Self-diffraction of laser beams in the case of resonant excitation of excitons in colloidal CdSe/ZnS quantum dots

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ABSTRACT

Self-diffraction of two types has been discovered in the case of resonant excitation of excitons in CdSe/ZnS quantum dots (highly absorbing colloidal solution) by powerful beams of mode-locked laser with picosecond pulse duration. I. The bleaching of exciton transition provokes the creation of transparency channel and laser beam's self-diffraction at the induced circular aperture. II. Self-diffraction arises for two laser beams intersecting in the cell with colloidal CdSe/ZnS quantum dots due to the induced transient diffraction grating. Nonlinear optical properties responsible for the observed self-action effects in CdSe/ZnS quantum dots are discussed and a method for estimating laser pulse duration is suggested.

Keywords: self-diffraction, quantum dots, exciton, transient grating, Stark effect, state-filling

1. INTRODUCTION

In recent years there has been a growth of activity in the field of nonlinear optical properties of excitons in colloidal semiconductor quantum dots (QDs). The nonlinearities of two types may arise in semiconducting QDs: fast (classical) nonlinearity of transparent media due to interaction of light with bound electrons (two-photon absorption, generation of harmonics, nonlinear refraction, etc.) and dynamic (resonant, strong) nonlinearity of absorbing media in the case of free carriers excitation (nonlinear absorption and refraction as a result of state filling and Stark shift of the basic electron-hole transition by induced electric field). Nonlinear optical effects in QDs are of great interest both for their fundamental properties and important possible application in science and engineering (optical limiting, saturable absorbers for Q-switched and mode-locked lasers, optical switching, etc.). The efficiency of nonlinear optical devices depends on the values of nonlinear changes of absorption and/or refraction. The magnitude of these nonlinearities becomes resonantly enhanced in the spectral vicinity of the absorption edge. While in bulk semiconductors different processes (exciton screening, band filling, renormalization of the energy gap, etc.) provide contribution to the nonlinear index of absorption and refraction, in semiconductor QDs the basic nonlinear effects are the saturation of exciton absorption as a result of state filling and Stark shift of exciton transition[1-6]. The dependence of discreet energy spectrum of QD upon its size allows to choose QDs with appropriate size to achieve one- and two-photon resonant excitation of the basic electron-hole (exciton) transition using the pulses of mode-locked Nd:YAG laser and its second harmonic.

The goal of our work is the investigation of nonlinear optical processes that arise in the case of one- and two-photon resonant excitation of the allowed basic exciton transitions of colloidal semiconducting CdSe/ZnS quantum dots (QDs) that lead to self-diffraction effects by powerful pulses of a Nd^{3+}:YAG mode-locked laser (1.165 eV) and its second harmonic (2.33 eV). Laser generates train of 20-25 pulses with 7 ns axial period and 30-35 ps pulse duration.

Self-diffraction is the self-action effect of light beams that spread in the medium with properties depending on the light intensity. Two types of self-diffraction process may arise in resonantly absorbing QDs. I. In the case of efficient nonlinear absorption (bleaching of the basic exciton transition) the high-power laser beam may create the transparency channel, and thus its self-diffraction may arise at induced aperture. II. Two powerful intersecting laser beams in absorbing or transparent nonlinear medium induce the diffraction grating due to periodic modulation of absorption and/or refraction and their self-diffraction at created grating may arise.

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2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Spherical CdSe QDs with a monolayer ZnS shell and preventing their coalescence trioctyl phosphine oxide hydrophobic layer on the outer surface were grown by metal organic synthesis in NFM LTD (Belarus). The nonlinear absorption and refraction of CdSe/ZnS semiconducting QDs in hexane (colloidal solution) were investigated in the case of one- and two-photon resonant excitation of the basic electron-hole (exciton) optical transition by powerful picosecond pulses of a Nd^{3+}:YAG mode-locked laser (1.165 eV) and its second harmonic (2.33 eV). To realize resonant excitation of excitons QDs of appropriate size (radius) were selected using their measured transmission spectra (inset II in Fig.1). The QDs' radius (2.4±0.3 nm) was determined by comparing the energy of the basic electron–hole optical transition $1S_{3/2}(h)-1S(e)$ (the energy of maximum of the inhomogeneously broadened absorption spectrum because of QDs' size dispersion and spectral half-width) with the theoretical dependence of CdSe QD's energy spectrum on its radius[7]. The density of QDs in colloidal solution was about 10^{17} cm^{-3}.

