

NONLINEAR OPTICAL PHENOMENA

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Self-diffraction of ultrashort laser pulses under resonant excitation of excitons in a colloidal solution of CdSe/ZnS quantum dots

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Abstract. **We report self-diffraction processes of two types under resonant excitation of the fundamental electron–hole (exciton) transition in a strongly absorbing colloidal solution of CdSe/ZnS quantum dots (QDs) by high-power picosecond laser pulses. In the first case the absorption saturation (bleaching) at the exciton transition frequency and the Stark shift of exciton absorption line lead to the formation of a transparency channel and self-diffraction of the laser beam from the thus induced round diaphragm. In the second case, self-diffraction of two laser beams, intersecting in a cell with a colloidal QD solution, occurs on the diffraction grating induced by these beams. The physical processes responsible for the nonlinear optical properties of CdSe/ZnS QDs and the found self-action effects are analysed.**

Keywords: *semiconductor quantum dots, self-diffraction, exciton, induced diffraction grating, absorption saturation, Stark effect.*

1. Introduction

In recent years, much attention has been paid to nonlinear optical properties of excitons in colloidal semiconductor quantum dots (QDs) (the fundamental electron–hole transition in QDs is referred to as exciton transition to emphasise the strong Coulomb electron–hole interaction in them). Optical nonlinearities of two types may arise in semiconductor QDs. The first is the inertialess (classical) nonlinearity in a transparent medium; it arises as a result of interaction of light with coupled electrons and is responsible for two-photon absorption, generation of harmonics, nonlinear change in the refractive index, etc. The second is the dynamic (resonant, strong) nonlinearity in an absorbing medium under excitation of free carriers (nonlinear absorption and refraction caused by occupation of states). In addition, a change in absorption and refraction can be caused by a Stark shift of the fundamental electron–hole transition under induced electric field.

Study of nonlinear optical effects in QDs is of great importance to gain a deeper insight into QD fundamental properties and for possible applications in science and technology (QD lasers, optical limitation, saturable absorbers for modulating the Q factor and laser mode locking, optical switches, etc.). The efficiency of nonlinear optical devices depends on the nonlinear change in absorption and/or refraction. These nonlinearities increase under resonant excitation of excitons. It is known that diverse processes (screening of excitons, band occupation, band gap renormalisation, etc.) may contribute to the nonlinear absorption and refraction indices of bulk semiconductors. At the same time, the main effects that are responsible for changes in the absorption and refraction (which depend on excitation light intensity) in semiconductor QDs are saturation of exciton absorption as a result of occupation of states and Stark shift of exciton transition [1–6]. Since the energy spectrum of QDs depends on their size, one can choose QDs of appropriate size to implement resonant one- and two-photon excitation of the fundamental electron–hole (exciton) transition using pulses of a Nd^{3+}:YAG laser with passive mode locking and its second harmonic.

In this paper, we report the results of studying the specific features of nonlinear and electro-optical processes that occur under one- and two-photon resonant excitation of allowed fundamental exciton transitions in colloidal CdSe/ZnS QDs and lead to self-diffraction effects. Self-diffraction is the self-action of light beams propagating in a medium whose properties depend on light intensity. Self-diffraction of two types may occur in resonantly absorbing colloidal QDs. When the absorption at the frequency of fundamental exciton transition is significantly reduced, a high-power laser pulse forms a transparency channel; as consequence, self-diffraction from the thus induced diaphragm may occur. When two high-power laser beams intersect in an absorbing or transparent nonlinear medium, they can form a dynamic diffraction grating because of periodic spatial change in absorption and/or refraction in the field of induced standing wave and, as a consequence, diffract from the induced grating (undergo self-diffraction).

