Quantum Dots and QED

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Abstract

High quantum dot (QD) efficiency may be explained by excitons generated in the quantum electrodynamics (QED) confinement of electromagnetic (EM) radiation during the absorption of the laser radiation. By the Mie theory, there is general agreement the laser photons are fully absorbed by QDs smaller than the laser wavelength. But how the absorbed laser photons are conserved by a QD is another matter. Classically, absorbed laser radiation is treated as heat that in a body having specific heat is conserved by an increase in temperature. However, the specific heats of QDs vanish at frequencies in the near infrared (NIR) and higher, and therefore an increase in temperature cannot conserve the absorbed laser photons. Instead by QED, the laser photon energy is first suppressed because the photon frequency is lower than the EM confinement frequency imposed by the QD geometry. To conserve the loss of suppressed EM energy, an equivalent gain must occur. But the only EM energy allowed in a QED confinement has a frequency equal to or greater than its EM resonance, and therefore the laser photons are then up-converted to the QD confinement frequency - the process called cavity QED induced EM radiation. High QD efficiency is the consequence of multiple excitons generated in proportion to very high QED induced Planck energy because at the nanoscale the EM confinement frequencies range from the vacuum ultraviolet (VUV) to soft x-rays (SXRs). Extensions of QED induced EM radiation are made to light emission from porous silicon (PS) and multi-photon excitation (MPE) of molecules.

Introduction

The efficiency of QDs is the electrical power produced as a percentage of the absorbed radiation. Efficiency in the conversion of photons to excitons in bulk semiconductors is usually based on the 1 photon – 1 exciton rule for photons having Planck energy greater than the band gap, the upper limit determined [1] to be about 31 %. The highest QD conversion efficiency [2] sometimes called carrier multiplication (CM) is typically about 66 %.

Currently, high QD efficiency is explained by impact ionization [3] that allows more than 1 exciton to be successively generated in the absorption of 1 photon with Planck energy greater than the band gap of the semiconductor. But impact ionization by successive absorption takes time while experiments [4] show the excitons are formed instantaneously. Further, impact ionization fails to explain [5] almost the same QD efficiencies found for the widely different CdSe and PbSe semiconductors.

Subsequently, the "coherent–CM" mechanism was proposed [6,7], but required very large Coulomb coupling that could not be experimentally [5] verified, thereby prompting the similar QD efficiencies found for the quite different CdSe and PbSe to be explained by *virtual* exciton states.

In this paper, QDs upon the absorption of laser photons generate multiple excitons in proportion to the Planck energy induced by QED induced EM radiation, the proportionality known since the 1950's for excitons [8] generated in bulk Ge under x-rays (XRs). *Virtual* exciton states are not necessary.

Prior applications of QED induced EM radiation were directed to frequency up-conversion of photons in evacuated nanovoids (NVs), say by bubbles in the electrification of flowing [9] liquids or by the Casimir [10] effect for gaps between solids. The only difference between QED confinement of photons in solid NPs and evacuated cavities is the refractive index, but even this difference is inconsequential because the refractive index may be treated as unity [11] for QDs small in relation to the photon wavelength, and therefore QED induced EM radiation in QDs is the same as that in NVs.

Theoretical Background

QED induced EM radiation for a laser photon absorbed in the QD is shown in Fig. 1. The QD is taken to be spherical of radius R having an EM confinement frequency beyond the VUV. By the Mie theory [12], a laser photon is fully absorbed in the QD having a diameter *D* less than the laser wavelength. Absent specific heat at VUV frequencies, the EM energy of the absorbed laser photon cannot be conserved by an increase in QD temperature. Instead, the laser photon absorbed in the QD momentarily has a frequency lower than the VUV confinement frequency, and therefore is suppressed by QED. To conserve the loss of suppressed photon energy under QED constraints, an equivalent amount of EM energy is gained at the EM confinement frequency. Depending on the QD diameters, the EM confinement frequencies vary from the VUV to SXRs. Because of this, the suppressed laser photon is up-converted to high Planck energies by QED induced EM radiation, the number of multiple excitons generated in proportion to the Planck energy.

