Nonlinear absorption of semiconducting quantum dots at one- and two-photon resonant excitation of excitons

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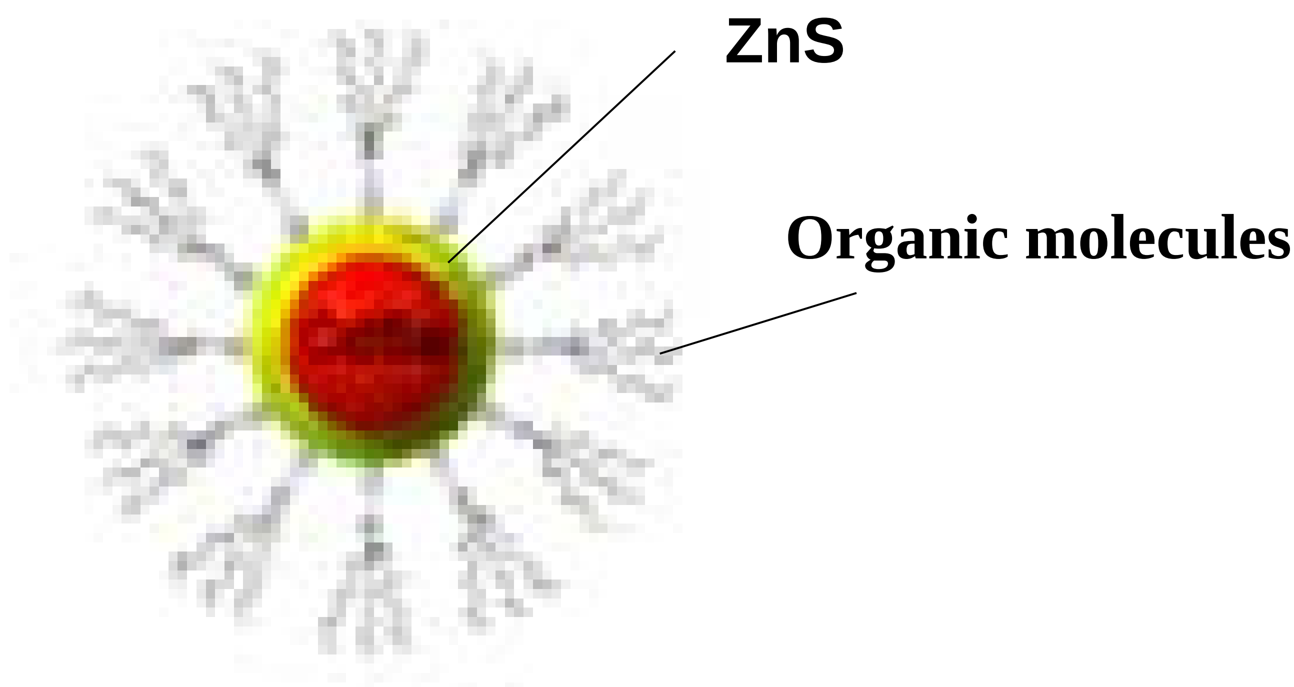
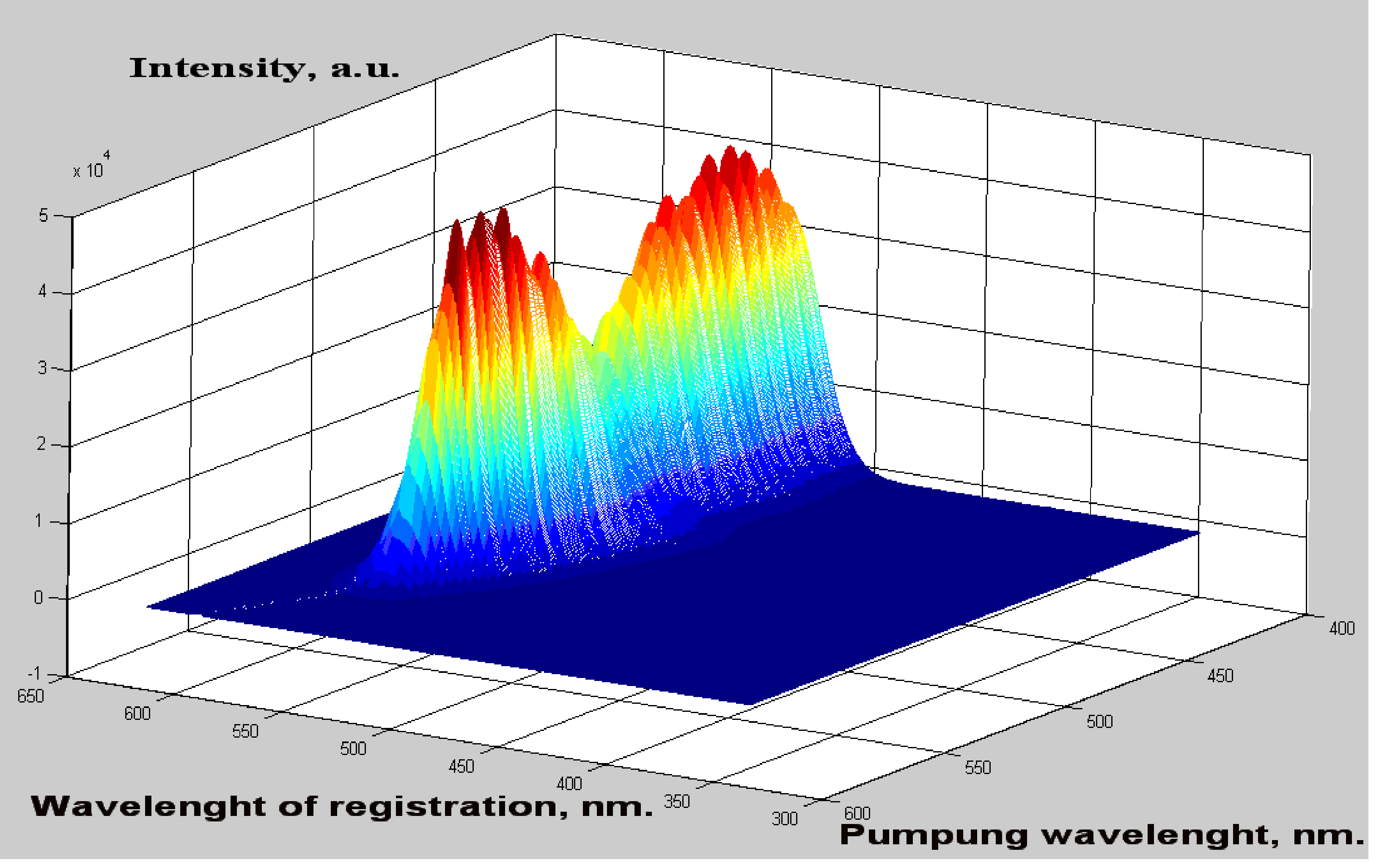
- **I. One-photon resonant excitation of excitons in CdSe/ZnS colloidal quantum dots by 30-ps pulses of Nd:YAG laser second harmonic:**
- **- anomalous nonlinear absorption (state filling in the case of variable excited-state lifetime);**
- **- formation of the transparency channel, strip-effect, Fresnel and Fraunhofer self-diffraction of laser beam.**

- **II. Two-photon resonant excitation of excitons in CdSe/ZnS quantum dots:**
- **- traces of luminescence allow to measure the coefficient of two-photon absorption and to reveal the influence of nonradiative Auger recombination;**
- **- two-photon absorption and limiting effect.**

