Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Impact of Lifetime Control on the Threshold of Quantum Dot Lasers

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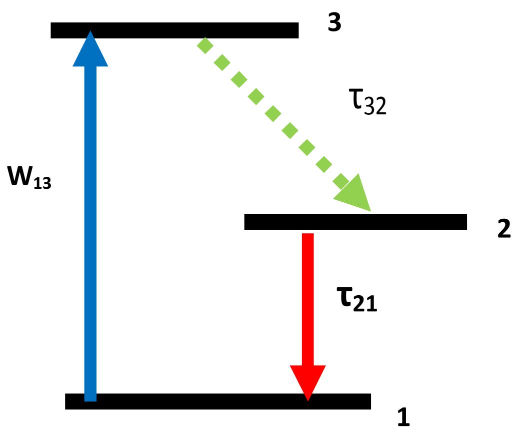
Supplementary Information

Laser Rate Equation for a Three-Level System



S1. Schematic showing various transitions in a three level laser.The blue arrow indicates excitation of electron from ground state to level 3, dashed green arrows indicate spontaneous emission and red arrow indicates laser transition.

Level 1, 2 and 3 represent ground state, first excited state and second excited state of a three level laser scheme. n_1, n_2 and n_3 are the electron population density in level 1,2 and 3 respectively. In a three level system, laser transition occurs between level 2 and level 1. Level 3 helps in the attainment of population inversion. For a typical three level system, τ_{32} is much smaller than τ_{21}. So for all practical purposes one may consider $n_3 = 0$[1]. We follow the notation in Reference 1.

The total electron density is given by,

$$n_{tot} = n_1 + n_2 + n_3 \sim n_1 + n_2 (\because n_3 = 0) \quad (1)$$

$W_p$excites electron to level 3. From level 3, electron undergoes a fast relaxation to level 2. The electrons in level 2 undergo both spontaneous and stimulated emission thus returning to the ground state. The rate of change of electron density in level 1 therefore can be written as,

$$\frac{\partial n_1}{\partial t} = \left(n_2 - \frac{g_2}{g_1} n_1\right) c\sigma\varphi + \frac{n_2}{\tau_{21}} - W_p n_1 \quad (2)$$

Here, c is the velocity of light in ms^{-1},$\sigma$is the stimulated emission cross section in cm^2 and $\varphi$is the photon flux density in photon per cm^3. $g_2$andg_1 are the degeneracy of level 2 and level 1 respectively. The first term on the right side of the equation accounts for stimulated emission, the second term accounts for spontaneous emission and the third term accounts for the depletion of electron density population from level 1 due to pumping of electrons to higher energy levels.

Since $n_3 = 0$,

$$\frac{\partial n_1}{\partial t} = -\frac{\partial n_2}{\partial t} \quad (3)$$

The inversion population density is the difference in the population density of level 2 and level 1 and can be defined as,

$$n = n_2 - \frac{g_2}{g_1} n_1 \quad (4)$$

From equation (1) and equation (4),n_1 and n_2 can be expressed in terms of n_{tot} and,

$$n_1 = n_{tot} - n_2 \quad (5)$$

$$n_1 = n_{tot} - n - \frac{g_2}{g_1} n_1 \quad (6)$$

$$n_1 \left(1 + \frac{g_2}{g_1}\right) = n_{tot} - n \quad (7)$$

$$n_1 = \frac{n_{tot} - n}{\gamma} \quad (8)$$

$$n_2 = n_{tot} - \frac{n_{tot} - n}{\gamma} = \frac{n_{tot}(\gamma - 1) + n}{\gamma} \quad (9)$$

The rate of change of inversion population density for a three level system therefore can be written as,

$$\frac{\partial n}{\partial t} = -\gamma n c\sigma\varphi - \frac{n + n_{tot}(\gamma - 1)}{\tau_f} + W_p(n_{tot} - n) \quad (10)$$

Here, $\gamma = 1 + \frac{g_2}{g_1}$ and $\tau_f = \tau_{21}$

The rate of change of photon flux within the laser resonator is,

$$\frac{\partial \varphi}{\partial t} = c\sigma\varphi x n - \frac{\varphi}{\tau_c} \quad (11)$$

At threshold the photon flux inside a resonator is very small and its rate of change can be neglected,

$$\frac{\partial \varphi}{\partial t} = 0 \tag{12}$$

The population density for inversion from equation (10) and (12) therefore can be expressed as,

$$n = \frac{1}{\tau_c c \sigma x} \tag{13}$$

At steady state,

$$\frac{\partial n}{\partial t} = 0 \tag{14}$$

$$-\frac{n + n_{tot}(\gamma - 1)}{\tau_f} + W_p(n_{tot} - n) = 0 \tag{15}$$

We consider $\frac{g_2}{g_1} = 1$.

