Three-photon absorption for nanosecond excitation in cadmium selenide quantum dots

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Abstract. We experimentally observe saturable absorption and dramatic three-photon absorption in various colloidal solutions of cadmium selenide quantum dots, with a strong size dependence witnessed for these properties. We also develop a model for the electronic portion of the nonlinearities that illustrates well the trends exhibited by our experimental data. The model incorporates six bands (three each in the valence and conduction bands). © *2007 Society of Photo-Optical Instrumentation Engineers.* [DOI: 10.1117/1.2823156]

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Due to their small size, ability to be embedded in other materials to affect the host's properties, ability to have their own properties easily tuned by slightly varying their size or composition, and the development of standard production techniques, quantum dots are rapidly showing promise in a wide range of applications. The nonlinear optical properties of quantum dots are important for many of these applications. One of these properties is multiphoton absorption. A theoretical model describing two-photon absorption in quantum dots was developed by Fedorov, Baranv, and Inoue,[1] with the effect being recently studied experimentally.[2] The relationship of nonlinearities of the quantum dots to the bulk material has been an issue of some debate. In particular, a recent study of the nonlinearities of CdSe quantum dots (essentially the same sample types as studied in this work) showed that the nonlinear properties were very similar to the bulk properties.[3] Several other studies[2,4,5] show instead that the nonlinear properties of the quantum dots differ greatly from those of the bulk material, and are critically dependent on dot size. The findings of this work are in line with these studies, seeing strongly size-dependent nonlinearities. Three-photon absorption has also recently been reported in CdS,[6] ZnO, and ZnS[7,8] quantum dot samples. The studies in ZnO and ZnS,[7] performed with femtosecond pulses to study purely electronic nonlinearities, saw a maximum value for the three-photon absorption of 0.016 cm^3/GW^2, with the values seen in CdS being approximately an order of magnitude smaller.[6] While these are relatively large with respect to those witnessed in dyes and other common absorbers, in this study we witnessed effective three-photon absorption values 3 to 7 orders of magnitude larger (4 to 9 orders of magnitude when corrected for volume concentration) than those previously reported for quantum dot samples by exciting with nanosecond pulses to access nonlinearities beyond purely electronic. Also, the previous studies were performed with long wavelength lasers (720 to 1000 nm), with the three-photon absorption becoming negligible at shorter wavelengths.[7] By identifying samples with extremely large values of three-photon absorption at visible wavelengths (532 nm for the current study), this result is of extreme importance for the development of nonlinear lithography,[9,10] where a key factor is minimizing λ/N, with N being the order of the absorption. In the current study, we carefully examine three-photon absorption in CdSe quantum dots as a function of dot size. We measured extremely large experimental values for the effective three-photon absorption coefficients. We further develop a six-band theoretical model to explain the relative values observed for the various dot sizes, though the absolute values differ from our results, as the model currently only accounts for the electronic portion of the nonlinearities.

A collection of CdSe core-shell quantum dot colloids and composites,[11] each with distinct dot properties and corresponding linear optical properties, have been provided by Evident Technologies (Troy, New York). Using standard open-aperture z-scan measurements, the nonlinear absorptions were studied as a function of dot size. For the data reported here, all of the measurements were made at $\lambda = 532$ nm, using the second harmonic of a 10-Hz, 6-ns Nd:YAG laser, with the pulse energies set at 90 μJ. For future studies, other wavelengths will also be explored using the optical parametric oscillator (which is tunable from 420 nm to more than 2 μm) pumped by the third harmonic of this system. In the results described here, the measurements were made on 1-cm-long samples of the pure quantum dot colloids (in toluene solution). Ongoing phases of the research are exploring how the nonlinearities described here are altered in the composite quantum dot materials.

Results of the open-aperture z-scans are shown in Fig. 1. In each case, the absorption coefficient was fit to the model:

$$\alpha = \alpha_o + \beta I + \gamma I^2, \tag{1}$$

where α_o is the linear absorption coefficient, β is the effective saturable absorption coefficient, and γ is the effective three-photon absorption coefficient. The intensity was determined using the measured energy (sampled before the z-scan apparatus), with the beam waist at points throughout the scan determined using the measured input waist, known lens parameters, and basic Gaussian optics calculations.