Colloidal CdSe/ZnS quantum dots

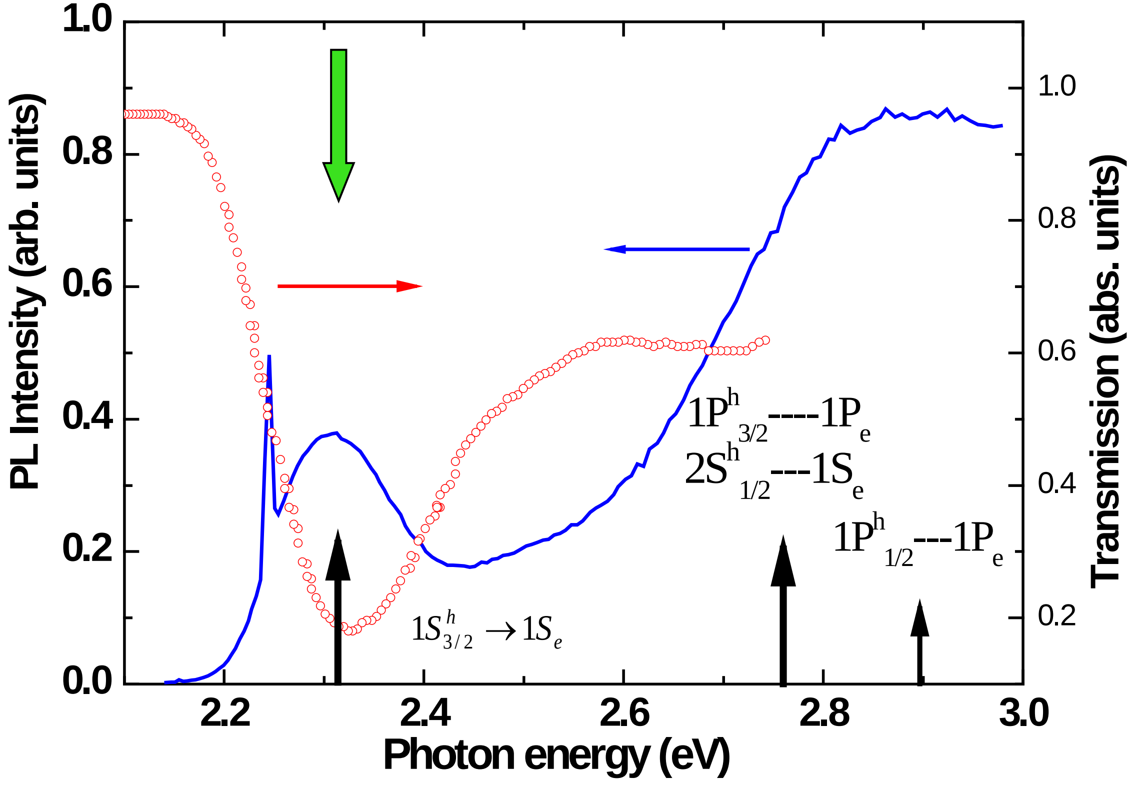


Photoluminescence excitation spectra of CdSe/ZnS quantum dots



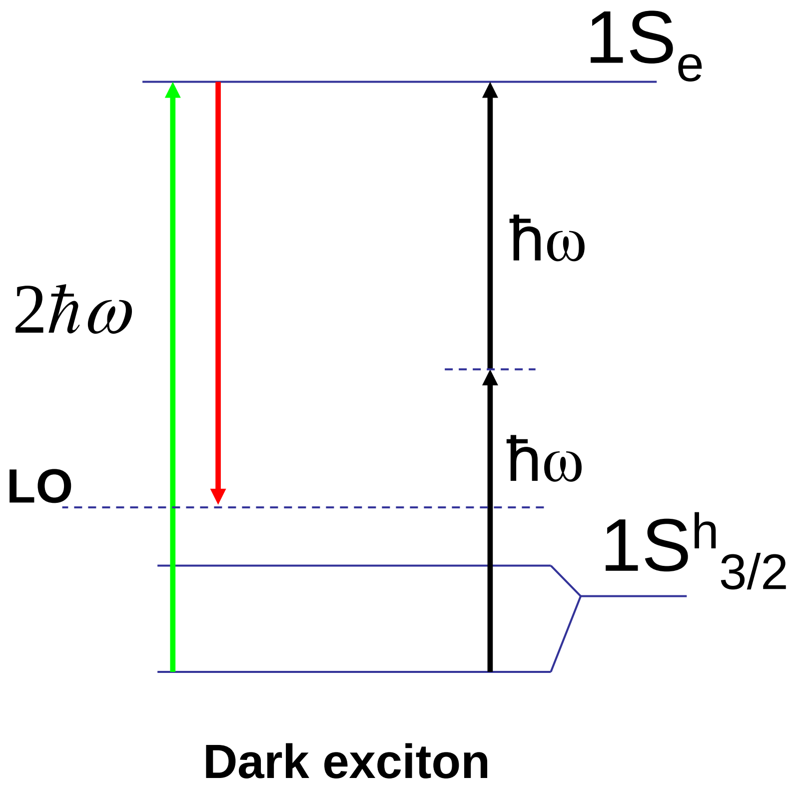
Transmission and Photoluminescence excitation spectra of CdSe/ZnS quantum dots.

$_{3/2}^{n} \rightarrow 1S_e$

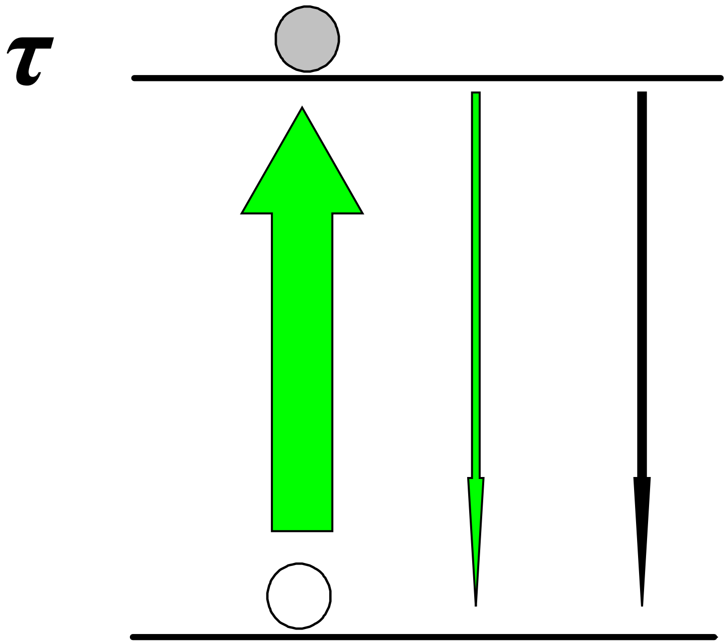


Radius of QDs is 2.5 ± 0.4 nm

One- and two-photon excitation of the basic electron-hole (exciton) transition and luminescence of CdSe/ZnS quantum dots



Resonant nonlinear absorption (state-filling effect) was discovered for the first time in 1926 by S.I.Vavilov in uranium glass.



τ (I) !

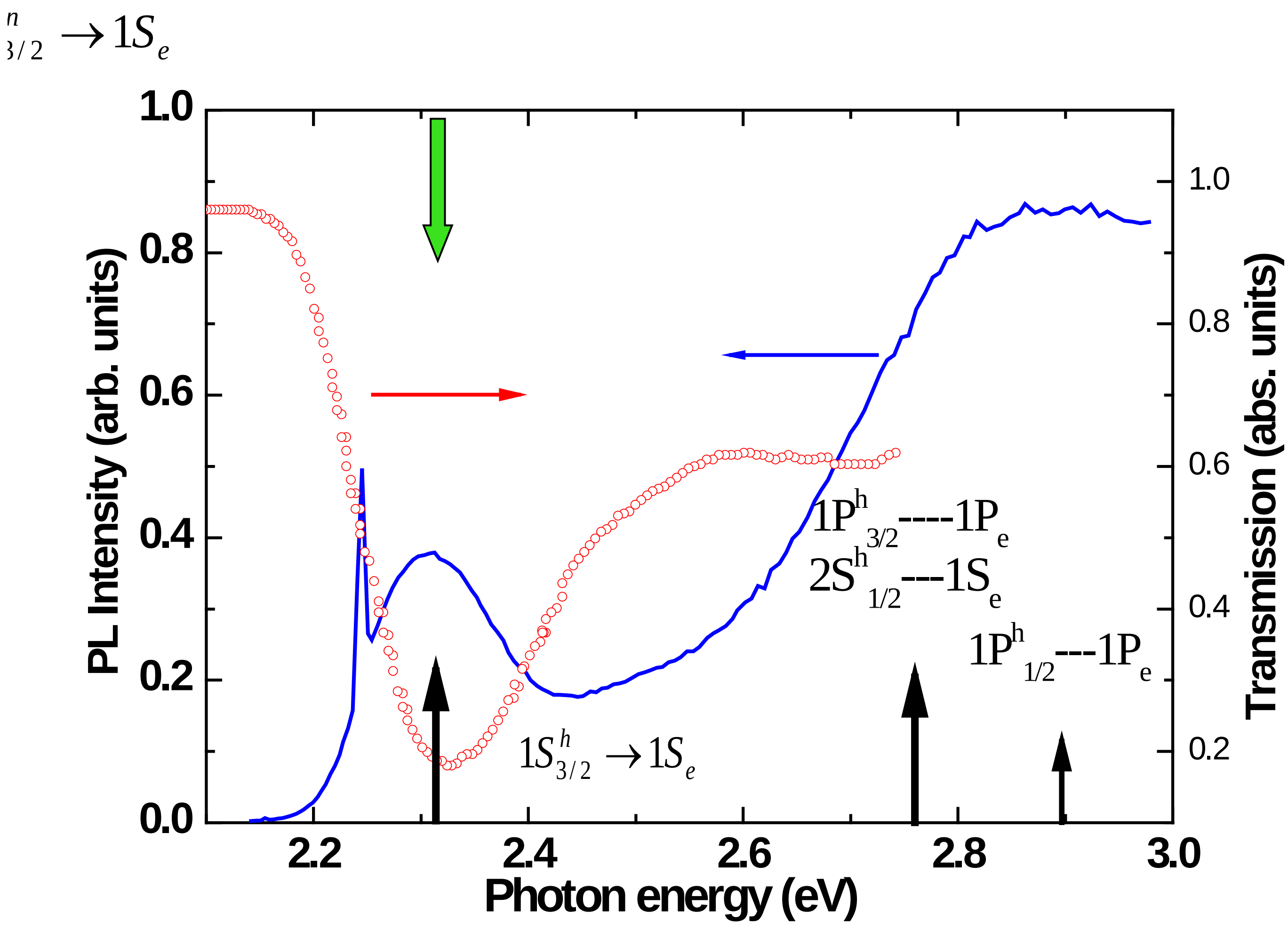
S.I. Wawilow u. W.L. Lewschin, Z. Phys. 1926, 35, 932