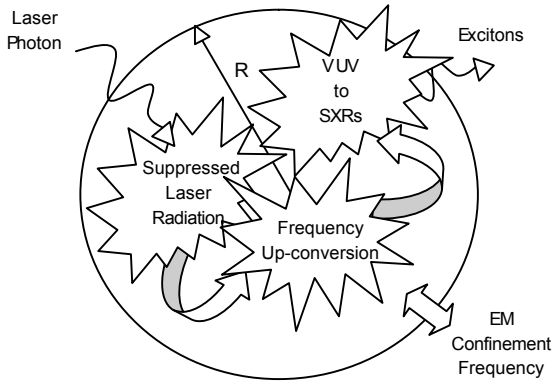

Figure 1 Spontaneous Multiple Excitons by QED

In contrast to QDs, micro dots (MDs) larger than the laser wavelength only partially absorb the laser radiation. MDs are only considered in this paper to contrast the differences with QDs. In MDs, the absorption of the laser photon follows classical theory and is conserved by an increase in temperature.

But this is not the case for QDs. Fig. 1 shows the laser photon at wavelength l_P absorbed by the QD according to the Mie theory. However, an increase in QD temperature is precluded by QED. Instead, the laser photon having a wavelength l_P longer than the QD confinement diameter D is shown suppressed only to be conserved by frequency up-conversion to VUV or SXR levels. Excitons are then produced in proportion to the Planck energy.

Similar to creating photons of wavelength l in box having walls separated by $l/2$ by supplying EM energy to the box, the QD diameter D defines the half wavelength $l_{EM}/2$ of the photon created from the absorbed laser photon. The EM confinement wavelength is,

$$l_{EM} = 2n_r D = 4n_r R \qquad (1)$$

where, the refractive index n_r corrects for the lower speed of light c in solids. Although $n_r > 1$ is applicable for MDs, for QDs [11] smaller than the laser photon wavelength l_P, $n_r = 1$.

Upon absorption, the laser photon is confined within the geometry of the QD. For the QD to conserve the absorbed photon by an increase in temperature, the specific heat must be finite. By the Einstein solid, the QD specific heat depends on the frequency of each degree of freedom (DOF) of the atoms as they respond at the EM confinement frequency to the absorption of the laser photon. Each DOF of the atom is treated as a harmonic oscillator by the Einstein-Hopf relation [13]. Fig. 2 shows the dispersion of average Planck energy E_{avg} of a single harmonic oscillator with wavelength l at temperature $T \sim 300$ K

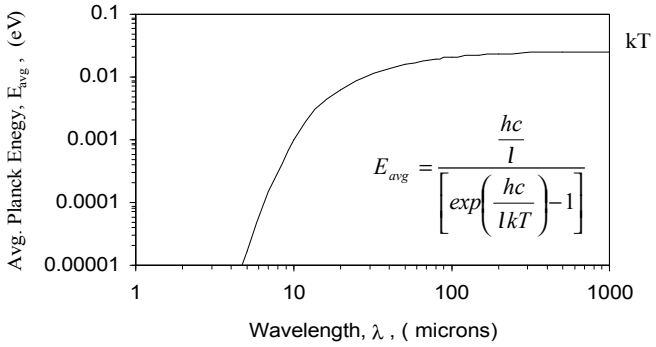

Figure 2 Harmonic Oscillator at T ~ 300K
In the inset, h is Planck's constant, k is Boltzmann's constant, and c is the speed of light.

For the QD as a collection of N_A atoms having 3 DOF, the total Planck energy U,

$$U = 3N_A \frac{\frac{hc}{l}}{\left[exp\left(\frac{hc}{lkT}\right) - 1\right]} \qquad (2)$$

The QD specific heat C is,

$$C = \frac{\partial U}{\partial T} \qquad (3)$$

In terms of the dimensionless specific heat C^*,

$$C^* = \frac{C}{3N_A k} = \frac{\left(\frac{hc}{lkT}\right)^2 exp\left[\frac{hc}{lkT}\right]}{\left[exp\left(\frac{hc}{lkT}\right)-1\right]^2} \qquad (4)$$

In the limit as the oscillator wavelength $l \rightarrow 0$, $C^* \rightarrow 0$. But EM confinement frequencies are only required to be higher than the NIR to have C^* vanish. The specific heat C^* at 300 K is illustrated in Fig. 3. QDs with D less than about 4 microns have vanishing specific heats with excitons at VIS levels produced for diameters D less the laser half-wavelength $l_P/2$.

