Correlated signals of the accumulated photon echo on CdSe – CdS quantum dots

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Abstract. The possibility of an observation of correlated signals of the accumulated photon echo under a three-photon excitation of a sample, which is an ensemble of semiconductor nanoparticles of “core – shell” type, by a femtosecond radiation of Ti:Sa laser is discussed. The phase matching conditions of such signals are obtained.

1. Introduction

Earlier, we predicted a possibility to observe the correlated free induction decay (CFID) signals [1]. Then, in paper [2], it was shown that the signals of stimulated photon echo (SPE) can also be correlated since they are in fact the same signals of free induction decay formed in a nonreversible system. Now let us pay attention to the fact that the correlation can exist also between the signals of accumulated photon echo (APE). The order of their excitation is similar to that of SPE, but at the presence of cumulative effect [3, 4]. The aim of this paper is to analyze the conditions of formation of the correlated APE responses on quantum dots CdSe – CdS. The peculiarities of a such quantum dots synthesis were presented in [5].

Correlated SPE signals as well as the correlation between APE signals in [1] is understood as their identity which is due to the presence of EPR pairs (Einstein-Podolsky-Rosen pairs [6]) formed in the sample under its multi-photon excitation by two crossed beams of Ti:Sa laser radiation. The exciting beams are of the same 800-nm wavelength but they have different wave vectors \( k_1 \) and \( k_2 \). In the case of correlated FID signals two different nonequilibrium EPR-gratings \( k_1 - k_2 \) and \( k_2 - k_1 \) simultaneously appear in a resonant medium as a result of excitation. The correlated signals are in fact the coherent responses scattered by these gratings in opposite directions. As for both correlated SPE and APE signals the situation is more complicated. There are two exciting pulses which act at one and the same area of a sample before the influence of the third (reading) pulse \( k_3 \). It is well-known fact that SPE as well as APE signals are formed due to the diagonal part of a density matrix after two exciting pulses. That is why in this case EPR-gratings \( k_1 - k_3 \) and \( k_3 - k_1 \) are the nonequilibrium population gratings formed after the action of two exciting pulses. The theory of EPR-gratings formation in nanostructured semiconductor sample under its multi-photon excitation by laser radiation was presented in [7]. The special case of the sample containing CdSe–CdS colloidal quantum dots was discussed in [2].
Now we should say a few words about the mechanism connecting the electrons in EPR-pairs in a semiconductor sample. In the experimental study [8] it was established that in the high density gas of carriers, which appears in CdS crystal under two-photon mode of its excitation, an essential role belongs to excitons and excitonic molecules. So, the EPR-pairs are seemed to be biexcitons. Since such femtosecond experiments are performed at room temperature, the phonons play the important role also. The situation is quite similar to Cooper pairs in superconductors when two electrons with opposite spins form a bound state through the exchange of phonons [9]. In our case the mechanism of EPR-pairs formation is more complicated since one should take into account the Coulomb screening [10].

2. Peculiarities of CdSe–CdS nanopowders

The development of nanotechnologies allows us to create and to investigate the nanodimensional objects with unique optical properties [9]. For example, there is such quantum size effect as the dependence of a forbidden band width on a nanoparticle size, which provides a possibility to control a wavelength of luminescence. Such nanomaterials can be used for a creation of optoelectronic emitters, quantum dots displays and new lasers.

Earlier, in [5], we have already reported about synthesis and study of semiconductor nanoparticles of “core – shell” type, where the CdSe nanoparticles play the role of a core covered by the CdS shell. The size of CdSe core was equal to 3–4 nm and related to the thickness of the shell as 2,5:1. It was found that in the presence of the CdS shell the luminescence caused by the femtosecond 800-nm Ti:Sa laser radiation increased in 8 times by contrast with the pure core and was due to the processes of both two- and three-photon absorption. The luminescence efficiency increases due to the specific configuration of energy zones, which leads to more effective excitation of the sample. A smaller number of internal elementary excitations decays nonradiatively. The band structure and the scheme of energy transitions between bands as well as the luminescence spectra of CdSe–CdS nanocomposites are shown in figure 1.

![Figure 1](image.png)

**Figure 1.** Band structure (a) and luminescence spectra (b) of CdSe–CdS nanoparticles, CB1 and CB2 are the conduction bands, \(v_i\) and \(k_i\) are the frequency and the wave vector of exciting pulses, \(i=1, 2, 3\).
One can see that for the particles of 3 nm size the emission maximum occurs at 540 nm, of 6.5 nm size – at 590 nm and of the 7 nm size – at 600 nm. So, we observe the luminescence from the conductive band CB1 while the excitation was performed to the conductive band CB2, i.e. the nonradiative transition CB1 → CB2 takes place. One may suppose that the nonequilibrium gratings \( k_1 \) - \( k_2 \) and \( k_2 \) - \( k_1 \) should disappear in this case. Nevertheless, it was shown by the authors of experimental study [10] and in our own experiments that with the three-photon excitation of the sample at 800 nm the population gratings exist both at 267 nm and 534 nm transitions. Due to the nonradiative relaxation the population grating at 267 nm transition disappears but it still exist at 534 nm transition and scatters coherently the correlated APE responses.