С.И.Вавилов «Микроструктура света», изд. АН СССР, Москва 1950
S.I.Vavilov "Microstructure of Light"

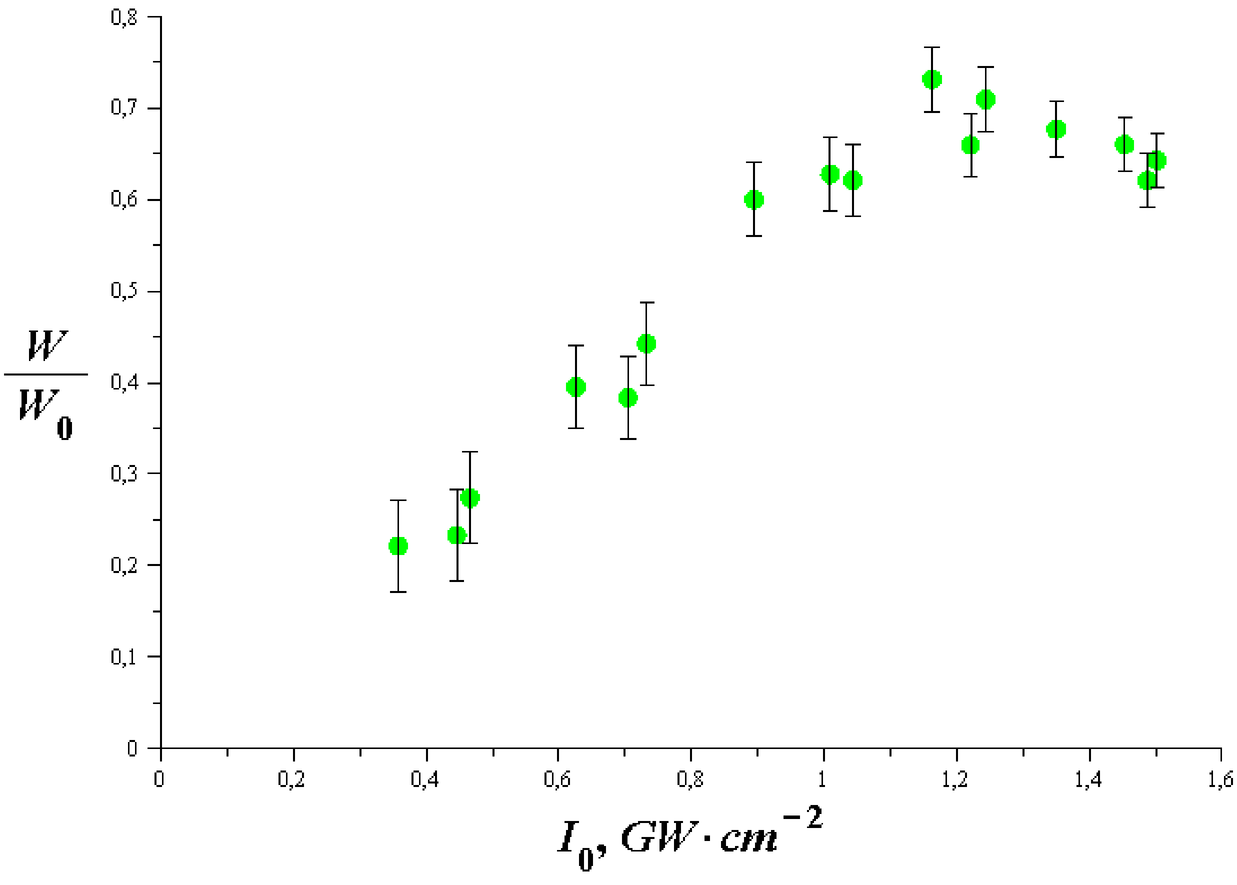
- Чем большее число молекул находится в возбуждённом состоянии при распространении света в среде, т.е. чем больше световая мощность, тем заметнее должна уменьшаться доля поглощаемой энергии, так как возбуждённые молекулы до своего возвращения в нормальное состояние перестают абсорбировать свет прежним образом. Поглощение должно, таким образом, зависеть от мощности светового потока.

- . If more molecules are in the excited state, that is the greater is the intensity of the exciting light, the noticeable must be the decreasing portion of the absorbed energy because the excited molecules cease to absorb light in former way before their return in normal state. Thus the absorption must depend on the intensity of the light beam

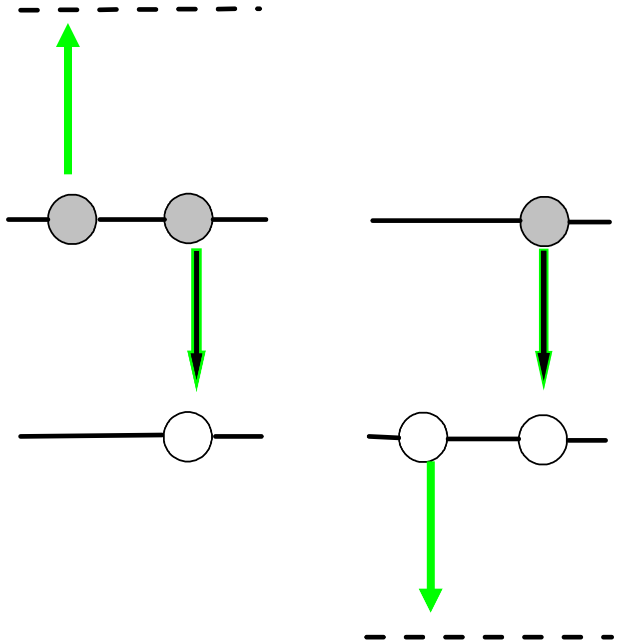
Transmission and Photoluminescence excitation spectra of CdSe/ZnS quantum dots.