The scheme of two beams' excitation of 1 mm cell with colloidal solution of CdSe/ZnS QDs with discovered output beams $I_{\pm1}$ and $I_{\pm2}$ and the photograph of their cross-section image at the screen is shown in Fig.1. The cell with colloidal QDs was excited by two equal intensity intersecting beams I_0. Two-photon resonant excitation of $1S_{3/2}(h)-1S(e)$ and $1P_{3/2}(h)-1S(e)$ allowed electron-hole transitions was realized by using the first and by the laser's second harmonic in the case of resonant one-photon excitation of $1S_{3/2}(h)-1S(e)$ transition (inset I in Fig.1).

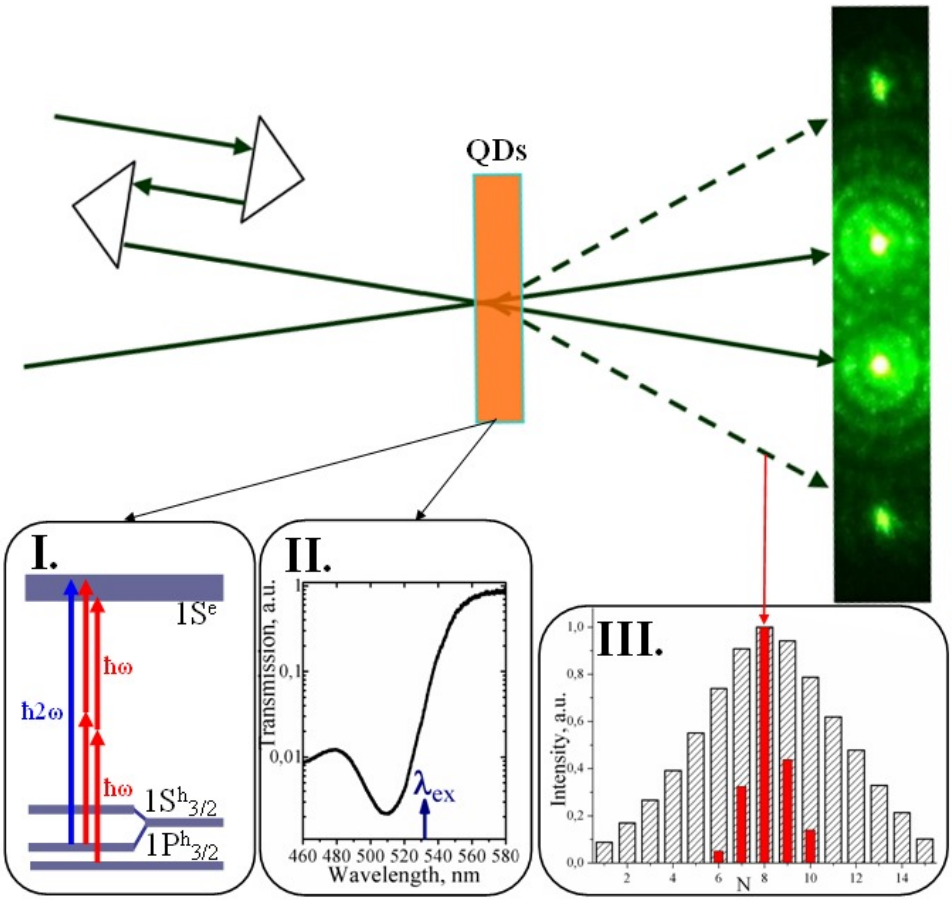

Fig.1. The scheme of two beams exciting the cell with colloidal solution of CdSe/ZnS QDs, diffracted output beams and the photograph of their cross-sections. Inset I: the allowed transitions for one- and two photon resonant absorption are shown schematically. Inset II: the transmission spectrum of colloidal solution of CdSe/ZnS quantum dots of (2.4 ± 0.3) nm radius and 10^{17} cm^{-3} density. Inset III: Incident and self-diffracted trains of pulses normalized to the maximum pulse intensity in corresponding train.

