CLSM, Nikon PCM2000). The setup is described extensively in chapter 2. Light of 468 nm or 477 nm from an Argon-Krypton mixed gas laser (Spectra Physics, 2060-10SA) was used for excitation (power density on the sample 0.5-500 kW/cm²). The measurements were performed using the larger of the two pinholes of the CLSM (i.e. 50 \mu m) and a 60× oil immersion objective (NIKON, PlanApo, NA 1.4).
Chapter 5

The two detection channels of the CLSM are coupled to the detectors by means of optical fibers. In the configuration applied here, one of the standard detectors (i.e. photomultiplier tubes) is replaced by a home-built spectrograph. In the spectrograph, a prism disperses the light (SF10-glass, 60mm equilateral), and a Peltier-cooled, back-illuminated CCD camera is used for detection (Princeton Instruments, NTE/CCD 1340). The spectral resolution is wavelength-dependent, and varies between ~1.5 nm and 5.5 nm (from 500 nm to 700 nm) in the measurements as presented here. The second standard photomultiplier tube is used to locate single QDs, employing a 590/60 bandpass filter (Nikon). After positioning the laser beam on a single QD the emission light is coupled into the spectrograph and the spectra are recorded at 5-100 ms dwell time. The total measurement time ranged from 1-30 minutes. The experiments were performed in ambient air and in a nitrogen atmosphere.

Data are corrected for background from the system and the sample by subtracting the average spectrum from time interval of the recording where the QD is not emitting. Data are corrected for the detection sensitivity of the setup using a calibrated tungsten bandlamp. The spectrum of the bandlamp is recorded and compared to the theoretical spectrum of a blackbody radiator of the same temperature. The spectra are fitted by a Lorentzian peak function for quantification of the integrated intensity, the peak position and the peak width.

5.3 Multi-state model of optically generated excitons

5.3.1 Energy states in quantum dots

The valence band and conduction band of a semi-conductor are separated by an energy bandgap. The bandgap in a quantum dot (QD) is larger than in the bulk material and is size-dependent (it increases with decreasing QD size). Furthermore, discrete, atomic like, energy levels are present in QDs. These phenomena can be understood in terms of the quantum confinement approach for carriers in the quantum dot (so called particle-in-a-box approach).

The QDs that are used in the experiments in this thesis have a CdSe core of approximately 5 nm in diameter. The QDs are coated with a ZnS shell with an estimated thickness of 4 or 7 monolayers for batch 1 or 2, respectively. The bandgap of bulk CdSe is 1.84 and 1.74 eV at 0 and 300 K, respectively. The average radius of the CdSe-core (~2.5 nm) is smaller than the exciton Bohr radius for excitons in bulk CdSe (~4.9 nm). Therefore, the positions of the carriers in the QD are strongly confined. The range where the particle radius is smaller than the Bohr radius is also referred to as the strong confinement regime (see e.g. Gaponenko).

In order to explain the observed reversible changes in the luminescence of the QDs, a model is presented here in which the creation and annihilation of electron-hole pairs is

* Here the particle radius is used to compare the quantum dot size with the Bohr radius. In the remainder of the thesis the QD size is defined by its diameter.
described. The model includes various states that an electron-hole pair can reach before it finally annihilates.

Figure 5-3 shows a schematic overview of the different states that a QD can be in, with none, or one electron-hole pair, or ionized with one charge. In the ground state (labeled ‘G’ in figure 5-3), the valence band is totally filled and the conduction band is empty (denoted by the gray and white color, respectively). Energy uptake by a quantum dot in the ground state, e.g. by photon absorption, can promote an electron from the valence band to the conduction band and create an electron-hole pair. For direct creation of an electron-hole pair the photon energy must be equal to or higher than the bandgap energy. After excitation, rapid intra-band relaxation (<1 ps) takes place to the lowest excited state. The created electron-hole pair in a quantum dot is commonly denoted as an exciton and is labeled ‘E’ in figure 5-3.

The exciton lifetime in a QD is between 1-100 nanoseconds and the electron-hole recombination can be radiative or non-radiative. If not averaged over long times, the line width of the emission spectrum results from homogeneous broadening and is consequently Lorentzian shaped. The homogeneous broadening is caused by phonon dephasing processes. The homogeneous line width is reported to increase approximately linear with the temperature and inversely quadratic with the QD size. The spectral resolution of the experimental setup may cause extra spectral broadening, in particular at low temperatures, where the line width of the QD emission is smallest.

Structural defects in a QD are important sources of non-radiative recombination of excitons. The defects can occur internally and at the surface of a quantum dot. The surface defects are particularly important, because a large fraction reside on the surface of the QD. For a 5 nm diameter QD over 25% of the atoms reside on the surface.