The measured nonlinear transmission of colloidal CdSe/ZnS quantum dots



Nonradiative Auger recombination in quantum dots



$\underline{\tau = \tau\,(I)}$

Nonlinear transmission of resonantly excited two-level system in the case of constant and variable excited-state lifetime

- **In the case of excited-state lifetime** $\tau_{ex} = const$

$$\frac{d}{d\tau}(\ln T) + \ln T = 2gf(\tau)(1-T) + \ln T_0$$

- **where** $\tau \equiv t/\tau_{ex}$; $g \equiv \sigma S_0 \tau_{ex}$; $f(\tau) = 0.5(1-\cos\pi\frac{t}{\Delta t})$

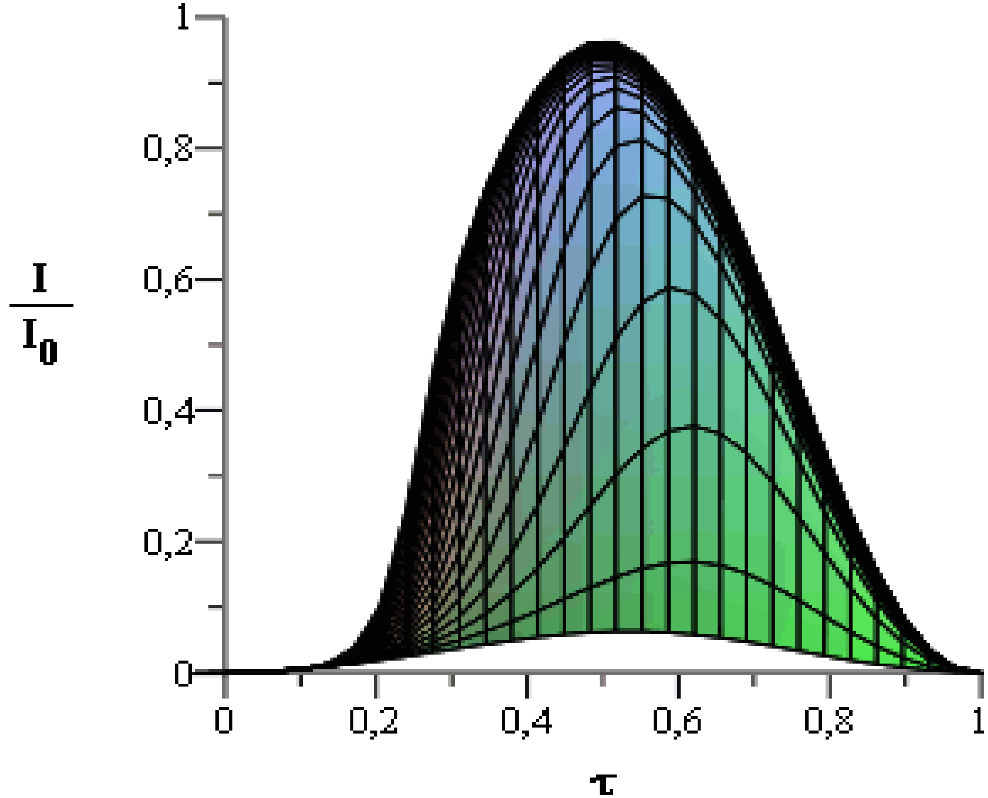
- **In the case of variable excited-state lifetime** $\tau_{ex} = \gamma S_0^{-2}$

$$\frac{d}{d\tau}(\ln T) + \ln T = 2\sigma\gamma I_0^{-1} f(\tau)(1-T) + \ln T_0$$

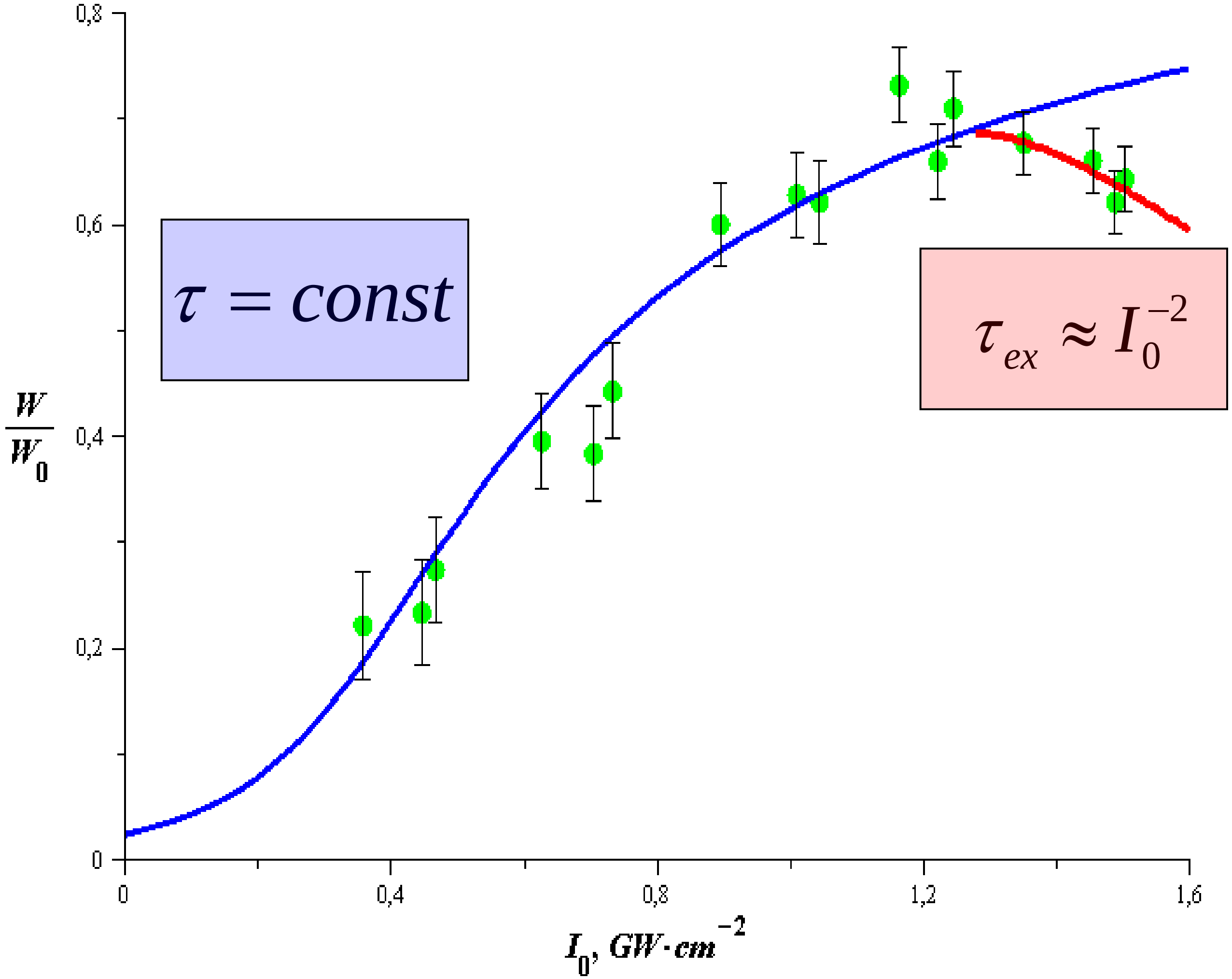
The profile of transmitted 30-ps laser pulse

(one-photon resonant excitation of excitons in CdSe/ZnS QDs – saturation effect)

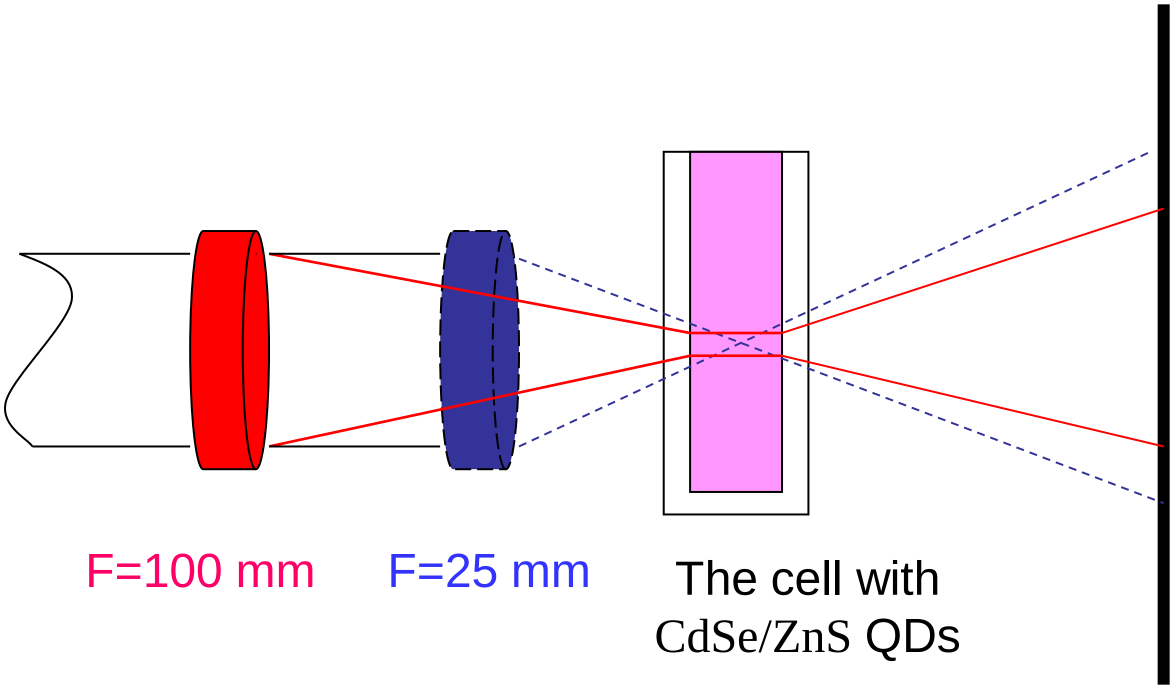
The change of the transmitted pulse profile at different input intensities



