Influences of Size and Relaxation Time on Optical Free Induction Decay in a Small Spherical CdSe/ZnS Quantum Dot Quantum Well

Qianqian Xu[a] and Duanzheng Yao[b]

[a] Department of Physics, Wuhan University, Wuhan 430072, China
[b] Key Laboratory of Acoustic and photonics Material and Devices, Ministry of Education,
Wuhan University, Wuhan 430072, China

Reprint requests to D. Y.; E-mail: Fax: 86 27 68752569; dzyao@whu.edu.cn

Z. Naturforsch. **64a,** 837 – 843 (2009); received February 23, 2009 / revised June 17, 2009

The optical free induction decay (OFID) induced by the transition between 1s and 1p state in a small isolated spherical CdSe/ZnS quantum dot quantum well (QDQW) has been studied numerically under the framework of effective-mass approximation. The size and relaxation time-dependent properties of the OFID have been obtained and analyzed. It shows that the OFID-change mechanisms dependent on shell thickness and core size are different. Moreover, the OFID signal decays sharply in amplitude and life as the transverse relaxation time being reduced while the change is slight to the longitudinal relaxation time. By comparing these two factors, we infer that the size mainly influences the amplitude of the decay signal and the delay time is basically determined by the relaxation time.

Key words: Optical Free Induction Decay; Quantum Dot Quantum Well; Quantum Size; Relaxation Time.
PACS numbers: 42.50.Md; 73.63.Bd; 83.60.Rs

1. Introduction

Since the advent of laser, research on the field of interaction between light and matter becomes more active and gains plentiful achievements. By now, series of nonlinear optical phenomena caused by the interaction between laser and atomic system have been studied theoretically and experimentally [1 – 5]. Among them, the optical coherent transient effect (OCTE) definitely arises from the matter irradiated by strong ultrashort pulses which last far shorter than the relaxation times. In this case, the interaction process is essentially important to be considered.

The optical free induction decay (OFID) is one of the important coherent transient phenomena, a type of electron sustained resonance in a short period of time, which appears after the resonant system was detuned by Stark switch or other methods. Brewer and Shoemaker developed the Stark-pulse technique to demonstrate an OFID in NH_2D in 1972 [6]. Several years later, the observation of OFIDs in NH_3 [7] and I_2 [8] as well as other gases with the method of Stark shift has been reported. In 2002, Unyob and other authors obtained an OFID in cold ^{85}Rb atoms with the heterodyne method [9]. But now, an ultrashort pulse is the optimum way to study a transient process and has been adopted both in theory [10] and experiment [11].

However, little attention about OFID has been focused on the attractive artificial quantum dot quantum well (QDQW) which has discrete energy levels and possesses the property of high chemical stability and strong luminescence. It is worthy to point out that CdSe/ZnS draws more attention of engineers and researchers due to the charming character of strong visible spectrum and high quantum yield [12, 13].

In this work, we investigate the OFID in an isolated small spherical QDQW (CdSe/ZnS) by numerical calculation. Under the framework of effective mass approximation, the two lowest energy levels (1s and 1p) in the conductive band and the related electron wave functions are obtained through solving the Schrödinger equation. It may be mentioned that this method has been adopted in some papers and proved to be an effective tool [14 – 16]. By paying attention to the energy interval and the electric dipole moment as well as the electron density, we explore the influence of sizes (core and shell) on the OFID signal. Additionally, the relationship between the properties of OFID signal and relaxation time is investigated. The results and conjectures are discussed in detail among Section 3.

2. Theory

The model we consider is an isolated spherical QDQW with a centric well (CdSe) and a shell barrier (ZnS) as shown in Figure 1. Due to the fact that the band gap of CdSe is smaller than that of ZnS, we choose the zero potential at the upper boundary of energy gap belonging to the core. The electron energy forms some discrete levels in the potential well. While a laser pulse with enough energy excites the system, an electron may absorb the energy and transit to relative energy level and vise versa.