Defects in the QD can also trap a charge carrier in a sub-bandgap state. In figure 5-3 ‘D’ indicates the different states of a QD in which a charge carrier is trapped. The charges can be trapped internally or at the surface of the QDs, depending on the positions of the defects. The vertical positions of the trapped charge carriers between the valence and conduction band are chosen randomly and do not represent the actual energy levels of the different defect-states with respect to each other or the bandgap. It is expected that the trapping processes take place from the lowest excited state, as a consequence of the fast intra-band relaxation. The sub-bandgap trapped charges have lifetimes that are a few orders of magnitudes longer (microseconds) than the exciton lifetime and mostly recombine without radiation. However, radiative electron-hole recombination at QD defect-state also occurs. The defect-state related emission is red shifted, because the available energy of the trapped state is less than that of the exciton state. The lifetime of the defect related emission in QDs is typically in the microsecond range.
Figure 5-3. Schematic overview of the different states of a quantum dot. The circles with the open and closed dots denote schematic representations of the states that will be used in figure 5-4. The thin lines denote the discrete energy levels. Closed and open circles denote electrons and holes, respectively. (G) Ground-state, with no electrons in the conduction band and no holes in the valence band. (E) Exciton-state: Lowest excited state, after photon absorption and intra-band relaxation. (D) Sub-bandgap trap-states (Defect-states), where one of the charge carriers is trapped between the conduction and the valence band. The charge carrier can be trapped in the bulk of the quantum dot or at the surface of the quantum dot. The vertical position of the trapped charge carriers is chosen randomly. (I) Positively and negatively QD ionization-states.
Besides the defect trapping states inside or at the surface of a QD one of the charges can also be trapped outside the QD. In this case an ionized QD remains (labeled by ‘1’ in figure 5-3). From measurements on QD solids, it was concluded previously that the ionization rate of the QD is lower than the intra-band relaxation 30, and as a consequence that the ionization starts from the lowest exciton state.

For CdSe/ZnS QDs, the electron has a larger probability to be expelled than the hole. In (bulk) CdSe, the electron has a lower effective mass than the hole 1, 3. As a consequence, the electron wave function extends into the ZnS shell, while the hole wave function has negligible probability of spreading into the ZnS shell 1. In ionized CdSe/ZnS QDs the expelled charge is therefore mostly the electron. This has been confirmed empirically using electrostatic force microscopy 31. The intermittence in the luminescence was observed to correlate with the creation of a higher positive charge of the QD.

In general, subsequent electron-hole pair creations in an ionized QD recombine non-radiatively and the ionized QDs are not emitting light 10, 32. The ionized states have long lifetimes (milliseconds-seconds) and are observed as the intermittency in the exciton emission. They are therefore referred to as the “dark” or “off” states of the QD. The ionization is generally believed to be an Auger process 9, 10, 12, but evidence other ionization processes has been reported as well 11, 30, 33. In the Auger process two electron-hole pairs are present in the QD simultaneously. The recombination of one pair then supplies the energy that is necessary to excite one of the remaining charge carriers outside the QD 3. The requirement of two electron-hole pairs implies quadratic dependence of the ionization rate on the light intensity.

However, several groups have reported linear dependence of the ionization rate on the excitation density 11, 30, 33, pointing out that the ionization occurs via a single electron-hole pair. The energy that is required to move one of the charge carriers outside the QD can be supplied by phonons 11, suggesting that the ionization is a thermally activated process. Banin et al. 11 concluded the thermal contribution to the ionization of QDs from the linear relationship between the on-times of the QDs with the excitation density (0.1-10 kW/cm²) and from the dependence of the blinking behavior on the temperature. Leatherdale et al. 30 report almost linear dependence of the number of free charge carriers outside the QDs on the light intensity in photoconductivity measurements on quantum dot solids. The linear relationship was observed down till excitation intensities as low as 2.5 mW/cm². However, The systematic deviation of the data points from the linear fits in their paper suggest the presence of additional, higher-order dependence on the excitation density as well.

The Auger and direct ionization processes do not longer depend quadratically or linearly, respectively, on the excitation density when employing high excitation densities. At saturation the exciton state density does not increase anymore with the excitation density. This occurs when the excitation rate of the quantum dot (i.e. the excitation photon flux multiplied with the excitation cross-section) becomes larger than the inverse average lifetime of an electron-hole pair. As a result, the emitted intensity does not
further increase with increasing excitation rate. The direct ionization process from the exciton state behaves similarly. Furthermore, the Auger ionization rate becomes linear with the excitation rate, instead of the square dependence predicted at low excitation rates. In organic dyes that have long-lived triplet states it is the triplet state that causes the saturation. In analogy to this (long-lived) defect-states are expected to cause saturation before the exciton state does, when present.

Because the process that leads to the off-state is assigned to photo-ionization of the QD the off-time intervals are related to the recombination of the ejected charge carrier with the ionized dot. The off-time distribution of ZnS coated CdSe QDs has been studied in detail in the past. A recent study by Kuno et al. provided evidence for an inverse power law behavior of the off-time intervals, i.e. $P(t_{\text{off}}) \propto t_{\text{off}}^{(1+a)}$. A good agreement between the experimentally observed off-time distribution over nine decades in probability density and five decades in time was observed, with $1+a = 1.6$.

The off-time interval distribution was observed to be excitation density independent. The most probable explanation for the inverse power law behavior is the existence of multiple ionization states and consequently a distribution of recombination rates. The same paper suggests that the most likely model for ionization and recombination is based on tunneling of charges.