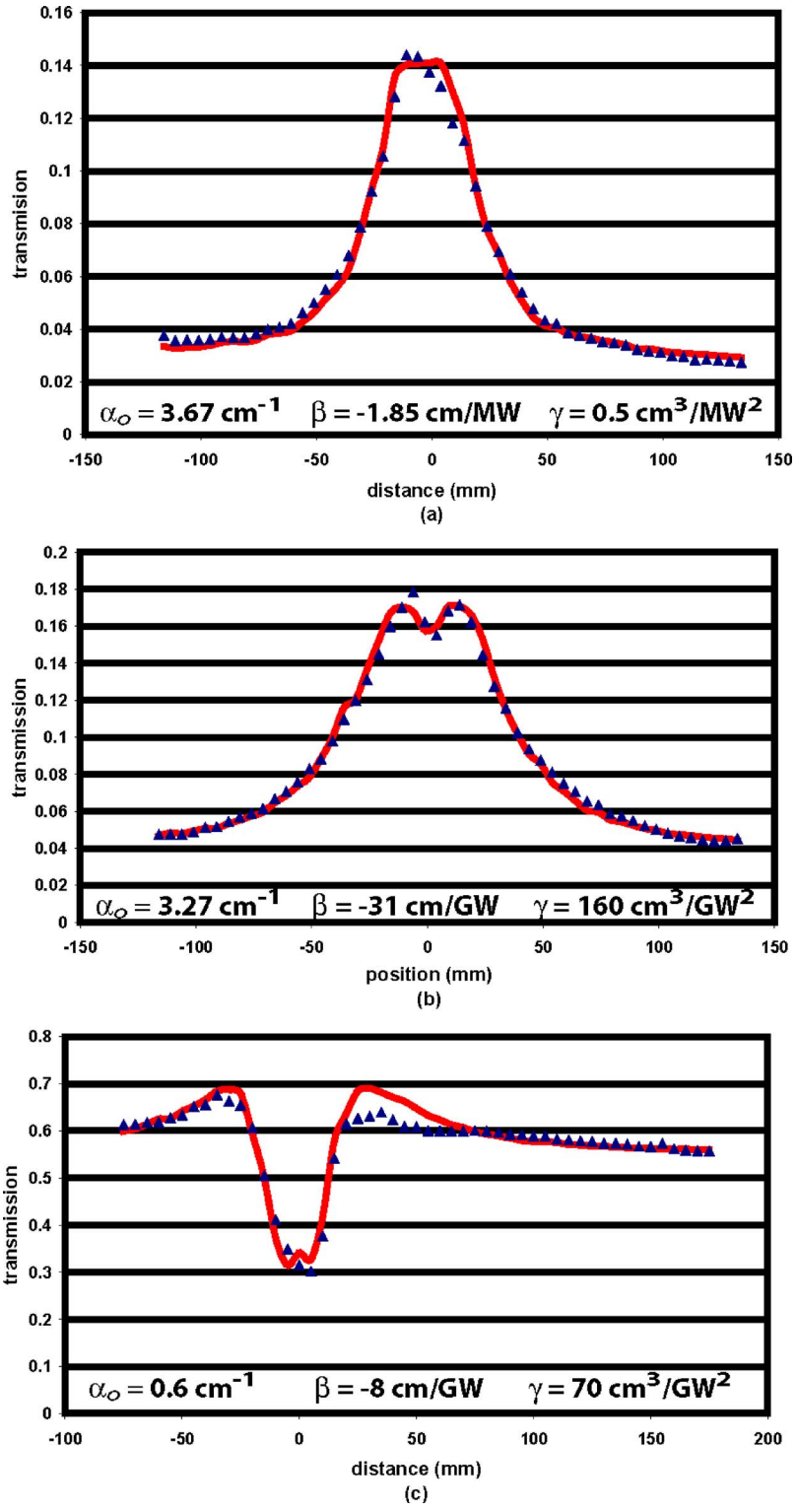

Fig. 1 Experimental results of open-aperture z-scans (dots) and analytical fits (solid lines) at 532-nm through 1-cm colloidal (in toluene) samples of CdSe quantum dots of diameter (a) 5.2, (b) 2.4, and (c) 1.9 nm. The best-fit values for linear absorption, effective saturable absorption, and effective three-photon absorption are shown.

The values given in the figure are for the colloidal samples, not extracted for the dots.

