# Incoherent Photon Echo from Inhomogeneous Ensemble of Semiconductor Colloidal Quantum Dots

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Photon echo is widely used in spectroscopic research of different media, including solid-state structures, liquids and gases. A large number of works devoted to the using of photon echo technique to study disordered structures: polymers, glasses and molecular crystals (see, *e.g.* [1] and references therein). This technique also is used in applications of quantum optics, in particular for the creation of optical memory and information processing. Generally, the photon echo signals generated by electronic transitions of so-called chromophores (*e.g.*, organic molecules dyes), specially introduced in a very low concentration into the studied transparent matrix. The optical spectra of the impurity are extremely sensitive to the parameters of local environment, which makes it possible to use them as special probes to study the internal dynamics in various matrixes [2]. Very promising in such type of studies could be semiconductor nanocrystals (quantum dots) characterized by unique and controlled photophysical properties. Due to the high photostability, semiconductor nanocrystals exceed the level of the quantum yield of conventional organic chromophores and make it easy to vary the spectrum of luminescence, which ensures their high practical value in areas such as organic photovoltaics, solar energy and quantum informatics. However, in spite of the obvious advantages of using a semiconductor nanocrystals as fluorescent probes, there are problems both with the preparation of the samples doped with quantum dots, and the detection of photon echo signal in such samples. There is a considerable interest not only to study regularities, describing the interactions of quantum dots with the environment, but also to study the photophysical properties of the quantum dots themselves.

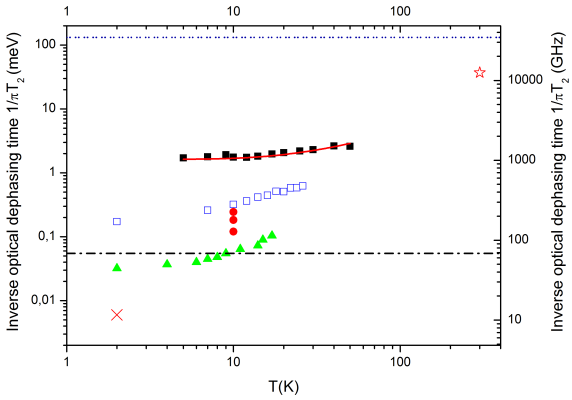


Figure 1: Temperature dependence of the inverse optical dephasing time measured in ensemble of 3–7 nm CdSe/CdS/ZnS quantum dots using incoherent photon echo (closed black squares). Red solid line is approximation of the obtained data by the Eq. (1). The temperature dependence of the homogeneous linewidths measured by accumulated photon echo for 3.6 nm CdSe quantum dots (open blue squares) [5] and high-resolution spectral hole burning in 9 nm CdSe/ZnS core-shell nanocrystals (green triangles) [7]. Data on photoluminescence spectroscopy of a single 4.3 nm CdSe/ZnS quantum dots (red circles) [8]. Homogeneous width measured at $T = 2$K by spectral hole-burning in ensemble of CdSe/ZnS quantum dots (cross) [9] and by luminescence spectromicroscopy at room temperature in single CdSe/CdS/ZnS quantum dots (asterics). Black dash dotted line represents a natural width and blue dotted line – a width of the luminescence spectrum measured in solution of 3–7 nm CdSe/CdS/ZnS quantum dots in toluene

This paper is devoted to experiments on photon echo performed in a wide range of cryogenic temperatures in an inhomogeneous ensemble of semiconductor quantum dots, spread on a glass substrate. We used CdSe/CdS/ZnS quantum dots (QD-light, Russia), dissolved in high concentration in toluene as an object of study. Declared variation of size of quantum dots was 3–7 nm. Spin coating technique wasn‘t used because of the large loss of the QD-solution during the creation of sample with sufficient optical density. An arrangement and procedure to spread quantum dots on a glass substrate have been developed

to prepare the samples [3]. Setup consists of two glass plates, perpendicular to each other. One of the plates is rigidly fixed, the other is fixed on a micrometric two-axis translation stage. A small amount of a concentrated solution of quantum dots was planted on the latter glass substrate using a dispenser. The substrate with a drop is then moved towards the stationary fixed plate until it touches the drop and the solutions spreads over the edge and is being held due to surface tension. Next, translating the stage, the solution is spread layer by layer on the substrate. Optimizing the speed of the plates motion and the distance between the plates, good quality films were produced with a high optical density. The process was visualized using a CCD-camera.