A consequence of the non-exponential behavior of the blinking is that the average on- and off-time are dependent on the experimental conditions, i.e. the recording time per spectrum and the total measurement time.

### 5.3.2 State-density distribution and ionization of single quantum dots

In this section a model is presented that describes the density of various states of a QD using the transition rates one state to another. The population distribution of the states can be applied to calculate the light output of a QD or model the ionization of a QD, including the influence of saturation. Figure 5-4 shows the states that are included in the model and the possible pathways from one state to another. The different defect and ionized states (‘D’ and ‘I’ states in figure 5-3) are each considered being a single state in the model.

The model assumes that photon absorption by a QD in the ground state (G) can only bring the QD in exciton state (E). The actual state of the electron-hole pair on excitation is ignored, because it relaxes fast and efficiently to the lowest exciton state. From the exciton state the QD can return to the ground state, go to the defect-state (D) when a charge carrier is trapped or go to the ionized state (I) when a charge carrier is expelled from the core. After absorption of a second photon the QD can go to a bi-exciton state (E→E+E). From the defect-state the QD can return to the ground state, go to a ‘bi-exciton defect-state’ (D+E) or go to the ionization-state (I) when one of the charge carriers is expelled. From the two bi-exciton states (E+E and D+E) the QD can return to the single exciton state, to the defect-state, or can be ionized. Ionization of the QD via a...
bi-exciton state thus requires two electron-hole pairs to be present in the QD, as in the Auger model.

The model is used to describe the population distribution of a QD states while ‘on’ and until it is ionized and therefore the return path(s) from the ionized state is (are) not included in this model. Because of its small probability, the ionization has negligible influence on the population distribution of the other states and is omitted from calculations. The ionization rate can still be extracted from a three state model that

\[ \text{G: ground state, E: lowest excited state, I: ionized states, E+E: bi-exciton state, } \]
\[ \text{D+E: bi-exciton-defect-state (i.e. defect-state after creation of a second electron-hole pair, contains one trapped charge and three free charges). The solid arrows denote transitions between states with photon absorption (upward arrows) or photon emission (downward arrows). Dashed lines denote transitions without photon emission. The transitions denoted by the curved, dotted arrows (E+E→D and D+E→E) are ignored in the three-state model.} \]
includes only the ground state (G), exciton state (E) and defect-state (D) with some additional assumptions. Firstly the population of the bi-exciton states (E+E and D+E) is assumed to be negligible. This is plausible, because the recombination of additional created electron-hole pairs is fast $^{10,37}$. The recombination of additional electron-hole pairs is enhanced, because each of the charge carriers can recombine with each of the two opposite charge carriers. Furthermore, the return paths from the bi-exciton states to the exciton and defect-states E+E→D and D+E→E (that are denoted by the two curved, dotted paths) are neglected, because they are expected to be less efficient than E+E→E and D+E→D. Under these assumptions the probabilities for the transitions E→E+E and D→E+D can be replaced by reduced probabilities that the bi-excitons are created followed by ionization of the QD.

When the assumptions are not made, a five-state model is required to calculate the excitation rate dependence of the ionization.

When the total number of dots is constant in time, the occupation density changes of the three states in time ($N'_g$, $N'_e$ and $N'_d$, for the ground, exciton and defect-states, respectively) can be written as follows:

$$N'_g = k_{exc} \cdot N_g - (k_R + k_{NR}) \cdot N_e$$
$$N'_e = k_d \cdot N_e - (k_{dr} + k_{dNR}) \cdot N_d$$
$$N'_d = -N'_g - N'_e = -k_{exc} \cdot N_g + (k_R + k_{NR}) \cdot N_e + (k_{dr} + k_{dNR}) \cdot N_d$$

In these equations $k_{exc}$ is the photon excitation rate from the ground state to the exciton state (G→E) and $k_R$ and $k_{NR}$ the radiative and non-radiative recombination rates from the exciton state (E→G). Furthermore, $k_d$ is the rate for entering a defect-state from the exciton state (E→D) and $k_{dr}$ and $k_{dNR}$ the radiative and non-radiative recombination rates from the defect-states back to the ground state (D→G). Two of the three equations of (5.1), plus the demand that the total number of dots is constant ($N'_g + N'_e + N'_d$) and a boundary (or begin) condition are required to calculate the density of states. In a steady state situation the population densities of the states do not change in time and each of the equations of (5.1) can be put to zero. In this case, it follows directly from the second equation of (5.1) that the ratio of the exciton and defect-state densities is independent of the excitation rate: $N_d/N_e = k_d/(k_{dr} + k_{dNR})$. When considering a single QD, the sum of the three state densities equals $N_g + N_e + N_d = 1$ and the three state densities are the average times that the QD spends in each of the three states. The three densities can be calculated as a function of the transfer rates between the different states:

$$N_e = k_{exc} \cdot \frac{k_{dr} + k_{dNR}}{(k_d + k_{dr} + k_{dNR}) \cdot k_{exc} + (k_d + k_R + k_{NR}) \cdot (k_{dr} + k_{dNR})}$$
$$N_d = k_d \cdot \frac{k_d}{(k_d + k_{dr} + k_{dNR}) \cdot k_{exc} + (k_d + k_R + k_{NR}) \cdot (k_{dr} + k_{dNR})}$$
$$N_g = 1 - N_e - N_d$$