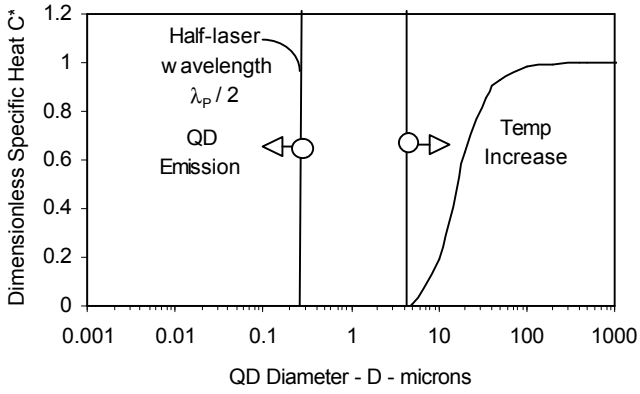

*Figure 3. Dimensionless Specific Heat C*at 300 K*

For a number of QDs, the collective response to laser irradiation consists of each QD emitting its own broadband EM spectrum as the laser photon is absorbed because the QD diameters are not identical. Both frequency-up and -down conversion of the absorbed laser photon may occur during EM confinement. For QDs, $l_P > l_{EM}$ and the laser photon undergoes frequency up-conversion, but for MDs having $l_P < l_{EM}$, the laser photon undergoes frequency down-conversion. The EM emission spectrum for a QD with $l_P > l_{EM}$ is depicted in Fig. 4

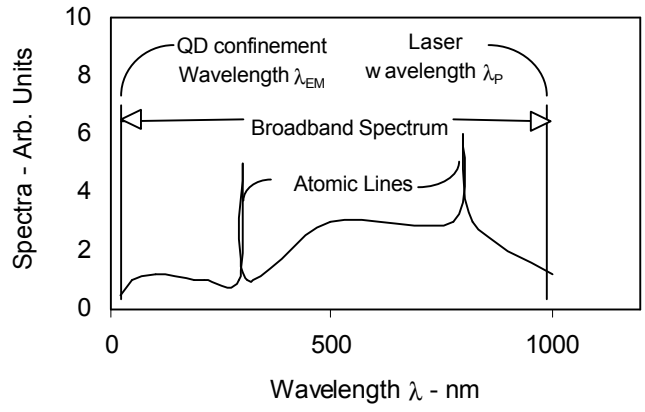

Figure 4. QD Emission Spectrum Induced by Laser Photon confinement in QDs.

Since the EM broadband spectrum is continuous, all quantum states of chemical species in the QD over the wavelength interval [$l_{EM,}$ l_P] are excited as shown by the atomic lines depicted in Fig. 4. In MDs, molecular bands in the wavelength interval [l_P, l_{EM}] are excited.

The Planck energy E induced in the QD or MD by the QED confinement,

$$E = \frac{hc}{2D} \quad (5)$$

The Planck energy E in terms of the QD diameter D is shown in Fig. 5. MDs with $D > 4$ microns increase in temperature. In contrast, QDs having $D < 0.25$ microns and $E > 2.5$ eV produce VIS excitons at Planck energy levels from the VUV to SXRs.

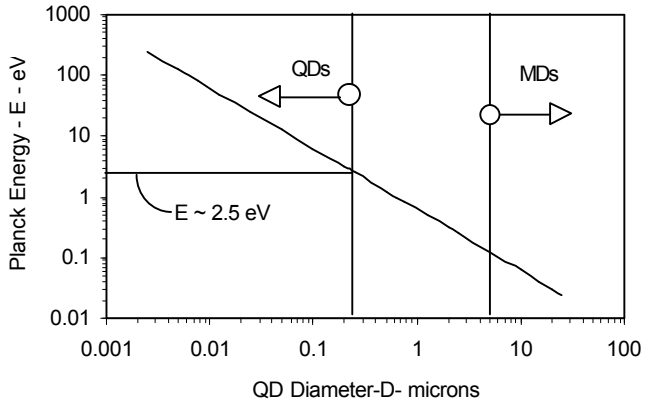

Figure 5. Planck Energy E v QD and MD Diameter D

By QED, the EM energy of the absorbed laser photon is conserved by an increasing its frequency to the EM confinement frequency, thereby inducing Planck energy far in excess of the typical semiconductor band-gaps. Excitons are formed in proportion to the Planck energy, thereby exceeding the 1 photon – 1 exciton rule for the bulk.

