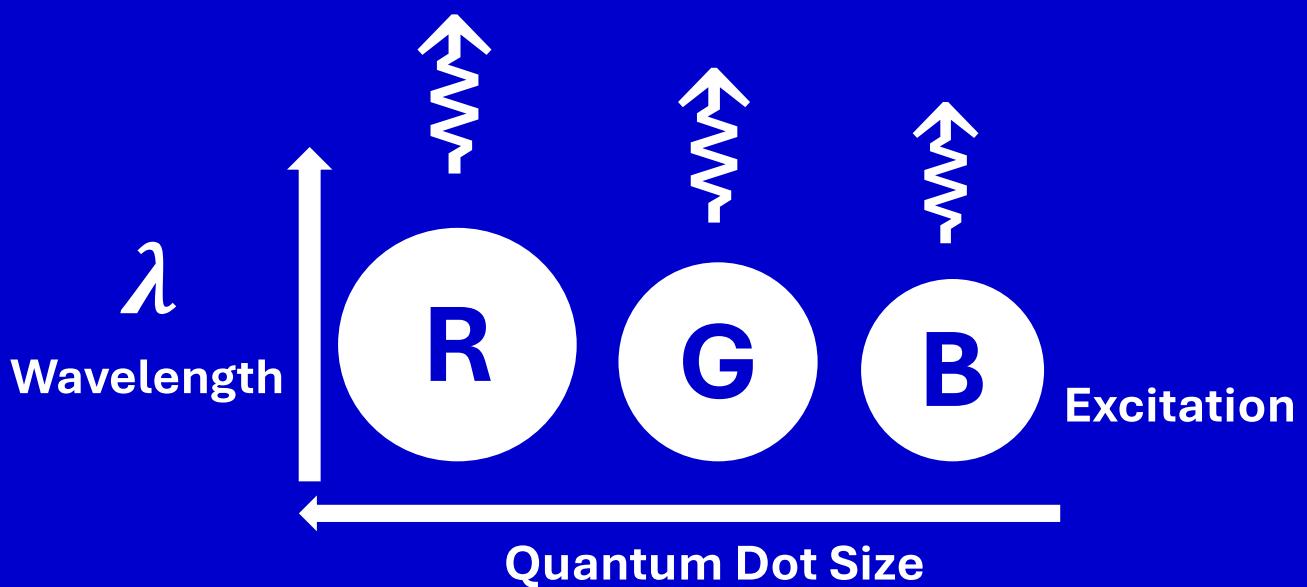


# Spectroscopy of CdSe Quantum Dots

By the end of this lab, you should be able to:

1. Synthesise CdSe quantum dots and monitor particle growth kinetics.
2. Record and interpret UV-visible absorption and fluorescence spectra.
3. Assess quantum confinement effects through spectral analysis.
4. Determine Stokes shifts and relate them to structural relaxation.
5. Demonstrate care, precision, and critical thinking in spectroscopic work.



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## 1. Introduction

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### 1.1. Aim and Objectives

The aim of this experiment is to investigate how quantum confinement influences the optical properties of semiconducting nanocrystals, specifically CdSe quantum dots. Nanocrystals are typically a few nanometres in diameter — larger than individual atoms but significantly smaller than bulk crystals — and exhibit properties that differ markedly from their bulk counterparts due to confinement effects. To explore this, you will synthesise colloidal CdSe nanoparticles using a kinetic growth method, controlling particle size through reaction time and surfactant stabilisation. You will then characterise the samples using UV-visible absorption and fluorescence spectroscopy, analysing features such as emission maxima, Stokes shifts, and excitation profiles. These measurements will allow you to determine particle size, assess quantum efficiency, and relate your findings to theoretical models such as the Brus equation, thereby gaining insight into the relationship between nanocrystal dimensions and band-gap energy.

### 1.2. Colloids

In this experiment you will prepare "colloids" of nanocrystalline CdSe — this means you will form discrete nanocrystals of CdSe that are dispersed in a solvent (1-octadecene). Large crystals of CdSe are insoluble and will crash out of solution, so you can only prepare a stable dispersion of CdSe by preventing the crystals from growing too large — i.e., restricting them to the sub-micron size. However, small crystals have a "natural" tendency to grow, either by capturing more feed material (dimers of CdSe in solution) or by fusing with other small crystals — a process known as Ostwald ripening. This is because atoms at the surface of the nanocrystal have a higher energy than particles in the bulk of the crystal. By fusing two particles together, the surface-to-volume ratio is reduced and the fraction of high energy atoms at the crystal surface therefore reduces. The energy of the fused crystal is consequently lower than the combined energy of the original crystals, and

there is a thermodynamic driving force for particle growth. Hence, unless you do something special to stabilise the crystals when they are in the nm size regime, they will grow steadily and form a precipitate in the bottom of the flask.