(5.2)
At low excitation rates the two excited state densities are approximately proportional to the excitation rate and flattens off at higher intensities. Figure 5-5A shows the exciton and defect-state densities as a function of the excitation rate. The numbers used to create the curves are mentioned in the figure caption. At higher excitation rates, the occupation densities of these states may no longer be assumed proportional to the excitation rate and saturation is evident. The dotted line shows the intensity, in the case where no saturation would be present (i.e. also neglecting saturation caused by the exciton state lifetime).

The thermally activated ionization is proportional to the state-density from which the QD is ionized. Therefore, similarly shaped curves are obtained as shown in figure 5-5A. The ionization rate $k_{ion}$ via the bi-exciton state (E+E) consists of an excitation component and an Auger ionization rate $k_{Au}$. The excitation rate to create the second electron-hole pair $(k_{exc})$ is proportional (though not necessarily equal) to that to create the first one $(k_{exc})$ and therefore the ionization rate is proportional to the excitation rate:

$$k_{ion} = c \cdot k_{Au} \cdot k_{exc}$$

The rate at which a QD enters the ionized state now becomes:

$$N_{ion}' = N_e \cdot k_{ion} = N_e \cdot k_{exc2} \cdot k_{Au} = N_e \cdot k_{exc} \cdot c \cdot k_{Au}$$

$$= k_{exc}^2 \cdot c \cdot k_{Au} \cdot \frac{k_{DR} + k_{dNR}}{k_d + k_{dDR} + k_{dNR}} \cdot k_{exc} + (k_d + k_{NR}) \cdot (k_{dR} + k_{dNR})$$

(5.3)

Figure 5-5B shows the $N_{ion}'$ as function of the excitation rate using eqs. (5.2) and (5.3). The ionization rate goes from square dependence at low excitation rates to linear.

Figure 5-5. (A) Density of the exciton state (solid line) and defect-state (dashed line) as a function of the excitation rate. The dotted line denotes the exciton state density when no saturation would occur. (B) Ionization rate as a function of the excitation rate using an Auger model. The dotted line shows the ionization curve belonging to the non-saturation situation. The values that are used to calculate the curves are: an exciton lifetime of $\tau_{exc} = 20$ ns ($k_{R} + k_{NR} = 5 \cdot 10^{7} \text{ s}^{-1}$), a defect lifetime of $\tau_{d} = 1 \mu$ s ($k_{dR} + k_{dNR} = 1 \cdot 10^{6} \text{ s}^{-1}$), a defect trapping probability of 1% ($k_d = 5 \cdot 10^{5} \text{ s}^{-1}$) and an ionization probability of $k_{ion} = k_{exc} \cdot 10^{-5}$. An excitation rate of $10^6 \text{ s}^{-1}$ corresponds to an intensity of 0.4 kW/cm$^2$, at 500 nm excitation wavelength and assuming an excitation cross-section of $10^{-15} \text{ cm}^2$. 14.
dependence at high excitation rates. The dotted line in figure 5-5B denotes the situation without saturation. The ionization starting from the (D+E)-state only differs by a constant factor from eq. (5.3). Which of the two ionization paths is dominant will depend on the different rates that are present in the system.

The non-radiative recombination pathways from the exciton and defect-states may include terms that are dependent on external influences, like oxygen mediated recombination pathways from the exciton and/or defect-state.

The three-state model cannot be applied when the dotted pathways of figure 5-4 are included, and a five-state model is required, that include the two bi-exciton states. The ratio of $N_e$ and $N_d$ now depends on the excitation rate. Dependent on which of the two pathways dominates, the exciton state density or defect-state density state will decrease at higher intensities. As a result, the ionization rates starting from (E+E) or (D+E) are differently shaped as well. The three-state model will be applied later to discuss intensity fluctuations that were observed in the QDs and to describe the influence of oxygen on the emission intensity of the QDs.

5.4 Results and Discussion

Luminescence spectra of individual CdSe/ZnS quantum dots from two batches were measured under different atmospheres and using different excitation intensities. The two batches differed in capping thickness. The estimated average capping thickness of batch 1 and 2 amounted to 4 or 7 monolayers, respectively. Clear differences were observed between the emission spectra of the individual quantum dots, even for dots of the same batch and under the same atmosphere. The QDs differed not only in emission wavelength, but also in emission intensity and blinking behavior. Two colocalized QDs...