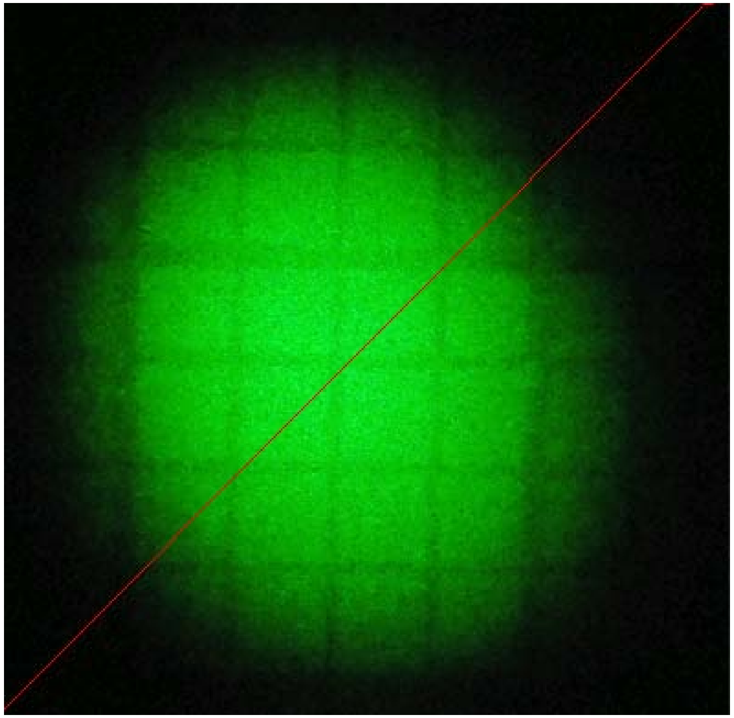
The measured and calculated nonlinear transmission of CdSe/ZnS QDs



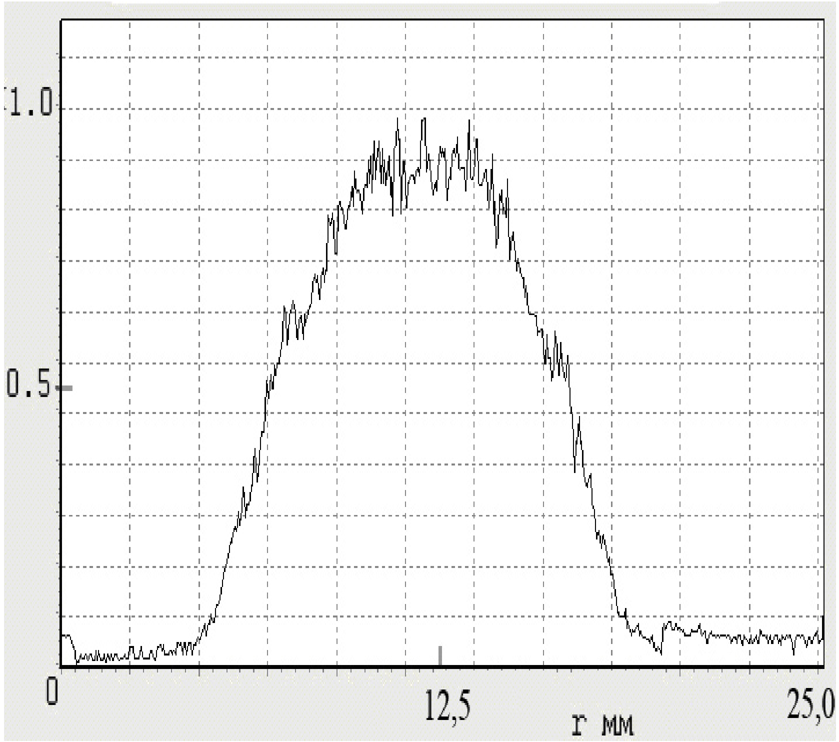
Self-diffraction of laser beam in colloidal solution of CdSe/ZnS quantum dots



The transmitted intensity profile of the laser beam in the cell with hexane and without quantum dots and diametrical distribution of the transmitted intensity



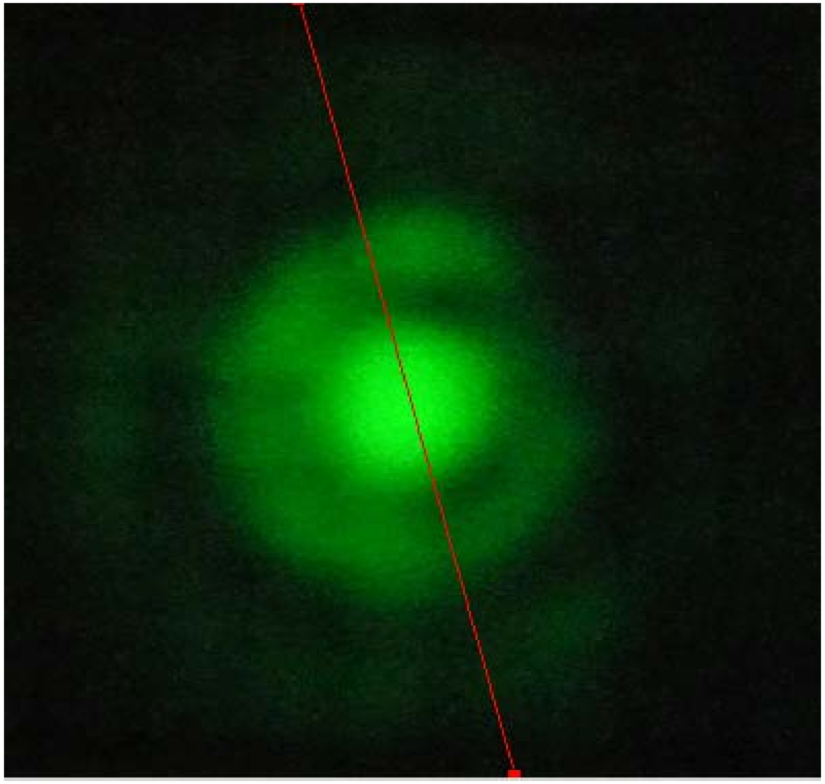
a)



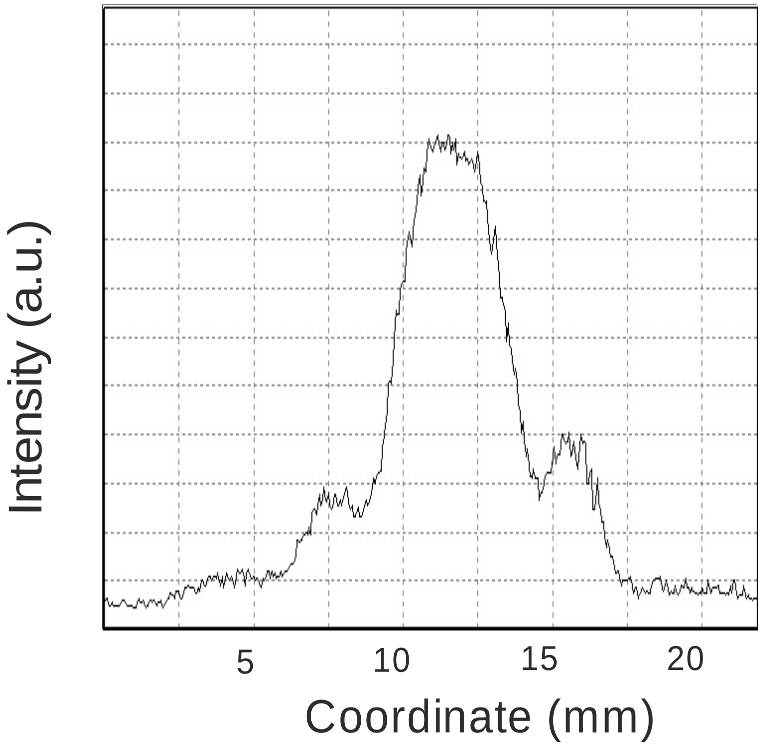
b)

Fresnel diffraction

The transmitted intensity profile of the laser beam at input intensity ***1 GW/cm^2*** and diametrical distribution of the transmitted intensity.