2. Experimental

Spherical CdSe QDs with a barrier ZnS monolayer and a hydrophobic layer on their surface (deposited to prevent them from coalescence) were grown by metal organic synthesis (NFM Ltd, Belarus). Nonlinear absorption and refraction of CdSe/ZnS QDs (in the form of a colloidal solution in hexane) were studied under one- and two-photon resonant excitation of the fundamental exciton transition by high-power picosecond pulses of the second (2.33 eV) and fundamental (1.65 eV) harmonics of the passively mode-locked Nd^{3+}:YAG laser. Irradiation was performed by a train of 25 to 30 35-ps laser pulses with a repetition rate of 7 ns. To perform resonant excitation of excitons, we chose QDs of desired size based on their previously measured transmission spectra (Fig. 1, top inset). The radius and size variance (2.4 ± 0.3 nm) of the QDs cho-

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sen were determined by comparing the position of the absorption peak and the half-width of the spectrum with the results of theoretical calculations of the dependence of the energy spectrum of CdSe QDs on their size [7]. Two-photon resonant excitation of allowed $1S_{3/2}(h)-1S(e)$ and $1P_{3/2}(h)-1S(e)$ electron–hole transitions was performed at the fundamental laser frequency, while single-photon resonant absorption of the allowed $1S_{3/2}(h)-1S(e)$ transition was implemented at the second laser harmonic (Fig. 1, bottom inset). The QD concentration in the colloidal solution was about 10^{17} cm^{-3}.

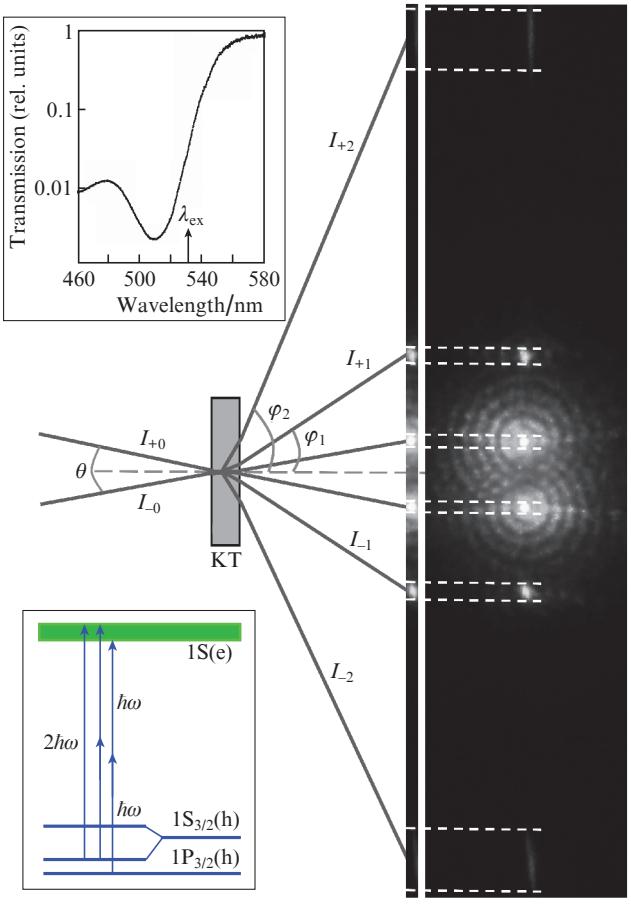

Figure 1. Schematic diagram of two-beam excitation of a colloidal CdSe/ZnS QD solution and diffracted beams at the output of a cell filled with a colloidal QD solution and a photograph of their cross section. The top inset shows the transmission spectrum of a colloidal CdSe/ZnS QD solution (the arrow indicates the one-photon excitation wavelength) and the bottom inset presents a schematic diagram of the one- and two-photon transitions corresponding to resonant absorption of excitons in CdSe/ZnS QDs.

A schematic diagram of two-beam excitation of a 1-mm-thick cell with a colloidal solution of CdSe/ZnS QDs and recorded diffracted beams with intensities $I_{\pm1}$ and $I_{\pm2}$, as well as the photograph of their cross section at the cell output, are shown in Fig. 1. Both beams intersecting in the cell had identical intensities. Photographing and measuring the intensity distribution over the output beam cross section were performed using a special computer-controlled camera with a linear dependence of the output signal on the input light intensity.