One way to stabilise the nanocrystals is to use an organic surfactant, comprising a long hydrocarbon chain with a functional group on one end that can bind to the nanocrystal surface. When the surfactant is dissolved alongside the nanocrystal feedstock, there is a competition between binding by the surfactant, fusion of crystals, and capture of new atoms. Initially fusion and atom capture tend to dominate, and the crystals grow in size. As a particle grows, however, binding by the surfactant becomes more favourable and eventually growth stops when the crystal is fully capped by ligand. The size at which this happens can be controlled in many ways, including varying the choice of surfactant, its concentration, and the reaction conditions.

The complete process of colloid formation is an important one and is typically described using a LaMer diagram. Before starting this experiment, you should carefully read References 1 and 2 learn about the thermodynamics and kinetics of colloid formation.

Refer Ref. 1 p. 9 for LaMer diagram, ‘the formation of a monodisperse system by controlled nucleation and growth’.  
**1.3. Quantum Confinement** I. Pre-nucleation, II. Burst nucleation, III. Controlled growth

You should recall from nearly-free-electron theory (NFET) that the magnitude of the band-gap in a bulk semiconductor is determined entirely by the periodic potential of the crystal lattice. It is not possible to modify the band-gap without altering the crystal structure, and therefore it is extremely difficult to control the optical properties of macroscale inorganic crystals. From a technological point of view, this is rather restrictive. For example, if we are designing a light-emitting diode, we would like to be able to control the exact colour of emission, or if we are making a solar cell, we would like to ensure the optical band-gap is optimised to the solar spectrum. This is not really possible with bulk semiconductors (short of choosing a completely new material which happens to be closer to our requirements). Quantum confinement provides us with an additional means of controlling the properties of semiconductors and is therefore of considerable scientific and commercial interest.

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In the Electronic Properties of Solids course, you will have studied the band structure of semiconductors in terms of nearly-free-electron theory. In NFET, we assume the electronic wave functions extend over the entire lattice (this is handled mathematically by enforcing periodic boundary conditions). However, if we reduce the size of the semiconductor sufficiently, the assumption of an infinitely extending periodic wave becomes invalid and the "walls" of the semiconductor begin to affect the shape, and hence properties, of the wave function.

Quantum confinement becomes important when the energy of confinement is comparable in magnitude to the optical gap of the bulk semiconductor — typically 2 to 3 eV for a semiconductor that absorbs in the visible region of the spectrum. When a nanocrystal is excited by absorbing a photon, an electron is promoted to the conduction band, leaving a hole behind in the valence band. In large crystals ( $> 100$  nm) the electron and hole are free to move around, but in a nanocrystal they are confined by the walls of the crystal.

In the first-year quantum chemistry course and the second-year electronic properties of solids course, you studied the particle in a box model, and should recall that the energy  $E$  of a particle of mass  $m$  in a one-dimensional box of length  $L$  is given by

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (1.1)$$

where  $n = 1, 2, 3, \dots$  is the principal quantum number. Hence the lowest energy state ( $n = 1$ ) is shifted by an amount

$$\Delta E = \frac{h^2}{8mL^2} \quad (2.2)$$

from "zero". If you do not remember this, then please refer back to your lecture notes. For a sphere of radius  $a$  this expression is modified to

$$\Delta E_e = \frac{h^2}{8ma^2} \quad (3.3)$$

and therefore, the smaller the nanocrystal the higher the confinement energy. In the discussion above "zero" corresponds to the energy of a non-confined electron, i.e., the energy the electron would have if it were in a large crystal that exhibited no quantum

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confinement. For an electron in the conduction band, this energy is the energy of the conduction band edge ( $E_c$ ).