Figure 5-6. (A) Spectrally resolved time trace of a CdSe/ZnS QD of batch 2 under nitrogen recorded with 100 ms dwell time using ~0.5 kW/cm² excitation density at 477 nm. The emission intensity is a stretched black-and-white representation and each vertical spectrum is the sum of 25 successive spectra. (B) Detail from the start of the start of the time trace. Each vertical line is a single spectrum recorded in 100 ms. Note that the horizontal axes of the two figures use different units.
were already shown in chapter 2 (figures 2-11 and 2-12). The two QDs emitted at different wavelengths and observed emission intensities were different as well. Figure 5-6 shows a plot of another QD in nitrogen. The wavelength is plotted vertically and the time is plotted horizontally. In the time interval of figure 5-6A it is seen that the dot emits for over 10 minutes. The first eight seconds of the total interval is illustrated in figure 5-6B and shows blinking and variations in the emission intensity and the emission wavelength of the QD in time.

The shape of the single dot emission spectra is described reasonably well by Lorentzian peaks, indicating that the broadening of the spectra is due homogeneous broadening. Figure 5-7 shows two measured emission spectra (symbols) of single QDs with their fitted Lorentz curves (solid lines). The fitted full width at half maximum (FWHM) of the emission peaks 16 and 14 nm for the left and right spectrum respectively. Typically, the FWHM of the emission peaks amounted to 12-20 nm. Line widths of single QDs at room temperatures have been reported between 15-25 nm. Extrapolation to room temperature of the data from a theoretical study predicted a line width of \( \Gamma \approx 5 \) nm for the QD size that we apply (5 nm in diameter). This difference is not understood. In the spectral shape we do not see a large contribution to the line width from inhomogeneous broadening. It might be that the linear dependence that was reported is not valid up to room temperature, or that the coefficients that were obtained from the paper do not accurately describe the line width for the QDs that were applied here.

The line width might be broadened due to heating of the QD from the photon energy that is not emitted as light. Assuming a heat capacity of 1 Jg\(^{-1}\)K\(^{-1}\) and a mass of approximately 10\(^{-18}\) g, the energy of 1 absorbed photon (500 nm) yields a temperature rise of 0.4 K when converted to heat. At high excitation rates, this can give a considerable heat production in a QD when the heat conduction to the surrounding air is poor. However, the theoretically linear relationship would predict unrealistically high temperatures to obtain the observed line widths.

The fit procedure was carried out on the time traces of the single QD spectra to analyze the time-resolved properties. In figure 5-8 the

**Figure 5-7.** Measured spectra of two single QDs (symbols) and the Lorentzian fit curves through the data points. The fits yielded for the left and right peak a FWHM of 16 and 14 nm respectively.

**Figure 5-8.** Wavelength of the emission maximum (from the Lorentz fits) as a function of time for the QD of figure 5-6.
positions of the emission maxima of the QD of figure 5-6 are plotted as a function of time. It was already seen in figure 5-6B that the emission of the QDs was not constant in time. The next sections will elaborate on the variations that were observed in the emission wavelength (§ 5.4.1) and observed intensity (§ 5.4.2 - § 5.4.4) of the QDs in time.

### 5.4.1 Random diffusion

The distribution of the emission peak positions forms a 10-15 nm broad band (see figure 5-8). This was observed for the QDs both in air and in nitrogen. The distribution of the peak positions is in agreement with the low temperature measurements on spectral diffusion on single quantum dots ⁹⁻¹². The random diffusion is further illustrated in the spectrally resolved time traces in figure 5-9 and the associate fitted positions of the emission maximums in figure 5-10. Clear variations in the position of the wavelength of the exciton emission are visible. The position of the emission maximum was often observed to be fairly constant during several frames and then jumped to another wavelength. This is particularly visible in figure 5-10A and C. Furthermore, a covariance between the spectral jumps and the intermittency of the emission seems present, in agreement with previously reported results ¹². Though the intensity did not always drop to zero between jumps in the emission wavelength of figure 5-10A (see vertical dotted lines), the intensity drops strongly suggest that the QD was in the off-state for a short period of time. Neuhauser et al. ¹² assigned the spectral jumps to a change in the electronic environment of the QDs after the ionization and recombination of the QD. This may imply that the expelled and captured charge carriers are not the same.

---

**Figure 5-9.** Spectrally resolved time traces of different QDs at different excitation intensities. On top of each of the time traces the integrated intensity under each of the curves is plotted in a gray scale (A) at 0.5 kW/cm² at 477 nm with a dwell time of 50 ms per spectrum; (B) at 5 kW/cm² at 477 nm with a dwell time of 10 ms per spectrum. The accolade shows an interval in which the dot is emitting at low, but rather constant intensity (C) at 20 kW/cm² at 468 nm with a dwell time of 5.2 ms per spectrum. Each vertical line is a single recorded spectrum.
5.4.2 Intensity fluctuations

Besides the on/off behavior that will be discussed in § 5.4.4, the QDs also show variations in the intensity while on. On top of each time trace of figure 5-9 the integrated intensities under the recorded spectra is shown. The fitted (integrated) intensities are plotted figure 5-10. The light-output is clearly not constant but showed variations in time. After an interval where the QD emitted at an approximately constant light output, jumps to another intensity were observed. This shows clearly in figure 5-10B.