3. RESULTS AND DISCUSSION

3.1 Self-diffraction of laser beam at induced aperture in colloidal CdSe/ZnS QDs in the case of one photon resonant excitation of excitons

The diffraction rings typical for Fresnel diffraction arise for the beams $I_{\pm 0}$ penetrated through the cell with QDs that hold the direction of incident beams (Fig.1). Their identical cross-section intensity distribution and number of rings depend on the intensity of the incident beam.

Additional experiment with single input beam of the laser's second harmonic (one-photon resonant excitation of excitons in CdSe/ZnS colloidal QDs) allows to distinguish the features of output beam's cross-section intensity distribution and its dependence upon the intensity of the incident beam (Fig. 2).

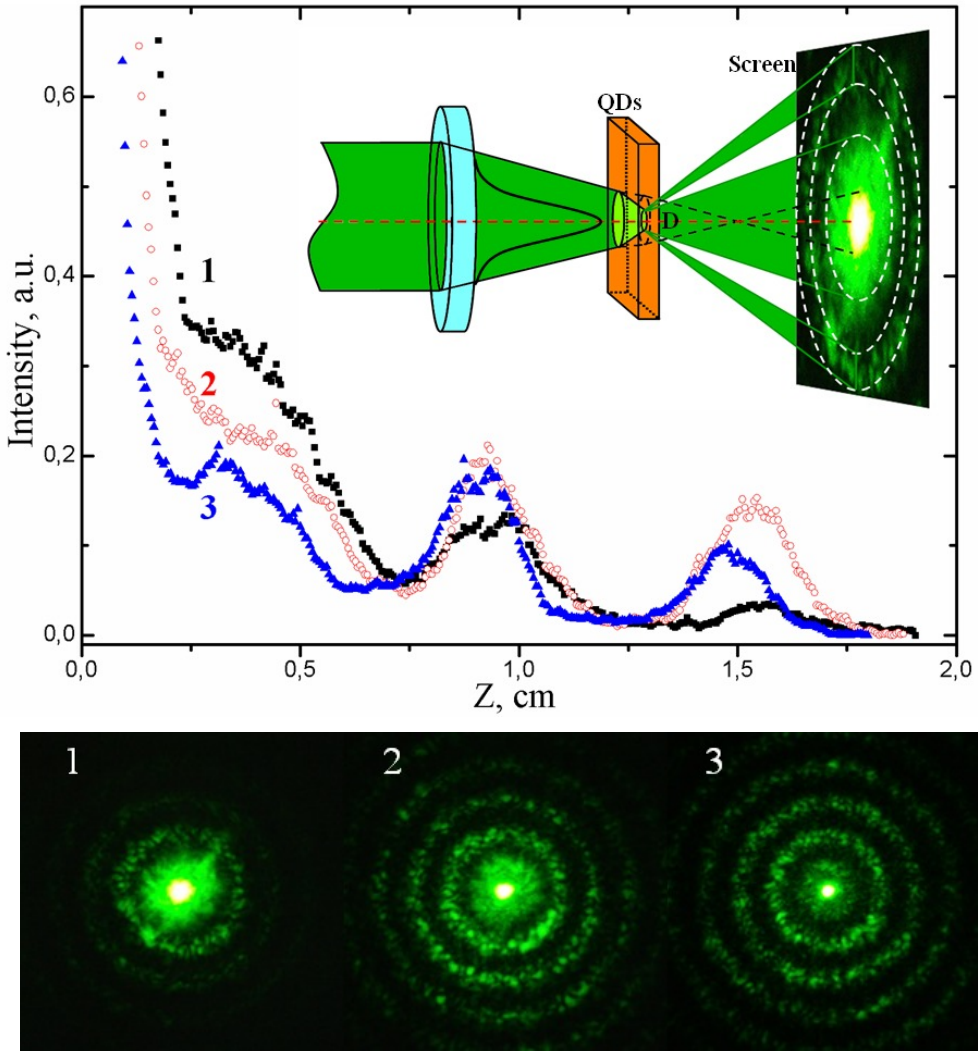

Fig.2. The dependence of diametrical intensity distribution (graphs and images) of diffracted output beam on the intensity of the incident beam (1-0.12, 2-0.18, and 3-0.28 GW/cm^2) formatting the transparency channel. Inset: dashed lines show the scheme of low intensity pulses propagation that undergone only linear absorption, solid lines - powerful pulses propagation that create the transparency channel and diffract at induced aperture.