There is an additional consequence of the small crystal size: the electron and hole are forced into close proximity and therefore experience a strong Coulomb attraction. This attraction lowers the energy of the electron by an amount

$$\Delta V_{e-h} = \frac{1.8e^2}{4\pi\epsilon a^2} \quad (4.4)$$

## Why 1.8?

Note, the factor of 1.8 comes from an integration of the smeared out 1s electron and 1s hole distributions and is related to the average separation of the electron and hole in the spherical crystal

If we apportion half of the Coulomb energy to the electron (and the other half to the hole) then, relative to the conduction band of the bulk crystal, the electron energy is shifted by an amount

$$\Delta E_e = \frac{h^2}{8m_e a^2} - \frac{0.9e^2}{4\pi\epsilon a} \quad (5.5)$$

By an analogous argument, the hole energy is shifted from the valence band edge by an amount

$$\Delta E_h = \frac{h^2}{8m_h a^2} - \frac{0.9e^2}{4\pi\epsilon a} \quad (6.6)$$

## Have you considered?

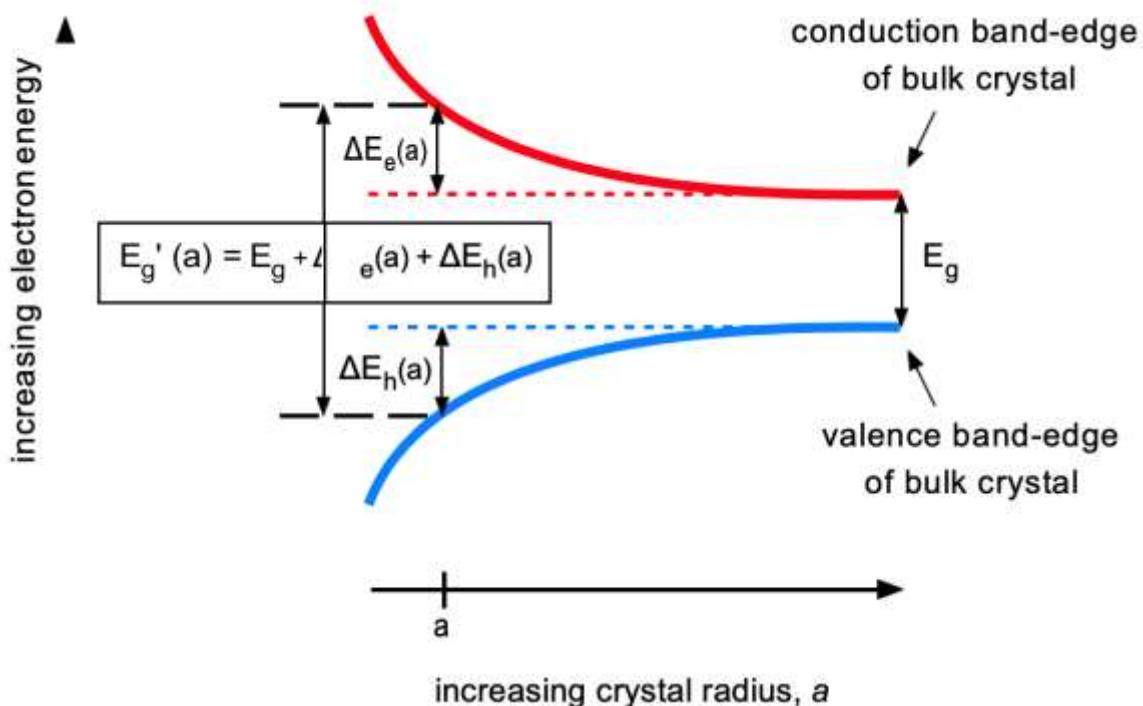
You should notice that the confinement energy varies as  $1/a^2$  whereas the Coulombic energy varies as  $1/a$  — which term will "win out" when the crystal is sufficiently small?

Also notice that the first term is positive, and the second term is negative — what is the physical significance of this?

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A typical energy level diagram shows the energies "from the electron perspective". Therefore, higher energy electron states appear higher in position on an energy level diagram (i.e. further up the page vertically). Holes are oppositely charged and therefore higher energy hole states appear lower in position on the energy level diagram (i.e., further down the page vertically). Hence, remembering that the energy shifts  $\Delta E_e$  and  $\Delta E_h$  are relative to the conduction band-edge and the valence band-edge, respectively, the energy level diagram as a function of crystal radius will appear as shown in **Figure 1**.

It is clear from **Figure 1** that the band-gap increases with decreasing particle size and is given by Eq.1.7 — known as the **Brus Equation**.