Under the framework of effective-mass approximation and the spherical coordinate, the steady Schrödinger equation of the electron appears as

$$\left\{-\frac{\hbar^2}{2m_i^* r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]+V_i(r)\right\}\Phi_{nlm}(r)=E\Phi_{nlm}(r), \tag{1}$$

where m_i^* and $V_i(r)$ are the effective mass of an electron and the potential in the ith region of the system, respectively, and

$$m_i^* = \begin{cases} m_1^*, \; r \le r_1, \\ m_2^*, \; r_1 < r \le r_2, \end{cases} \tag{2}$$

$$V_i(r) = \begin{cases} 0, \;\; 0 < r \le r_1, \\ V_c, \; r_1 < r \le r_2, \\ \infty, \; r > r_2, \end{cases} \tag{3}$$

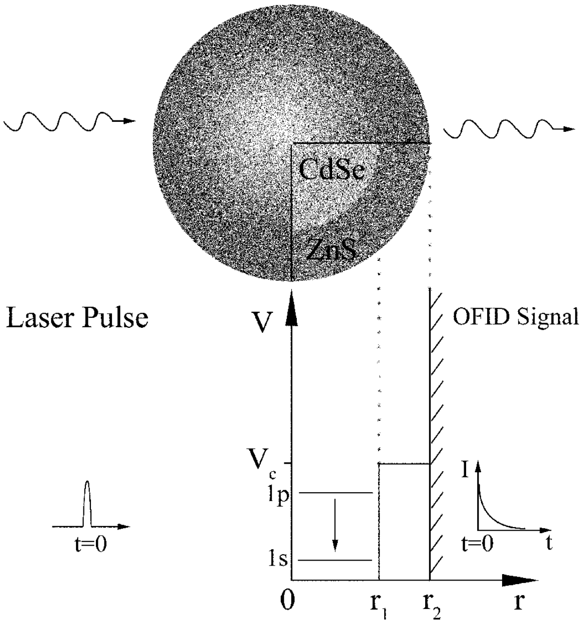

Fig. 1. Model of CdSe/ZnS QD with two energy levels (1s and 1p) in the potential well irradiated by a short laser pulse. Core: CdSe; shell: ZnS.

The wave function of an electron in a spherically symmetric potential and shape can be written as

$$\Phi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi), \tag{4}$$

where $R_{nl}(r)$ is the radial wave function and $Y_{lm}(\theta,\varphi)$ the spherical harmonics which are unrelated to the potential $V_i(r)$ but completely depend on θ and φ.

In the following study, we just limit our calculation to the intra-band transition between 1s and 1p (the lowest two energies in the conduction band which also satisfy to promise that the conclusions deduced from effective mass approximation are efficient [17, 18]. To get the wave function Φ_{1l} we can only consider $R_{1l}(r)$, because $Y_{lm}(\theta,\varphi)$ is independent of the radius of the QD. The radial wave function $R_{1l}(r)$ can be expressed as

$$R_{1l}(r) = \begin{cases} A_1 j_l(k_{1l}r) + B_1 n_l(k_{1l}r), & r \le r_1, \\ A_2 h_l^{(1)}(i\kappa_{1l}r) + B_2 h_l^{(2)}(i\kappa_{1l}r), & r_1 < r \le r_2, \\ 0, & r > r_2, \end{cases} \tag{5}$$

where j_l, n_l, and h_l are the l order spherical Bessel function, spherical Neumann function, and spherical Hankel function, respectively, A_1, A_2, B_1, and B_2 are the normalization constants and k_{1l} and κ_{1l} are wave vectors, which are expressed as

$$k_{1l} = \sqrt{2m_1^* E/\hbar^2}, \tag{6}$$

$$\kappa_{1l} = \sqrt{2m_2^*(V_c - E)/\hbar^2}, \tag{7}$$

According to the boundary conditions, we get

$$\begin{aligned} &B_1 = 0, \\ &R_{1l}(r_2) = 0, \\ &R_{1l,1}(r_1) = R_{1l,2}(r_1), \\ &\frac{1}{m_1^*}\left.\frac{\mathrm{d}R_{1l,1}}{\mathrm{d}r}\right|_{r=r_1} = \frac{1}{m_2^*}\left.\frac{\mathrm{d}R_{1l,2}}{\mathrm{d}r}\right|_{r=r_1}. \end{aligned} \tag{8}$$

From the equations above, the energy and the wave function of the electron below the shell potential can be obtained when the normalization constants have been gotten from the normalization condition by numerical calculation.