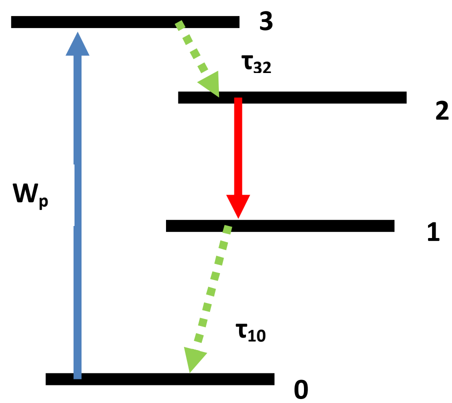
The equation for fluence now becomes,

$$W_p = \frac{n + n_{tot}}{\tau_f(n_{tot} - n)} = \frac{\frac{1}{\tau_c c \sigma x} + n_{tot}}{\tau_f\left(n_{tot} - \frac{1}{\tau_c c \sigma x}\right)} = \frac{1 + n_{tot}\tau_c c \sigma x}{\tau_f(n_{tot}\tau_c c \sigma x - 1)} = \frac{\tau_f + \alpha}{\tau_f(\alpha - \tau_f)} \tag{16}$$

The pump fluence required to achived threshold condition in a three level system is

$$f(threelevel) = \frac{\tau_f + \alpha}{\tau_f(\alpha - \tau_f)\sigma_A} \tag{17}$$

Laser Rate Equations for Four Level System:



S2. Schematic showing various transitions in a four level laser. Blue arrow indicates excitation of electron from ground state to level 3, dashed green arrows indicate spontaneous emission and red arrow indicates laser transition.

The net electron population density in a four level scheme is a sum of electron density in level 0, 1, 2 and 3. Here level 0 represents the ground state. The rate of transition of electrons from level 3 to level 2 is extremely fast as compared to other transition rates. Due to this, one can assume, $n_3 = 0$ and can write the total electron density as,

$$n_{tot} = n_0 + n_1 + n_2 \tag{18}$$

The laser transition in a four level system occurs between level 2 and level 1. Hence, it is necessary to consider the rate of change of electron density in these two levels.

The electrons occupy level 2 on excitation due to pump as well as due to stimulated absorption from level 1. The population density of level 2 is depleted because of spontaneous emission to level 1 and ground state as well as due to stimulated emission. Thus the overall rate of change of n_2 can be represented as,

$$\frac{\partial n_2}{\partial t} = W_p n_0 - \left(n_2 - \frac{g_2}{g_1} n_1\right) c\sigma\varphi - \left(\frac{n_2}{\tau_{21}}\right) \tag{19}$$

Level 1 is populated due to stimulated and spontaneous emission from level 2 and depopulated due to spontaneous decay and stimulated absorption from level 1. This can be summarized as,

$$\frac{\partial n_1}{\partial t} = \left(n_2 - \frac{g_2}{g_1} n_1\right) c\sigma\varphi + \frac{n_2}{\tau_{21}} - \frac{n_1}{\tau_{10}} \tag{20}$$

At steady state,

$$\frac{\partial n_1}{\partial t} = \frac{n_2}{\tau_{21}} - \frac{n_1}{\tau_{10}} = 0 \tag{21}$$

$$n_1 = \frac{n_2 \tau_{10}}{\tau_{21}} \tag{22}$$

The inversion population density arises due to difference in the population of level 2 and level 1.

$$n = n_2 - n_1 = n_2\left(1 - \frac{\tau_{10}}{\tau_{21}}\right) = n_2\left(\frac{\tau_{21} - \tau_{10}}{\tau_{21}}\right) \tag{23}$$

$$n_2 = n\left(\frac{\tau_{21} - \tau_{10}}{\tau_{21}}\right)^{-1} \tag{24}$$

$$n_1 = n\left(\frac{\tau_{21} - \tau_{10}}{\tau_{21}}\right)^{-1} \frac{\tau_{10}}{\tau_{21}} = n\frac{\tau_{10}}{\tau_{21} - \tau_{10}} = n\frac{\tau_d}{\tau_f - \tau_d} \qquad (\tau_{21} = \tau_f; \tau_{10} = \tau_d) \tag{25}$$