We attribute the observed output cross section intensity distribution of the beams $I_{\pm 0}$ in Fig.1 and output beam in Fig.2 to self-diffraction at circular aperture that arise due to the creation of transparency channel as a result of the bleaching (decreasing of exciton absorption) in CdSe/ZnS QDs at resonant excitation by powerful picosecond pulses of Nd:YAG-laser's second harmonic[2-6]. Due to self-action effect the powerful laser beam initiating the decreasing of

exciton absorption can "prepare" the transparency channel and penetrate through the cell with colloidal QDs. While penetrating through the cell the beam with Gaussian cross section intensity distribution loses low intensity peripheral parts due to stronger absorption than at its center ("strip"- effect[8, 9]). Thus induced rigid circular aperture and Fresnel self-diffraction of the beam producing this aperture arise. The output beam cross-section intensity distribution for three trains of pulses with different maximum pulse intensities is shown in Fig.2. This distribution is partly masked by bright spot in the centre arising because of linear 3 % transmission of the sample (inset II in Fig. 1). The latter allows to explain why only the tendency for arising the minimum intensity of the diffracted beam in the centre (curve 3 in Fig.2) was observed.

It is possible to measure the diameter of the induced aperture at different intensities of laser beam: $D_m = 2\sqrt{m\lambda b}$; where m is the number of opened Fresnel zones, λ – the wavelength of exciting beam, and b – the distance between the cell with QDs and the screen. The Gaussian laser beam with measured 600 μm diameter (full width at half maximum intensity) at the input of the cell (inset in Fig.2) creates rigid aperture with calculated 340 μm in the case of one and 500 μm diameter in the case of two open Fresnel zones. This result proves "stripping" of the beam while transparency channel is created.

To clarify the physical processes responsible for the creation of transparency channel and induced aperture we have measured the dependence of the energy of picosecond pulses transmitted through the cell with colloidal CdSe/ZnS QDs upon the energy of corresponding 3-ns delayed input pulses (Fig. 3) using oscillograms obtained using special fast coaxial photo-detector and oscillograph (time resolution ≤1 ns).

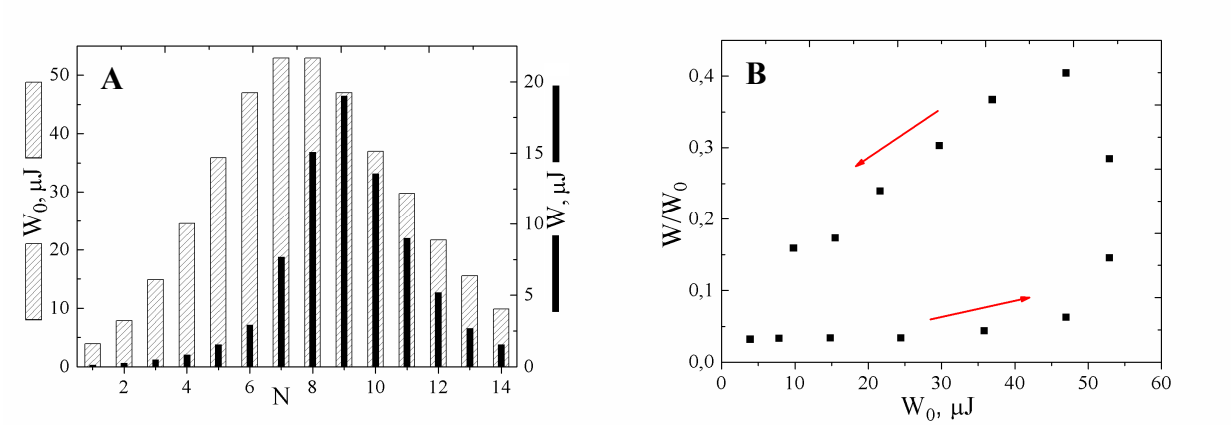

Fig.3. A. The histogram: shaded rectangles – the energies of input 3-ns delayed pulses of the train, blackened rectangles – the corresponding energies of transmitted through the cell with colloidal CdSe/ZnS QDs pulses. B. The dependence of transmission W/W_0 on single exciting pulse energy W_0: each point is for corresponding pair of pulses and the direction of increasing pulse's number is shown by arrow.