All we have done above is to obtain the electric dipole moment, which depends on the wave function related to the two energy levels we considered and the mathematical expression can be written as $\mu_{sp} = \langle \Phi_{10} | -er | \Phi_{11} \rangle$. Then the radiation intensity reads [19]

$$I(t) = \frac{\mu_0}{\bar{v}k^2}\sqrt{\pi}\omega_0^3 NL\mu_{sp}E_0^2\Omega\left(\frac{1}{\sqrt{1+\Omega^2T_1T_2}}-1\right)\exp\left[-\left(\frac{\Delta_1}{k\bar{v}}\right)^2\right]\exp\left[-\frac{t}{T_2(1+\sqrt{1+\Omega^2T_1T_2})}\right], \quad (9)$$

where T_1 and T_2 are the longitudinal relaxation time (means the energy relaxation) and the transverse relaxation time (means the phase relaxation), respectively. Ω is the Rabi frequency related to μ_{sp}. Other parameters can be considered as constants because we just focus on qualitative analysis.

3. Results and Discussions

In this section, we present a detailed numerical study on optical free induction decay in an isolated small spherical QDQW (CdSe/ZnS) with low excitation. Suppose that the QDQW is irradiated by a 150 fs laser pulse with the electric field amplitude of 5×10^7 V/m and preset the system under a near-resonant excitation state, then the QDQW possesses the ability of photoluminescence. At time $t = 0$, the pulse vanishes. Afterward, the QDQW will remain irradiation but in a form of free induction decay because the excited system needs time to recover.

For simplifying the model, we restrict our investigations under the weak excitation regime and the lower temperature for ignoring the many-body effects. Besides, we escape from the exciton effect through limiting the size of the QDQW less than the exciton Bohr radius in bulk CdSe [20]. If without specification, the parameters used in the calculation are as follows: $m^*_{e,\mathrm{CdSe}} = 0.13m_0$, $m^*_{e,\mathrm{ZnS}} = 0.28m_0$, $V_c = 0.9$ eV, $T_1 = T_2 = 300$ fs [21], and $N_a^0 - N_b^0 = 5 \times 10^{24}$ m^{-3}.

To begin with, the size dependent effect which means what to the radiation signal happens while changing the shell or the core radius of the QDQW, is studied. With caution, we only consider the electron transition between 1s and 1p in the potential well for the reason that effective-mass approximation is more accurate when applied in finite potential well [21 – 23]. Besides, we limit the radius of the QDQW among 2 ~ 3.5 nm for the exciton Bohr radius in bulk CdSe is about 5 nm. The thickness of the shell is restricted to less than 0.5 nm because a comparatively thick shell will bring an additional problem of surface passivation to the core.

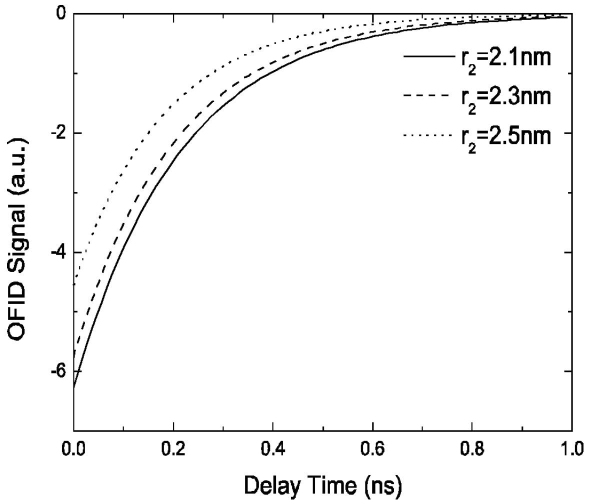

Fig. 2. Optical free induction decay signal varied with different r_2 (2.1 nm, 2.3 nm, and 2.5 nm) under certain r_1 (2 nm).

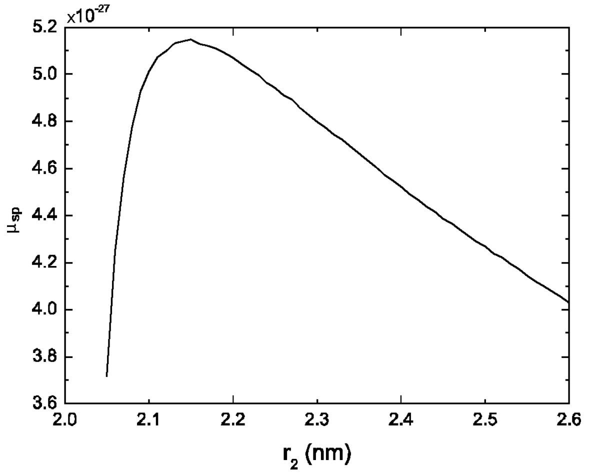

Fig. 3. Transition dipole moment μ_{sp} presented as a function of the radius r_2 of the CdSe/ZnS QD under the condition that the core radius is steady at 2 nm.