At threshold, the terms involving photon flux becomes negligible and hence can be ignored. At steady state equation (20) gets reduced to,

$$W_p n_0 - \frac{n_2}{\tau_f} = 0$$

$$W_p(n_{tot} - n_2 - n_1) - \frac{n_2}{\tau_f} = 0$$

$$W_p = \frac{n_2}{\tau_f(n_{tot} - n_2 - n_1)}$$

$$W_p = \frac{n\left(\frac{\tau_f - \tau_d}{\tau_f}\right)^{-1}}{\tau_f\left(n_{tot} - n\frac{\tau_f}{\tau_f - \tau_d} - n\frac{\tau_d}{\tau_f - \tau_d}\right)}$$

$$W_p = \frac{n\frac{\tau_f}{\tau_f - \tau_d}}{\tau_f\left(n_{tot} - n\frac{\tau_f}{\tau_f - \tau_d} - n\frac{\tau_d}{\tau_f - \tau_d}\right)} = \frac{n\tau_f}{\tau_f\left(n_{tot}(\tau_f - \tau_d) - n(\tau_f + \tau_d)\right)} \quad (26)$$

Substituting expression for n from equation (13) into equation (26) we get,

$$W_p = \frac{1}{\left(n_{tot}\tau_c c\sigma x(\tau_f - \tau_d) - (\tau_f + \tau_d)\right)} = \frac{\tau_f}{\alpha(\tau_f - \tau_d) - \tau_f(\tau_f + \tau_d)} \qquad \left(n_{tot}\tau_f\tau_c c\sigma x = \alpha\right)$$

The pump fluence required to achieve onset of lasing action in case of a four level system is,

$$f(fourlevel) = \frac{\tau_f}{\sigma_A\left(\alpha(\tau_f - \tau_d) - \tau_f^{\,2}\right)} \qquad \because \tau_f \gg \tau_d \quad (27)$$

Effects of Quantum Yield on Quantum dot lasing

For quantum dots, we have considered an ideal situation where the system has a unit emission quantum yield. However, in a real system, one needs to take non-radiative process into consideration since they are major loss contributors. This modifies the rate equations as follows:

$$\frac{dN}{dt} = W_p(1 - N - B) - W_pN + 2c\sigma\varphi(1 - N - B) - 2Nc\sigma\varphi + 2Bc\sigma\varphi + \frac{B}{\tau_B} - \frac{N}{\tau\prime} \quad (28)$$

$$\frac{dB}{dt} = W_pN + c\sigma\varphi(N - 2B) - \frac{B}{\tau_B} \quad (29)$$

$$\frac{d\varphi}{dt} = 2Bc\sigma x\varphi - 2c\sigma x\varphi(1 - N - B) - \frac{\varphi}{\tau_C} \quad (30)$$

Where, $\frac{1}{\tau\prime} = \frac{1}{\tau} + \frac{1}{\tau_{NR}}$; here τ is the radiative life time of a single exciton and τ_{NR} is the non-radiative lifetime of a single exciton. τ' is related to the sample quantum yield as $Q = \frac{\tau\prime}{\tau}$. Note that α remains a function of τ alone.

At the threshold, $1 - N - B = B$ and the photon flux density is small enough to be neglected. At steady state, the rate equations can be set to zero. Solving the rate equations with the stipulated conditions yields

$$f(threshold, QDXX) = \frac{W_p}{\sigma_A} = \frac{\tau + \sqrt{\tau^2 + \frac{4(4\alpha^2 - \tau^2)\tau_B}{\tau'}}}{2\sigma_A(2\alpha - \tau)\tau_B} \tag{31}$$

For a quantum dot lasing under single exciton regime, the rate equations for single exciton and biexciton probability remains same as equation (28) and (29). The rate equation for photon flux density is,

$$\frac{d\varphi}{dt} = c\sigma\varphi x N - 2c\sigma x\varphi(1 - N - B) - \frac{\varphi}{\tau_C} \tag{32}$$

For lasing under single exciton regime, the threshold condition is $1 - N - B = N$. At threshold, the photon flux density is small enough to be neglected. Solving the rate equation under steady state conditions results in,

$$f(threshold, QDX) = \frac{W_p}{\sigma_A} = \frac{(\alpha-\tau) \pm (\alpha-\tau)\sqrt{1 - \frac{4\tau_B\tau(2\alpha+\tau)}{\tau'(\alpha-\tau)^2}}}{2\tau\tau_B} \tag{33}$$

$$f(threshold, QDX, \tau_B = 0) = \frac{(2\alpha+\tau)}{\sigma_A\tau'(\alpha-\tau)} \tag{34}$$