The PE-measurements were performed using the home-build incoherent photon echo spectrometer based on a resonator-less super-luminescence dye-source (see, *e.g.* [4] for detailed description). The optical scheme of the setup consists of two optical channels. One with the stable delay and another one with precisely controlled delay. The delay between two excitation pulses can be changed by variation of the optical length in one of channels (in a range of 5.6 fs to 4 ns with a step of 5.6 fs). PE signals were detected using a CCD-camera Cooke SensiCam HighSpeed. The sample was placed into the measuring chamber of an optical helium cryostat (RTI, Chernogolovka, Russia) with temperature regulation in the range of 4.5K to room temperature with accuracy of 0.1K.

IPE decay curves (dependence of IPE signal intensity on the delay time between 1st and 2nd pulses) were measured by controlled moving of reflecting prism along mechanical delay-line. The typical 2-pulse Incoherent photon echo (2IPE) decay curve consists of sharp intensive peak in the region of zeros delays and tail. In order to find the optical dephasing time $T_2$ we fit this tail with the standard expression $I = I_0 + Cexp(-4\tau/T_2)$, where $I_0$, $C$ and $T_2$ are fitting parameters. The procedure was repeated in our measurements at different temperatures from 4.5K and up to 50K, thus the temperature dependence of the inverse optical dephasing time was found. This dependence is shown in Fig. 1.

The experimental data approximated by the formula (see, *e.g.* [5]):

$$\Gamma = \Gamma_0 + \Gamma_{sample} + AT + B/(exp(C/k_BT) - 1). \quad (1)$$

Fig. 1 shows the results of the other studies (see caption under the figure). The lowest dash dotted line displays the natural width $\Gamma_0 = 1/2\pi T_1$ measured by luminescence kinetics study in a solution of CdSe/CdS/ZnS quantum dots in toluene ($T_1$ = 12 ns). For comparison the results obtained by the other ensemble averaging measurements, such as accumulated photon echo [6] and hole-burning technique [7] are depicted on the figure. Finally, an experimental data on the measurement of (homogeneous) luminescence spectra of single CdSe/ZnS quantum dots [8] is given together with the width of single CdSe/CdS/ZnS quantum dot spectrum measured at room temperature. The values of widths obtained for single quantum dots are below the temperature dependence of the inverse time of the optical dephasing measured by the PE methods. This may be due to the fact that our measurements were performed in the inhomogeneous (by size and form) ensemble of quantum dots, hence such a dispersion leads to an additional broadening. Accurate measurements by hole-burning technique using modulated low-intensity laser excitation reveal the narrowest value of homogeneous line-widths in ensemble of 9 nm CdSe/ZnS semiconductor nanocrystals [7] down to 6 $\mu$eV at $T$ = 2K [9].

Also, the figure shows the width of the luminescence spectrum of single CdSe/CdS/ZnS quantum dots measured at room temperature (asterisk). The highest dotted line in the figure corresponds to the width of the luminescence spectrum measured at room temperature in a solution of quantum dots. This value characterizes the maximum possible width of the inhomogeneous broadened spectrum of an ensemble of quantum dots.

In the investigated temperature range, the temperature dependence of the inverse optical dephasing time is characterized by the presence of an additional (with respect to the natural width) broadening. The value $\Gamma_{sample}$ of this broadening is seems to be independent on temperature, and apparently, can be interpreted as a characteristic of the sample under study associated with fast intrinsic dynamics in QD, with distribution of quantum dots in size and shape, and also with the inhomogeneous distribution of local fields near each quantum dot.

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