3. Laser beam self-diffraction from an induced diaphragm in a colloidal CdSe/ZnS QD solution under resonant single-photon excitation of excitons

Diffraction rings, which are typical of Fresnel diffraction, were found for the beams passed through a strongly absorbing colloidal QD solution without changing their direction (see Fig. 1). The transverse intensity distribution is identical for these beams, and this distribution, as well as the number of diffraction rings, depends on the input beam intensity.

An additional experiment on excitation of a colloidal QD solution by one laser beam allowed us to reveal specific features of the transverse distribution of output beam intensity and its dependence on the excitation intensity (Fig. 2).

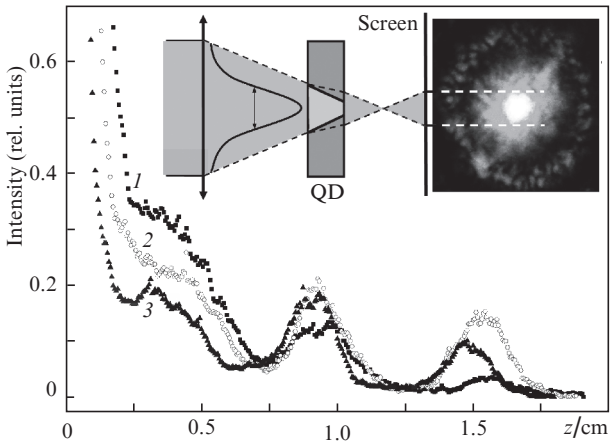

Figure 2. Transverse output beam intensity distribution at different intensities of the excitation beam (forming the transparency channel): (*1*) 0.12, (*2*) 0.18, and (*3*) 0.28 GW cm^{-2}. The inset schematically shows the propagation of low-intensity beams, which undergo only linear absorption (dashed lines), and high-intensity beams, which form a transparency channel (solid lines).

We explained the found transverse intensity distribution for the beams with retained propagation direction at the cell input by the self-diffraction from a round diaphragm (round 'hole'), which arises due to the excitation of a 'transparency channel' as a result of decreasing exciton absorption (bleaching) in CdSe/ZnS QDs under resonant excitation by high-power picosecond pulses of the second harmonic of the Nd^{3+}:YAG laser [2–6]. Due to the self-action effect (propagation of a light beam with a limited cross section in a medium whose local parameters depend on the light intensity), a high-power second-harmonic laser beam, which initiates reduction in exciton absorption, forms a transparency channel and passes through a cell containing a colloidal solution with a high QD concentration, characterised by high linear exciton absorption (transmission less than 3%). When passing through the cell, a beam with a Gaussian transverse intensity distribution 'loses' its intensity in the periphery region because of the higher absorption in comparison with its central part (beam stripping effect) [8, 9]), which leads to the formation of a round diaphragm with sharp edges and Fresnel self-diffraction of the beam producing this diaphragm.

Figure 2 shows the intensity distribution in the second-harmonic laser beam cross section at the output of the cell with CdSe/ZnS QDs for three trains of pulses having different maximum intensities. This distribution is partially obscured by the bright spot in the centre, which is due to the low (about 3%) linear transmission of high-power second-harmonic radiation (Fig. 1, upper inset). This circumstance explains only the tendency to the occurrence of intensity minimum in the centre at an excitation intensity of 0.28 GW cm^{-2} [Fig. 2, curve (*3*)].

Based on the results obtained, the diameters of the induced diaphragms can be measured at different excitation intensities: $D_m \cong 2\sqrt{m\lambda b}$, where m is the number of open Fresnel bands and b is the distance between the cell and screen. Calculations showed that a Gaussian laser beam with a measured diameter of 0.6 mm (FWHM intensity) at the cell input forms a diaphragm 0.34 mm in diameter for one open Fresnel band and 0.5 mm for two bands. The decrease in the beam diameter at the output of a QD-containing cell with respect to the beam diameter at the input confirms the effect of stripping, which gives rise to a transparency channel.