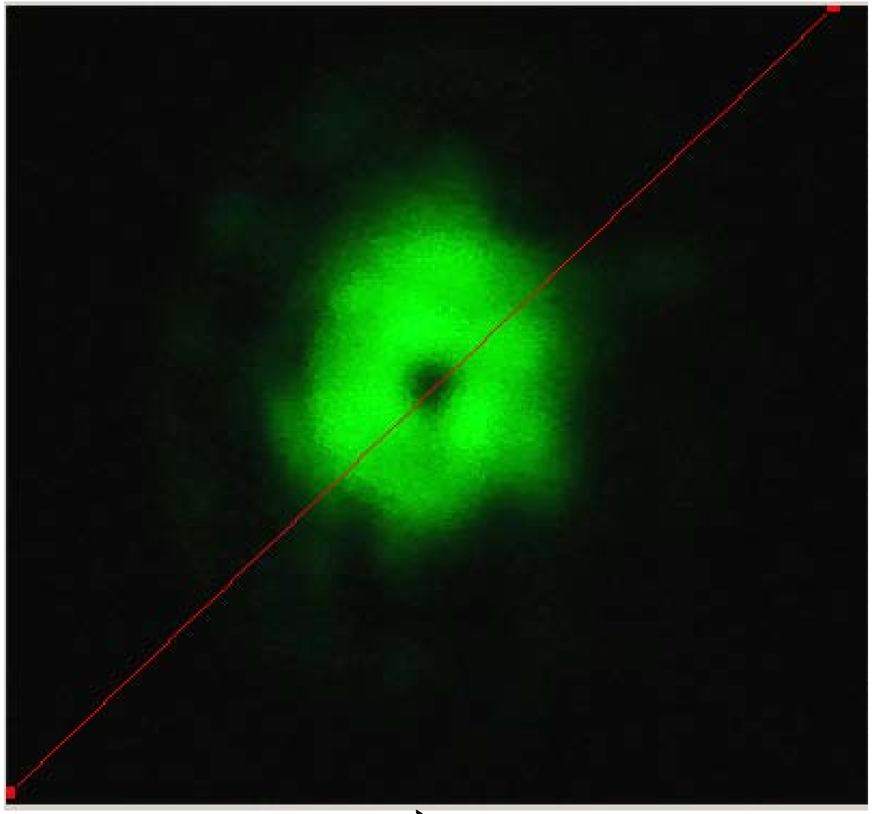
a)



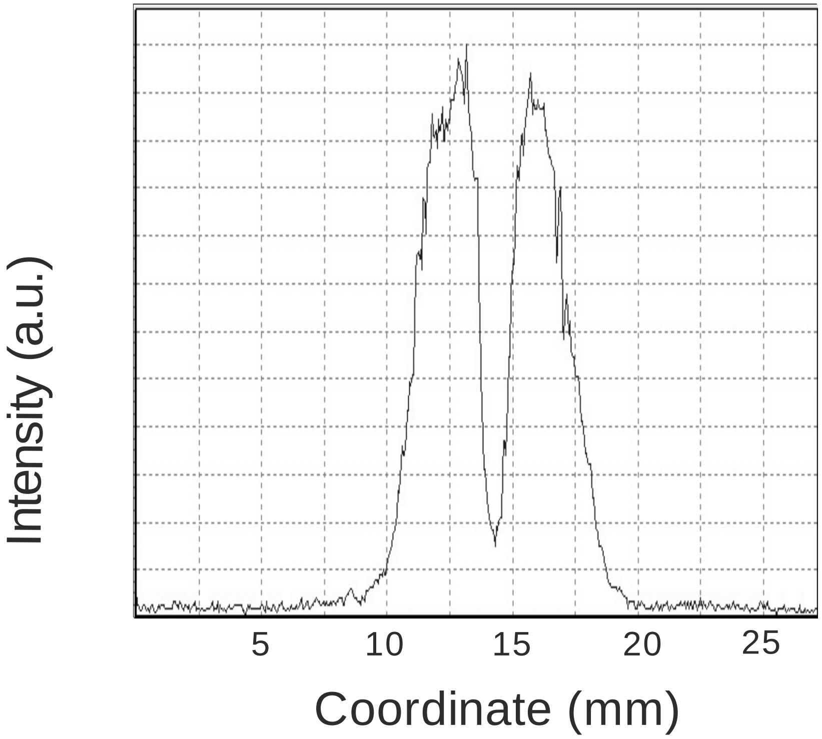
b)

Fresnel diffraction

The transmitted intensity profile of the laser beam at input intensity **1.2 *GW/cm²*** and diametrical distribution of the transmitted intensity.



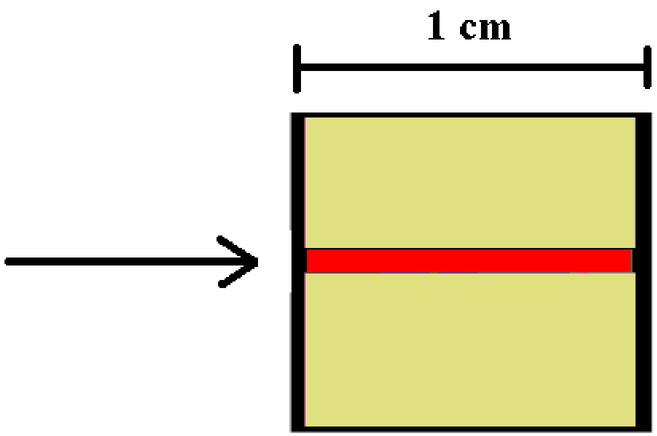
a)



b)

The trace of luminescence

(z-dependence of luminescence intensity in the case of resonant two-photon excitation of excitons in CdSe/ZnS colloidal quantum dots)



The cell with colloidal CdSe/ZnS QDs

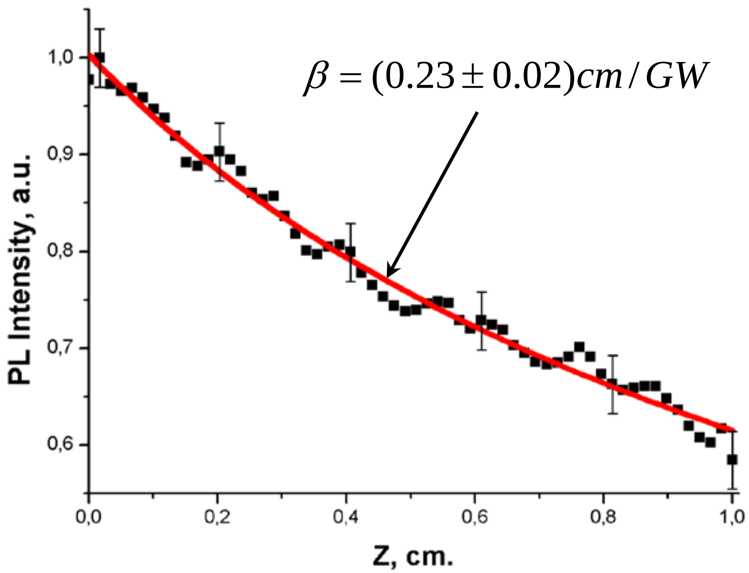
Photocamera

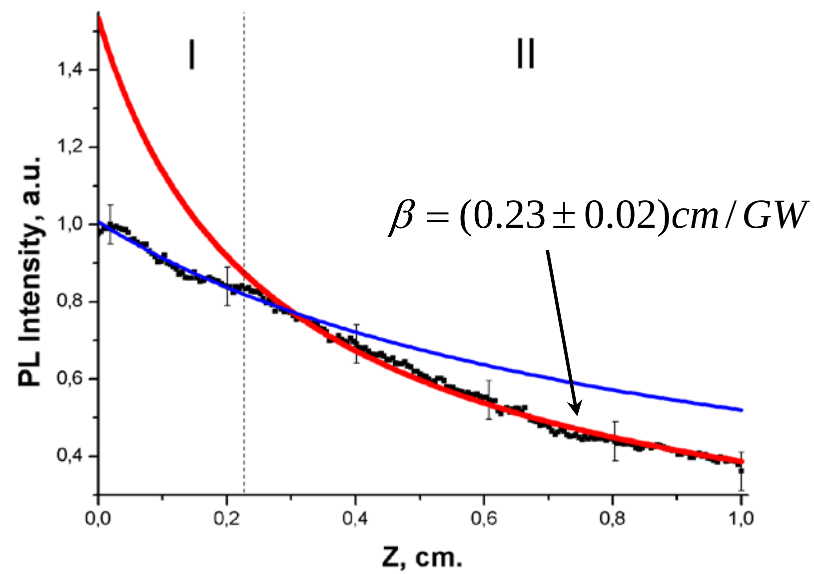
The trace

The measured and calculated z-dependences of CdSe/ZnS quantum dots' luminescence traces