For one thing, we discuss the influence of an increasing shell on the OFID signal through steady r_1 (2 nm) with varied r_2 (2.1 ~ 2.5 nm) shown in Figure 2. It is found that the OFID signal becomes weaker

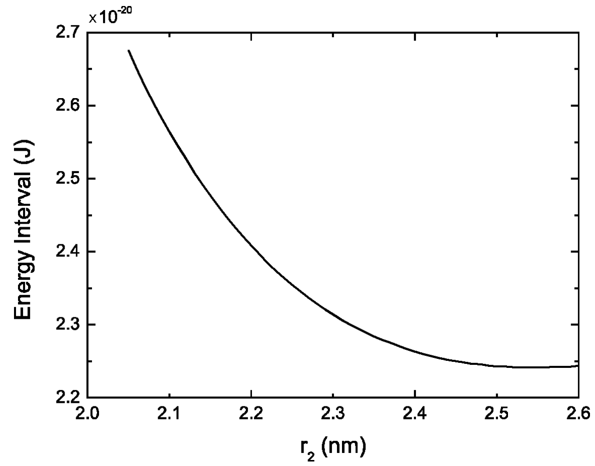

Fig. 4. Relationship between energy interval and radius r_2 of the CdSe/ZnS QD. The core radius is steady (2 nm).

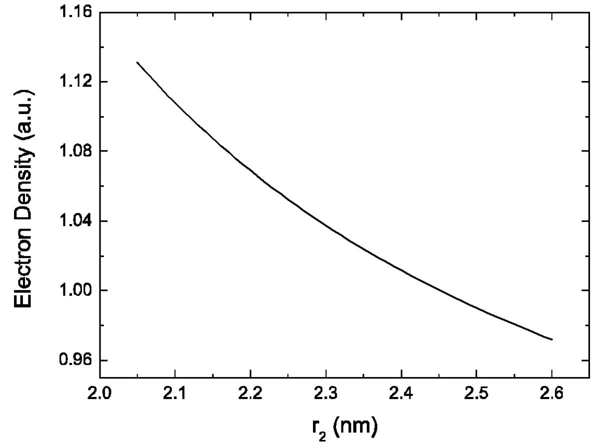

Fig. 5. How electron density of 1s state in the core depends on the radius of the CdSe/ZnS QD with stable core radius (2 nm).

obviously along the increase of r_2 and fades away exponentially almost in one picosecond. To explain the results clear, we review the relationship between electric dipole moment and r_2 (Fig. 3). The curve is nonmonotonous with varying r_2 of a steep rise at first (last less than 2 nm) and a relative slow decrease following. As we can see, the first point (2.1 nm) we selected is at the upward section whereas the other two are at the downward section, and the difference between the former two is smaller than the later two, which is the reason of low discrimination between the two downside curves in Figure 2.

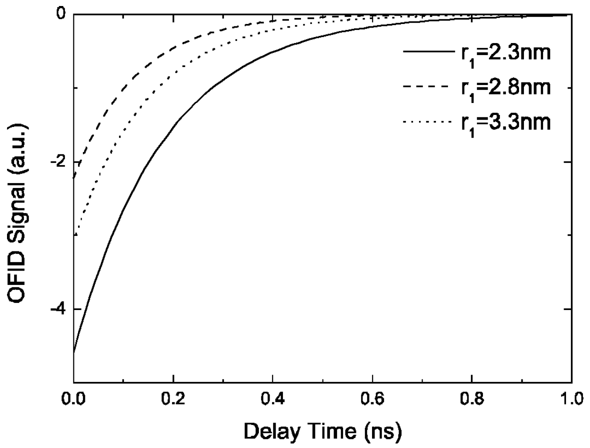

Fig. 6. Optical free induction decay signal varied with different core radius (2.3 nm, 2.8 nm, and 3.3 nm) under certain shell thickness (0.5 nm).