To reveal the physical processes leading to the formation of a transparency channel and induced diaphragm, we measured the dependence of the energy W of individual picosecond train pulses passed through the QD-containing cell on the energy W_0 of the corresponding input train pulses (Fig. 3). We believe the specific features of the dependence of the transmission W/W_0 on W_0 (Fig. 3b) to be due to the competition of two coexisting processes: occupation of states and red Stark shift of the fundamental electron–hole transition in CdSe/ZnS QDs. For the first part of the excitation train, the red Stark shift of the exciton transition may initiate a rise in absorption (Fig. 1, upper inset), which is only partially compensated for by occupation of QD states. The significant bleaching for the pulses of the central part of the train and even increased transmission for pulses with reduced energy can be assigned to the coexistence of both effects, which lead to a decrease in absorption at the exciton transition frequency. At a high level of excitation by pulses of the central part of train, the experimental results (Fig. 3) can be explained by the dominance of the large red Stark shift of the exciton transition in CdSe/ZnS QDs in induced electric field; this shift is likely to exceed the width of exciton absorption spectrum because of the accumulation effect. Saturation (occupation of states) and Stark effect are characterised by different dynamic properties. The relaxation time of the induced electric field, which arises when a carrier is captured by the QD surface [6], may exceed the axial period (the time interval between pulses in the train, 7 ns); the relaxation time of excited excitons is much shorter than the axial period [10]. The red thermal shift of the exciton absorption spectrum of colloidal CdSe/ZnS QDs was measured to be only about 0.5 Å per 1 K; hence, we could neglect the sample heating for the used range of excitation energies of picosecond second-harmonic laser pulses.

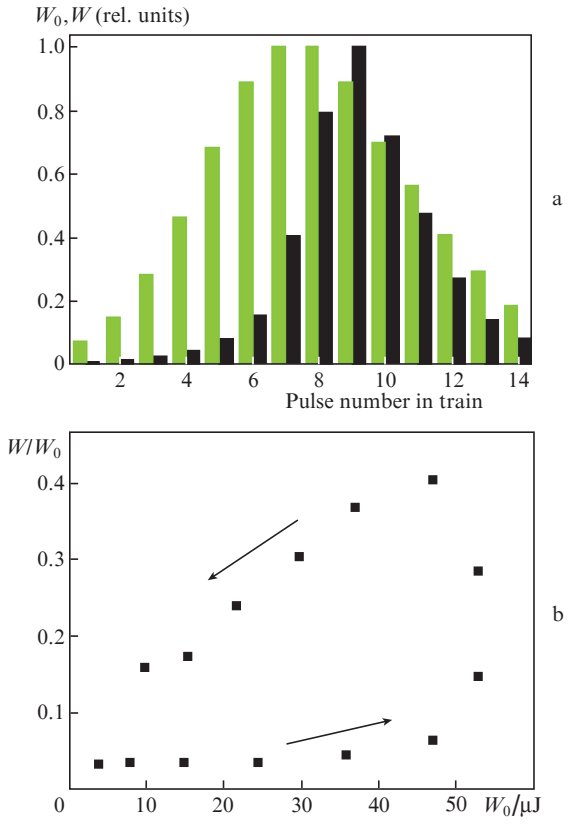

Figure 3. (a) Energy histogram of the input pulse train delayed by 3 ns (gray rectangles) and the pulses transmitted through the colloidal CdSe/ZnS QD solution (black rectangles) and (b) the energy dependence of transmission for a separate pulse train. Each point corresponds to a pair of pulses. The arrows indicate the direction of increase in the pulse number.

4. Self-diffraction from induced diffraction grating under one-and two-photon resonant excitation of excitons in CdSe/ZnS QDs

Along with the two beams at the output of the cell with colloidal QDs, which retained the propagation directions of the two input beams crossed in the cell at an angle θ, we found beams with intensity $I_{\pm 1}$ for one- and two-photon excitation and $I_{\pm 2}$ for one-photon resonant excitation of the fundamental exciton transition in CdSe/ZnS QDs (see Fig. 1). We believe them to be the first- and second-order diffracted beams – products of the self-diffraction of input beams with intensity $I_{\pm 0}$ from the time-dependent diffraction grating with a period $\Lambda = \lambda/[2\sin(\theta/2)]$, induced by the aforementioned input beams. The measured propagation angles of self-diffracted beams, $\varphi_1 = 33°$ and $\varphi_2 = 67°$ for the first and second diffraction orders, respectively, coincide with the calculated values $\varphi_\kappa = \arcsin[(2\kappa + 1)\sin(\theta/2)]$ (the angle between the laser beams at the cell input is $\theta = 21°$).