We attribute the dependence of single pulse transmission W/W_0 on W_0 (Fig.3 B) to competition and coexistence of two processes – to state filling and Stark shift of the basic electron-hole transition in CdSe/ZnS QDs. For the front part of the train the red Stark shift of exciton transition may initiate the increasing of absorption (see inset II in Fig.1) which is probably only partly compensated by decreasing of absorption as a result of state-filling in QDs. Strong bleaching of the pulses of train's central part and even the increasing of transmission for pulses with decreasing energy may be attributed to coexistence of both effects leading to bleaching of exciton transition in QDs. At high excitation for the pulses of central part of the train the red Stark shift due to induced electric field may overcome the absorption maximum of excitons (see inset II in Fig.1) and even be enhanced by next pulses due to its accumulation. The state-filling and Stark effect have different kinetic properties. While the relaxation time of resonantly excited excitons is much less[10] than the axial period of the train (the time interval between the exciting pulses was 7 ns) the relaxation time of induced electric field that arise due to the trapping of carrier at QD's surface states[6] may exceed axial period. The measured red thermal shift of exciton absorption spectrum of CdSe/ZnS colloidal QDs about 0.5 Å per 1 degree and the estimated heating of the sample at utilized energies of exciting picosecond pulses of the laser's second harmonic allows to exclude this inertial effect as essential one.

3.2 Self-diffraction at an induced diffraction grating in the case of one- and two photon resonant excitation of excitons in CdSe/ZnS colloidal QDs

Besides two output beams $I_{\pm 0}$ holding the direction of two input beams I_0 intersecting the cell with colloidal CdSe/ZnS QDs at angle θ the beams $I_{\pm 1}$ for one- and two-photon and $I_{\pm 2}$ for one-photon resonant excitation of the basic exciton transition were discovered (Fig.1). We attribute these beams to self-diffracted $I_{\pm 0}$ beams of the first and second order at the induced transient grating with period $\Lambda = \frac{\lambda}{2\sin(\theta/2)}$. The measured angles of diffracted beams (33º for the first and 67º for the second order of diffraction, θ=21º) coincide with that calculated.

Different physical processes may condition the appearance of induced transient grating. We suppose that at one-photon resonant excitation of excitons by picosecond pulses of the second harmonic of Nd:YAG-laser periodic change of nonlinear absorption arising as a consequence of state-filling and Stark-shift of exciton transition in CdSe/ZnS QDs[2-6] creates amplitude grating. The nonlinear change of absorption is accompanied by nonlinear change of refraction[1]. The latter effect dominates when the wavelength of exciting beam is shifted from exact resonance. The slight shift from resonance to longer wavelength in our case (inset II in Fig.1) may provoke the creation of phase grating as a reason of periodic coefficient of refraction nonlinear decreasing. Efficient first order self-diffraction is confirmed by the observed diffraction rings for $I_{\pm 1}$ beams (Fig.1). The intensity of $I_{\pm 1}$ beams is sufficient to create in their turn transparency channels and to be diffracted at rigid circular aperture.

We attribute the observed $I_{\pm 1}$ beams in the case of two-photon resonant excitation of excitons in colloidal CdSe/ZnS QDs to self-diffracted beams at induced transient phase grating. The formation of induced amplitude grating due to resonant two-photon absorption of excitons in CdSe/ZnS QDs is improbable. The change of transmission $T_0 - T$ is insufficient (less than 10%). The estimated nonlinear transmission $T \equiv \frac{I}{I_0} = \frac{1}{1+\beta z I_0} \geq 0{,}91$ (the coefficient of two-photon absorption β≈1cm/GW [11], the dimension of domain excited by two intersecting in the cell laser beams $z \leq 0{,}1$cm, and I_0 did not surpass 1GW/cm^2. However the induced change of refraction[12] $\Delta n \equiv n - n_0 = \frac{12\pi^2 \chi^{(3)}}{c n_0^2} I_0 \cong 10^{-3}$ is sufficient for the transient phase grating formation. In the last expression n_0 is the linear refractive index, c - the velocity of light, the third order nonlinear susceptibility $\chi^{(3)} \cong -7 \cdot 10^{-10}\, cm^3 erg^{-1}$ [12], and input intensity I_0=1GW/cm^2. Such great value of $\chi^{(3)}$ compared with that of solvent (hexane) may be attributed to its increasing in the case of intermediate resonance in transparent for laser radiation media[13] (resonance for two photons' summary energy in our case).