**Figure 1:** Variation in energy of the valence and conduction bands with size.

$$E'_g = E_g + \frac{h^2}{8(m_e^* + m_h^*)a^2} - \frac{1.8e^2}{4\pi\epsilon a} \quad (7.7)$$

Effective band gap  
energy  $E'_g$  vs radius  $a$

The asterisk on the electron and hole masses signifies that we are dealing with effective masses and not free masses. (Again, refer to your lecture notes on the electronic properties of solids if you do not remember what this means). From the literature, find

values for  $m_e$ ,  $m_h$ ,  $E_g$ , and  $\epsilon$  and draw a plot of the energy gap versus radius using Excel.

You will need this for your later calculations.

In this experiment, you will synthesise CdSe quantum dots of varying sizes and perform spectral analysis on the obtained samples. Since the band gap energy of the nanoparticles lie in the visible range, UV-visible absorption and fluorescence spectroscopy are suitable for analysis. Before starting the experiment, carefully read Reference 2 by Murphy and Coffer, which provides an excellent overview of the preparation and properties of quantum dots.

## 2. Experimental

### Safety Point!

All synthesis work MUST be done in a fumehood (**Figure 2**). Wear gloves at all times and avoid spilling chemicals. Cadmium and selenium are toxic and must be handled carefully.

### 2.1. Notes

You have been provided with stock solutions of Cd(oleate) and SeTOP in octadecene (ODE). The quantities provided should be sufficient for five runs of the experiment. The Cd(oleate) solution was prepared by heating CdO and oleic acid in ODE at 180 °C for 30 minutes resulting in complete conversion of CdO to Cd(oleate). The SeTOP solution was prepared by mixing Se powder and trioctylphosphine (TOP) in ODE at room temperature resulting in complete conversion to SeTOP. The concentrations of each component in the stock solutions will be provided with the solutions. Your risk assessment should be based on the individual components used to prepare the two stock solutions.

Both solutions are mildly air-sensitive and have been prepared and sealed under nitrogen. For the purposes of your experiment, you should clamp the vial, remove the cap, and use

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a flat-ended needle to withdraw solution into the corresponding glass syringe. Once you have extracted the liquid you should re-seal the vial immediately to limit degradation.

You may observe that the cadmium solution has a white cloudy appearance. If this is the case gently warm the vial with the black hair dryer.

## 2.2. Synthesis

You will synthesise the CdSe nanoparticles using the Cd(oleate) and SeTOP stock solutions. The synthesis is based on a so-called kinetic growth method, in which the particle size is determined by the reaction time.

To start, secure a 25 mL 2-neck round-bottomed flask into the heating block on the hotplate. Attach the reflux condenser and connect up to the water line. Add a magnetic stirrer bar into the flask.

Transfer 10 mL of the Cd(oleate) solution into the 25 mL round bottom flask using the glass syringe (and flat-ended needle) provided. Place a glass stopper into the side-arm of the flask. Using the temperature controller, heat the solution to 215°C. When the temperature controller is stable at 215°C, allow the solution temperature to homogenise by waiting for 10-15 minutes.

### Watch the Heat!

Note that the red LCD value on the hotplate needs to be higher than the temperature set on the temperature controller; setting the value too high on the plate may cause the temperature on the controller to oscillate so keep an eye on the temperature, you want this to be as stable as possible!

When you are ready, remove the stopper and rapidly inject 1 mL of the selenium precursor solution using the syringe (and the second flat-ended needle) into the side arm of the reaction vessel. Fuming of the solvent will occur so keep the sash of the fume hood as low as possible and observe common sense. When you are ready, remove the stopper and rapidly inject 1 mL of the selenium precursor solution using the syringe (and the

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second flat-ended needle) into the side arm of the reaction vessel. Fuming of the solvent will occur so keep the sash of the fume hood as low as possible and observe common sense.



**Figure 2:** Fume hood and equipment used for quantum dot synthesis.

## Sample Storage

Your vials should be capped and stored in the fumehood between lab sessions.

You should start **timing the reaction** from the instant the Se precursor is injected. Use a **Pasteur pipette** to extract some of the reaction solution — only a small amount is needed, approximately the length of the narrow part of the pipette. You should **immediately quench** the pipetted solution — i.e., terminate the reaction — by **transferring it to a sample vial** containing **2–3 mL of toluene** at room temperature. In the first instance you should aim to **obtain 9 or 10 samples within 3 minutes at regular intervals**, but once you have a feel for how the reaction runs, you may allow for a longer reaction time, or take more samples. This is **left to your discretion**. During extraction, you may find that you need to extract more solution, depending on the sensitivity of the spectrometers.