A diffraction grating can be induced due to different physical processes. We believe that, under single-photon resonant excitation by picosecond pulses of the second harmonic of Nd^{3+}:YAG laser, the periodic change in the nonlinear absorption (which is due to the occupation of states and red Stark shift of the exciton absorption spectrum in CdSe/ZnS QDs [2–6]) may induce an amplitude diffraction grating. The nonlinear change in absorption is accompanied by a nonlinear change in refraction [1]. The latter process may dominate at a small detuning of the excitation wavelength from the resonance. In our case a small red shift from the resonant wavelength (Fig. 1, bottom inset) may lead to the formation of an induced phase diffraction grating due to the periodic nonlinear decrease in the refractive index of colloidal QD solution. The significant efficiency of the first-order self-diffraction (high diffracted-beam intensity) is confirmed by the detection of diffraction rings for the pulses with $I_{\pm 1}$ (Fig. 1).

The intensity of these pulses is sufficient for the formation of transparency channels and self-diffraction from a round diaphragm in their propagation directions.

We assign the beams with $I_{\pm 1}$, observed in the case of two-photon resonant excitation of excitons in colloidal CdSe/ZnS QDs by laser pulses at the fundamental frequency, to the beams that underwent self-diffraction on the induced phase grating. Apparently, an amplitude grating is unlikely to be formed in this case. The nonlinear change in transmission, $T_0 - T$, is small (less than 10%). Estimation of the nonlinear transmission in a transparent medium at the laser fundamental frequency yields

$$T \equiv \frac{I}{I_0} = \frac{1}{1 + \beta z I_0} \leqslant 0.91$$

(the two-photon-absorption coefficient $\beta \cong 1$ cm GW^{-1} [11], the size z of the excitation region in the case of beam intersection in the cell does not exceed 0.1 cm, and the pulse intensity $I_0 \leqslant 1$ GW cm^{-2}). However, the induced change in the refractive index [12],

$$\Delta n \equiv n(I_0) - n = \frac{12\pi^2 \chi^{(3)}}{c n_0^2} I_0 \cong 10^{-3},$$

is, apparently, sufficient to form a phase diffraction grating. Here, n is the linear refractive index, c is the speed of light, $\chi^{(3)} \cong -7 \times 10^{-10}$ cm^3 erg^{-1} [12] is the third-order nonlinear susceptibility, and $I_0 = 1$ GW cm^{-2} is the input intensity. The aforementioned value of $\chi^{(3)}$ is large in comparison with the third-order nonlinear susceptibility for the solvent (hexane), which is apparently due to the increase in $\chi^{(3)}$ occurring when the intermediate resonance is attained in a medium transparent for laser radiation [13] (in our case, the exciton resonance in QDs for the total energy of two photons).

5. Conclusions

We (i) revealed self-diffraction of a laser beam from a transparency channel induced by this beam under one-photon resonant excitation of excitons in colloidal CdSe/ZnS QDs and self-diffraction of two laser beams from a diffraction grating formed by these beams under one- and two-photon resonant excitation of excitons in QDs and (ii) established the physical processes responsible for these self-action phenomena. Under single-photon resonant excitation of excitons in CdSe/ZnS QDs, a transparency channel in the colloidal solution with a high QD concentration and an induced diffraction grating arise as a result of coexisting and competing processes of saturation of the fundamental electron–hole (exciton) transition and the red Stark shift of the exciton absorption spectrum. Under two-photon resonant excitation of excitons in colloidal CdSe/ZnS QDs, the self-diffraction of the beams forming a diffraction grating is apparently their diffraction from the induced phase diffraction grating, which arises as a result of a significant nonlinear change in the refractive index upon four-wave mixing in a transparent nonlinear medium with a large cubic nonlinearity $\chi^{(3)}$ (i.e., in a medium where one of virtual levels coincides with the real level at a intermediate resonance for the total energy of two photons).

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