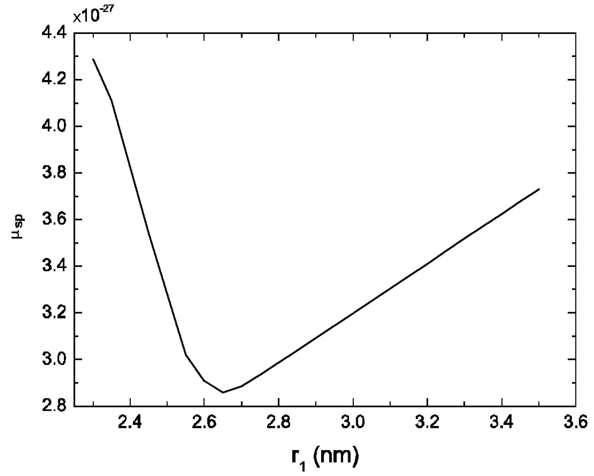

Fig. 7. Transition dipole moment μ_{sp} presented as a function of the radius of the core under the condition that the shell thickness is steady at 0.5 nm.

Generally speaking, two factors result in the lineshape of the electric dipole moment along increasing r_2. The first one is the energy interval between the two energy levels. In the region we study, the energy interval between 1s and 1p reduces fast and becomes smooth at last (Fig. 4). That means the thicker the shell, the narrower the energy level interval. This phenomenon has been observed in some experiments and deduced in several papers [25–27]. The influence of the energy interval on μ_{sp} must be that narrow energy interval induces big overlapping of the two related wave functions so that the electron can transit easy between the two energy levels and form a high transition dipole moment. However, the description does not correspond to the curve when r_2 grows bigger in

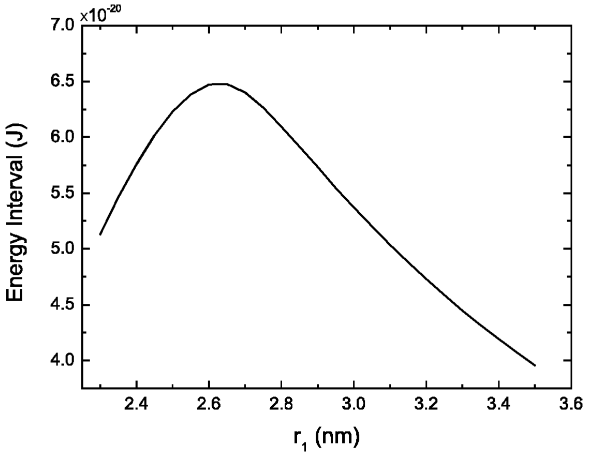

Fig. 8. Relationship between energy interval and the radius of the core. The shell thickness is steady (0.5 nm).

Figure 3 because the electron density (the other factor) makes μ_{sp} lessening. Just as we thought, the electron density in the core exhibit a significant drop as the shell becomes thick (Fig. 5). Thereafter, the competition between energy interval and electron density determine the forward of the transition dipole moment. When the shell is thin, the electron tends to stay in the core and the energy interval manifest as gradual decrescendo. The two factors are beneficial to the electron transition between the two energy levels. Along the shell grows, the electron inclines to transfer into the shell, so μ_{sp} inevitable decrease despite the gradually decrescent energy interval. That is the origin of the subdued OFID signal as r_2 increased. Similar conclusions about the competition have been investigated by theory in detail [28 – 30].

For another, we applied the same method to reveal the influence of increased r_1 on the OFID signal. To the three points of r_1, the OFID signal of the third is minor than the first but major than the second with the same shell thickness of 0.5 nm (Fig. 6), i. e., there must be a minimum signal exist. Considering the relative μ_{sp} and the energy interval, the whole current of μ_{sp} appears with a rise first and a following down as r_1 grows (Fig. 7) while the energy interval varies totally at contrary trend (Fig. 8) [27]. It abide the regular mentioned above that the narrower (bigger) the energy interval, the higher (lower) the transition dipole moment. As distinct from the r_2-related energy interval, the r_1-related energy interval has a rising part when the core is small due to the energy of the 1p state drops tiny slower than the 1s state at the beginning.