The fluctuations are explained by changes in the symmetry of the electronic state of the QD that affects the oscillator strength for radiative transition. It was suggested that the creation of defects may alter the symmetry of the QD and that that part of the created defects might be reversible. A redistribution of the local electric fields around the QDs, which is also held responsible for the spectral jumps may cause changes in

---

Figure 5-10. (A, B and C) Intensities (upper panes) and wavelengths of the emission maximums (lower panes) of the spectrally resolved time traces of figure 5-9A, B and C, respectively. The vertical lines in (A) denote points in time where intensity drops accompany jumps in the emission intensity and wavelength of the QD.
the luminescence quantum yield. If this is the case, the covariance that was found
between the luminescence intermittency and the spectral jumps\textsuperscript{12} is also expected to
occur between the intermittency or spectral jumps and the jumps in the intensity.
Qualitatively, such a covariance seems visible between in the fitted times traces of the
intensities and positions of the emission maximums. Future research will have to reveal
whether the correlation can also be proved quantitatively.
In terms of the transition rates between the different states that were used in figure 5-4
and eq. (5.2), the influence of variations in those rates can be looked at closer to analyze
the processes that influence the luminescence intensity. A change in the oscillator
strength of the radiative transition will change the radiative recombination rate ($k_R$, solid
line in figure 5-4), the exciton state lifetime ($\tau_E = 1/(k_R + k_{NR} + k_d)$) and the
luminescence quantum yield ($Q = k_R/(k_R + k_{NR} + k_d)$). Because the numerator of the
luminescence quantum yield changes faster than the denominator with $k_R$, a reduced
luminescence intensity will correlate with a longer luminescence lifetime of the QD
(when the other rates are unchanged).
A new (photo-induced) defect may affect both the non-radiative relaxations from the
exciton state: i.e. recombination to the ground state ($k_{NR}$, dashed line in figure 5-4, $E\rightarrow G$)
and entering of a defect-state ($k_d$, $E\rightarrow D$). Now, a lower luminescence intensity is
accompanied by a shorter luminescence lifetime (when $k_R$ is unchanged).
At excitation intensities around saturation, the change in the rate to enter a (long-lived)
defect-state $k_d$ has an additional effect on the intensity. A larger probability to enter the
defect-state does not only lead to a decrease in the intensity and exciton lifetime. At
saturation it also interrupts the fast excitation-relaxation ($G\rightarrow E\rightarrow G$) process and gives
an additional increase in the intensity. Moreover, if $k_d << k_R + k_{NR}$ a significant reduction
in the intensity may be observed at saturation, while the fluorescence lifetime is hardly
affected. The measurement of the exciton lifetime $\tau_E$ could reveal useful information on
the background of the intensity variations.

5.4.3 Influence of oxygen on the emission count rate
The QDs were studies in two different atmospheres. This had much impact on the
irreversible properties of the QD luminescence, as will be discussed in chapter 6.
Another observation was that the CdSe/ZnS QDs emitted brighter in air than in
nitrogen, i.e. higher detection count rates were observed in air than in nitrogen when the
QDs were in the on-state. The higher emission count rates in air were significant for
both batches, in spite of the rather large standard deviations (see table 5-1). The large
standard deviations are explained by differences between the individual QDs, shot noise
(the maximum observed intensities were considered, rather than the average intensities)
and the position of the QD, i.e. the QD is not always exactly centered in the illumination
focus, resulting in a reduced excitation rate and collecting efficiency.
Additional experiments were carried out at ~14, 50 and 500 kW/cm² for batch 2 and the results are presented in table 5-2. The difference at 14 kW/cm² amounted to almost a factor of 3 between air and nitrogen. At 50 kW/cm² the difference was much smaller and at 500 kW/cm² the QDs under nitrogen or air yielded no significant difference in the emission count rates. The higher light output in air below 100 kW/cm² can be explained by saturation kinetics of the QDs. A possible explanation of the higher light output in air below 100 kW/cm² is an enhanced relaxation of the defect-states by oxygen (see figure 5-4: D→G). The lifetime of defect-states is typically ~1 µs. When a charge carrier is trapped in a defect-state, the normal absorption-emission cycles of the exciton (G→E→G) (with nanosecond lifetimes) is interrupted, until the trapped charge carrier recombines, radiatively or non-radiatively and the QD relaxes to the ground state.

The enhanced light output in the presence of oxygen by faster defect-state relaxation requires that the long-lived defect-state indeed causes saturation of the QDs. The excitation levels applied here are in the range where saturation of single QDs has been reported to occur, between 10-100 kW/cm². To estimate whether saturation by a long-lived defect-state is expected at the count rates that were reported here the average time interval between two photon emissions was compared with the defect-state lifetime. Detection count rates in the order of 10⁵ counts/s were measured. This corresponds to average time intervals of 500 ns between subsequent photon emissions assuming a 5% overall detection efficiency of the setup. In this situation, the exciton relaxation E→D to a defect-state that has a microsecond lifetime will indeed reduce the number of emitted photons. An extra return path to the ground state (by oxygen) reduces the defect-state lifetime and will enhance the photon output. A similar situation has been reported for organic dye molecules where higher fluorescence light yields were measured by shortening of the triplet state by oxygen. Further support for the explanation is found in literature on other II-VI semiconductors like CdS and ZnS, where it has been established that oxygen can quench the defect related emission. These measurements suggest an extra (non-radiative) relaxation path from the defect-state by oxygen and agree with the higher light output of the exciton emission in the presence of oxygen.

