Photon echo in the ensemble of semiconductor quantum dots spread on a glass substrate

K R Karimullin$^{1,2}$, M V Knyazev$^1$, A I Arzhanov$^2$, L A Nurtdinova$^3$ and A V Naumov$^{1,2}$

$^1$ Institute for Spectroscopy RAS, 108840 Moscow Troitsk 5 Fizicheskaya st.
$^2$ Moscow State Pedagogical University, 119991 Moscow 29 Malaya Pirogovskaya st.
$^3$ Kazan Federal University, Institute of Physics, 420097 Kazan 18 Kremlevskaya st.

E-mail: kamil@isan.troitsk.ru

Abstract. Simple procedure to prepare samples containing semiconductor quantum dots was developed. Test photon echo measurements in the ensemble of quantum dots spread on a glass substrate were performed to study optical dephasing processes.

1. Introduction

Photon echo is widely used in spectroscopic research of solid-state structures, liquids and gases [1]. 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., [2]). Photon echo signals generated by electronic transitions of so-called chromophores (e.g., organic molecules dyes), specially introduced into the studied matrix in a very low concentration. The optical spectra of impurity centers 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 [3, 4].

Very promising in these studies could be semiconductor nanocrystals (quantum dots) with unique and controlled photophysical properties [5]. Due to the high photostability, semiconductor nanocrystals exceed the level of the quantum yield of conventional phosphors 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. Nowadays, a few papers on the detection of photon echo signals in the solid-state materials doped by quantum dots were published (see, e.g. [6, 7]). It should be noted, that 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. This paper is devoted to test experiments on photon echo and four-wave mixing in an ensemble of semiconductor quantum dots, spread on a glass substrate, using a developed technique in order to study the possibility of performing measurements over the wide range of low temperatures.

2. Preparation of samples

As the object of study CdSe/CdS/ZnS quantum dots (QD-light, Russia), dissolved in high concentration in toluene, were selected. 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.

Figure 1. Schematic drawing of the setup for spreading of quantum dots on a substrate: two-axis micrometric motions (1), a glass plate (substrate) for the sample application (2), a glass plate spreading the quantum dots (3) with its support (4).

Setup (figure 1) 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 solution 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 (figure 2). 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.

Figure 2. The image of the luminescent sample - a thin layer of quantum dots CdSe / CdS / ZnS (1) spreaded by the glass plate (2) on a glass substrate (3). The thickness of the plate (2) is 1 mm. Plate boundary circled with thin white lines to improve the contrast of the image.

3. Experimental results

The experimental data were obtained in the Molecular Spectroscopy Department of the Institute for Spectroscopy RAS by means of a unique incoherent photon echo spectrometer, developed by prof. Yu.G. Wainer in 1990 [8] and modified in recent years (see, e.g. [9, 10]).

At the heart of the setup is cavityless superluminescent light source on a dye (an ethanol solution of Rhodamine-6G) transversely pumped by second harmonic of a pulsed solid-state YAG:Nd laser (LS-2131M -10-FF, Lotis TII, Belarus). Optical scheme of the spectrometer consists of several time delay lines. The first and second form, respectively, first and second laser pulses. The delay between pulses is adjusted by changing the optical length of the first line; a second delay line is of a fixed length. Precision mechanism provided with a stepper motor can adjust the delay between the first and second pulses in the range from 5.6 fs to 4 ns with 5.6 fs minimal step. The sample is placed in the measuring chamber of an optical helium cryostat (RTI, Chernogolovka) with a high-precision control of
temperature using the temperature controller Lakeshore 93C. Accurate overlapping of the focused laser beams on the test sample was performed using a confocal fluorescent visualizer [11, 12], which allows to increase the intensity of the photon echo signal generation by an order of magnitude. Signal detection was carried out with high-speed CCD camera (Cooke Corporation SensiCam HighSpeed CCD).

Figure 3 shows a decay curve of the four-wave mixing signal measured at the room temperature in an ensemble of CdSe / CdS / ZnS quantum dots spread on a glass substrate and placed inside the optical cryostat.