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Once you are comfortable running the experiments, you are free to extend the experiment by varying the reaction temperature (stay in the range of 180–230 °C), by varying the molar ratio of Cd to Se, or by increasing the molar ratio of the oleic acid ortrioctylphosphine.

Have you considered?

What roles do oleic acid and trioctylphosphine play in this experiment?

## 2.3. Instrumentation

Ref 3. p.3 ‘The oleic acid acts as a surfactant, binding to the exterior of the crystal lattice and allowing for the crystals to remain soluble in the octadecene.’

Using the UV-Vis absorption spectrometer and fluorimeters, you should obtain absorption, excitation, and emission spectra for all your samples. This should be done on the same day as you obtain the samples, as the spectral properties may be affected over time. Use cuvettes provided for both instruments.

This experiment is just as much about exploring quantum confinement as it is about obtaining high quality spectroscopic data. You are expected be scrupulous in your analyses.

Lab Safety

All samples for analysis must be prepared in your fume hood

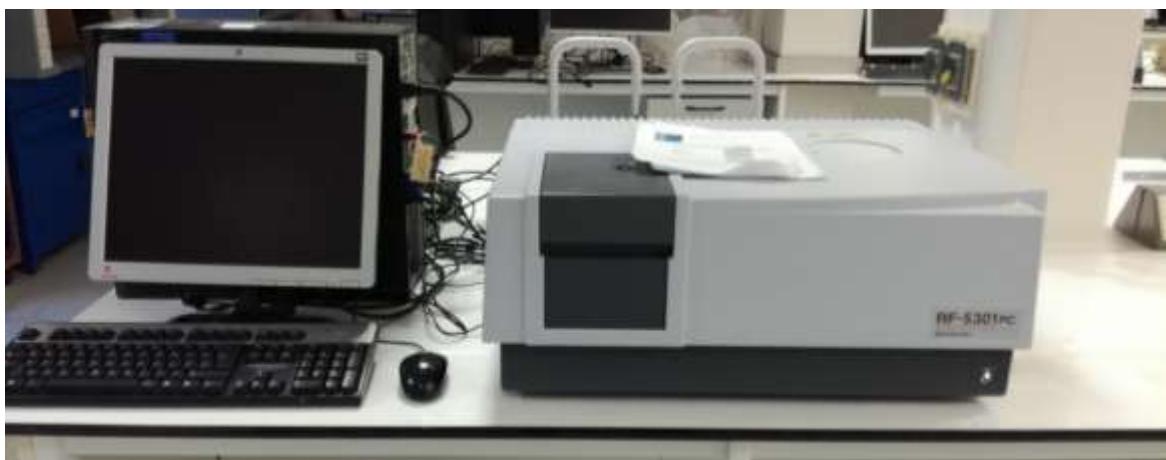
### 2.3.1. UV-Visible Absorption Spectroscopy

The absorption spectra of your samples should be measured on the Thermo Unicam UV 500 spectrometer in the middle of the lab. Instructions for use can be found next to the spectrometer (also available from the Laboratory Technician).

### 2.3.2. Fluorescence Spectroscopy

The fluorescence excitation and emission spectra are to be recorded using the Shimadzu RF- 5301PC fluorescence spectrometers (**Figure 3**). On the PC, find the RFPC

software icon on the desktop and follow the instructions provided next to the instrument (also available from the Laboratory Technician).



**Figure 3:** Fluorescence spectrometer used to measure excitation and emission spectra.

### 2.3.3. Saving Data

For saving the spectra, it is best to export the data as ASCII, text or CSV (comma separated variable) so that the data can be easily imported into Excel or other analysis programs.

## 2.4. Disposal of Samples

Samples and unused reactant solution must be poured into the heavy metal waste bottles available in your fumehood. Vials and reaction flasks should be rinsed with acetone into the heavy metal waste and then washed as normal using detergent solution.

### Keep Cd and Se Out of the Sink

Under no circumstances should samples or solutions containing cadmium or selenium be poured down the sink or into hydrocarbon waste as these are heavy metals and highly toxic and must be disposed of carefully.

## 3. Results and Discussion

Ref. 3 p. 2: As nanocrystals grow, their peak emission quickly approaches the band gap of bulk CdSe (730 nm).