### Table 5-1. Maximum light output of QDs between batch 1 and 2 in ambient air and dry nitrogen using ~20 kW/cm² excitation density at 468 nm.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Ambient</th>
<th>n</th>
<th>Detection count rate at 20 kW/cm² (photons/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1</td>
<td>Nitrogen</td>
<td>4</td>
<td>(1.2 ± 0.7) · 10⁵</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>5</td>
<td>(2.0 ± 1.2) · 10⁵</td>
</tr>
<tr>
<td>Batch 2</td>
<td>Nitrogen</td>
<td>8</td>
<td>(1.8 ± 1.1) · 10⁵</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>14</td>
<td>(2.8 ± 1.8) · 10⁵</td>
</tr>
</tbody>
</table>
Chapter 5

The difference in light output of the QDs in air and dry nitrogen disappeared for the highest excitation density (500 kW/cm²). This indicates that the difference in the defect-state lifetime in air and nitrogen has disappeared. At such high excitation intensities it is possible that the trapped state is annihilated after creation of a second electron-hole pair \( (D \rightarrow D+E \rightarrow E) \), see figure 5-4). This would yield a reduction of the defect-state lifetime at higher excitation intensities. A similar effect is obtained when the exciton in the defect-state absorbs a new photon removing the trapped charge carrier from the intra-band state. The shorter defect-state lifetime in the presence of oxygen reduces the probability to create a second electron-hole pair of a QD in air.

For much lower excitation intensities (<0.1 kW/cm²) exactly the opposite behavior has been reported. QDs were followed while repetitive switching the ambient between argon and oxygen, observing lower luminescence intensities in oxygen. The decrease in the intensity in the presence of oxygen is most likely explained a reduction in the luminescence quantum yield. This result does not contradict the results that are presented here, because of the large difference in excitation intensities that were applied. An excitation density of 0.1 kW/cm² at 500 nm excitation wavelength and assuming an excitation cross-section of \( 10^{-15} \) cm² yields an average time of ~4 µs between two successive excitations of the QD. The average time between two excitations is not shorter than the defect lifetime (~1 µs) and the defect-state lifetime does hardly form a bottleneck for the exciton emission process. Therefore a reduction of the defect-state lifetime will hardly affect the light output at low excitation intensities.

The increase in the detection count rate that is presented here suggests that the influence of the defect-state quenching is larger than the quenching effect on the exciton emission that is observed at low intensities. This is illustrated in figure 5-11, where two exciton density curves are shown. The dashed curve is calculated using higher non-radiative recombination rates from the exciton and defect-states, accounting for oxygen quenching of the exciton and defect-states. The exciton luminescence intensity equals the exciton state density \( (N_e) \), multiplied with the radiative recombination rate \( (k_R) \). At low excitation rates the luminescence intensity is lower for the dashed curve (with oxygen), while it is higher at high excitation rates. Apparently the measurement that are

<table>
<thead>
<tr>
<th>Ambient</th>
<th>( n )</th>
<th>Detection count rate at 14 kW/cm² (photons/s)</th>
<th>( n )</th>
<th>Detection count rate at 50 kW/cm² (photons/s)</th>
<th>( n )</th>
<th>Detection count rate at 500 kW/cm² (photons/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>9</td>
<td>((0.5 \pm 0.2) \cdot 10^5)</td>
<td>13</td>
<td>((1.3 \pm 0.6) \cdot 10^5)</td>
<td>11</td>
<td>((2.0 \pm 1.1) \cdot 10^5)</td>
</tr>
<tr>
<td>Air</td>
<td>7</td>
<td>((1.4 \pm 0.4) \cdot 10^5)</td>
<td>13</td>
<td>((1.9 \pm 0.5) \cdot 10^5)</td>
<td>7</td>
<td>((1.6 \pm 0.6) \cdot 10^5)</td>
</tr>
</tbody>
</table>

Table 5-2. Maximum light output of QDs of batch 2 in ambient air and dry nitrogen using three different excitation intensities at 477 nm.
Luminescence spectroscopy of single CdSe/ZnS quantum dots: Reversible properties

Figure 5-11. Exciton state density as a function of the excitation density. The solid curve shows the calculation in dry nitrogen, with the same rates that were also used in figure 5-5. The dashed curve shows the result of a calculation, in which higher non-radiative recombination $k_{NR}$ and $k_{INR}$ rates are used to account for the influence of oxygen on the non-radiative recombination.

presented here are on the high excitation side of the crossing point between the curves, while the results by Koberling et al. ⁴² are on the low excitation side.