![Graph](image)

**Figure 3.** Four-wave mixing signal decay curve measured in an ensemble of CdSe / CdS / ZnS quantum dots on a glass substrate at the room temperature.

The decay curve characterized by a good "signal-to-noise" ratio and has a symmetrical form, inherent to a measurements at high (non-cryogenic) temperatures. At the room temperature, a decay time is comparable to the resolution time of the incoherent photon echo spectrometer (tens of femtoseconds). With decreasing temperature the shape of curve, as a rule, changes: in addition to zero delay maximum, corresponding to the four-wave mixing signal, the decline of the photon echo signal is observed in the region of positive delays. Analyzing that signal within the frameworks of various models the information about the times of relaxation processes in the investigated material is obtained.

4. Conclusion
A technique for preparing samples with semiconductor quantum dots with a sufficient optical density to perform photon echo and four-wave mixing measurements was developed. The measurements demonstrated the possibility to use these samples to study phase relaxation parameters in an ensemble of semiconductor quantum dots at low temperatures.

This work was supported by the Russian Foundation for Basic Research (projects Nos 15-32-21100-mol_a_yed – study of new optical materials for nanooptics and 14-29-07270-ofi_m – study of optical dephasing processes in quantum dots). The authors are members of leading scientific school of Russian Federation “Spectroscopy of atoms, molecules and condensed matter” (No 7035.2016.2).

References
[1] Manykin E A and Samartsev V V 1984 *Optical echo spectroscopy* (Moscow: Nauka)
[2] Vainer Yu G, Kol’chenko M A, Naumov A V, Personov R I and Zilker S J 2000 Photon echoes in doped organic amorphous systems over a wide (0.35-50 K) temperature range *J. Luminescence* **86** 265-72
[3] Naumov A V 2013 Low-temperature spectroscopy of organic molecules in solid matrices: from the Shpol'skii effect to laser luminescent spectromicroscopy for all effectively emitting single molecules Physics-Uspekhi 56 605-22

[4] Magarian K A, Fedyanin V V, Karimullin K R, Vasilieva I A and Klimusheva G V 2013 Luminescence properties of CdSe nanocrystallites in cadmium alkanoate glasses J. Phys.: Conf. Series 478 012007

[5] Karimullin K R and Naumov A V 2014 Dyes characterization for multi-color nanodiagnostics by phonon-less optical reconstruction single-molecule spectromicroscopy J. Luminescence 152 15-22

[6] Salvador M R, Graham M W and Scholes G D 2006 Exciton-phonon coupling and disorder in the excited states of CdSe colloidal quantum dots J. Chem. Phys. 125 184709

[7] Poltavtsev S V, Salewski M, Kapitonov Yu V, Yugova I A, Akimov I A, Schneider C, Kamp M, Hofling S, Yakovlev D R, Kavokin A V and Bayer M 2016 Photon echo transients from an inhomogeneous ensemble of semiconductor quantum dots Phys. Rev. B 93 121304(R)

[8] Vainer Yu G and Gruzdev N V 1994 Dynamics of organic amorphous media at low-temperatures - an incoherent photon-echo study of resorufin in ethanol-d and ethanol-d(6) at 1.7-35 K I. Experimental procedure and main results Optics and Spectroscopy 76 252-8

[9] Knyazev M V, Karimullin K R and Naumov A V 2014 Using 2D-detectors in experiments on the photon echo Proc. Samara Sci. Center RAS 16 13-6

[10] Karimullin K R, Knyazev M V and Naumov A V 2014 Photon echoes in an impurity polymer: New data on the low-temperature processes of phase relaxation and their relationship to the broadening of zero-phonon lines of single molecules Bull. Russ. Acad. Sci. Phys. 78 1254-9

[11] Karimullin K R, Knyazev M V, Eremchev I Y, Vainer Yu G and Naumov A V 2013 A tool for alignment of multiple laser beams in pump-probe experiments Meas. Sci. Technol. 24 027002

[12] Karimullin K R, Knyazev M V, Vainer Yu G and Naumov A V 2013 A luminescence visualizer for exact convergence of laser beams in photon-echo spectroscopy, four-wave mixing, and related techniques Optics and Spectroscopy 114 859-62