3.3 Estimation of the laser pulse duration

We have measured the dependence of the diffracted beam's energy W (the energy meter OPHIR was used) upon the delay time Δτ (Fig.1). In the case of two identical Gaussian laser beams spreading with a delay Δτ and creating diffraction grating in colloidal QDs the intensity distribution over time (Fig. 2):

$$I(t) = \frac{W/S}{\sqrt{\pi/2\ln 4}\,\tau^2}\left(\exp\left\{-\frac{2t\ln 4}{\tau^2}\right\} + \exp\left\{-\frac{2(t-\Delta\tau)\ln 4}{\tau^2}\right\}\right), \quad (1)$$

where S is the measured cross section of the laser beams, τ is the duration of laser pulses.

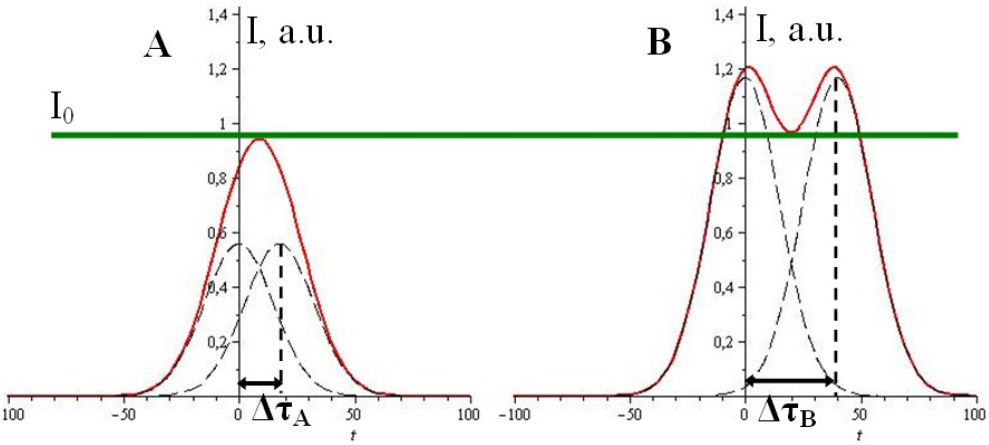

Fig.4. Intensity distributions of the interacting pulses for two different energies (W_B= $2W_A$) and corresponding time delays ($\Delta\tau_A$=17.5 ps, $\Delta\tau_B$=40 ps).

The delay between laser pulses at which the first order self-diffracted beams have the energy W_0 (that corresponds to the intensity I_0) depends only on the energies of interfering pulses. Self-diffraction at the delay corresponding to the fixed energy W_0 dominates for the pulse of maximum energy in the train (inset III in Fig.1). The intensity I_0 was calculated for the case of equal intensities of interacting pulses (for the time $\Delta\tau_{A,B}$ / 2), when the intensity of diffracted beam exceeds maximum value (Fig.2). We have estimated laser pulse duration (τ=35 ps) by equating the intensity I_0 calculated for the cases A and B:

$$\tau = \sqrt{\frac{\ln 2(\Delta\tau_B^2 - \Delta\tau_A^2)}{\ln W_B / W_A}}, \qquad (2)$$

where W_A, W_B are the pulses energies, $\Delta\tau_A$, $\Delta\tau_B$ – corresponding delay times.

4. CONCLUSIONS

Two discovered types of self-action process in the case of powerful picosecond laser pulse interaction with resonantly excited excitons in colloidal CdSe/ZnS QDs – self-diffraction at induced aperture and diffraction at induced transient diffraction grating – were explained by different competing and coexisting processes. In the case of one-photon resonant excitation of excitons the creation of transparency channel and Fresnel diffraction at rigid circular aperture was attributed to dominating state-filling and Stark effects. Self-diffraction of two intersecting in the cell with colloidal CdSe/ZnS QDs laser beams in the case of one-photon resonant excitation of excitons may be explained by diffraction at transient induced amplitude and phase gratings. We attribute self-diffraction in the case of two-photon resonant excitation of excitons to dominating diffraction at phase grating that arise due to nonlinear refraction conditioned by third order nonlinear susceptibility whose value is increased because of intermediate two-photon resonance. A method for estimating laser pulse duration is suggested and probed.

Acknowledgement

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