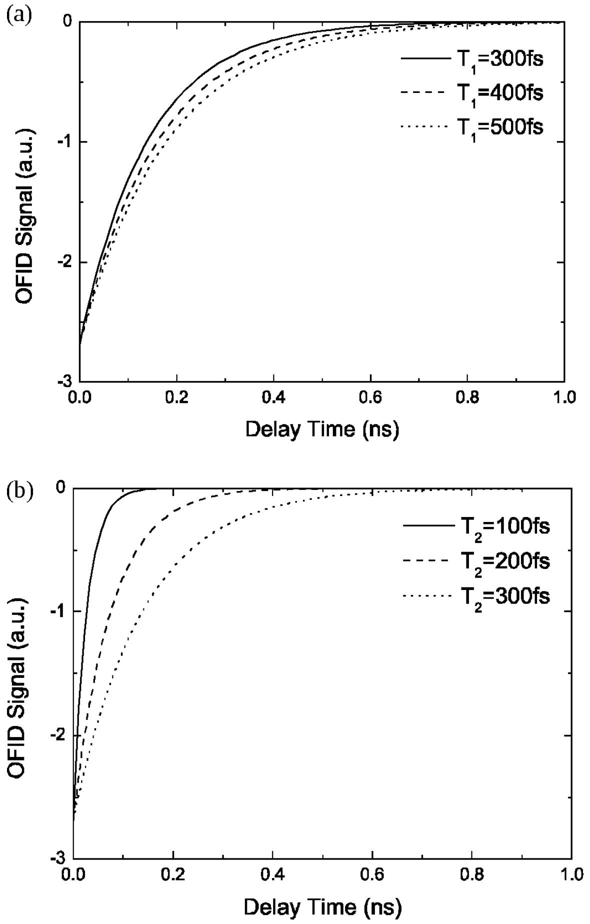

Fig. 9. Optical free induction decay signal changed with (a) different longitudinal relaxation time and (b) different transverse relaxation time while the other is certain (300 fs).

In addition, our efforts are focused on understanding the affection attributed to longitudinal relaxation time (T_1) and transverse relaxation time (T_2). Of course, we change the two parameters independently and set r_1 and r_2 at 2.5 nm and 3 nm, respectively. The OFID signals related to different relaxation times decay from the same amplitude but in different rates (Fig. 9). It is obviously to see that the affection of T_2 to the signal is more significant than T_1 and the relative conclusion can be easy deduced from the (9). The OFID signal decays sharply as T_2 decreased and the delay time shorten almost at the same rate.

Finally, we roughly compare the influences of size with the affection of relaxation time. While the size of core or shell varies, the amplitude of the decay signal produces an obvious fluctuation but the life span has tiny difference (Fig. 2 and Fig. 6). In contrast, relaxation time makes great difference on the delay time of the signal, with the same maximum amplitude (Fig. 9).

4. Conclusion

Under the framework of effective-mass approximation, we explore the OFID in an isolated small spherical QDQW (CdSe/ZnS) through numerical calculation. The results reveal that all the decay signals vanish in one nanosecond without other external influence. For the case of changing the thickness of the shell, competition between energy interval of the two energy levels and electron density induces a transition dipole moment abides the tendency of rise first and down later, and the decay signal follows the same tendency. While keeping the shell thickness but changing the core radius, the OFID signal decreases rapidly at the beginning and then increases because the energy of 1p state drops slight slower than the 1s state initially and faster afterward, which makes the energy interval big first then small. These conclusions imply that there exists an optimum size of the QDQW in an ultrafast electro-optic device to enhance or minish the free induction decay signal. By altering the longitudinal and the transverse relaxation time independently, we investigate the influence of them on the OFID signal and draw the conclusion that the signal decays remarkably fast in amplitude and life span as T_2 minish while slightly as T_1 minish. The influence can offer the opportunity to adjust the response time of devices because the transverse relaxation time (which is sensitive to temperature and impurity, as well as electric field) plays a major role on the duration of the decay signal. Comparing the influence of size and relaxation time, we can conclude that size mainly influences the amplitude of the decay signal and the relaxation time basically determines the delay time. This study can provide references for the design of related ultrafast electro-optic devices and is useful to the research on transient behaviour about relaxation property.