Some of the time resolved spectral images showed a second emission band at the highest excitation density of ~500 kW/cm² (figure 5-12). The peak was blue-shifted compared to the main exciton peak (i.e. a higher energy than the exciton emission band). There appeared to be a correlation between the on/off behavior of the second peak and the main peak: it was only visible when the main peak was strongly emitting. This suggests that the blue-shifted emission band is not caused by a second (independent) QD and that it is no fluorescence from the system. A second QD was expected to blink independently, as followed from measurements with 2 QDs present in the focus (see figure 2-9). Fluorescence from an element in the system (e.g. an optical filter) is unlikely, because no blinking in the signal would have been expected in that case. A possible physical explanation would be the occurrence of bi-exciton emission. The blue-shift could then be explained by the Pauli exclusion principle that states that

Figure 5-12. (A) Spectrally resolved time trace of a QD of batch 2 using ~500 kW/cm² at 477 nm. (B) Average of several successive spectra of two different time intervals in which the second peak was visible. The vertical lines are included to show the energy difference between the two emission bands.
the two excitons cannot occupy the same energy level. Since the first exciton was already in the lowest energy state, the second exciton will have a higher energy.

### 5.4.4 Blinking

The blinking behavior of the QDs of batch 1 and 2 was analyzed by determining the on- and off-time distributions from the spectral time-traces. The exciton emission intensity was used as a means to distinguish between the on- and off-state of the QD. A threshold just above the background level was used to discriminate between the on- and off-state. A graph of the off-time duration distribution of one of the QDs in nitrogen is plotted in figure 5-13 on a single logarithmic scale. A single off-state with a constant recombination rate would have yielded an exponential decay of the off-time distribution and consequently a straight line (see figure 5-13). Here, a deviation from the straight line is visible at the shorter and longer off-time durations, in agreement with earlier reports \(^9,^{11},^{32}\). The deviation is explained by the existence of a distribution of off-states, rather than a single off-state and a distribution of off-states yields an inverse power law for the observed off-time distribution.

To investigate whether oxygen or the capping thickness has influence on the blinking behavior of the QDs, the on/off time distributions were studied for various QDs from both batches both in air and in nitrogen. The results of the QD blinking analysis of the different batches and different atmospheres are not yet reliable, mainly due to artifacts in the data-analysis. Such artifacts result from variations in the recorded emission intensity and the emission intensity level that was used to distinguish between on and off. As can be seen by comparing figure 5-9A and B with figure 5-10A and B, frames are sometimes incorrectly assigned to be on or off, using a threshold to discriminate between on and off. The intensity drops between the wavelength and intensity jumps in figure 5-10A (see dotted vertical lines) strongly suggest that the QD has been off in between, while the analysis considers the QD to be on during the entire time interval from ~4.75-7.25 s. Oppositely, from the time resolved emission in figure 5-9B the QD appears to be emitting during the entire interval from 39.9-40.2 s, while the fit analysis of this time trace (figure 5-10) yields an off time in between. These errors are inherent to the data-analysis.

![Figure 5-13. Off-time distribution of a CdSe/ZnS QD of batch 1 in dry nitrogen with 6 ms dwell time, using \(~20\ kW/cm^2\) excitation density at 468 nm. The straight line shows the best exponential fit through the data.](image)
to the used techniques to measure and analyze the data. The recorded intensity depends on the fraction of time that the QD was emitting during the recording of a (single) spectrum. This will partly depend on the dwell time and excitation density. The analysis of the blinking behavior may be improved using a different setup that can use shorter dwell times to study the blinking behavior. Further improvement is expected using an analysis technique that includes the derivative of the intensity in time additional to the absolute intensity.

Other variations that complicate the blinking analysis and that are difficult to exclude are the variations in light output of the QDs. The light output varies strongly from dot-to-dot, is not constant in time (§ 5.4.2) and depends on the atmosphere (§ 5.4.3). It will be shown in chapter 6 that the QDs degrade in time during illumination. As a result of the degradation, the light output decreases in time. Furthermore, the degradation and the total recording time of the QDs depends on the atmosphere. This implies that the blinking behavior may change in time and that the fitted inverse power coefficients depend on the time interval that is analyzed. Indeed, the QDs appeared to be off for longer time intervals later in the recording of a QD. We have not been able to quantify this yet, but this will be assessed in future studies.

### 5.5 Conclusion

In this chapter, time-resolved fluorescence measurements were presented on single CdSe/ZnS core-shell quantum dots (QDs). The QDs show spectral diffusion at room temperature and large variations in the light output. A significant influence of the atmosphere is observed on the light output of the QDs. An increased emission count rate is observed for the QDs in air compared to nitrogen. This can be explained by quenching of the defect-state by oxygen in the regime where the long lifetime of the defect-states limits the maximum light output of a QD. During and between on-state intervals of the QD luminescence intensity fluctuations are observed that seem to covariate partly with spectral variations. Exciton lifetime measurements may provide valuable information on the mechanism that is responsible for the intensity variations. Finally, at very high excitation intensities (500 kW/cm²) a weak, blue-shifted emission band has been observed in addition to the normal exciton emission band. Possibly this emission band originates from bi-exciton emission.

### Reference List