QDs avoid the limitation of the 1 photon – 1 exciton rule in the bulk because QED induces the absorbed laser photon to increase its frequency to VUV/SXR levels, thereby providing Planck energies far beyond the band-gap necessary for generating multiple excitons. For bulk Ge, every 2.5 eV of XR energy [8] generated 1 exciton. Recently, 3 – NIR laser photons at 800 nm were found [6] to generate 7 excitons in QDs of PbSe. Fig. 6 shows Planck energy E and the number of excitons for Ge, and Fig. 7 gives the number of excitons v Planck energy E for PbSe and Ge. At the upper limit, the 1 nm PbSe QD inducing SXR Planck energies of 621 eV requires a pulsed NIR femtosecond laser [6] supplying about 400 NIR photons at 800 nm to generate 870 excitons.

QDs generate multiple excitons in proportion to the Planck energy [8] induced by QED. However, the number of excitons depends on the laser energy available. The number N of QED induced photons depends on the laser flux F,

$$N = \frac{p}{4}\frac{D^2 F}{E} \quad (6)$$

At a low level NIR laser flux $F \sim 1\text{x}10^{12}$ W/ cm^2, the number N of QED photons is shown in Fig. 8. The 1 nm QD produces about $1\text{x}10^{14}$ – 621 eV QED photons.

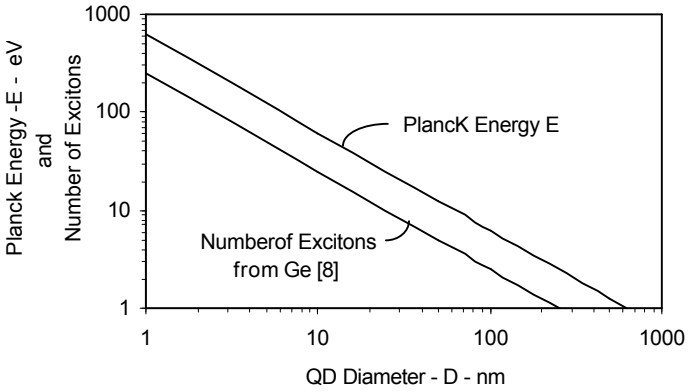

Figure 6 Planck Energy and Number of Excitons v QD Diameter

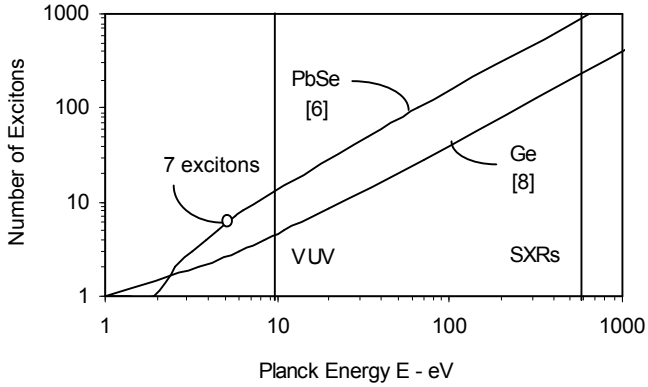

Figure 7 Numbers of Excitons v. Planck Energy for Ge and PbSe

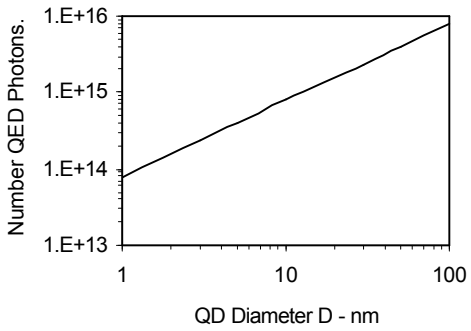

Figure 8 Number of QED Photons . QD Diameter at F = 1x10^{12} W/cm^2

Extensions

QED induced EM radiation in QDs is extended to explain similarities with light emission in PS and MPE.

Emission from Porous Silicon

Fundamental in the QED explanation of QD efficiency is the controversy [14] over whether the QD luminescence following laser illumination is thermal radiation (TR) or photoluminescence (PL). Here, TR is blackbody radiation depending on temperature, while PL is light emission in transitions between quantum energy states.

QD luminescence begins in 1990 with the discovery [15] of luminescence from PS. At that time, PS luminescence was explained by the quantum confinement of electrons in the thin pore walls, the surrounding evacuated pores acting as potential barriers. But this simple explanation for QED confinement is even now difficult to understand because of the obvious question:

How did the electrons become trapped in the PS pore walls?