On account of the limitation of the model and the calculation method, there is a vast development space in this field. It is more beneficial to develop a proper model and method to investigate transient behaviour in a small QDQW which is consistent with experimental results.

Acknowledgement

This work was financially supported by the National Natural Foundation of China under the Grant No. 10534080.

[1] H. Tsunetsugu and E. Hanamura, J. Phys. Soc. Jan **55**, 19 (1986).

[2] T. Guenther, Ch. Lienau, Th. Elsaesser, M. Glanemann, V. M. Axt, T. Kuhn, S. Eshlaghi, and A. D. Wieck, Phys. Rev. Lett. **89**, 057401 (2002).

[3] Y.-B. Han, J.-B. Ding, S. Ding, D.-J. Chen, Q.-Q. Wang, Optics Express **13**, 9511, (2005)

[4] C. Van Vlack and S. Hughes, Opt. Lett. **32**, 187 (2007).

[5] E. Goulielmakis, M. Schultze, M. Hofstetter, V. S. Yakovlev, J. Gagnon, M. Uiberacker, A. L. Aquila, E.M. Gullikson, D. T. Attwood, R. Kienberger, F. Krausz, U. Kleineberg, Science **320**, 1614 (2008).

[6] R. G. Brewer and R. L. Shoemaker, Phys. Rev. A **6**, 7 (1972).

[7] M. Loy, Phys. Rev. Lett. **36**, 1454 (1976).

[8] R. G. Brewer, and A. Z. Genack, Phys. Rev. Lett. **36**, 959 (1976).

[9] S.-I. Nagahama, T. Yanamoto, M. Sano, and T. Mukai Jpn. J. Appl. Phys. **41**, 5 (2002).

[10] L. de Araujo, Phys. Rev. A **74**, 43415 (2006).

[11] A. Monmayrant, B. Chatel, and B. Girard, Phys. Rev. Lett. **96**, 103002 (2006).

[12] D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase, and H. Weller, Nano Lett. **1**, 207 (2001).

[13] M. C. Neves, M. A. Martins, P. C. R. Soares-Santos, P. Rauwel, R. A. S. Ferreira, T. Monteiro, L. D. Carlos, and T. Trindade, Nanotechnology **19**, 9 (2008).

[14] G. Mei, S. Carpenter, L. E. Felton, and P. D. Persans, J. Opt. Soc. Am. B **9**, 9 (1992).

[15] D. Schooss, A. Mews, A. Eychmüller, and H. Weller, Phys. Rev. B **49**, 17072 (1994).

[16] B. Li, A. F. Slachmuylders, B. Partoens, W. Magnus, and F. M. Peeters, Phys. Rev. B **77**, 115335 (2008).

[17] G. Pellegrini, G. Mattei, and P. Mazzoldi, J. Appl. Phys. **97**, 073706 (2005).

[18] Y. Nosaka, J. Phys. Chem. **95**, 5 (1991).

[19] S. Shi, G. Chen, W. Zhao, and J. Liu, in: Nonlinear Optics, Xidian University Press, Xi'an 2003, p. 249.

[20] Y. Kayanuma, Phys. Rev. B **38**, 9797 (1988).

[21] V. I. Klimov, and D. W. McBranch, Phys. Rev. Lett. **80**, 4028 (1998).

[22] A. S. Y. Wang, W. Mahler, and R. Kasowski, J. Chem. Phys. **87**, 8 (1987).

[23] M. Royo, J. Planelles, and M. Pi, Phys. Rev. B **75**, 33302 (2007).

[24] B. Pejova and I. Grozdanov, Mater. Chem. Phys. **90**, 35 (2005).

[25] O. Millo, D. Katz, Y. Cao, and V. Banin, Phys. Rev. Lett. **86**, 5751 (2001).
[26] Z. Dai, J. Sun, L. Zhang, S. Huang, and J. Zhang, Physica B **324**, 373 (2002).
[27] L. Jdira, P. Liljeroth, E. Stoffels, D. Vanmekelbergh, and S. Speller, Phys. Rev. B **73**, 115305 (2006).
[28] L. E. Brus, J. Chem. Phys. **79**, 6 (1983).
[29] J. W. Haus, Phys. Rev. B **47**, 7 (1993).
[30] S. Gong and D. Yao, J. Phys. Condens. Matter. **18**, 10989 (2006).