The impact of quantum yield on thresholds is rather simple to evaluate. In particular, we can substitute $\tau' = Q\tau$ into equations 31, and 34 to get:

$$f(threshold, QDXX) = \frac{W_p}{\sigma_A} = \frac{\tau + \sqrt{\tau^2 + \frac{4(4\alpha^2 - \tau^2)\tau_B}{Q\tau}}}{2\sigma_A(2\alpha - \tau)\tau_B} \tag{35}$$

$$f(threshold, QDX, \tau_B = 0) = \frac{(2\alpha+\tau)}{\sigma_A Q\tau(\alpha-\tau)} \tag{36}$$

From these relations it is obvious that a sub-unity quantum yield has a stronger impact on single exciton lasing than on biexciton lasing. Biexcitonic lasing is less sensitive to nonradiative decay simply due to the much shorter lifetime exhibited by biexcitons. Figure S3 compares the thresholds of QDs with 10% and 100 % Quantum yields under single and biexcitonic lasing conditions.

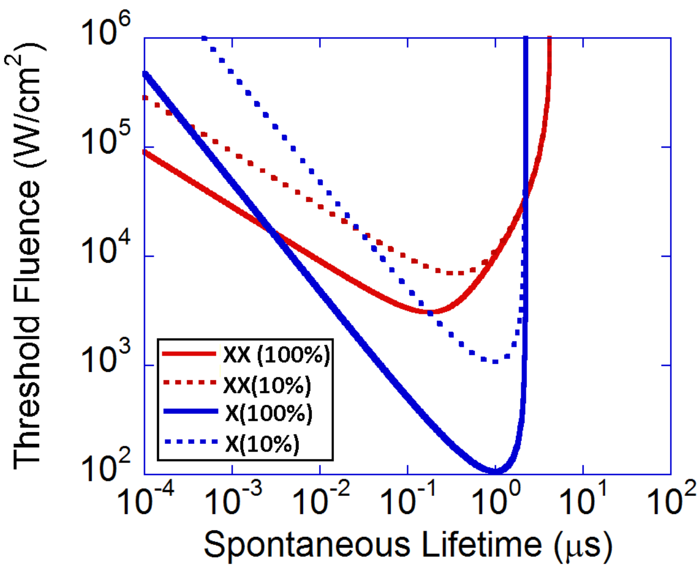


Figure S3. Quantum yield dependence of ASE thresholds under the single and biexciton gain regime.

Impact of formation of higher order excitons in QDs

Unlike solid state phosphors, QDs can also be populated by higher order excitations *viz.* tri-excitons, etc. that increasingly exhibit shorter lifetimes, limited by non-radiative decay. The formation of these excitations has little bearing on the phenomena discussed in this paper, and therefore has been neglected altogether. As an illustration, we consider three situations where a QD starts from having one, two and three excitons respectively. While triexcitons do decay rapidly (here ~7 times faster than biexcitons, as suggested in Klimov et. al., Science 2000),[2] their decay only leads to the eventual formation of biexcitons. In a sum of rates picture that has been found applicable in such a situation, there is no change in the amount of time for which biexcitons persist in the system. The presence of multiexcitons thus does not change the overall population that persists at the QD band edge in any manner, and is consequently ignored. As shown in the figure S4, there is no change to the amount of time for which the system is optically transparent either.

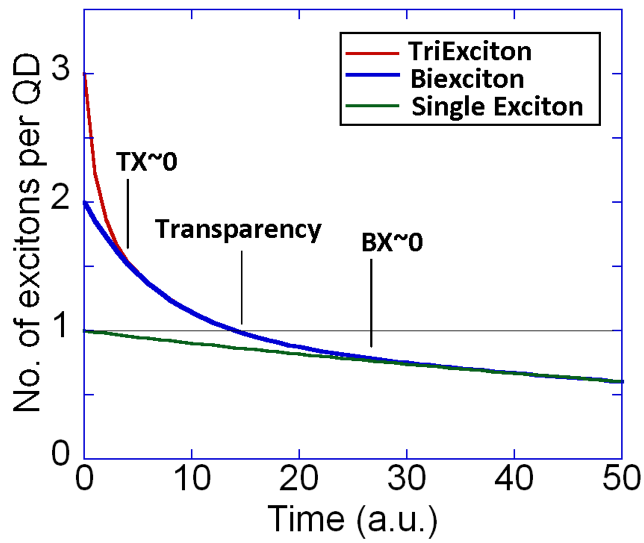


Figure S4. Schematic of the effects of higher order excitons on the gain behaviour of QDs. The ensemble starts variously from 1, 2 and 3 excitons per QD. It is observed that due to their rapid decay to biexcitons, the gain properties of higher order QD excitations have little difference from the properties of biexcitons.

1. W. Koechner, *Solid State Laser Engineering*. (Springer-Verlag, New York, 2006).

2. Klimov V. I. et. al., *Science* 2000, **287**, 1011.