Indeed, understanding how the electron becomes trapped in the PS walls is central to the explanation of PS and QD luminescence. For QDs, the usual explanation [16] is that the laser creates free excitons, say in the GaAs surrounding the QD, the excitons then diffusing into the QD to relax down to the lowest energy level in the QD. But this is unlikely because the potential confining the electron within the QD would certainly block an electron external to the QD from entering and occupying the lower QD states. Similar arguments can be made against the electrons confined in PS. Clearly, another mechanism is operating to trap the electron in the PS and QDs, and it is plausible that the same mechanism would explain the formation of excitons in QDs. Here, cavity QED induced EM radiation is proposed as the mechanism by which the excitons are produced and electrons trapped in the in the QDs and PS.

> Trapping the electron in PS or QDs proceeds spontaneously by QED induced EM radiation at the instant the laser photon is absorbed. The electron need not be trapped in the PS or QD prior to the absorption of the laser photon for PS or QD luminescence.
>
> The electron does not migrate into the QDs, but is created by QED induced VUV radiation upon laser absorption by the photoelectric effect.

Recently, a key experiment [14] was performed to determine whether PS luminescence was TR or PL. The experiment showed the PS luminescence in a vacuum was quenched by gas pressure. On this basis, it was concluded that the luminescence cannot be PL because the transitions between energy states would have to depend on the pressure of the surrounding gas. Since quantum levels do not depend on gas pressure, PS luminescence was concluded not to be PL, and by default could only be TR.

But this argument is based on the premise that PL and TR are the only mechanisms by which PS luminescence may occur. If the gas adsorbed in the PS changes its dimensions at the nanoscale, quenching may very well occur. Moreover, blackbody emission requires very high temperatures to sustain IR, VIS, and UV emissions, e.g., a temperature of 14,000 K is required to sustain a near IR photon at 1.4 eV. Since the PS has to vaporize to produce the near IR photon, it

follows that TR is also not the source of luminescence. However, TR increases the temperature of the bulk that can give the impression that high laser heating is causing the luminescence rather than by the change in EM confinement of the laser photon in the PS as required by QED induced EM radiation.

> The QD or PS substrate may very likely increase to high temperatures, but this not the cause of luminescence. Rather, it is the tendency of local confined QED regions that absorb NIR laser radiation to undergo frequency up-conversion to VUV levels that excites the electronic states. Bulk temperatures in QDs and PS are far lower than the blackbody temperatures necessary to directly excite the spectral peaks.

In 1992, PS luminescence was proposed [17] caused by quantum confinement in the MPE up-conversion of IR laser radiation in a double-resonance-enhanced nonlinear-optical process. The similar PL spectra found for PS irradiated with IR and UV photons was taken as confirmation of the high efficiency of MPE of IR photons in producing the equivalent UV photon despite the well-known inefficiency of MPE. Quantum confined IR radiation is also the basis for cavity QED induced EM radiation, but differs from [17] in that the absorbed IR laser radiation is frequency up-converted to VUV levels that produce the PS luminescence.

> QED induced EM radiation is a quantum confinement effect. But the quantum confinement is that of the IR laser radiation being absorbed by submicron entities in the PS. Subsequent frequency up-conversion produces the higher EM energy that excites the PS.
>
> MPE is an inefficient mechanism for up-converting IR photons to the VUV. In contrast, QED induced EM radiation is highly efficient way of frequency up-conversion of IR radiation to VUV levels.

Later in 1995, PS luminescence was proposed explained [18] by MPE. PL spectra excited by IR laser pulses at wavelengths from 0.532 to 4.9 microns were found similar to that obtained by UV excitation having Planck energy above the Si band gap, and therefore the MPE was taken to be confirmed independent of the photon energy. However, the MPE required 7 photons at 4.9 microns to produce a single 1.77 eV photon which is again questionable because MPE is known as an inefficient IR frequency up-conversion process.

> QED induced EM radiation relies on the QED confinement of the absorbed laser photon to the necessary Planck energy and does not depend on the IR photon energy level. Individual IR photons simply increase the EM energy in the EM confinement with the frequency up-conversion depending on the size of the QD. The process is continuous and all quantum states between the laser frequency and the EM confinement frequency of the QD are excited.

In 2000, PS luminescence in free-standing films [19] was thought caused by TR at temperatures measured at about 1000 K. In fact, the high temperatures are consistent with the hypothesis earlier advanced [20] that PS luminescence is not caused by any kind of exotic excitation process, but simply by TR. However, TR cannot explain the more recent [21] finding of C_2 emission from nano-carbon under microwave radiation in a vacuum.