$$S_0 = 1.5 GW / cm^2$$

$$S_0 = 3 GW / cm^2$$





The dependence of luminescence intensity upon distance (trace of luminescence)

- **In the case of negligibly small linear absorption the change of intensity:**

$$S_T = S_0 /(1 + \beta z S_0)$$

At moderate intensities of excitation when less than one electron-hole pair (less than one exciton) is excited in a single QD and nonradiative Auger recombination is suppressed the intensity of luminescence is proportional to the number of absorbed photons (absorbed energy):

$$I(z) \approx \tau\left[S(z) - S(z + \Delta z)\right]$$

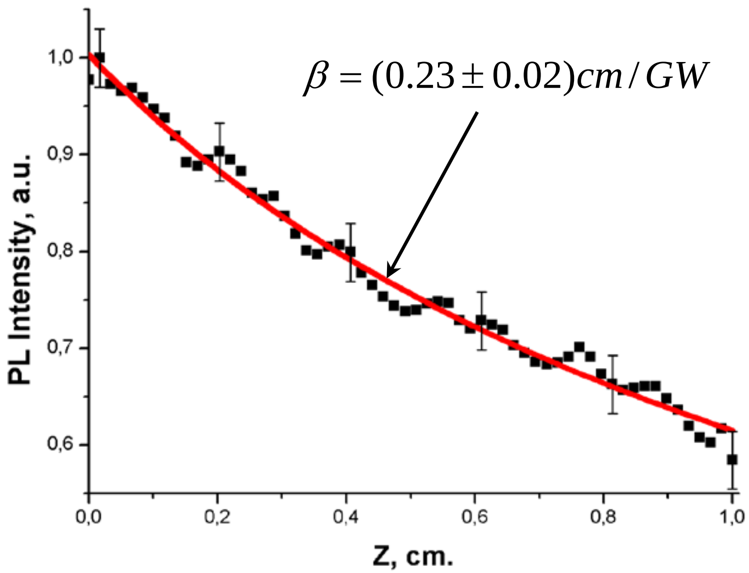
- **Thus, in the case when** $\Delta z \to 0$ $\quad I(z) \approx \tau \dfrac{\beta \Delta z S_0^2}{1 + 2\beta z S_0 + (\beta z S_0)^2}$

- **The measured ratio of the intensities of luminescence:**

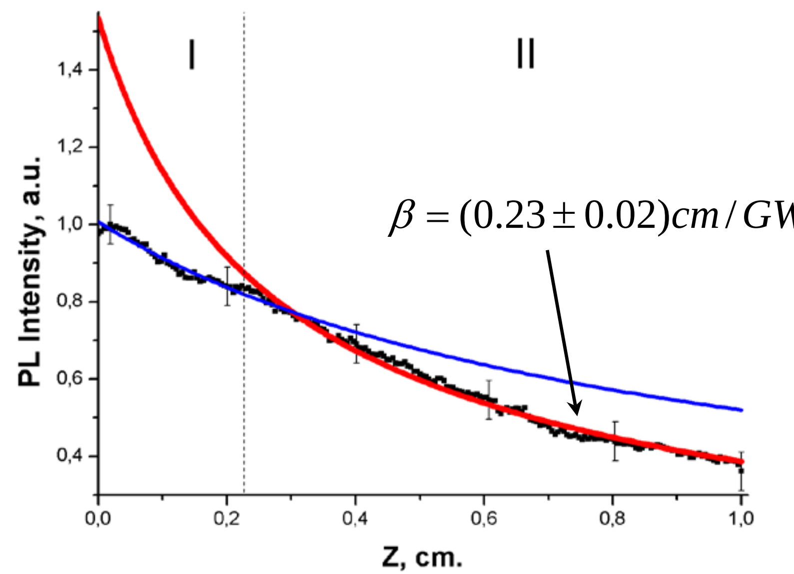
$$\frac{I(z_2)}{I(z_1)} = \frac{1 + 2\beta z_1 S_0 + (\beta z_1 S_0)^2}{1 + 2\beta z_2 S_0 + (\beta z_2 S_0)^2}$$

The measured and calculated z-dependences of CdSe/ZnS quantum dots' luminescence traces