### 3.1. Kinetics of Particle Growth

For each of the reaction mixtures you investigate, you should plot the position of the emission maximum against time. You should aim to plot the data whilst the reaction is proceeding as this will provide you with real-time information about how the reaction is proceeding and, in particular will ensure that you obtain measurements at appropriate intervals (i.e., not too frequently or infrequently). Afterwards, you should use Equation 1.7 to obtain plots of the (mean) particle size versus time. How does the particle diameter vary with time, e.g., does it increase linearly with time? If not, explain why this might be? Refer to the paper by Overbeek to understand how different growth mechanisms can affect the growth kinetics. Determine which growth mechanism is consistent with your data. (This will be discussed in the viva so be sure to read the paper).

### 3.2. Optimum reaction conditions

See if you can determine a set of reaction conditions that provide good control over the reaction (for example slow steady particle growth), while also yielding highly fluorescent particles. To obtain meaningful data, you should compare particles of the same approximate size only (i.e. particles with the same emission peak). The samples will have been obtained using different reaction conditions and will therefore be of different concentrations. To correct for this, you should measure the absorption spectra of each sample in order to determine the fraction of incident photons that are contributing to the emission. You should also measure the emission spectra under identical conditions (i.e. using the same slit widths, excitation wavelengths, integration times etc) so that the intensity measurements are comparable with one another.

Only AVERAGE size can be determined  
- use TEM to confirm size distribution!

i.e. need to NORMALISE the emission peaks

Ref 3. p.1: 'The resulting CdSe nanocrystal solutions yield high quality absorbance and emission spectra with particle sizes ranging from approximately 1.8 nm to 4.0 nm and emission wavelengths ranging from 490 nm to 580 nm.'

## Hints & Tips

- Note, you will probably need to dilute the solutions before doing the measurements in order to minimise self-absorption effects.
- Use the same dilution factor in all cases (or else correct for the different degrees of dilution when presenting your data).

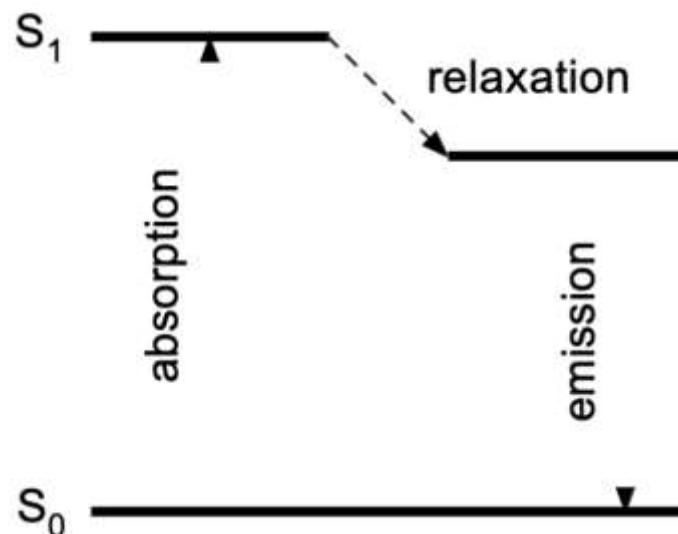


**Figure 4:** UV light table used to visualise quantum dot samples.

Once you have identified your best-performing quantum dot samples, place them on the UV light table provided (**Figure 4**) and take a photograph of their emission.

### 3.3. Stokes Shift

The absorption maximum occurs at a higher energy than the emission maximum and the energy difference is known as the Stokes shift. The origin of the Stokes shift is structural relaxation of the crystal immediately after it is promoted to the excited state by absorption of a photon, with the excess energy being shed in the form of heat (a process known as internal conversion). The crystal subsequently relaxes back to the ground-state, emitting a photon of slightly lower energy than the absorbed photon. The process is summarised in **Figure 5**.



Ref. 3 p.2: The value of the Stokes shift for different sizes of CdSe QD are relatively constant.

**Figure 5:** Nature of Stokes shift.

For all data, you should plot a graph of peak emission wavelength vs peak absorption wavelength and work out an approximate Stokes shift for the CdSe nanoparticles.



### 3.4. Excitation Measurements

Considerable insight into the emission process can be obtained by comparing the excitation spectrum and the absorption spectrum. Write down the relationship between the excitation spectrum, the absorption spectrum, and the quantum efficiency. Hence, explain how the wavelength dependence of the quantum efficiency may be determined from a comparison of the absorption and excitation spectra.

### 4. References

1. J. Th. G. Overbeek, *Adv. Colloid Interface Sci.*, 1982, **15**, 251–277. DOI: [10.1016/0001-8686\(82\)80003-1](https://doi.org/10.1016/0001-8686(82)80003-1)
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