Laser Dissociation of Molecules

The applicability of cavity QED induced EM radiation to QDs and PS as an alternative to MPE suggests that other areas of physics where MPE is a well established phenomenon [14] might also be similarly explained. One such area is the multi-photon dissociation (MPD) of polyatomic and macromolecules by IR lasers. After all, a molecule like a QD or PS having a small number of atoms should follow the same physics.

In 1971, MPE was performed [22] with 10.6 micron CO_2 IR laser radiation of absorbing gases, e.g., NH_3, CCl_2F_2, and C_3H_6. The laser induced MPD luminescence was instantaneous followed by delayed sparking. The instantaneous phase was thought [23] to be caused by collisionless uni-molecular MPD of single molecules up the vibrational ladder, while the sparking was caused from collision-induced fragments. The C_2 Swan bands centered at 516 and 563 nm observed [22] in the IR laser induced luminescence from C_3H_6 suggested that by MPE the IR radiation would reveal the Swan bands in all hydrocarbon gases.

> TR finds difficulty in producing detailed C_2 band structures, but the spectral bands are a natural consequence of PL from the QED induced EM radiation produced in the molecule upon IR radiation. Swan bands centered at 516 and 563 nm having Planck energies of 2.4 and 2.2 eV cannot be explained by blackbody temperatures of about 24,000 degrees because any solid state materials would vaporize.

Nevertheless, the issue of whether IR induced MPD of molecules is TR or PL continued [24] with the argument that before a molecule dissociates, the thermal energy from the IR excitation may be regarded as randomized in all its vibrational modes. But slow thermal heating with IR photons does not occur because QED forbids the molecule to increase in temperature.

> In cavity QED induced radiation, IR radiation of a molecule is conserved not by an increase in temperature, but by conversion to Planck energy at the frequencies of all vibration states. It is not thermal energy that is randomized in the vibration modes as currently thought, but rather the EM energy of the absorbed IR photon.

In the rapid MPD of a molecule under IR radiation, the increase in Planck energy that occurs instead of a temperature increase causes the molecule to dissociate as if irradiated by EM radiation in excess of its dissociation energy. However, this is not the MPD thought to occur by MPE of TR. For example, the IR laser MPD of silylene [25] showed detailed SiH_2 structure near 17,250 cm^{-1} or 2.14 eV that cannot be explained by MPE, but rather by the spontaneous conversion of absorbed IR photons into all quantum states by QED induced EM radiation.

Conversely, an argument may be made that the laser induced luminescence [26] from gas phase C_{60} and C_{70} fullerenes is TR because the fullerene spectra has the same shape as that for a tungsten filament at 3000 K, although the tungsten produces a far brighter light. Absent C_2 emission, the fullerene spectra are essentially those of blackbody radiation at 3000 K. In contrast, the C_2 bands from the microwave irradiation of nanocarbon [21] are observed as the temperature reached 3915 K. But blackbody radiation cannot explain the C_2 bands. It is likely the nanocarbon substrate at 3915 K is emitting blackbody radiation and adjacent submicron QED confinement entities are producing the C_2 bands by cavity QED radiation.

Conclusions

- QDs generate multiple excitons in proportion to the Planck energy induced by QED. However, the number of excitons depends on the laser energy available. At the upper limit, the 1 nm PbSe QD inducing SXR Planck energies of 621 eV requires a pulsed NIR femtosecond laser supplying about 400 NIR photons at 800 nm to generate 870 excitons.

- The transfer of an external electron into PS or QDs does not occur by diffusion through the same barrier that eventually confines it in the PS or QD. Instead, the electron is trapped as a consequence of QED induced EM radiation at the instant the laser photon is absorbed.

- It is the EM confinement of the photon that is crucial to QD and PS. The confinement of the electron is almost inconsequential to production of excitons.

- Laser photon frequency is increased upon absorption to the EM confinement frequency of the QD or PS, thereby exciting the semiconductor with high Planck energy. It is the momentary high Planck energy that produces excitons by PL.

- Blackbody radiation cannot explain the detailed structure of Swan bands found in the dissociation of hydrocarbon gases under IR radiation unless it is frequency up-converted.

- Similar to QDs and PS, molecular dissociation by IR lasers does not occur by MPE. Instead, laser induced MPD occurs by the collisionless process of cavity QED induced EM radiation.

- MPE excitation of high energy quantum states is very inefficient. In contrast, high energy states are excited by QED induced EM radiation at a high efficiency.

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