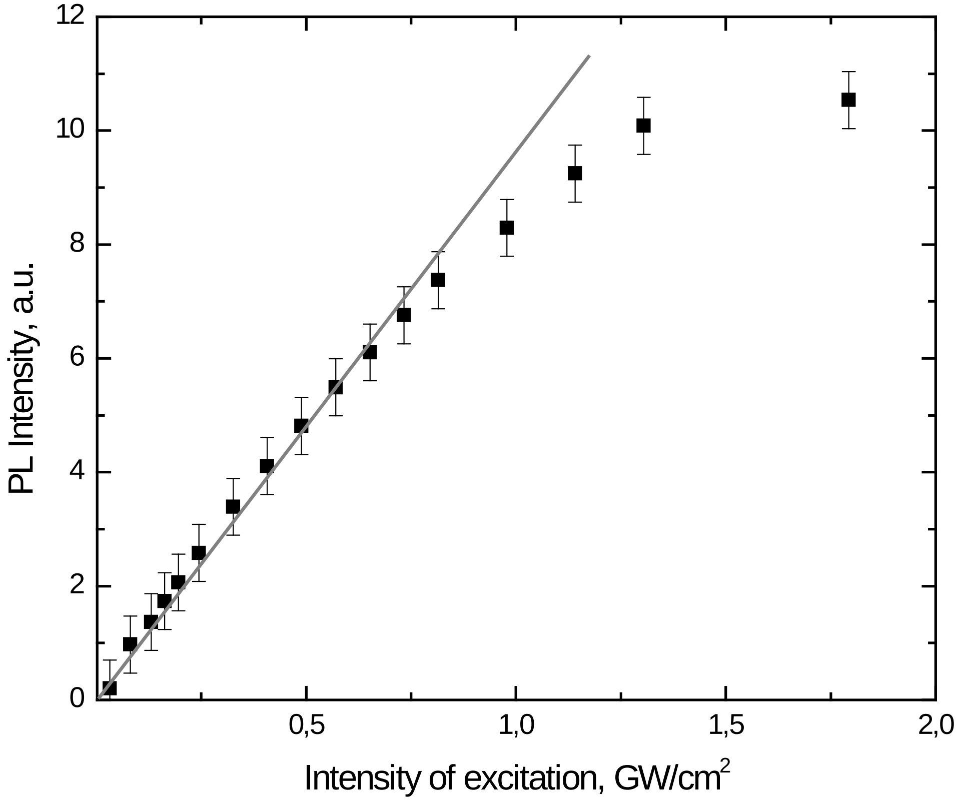
$S_0 = 1.5 GW/cm^2$



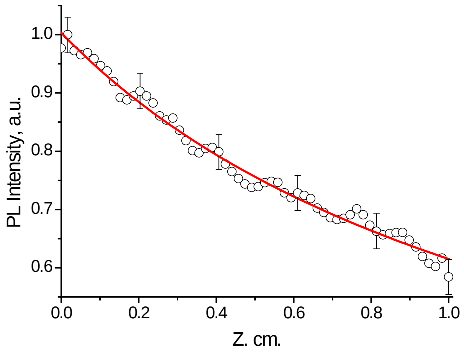
$S_0 = 3 GW/cm^2$

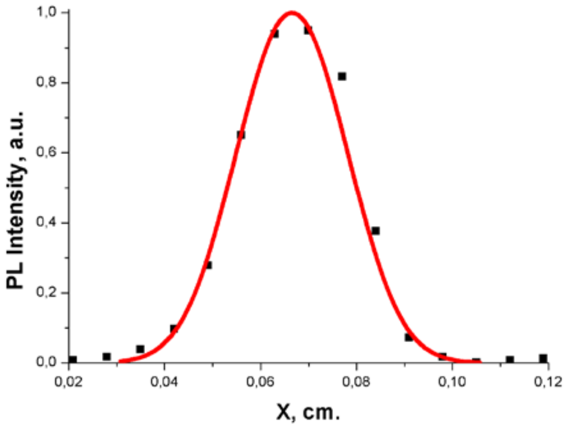


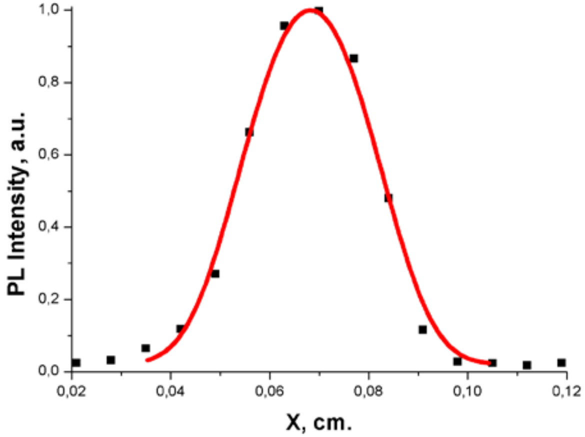
Nonlinear dependence of luminescence intensity upon the intensity of 100 fs laser pulses



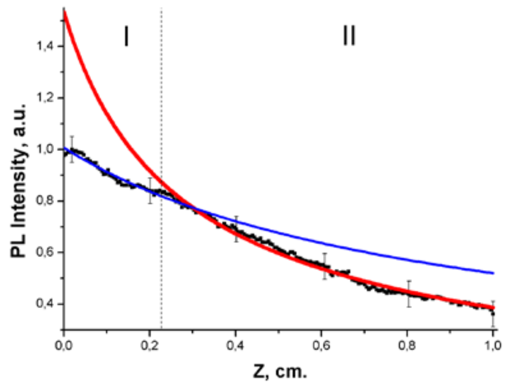
The diametrical distribution of luminescence intensity for different parts of the trace

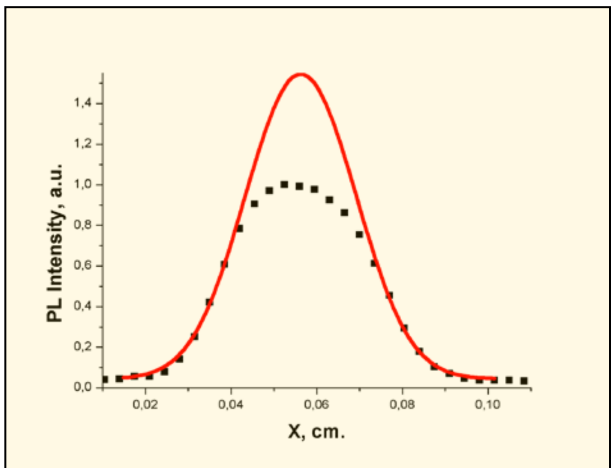


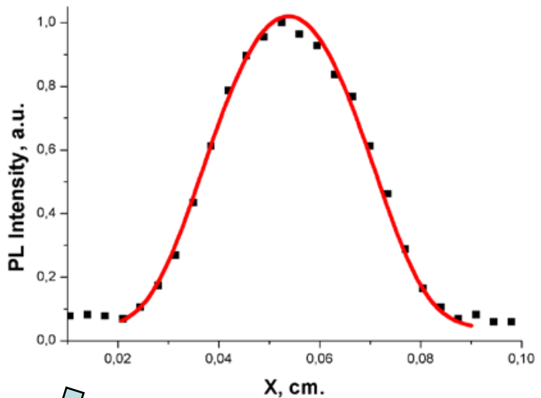




The diametrical distribution of luminescence intensity for different parts of the trace



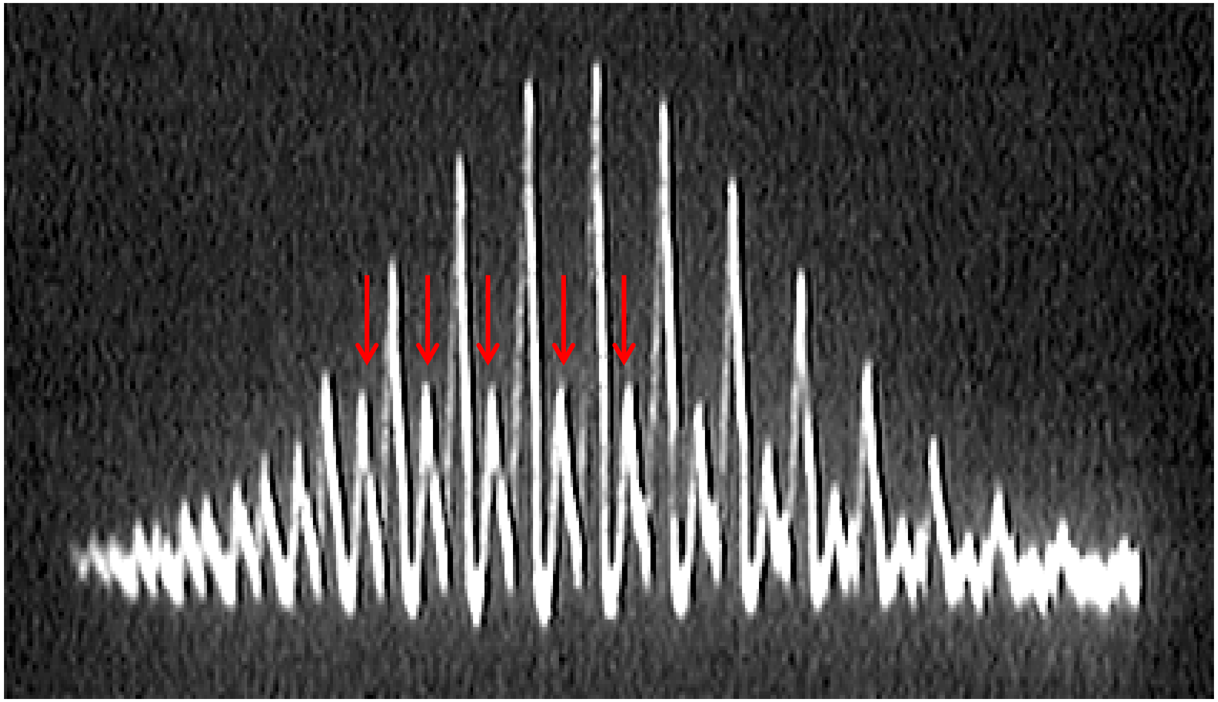




Limiting effect in the case of resonant two-photon excitation of excitons in colloidal CdSe/ZnS quantum dots. If $\beta z S_0 >> 1$ the transmitted intensity

$$I_T = 1/\beta z$$

The oscillogram of pulses transmitted through the cell with colloidal CdSe/ZnS quantum dots (pointed by red arrows) and 3 ns delayed pumping pulses.



Summary

- **We have explained the revealed nonlinear anomalous absorption of excitons in the case of exact resonance for the majority of CdSe/ZnS quantum dots having size dispersion by state-filling of two-level system with variable excited-state lifetime.**

- **The bleaching of CdSe/ZnS quantum dot's colloidal solution is accompanied by formation of the transparency channel, by strip effect, creation of induced "rigid" aperture, and Fresnel or Fraunhofer self-diffraction – self-action phenomenon when the laser beam affects the parameters of the medium and the modified medium influences the beam's propagation.**

- **The method of two-photon nonlinear absorption investigation utilizing the measured traces of luminescence (the dependences of colloidal CdSe/ZnS quantum dot's luminescence intensity upon distance) has allowed us to define the values of two-photon absorption coefficients, to reveal the influence of nonradiative Auger recombination, and to realize the limiting effect – invariable transmitted intensity of 30-ps laser pulses at input intensities exceeding limiting threshold.**