3. Correlated APE signals on CdSe–CdS nanoparticles

The order of APE excitation is well known [3, 11]. The sample is firstly acted by \( n \) pairs of exciting pulses with wave vectors \( k_1 \) and \( k_2 \), and then the APE signal is red out by means of the separate pulse with the wave vector \( k_3 \). The APE signal is in fact the co-phased set of \( n \) SPE signals. In this paper we suggest to use the four-wave mixing technique for SPE generation and, namely the experimental scheme presented in [12], but instead of single exciting pulses \( (k_1 \) and \( k_2) \) we shall consider the periodic two-pulse train. One of the convenient regimes of an excitation is realized when the exciting pulse \( k_1 \) acts at the angle of 30° to the axis of the sample, the exciting pulse \( k_2 \) – at the angle of 150° and the readout pulse \( k_3 \) – at the angle of 90°. In this case one of the expected correlated APE signals will be directed along \( k_2 \), the second one – along \( k_1 \) (both signals has the carrier wavelength equal to 267 nm × 2 = 534 nm which differs from the carrier wavelength of the exciting pulses) and the third one will not be emitted. Since each of exciting pulses should propagate in its own direction we have three channels (1, 2, 3) illustrated in figure 2.

![Figure 2](image)

*Figure 2.* Three-channel (1, 2, 3) regime of an excitation of the correlated APE signals. I and II are two pairs of exciting pulses with wave vectors \( k_1 \) and \( k_2 \), \( k_3 \) is a wave vector of a readout pulse, \( \tau, \tau', \tau'' \) are time intervals, \( S \) is a sample.

The corresponding scheme of a multipulsed excitation of APE signal similar to that from [12] is presented in figure 3. The optical regenerative amplifier ORA1 participates in the formation of pulses with wave vectors \( k_1', k_2' \) and also of the readout pulse \( k_3 \), while the optical regenerative amplifier ORA2 serves to the formation of pulses with wave vectors \( k_1'', k_2'' \). As a result two pairs of exciting pulses with a certain time delay between them are produced.

For such mutual spatial arrangement of the wave vectors of exciting pulses the phase matching conditions of correlated APE signals can be written as

\[
\begin{align*}
k_4 &= -k_1 + k_2 + k_3, \\
k_5 &= k_1 - k_2 + k_3, \\
k_6 &= k_1 + k_2 - k_3 = 0.
\end{align*}
\]

The situation is illustrated in figure 4.
Figure 3. Experimental scheme of an excitation of the correlated APE signals on nanostructured quantum dots CdSe–CdS. \( k'_1, k''_1, k'_2, k''_2, k_3 \) are the wave vectors of exciting pulses, \( k_4 \) and \( k_5 \) are the wave vectors of the correlated APE signals, DL is a delay line, D is a detector, S is a sample, STM is a semitransparent mirror, SM is a spherical mirror, ORA1 and ORA2 are optical regenerative amplifiers.

Figure 4. Phase matching conditions of the correlated APE signals (\( k_4 \) and \( k_5 \)) under a three-photon excitation of the nanostructured CdSe–CdS sample at 800 nm. The carrier wavelength of the correlated APE signals is equal to 534 nm.

Let us briefly discuss the method of calculation of the correlated APE signals. Following [13] we write the intensity of optical coherent responses emitted into the solid angle \( \Delta \Omega \) as

\[
\Delta I(k_{res}, t) = I_0(k_{res}) F(t) F^*(t) \Delta \Omega ,
\]

(4)
where $I_d(k, \omega)$ is the intensity of a three-quantum spontaneous radiation of an isolated electron in the direction of $k_{res}$,

$$F(t) = \frac{1}{2} \int_0^\infty d(\Delta \omega) g(\Delta \omega) \sum_{j=0}^{N} W(\Delta \omega, r_j, t) e^{-i(k_{res} \cdot r_j)}.$$

$\Delta \omega = \omega - 3\omega_c$ is a detuning parameter, $g(\Delta \omega)$ is a distribution function of $\Delta \omega$, $W(\Delta \omega, r_j, t)$ is an element of a density matrix of an electron system, corresponding to a coherent response. The electrical field of the correlated APE signal $(k_i)$ is equal to [11]:

$$E_{CAPE} = -NE_0(R) \frac{1}{2} \frac{\partial G}{\partial \omega} \frac{\partial G}{\partial \omega} Ge^{-i(\Delta \omega(3t-t'-\tau'))} e^{i(-k_1+k_2+k_3-k_{CAPE} \cdot r)} e^{2\pi \frac{\tau'}{T_i}} \left[ \frac{1 - \exp(-n\tau'/T_i)}{1 - \exp(-\tau'/T_i)} \right],$$

where $N$ is a number of nanoparticles, $\theta_j$ is an area of $\eta$-th pulse, $\tau$, $\tau', \tau''$ are the time intervals illustrated in figure 2, $n$ is a number of pulse pairs, $G$ is a parameter. It is worth mentioning that all calculations are provided using the approximation of small pulse areas $\sin \theta \alpha \approx \theta \alpha$. We suppose that, despite the smallness of a three-photon excitation cross-section ($10^{-7}$ cm$^6$ s$^{-2}$ photon$^{-2}$), these coherent responses are still observable [10]. The possibility to observe the correlated APE signals was also noted in [14].

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