The results shown in Fig. 1 demonstrate several important features. First, as is well known, by reducing the size of the quantum dots, the material becomes increasingly transparent at wavelengths where the bulk material is opaque. The 5.2-nm and 2.4-nm-diam samples are strongly absorbing at 532 nm, while the 1.9-nm sample passes the

majority of the incident light. Second, the absorption starts to strongly saturate as the intensity is increased for each of the samples studied. Notice that the saturable absorption is represented by a negative value of β, whereas a positive value would imply two-photon absorption. Finally, the most dramatic result is the large three-photon absorption witnessed in all cases. Notice that the strength of the effect, as measured by the value of γ, decreases in this case with decreasing dot size. However, as the linear and saturable absorption coefficients are also decreasing, the relative effect of the three-photon absorption actually increases with decreasing dot size. For the correctly chosen combination of dot size and wavelength, it is thus possible to make three-photon absorbers using quantum dot samples that have low linear and two-photon absorptions. The potential applications from high-quality multiphoton absorbers are numerous, with one of much current interest being nonlinear lithography.[9,10]

It is possible to estimate the three-photon absorption cross section for quantum dots from estimates on bulk materials. Estimates for CdSe of the bulk absorption are of the order of 0.001 to 0.005 cm^3/GW^2.[12] To estimate the results for dots, this result is multiplied by $2(2l+1)\phi\rho^2/\Delta E\rho_b(E_{3\gamma})V$, where l is the angular momentum of the resonance state, ϕ is the volume concentration of dots ($\sim$0.1 for the system reported in this work), ρ^2 is the third-order Maxwell-Garnett field correction (this can be as large as $\sim 10^{13}$), ΔE is the resonance energy uncertainty ($\sim$.07 eV for a narrow resonance), $\rho_b(E_{3\gamma})$ is the bulk density of states at resonance, and V is the dot volume. For the $l=3$ resonance in 1.9-nm dots, this yields an estimate in the range of 0.1 cm^3/GW^2. This is 1 to 2 orders of magnitude less than that which was observed in this study.

To analyze the three-photon absorption in quantum dots in more detail, the following model is proposed. The model assumes spherical dots and electron (hole) wave functions of the form

$$\Psi = \varphi(n,l,m)u_{c,v}, \tag{2}$$

where the envelope functions $\phi(n,l,m)$ are the eigenfunctions for a spherical well, and u_{cv} are the Bloch functions for the bulk material in the conduction and valence bands. For a specific hole state characterized by a set of quantum numbers (n,l,m), there are two types of three-photon transitions to an electron in the conduction band. One set of transitions involves only interband transitions and has the selection rules $\Delta(n,l,m)=0$. The second type of transition involves interband and intraband transitions. As shown in Federov, Baranv, and Inoue,[1] the matrix elements for intraband transitions for small quantum dots can be comparable, and in some cases even larger, than the interband transitions. This could afford a possible enhancement of multiple-photon absorption. For this second type of transition, the selection rules for three-photon absorption are $\Delta l=0, +2, -2$; $\Delta m=0, +1, -1, +2, -2$.

The intraband matrix elements are proportional to the expectation values of the momentum operator taken with respect to the spherical well envelope functions. These all have a factor of $\xi(n,l)\xi(n',l')/[\xi^2(n',l')-\xi^2(n,l)]$, where $\xi(n,l)$ are zeros of the spherical Bessel functions. The magnitude of this factor is a maximum when $n'=n$. Therefore, this approximate selection rule is used for the six-band model, even though there are resonant transitions such as 4F(h)$\rightarrow$5F(e) (7.04 eV), which violate this selection rule. For three-photon transitions of the first type, a simple two-band model is reasonable. However, for transitions of the second type, it is necessary to consider up to six bands for transitions where the resonance energy is $E_g+E_e(n,l')-E_h(n,l)$, where E_g is the bulk bandgap and $E_{e,h}(n,l)$ are the spherical well energies with

$$E_e(n,l) = \hbar^2\xi^2(n,l)/2R^2m_e,$$

$$E_h(n,l) = -\hbar^2\xi^2(n,l)/2R^2m_h, \tag{3}$$

where the bandgap energy E_g is 1.7 eV for CdSe, and for the effective masses, $m_e=0.13m$, $m_h=0.45m$, and m is the electron mass.

Using perturbation theory, the interband transition contribution to the three-photon absorption coefficient γ for microdots of radius R embedded in a nonabsorbing medium, at a resonance $3\hbar\omega$ energy, can be written as

$$\gamma = \frac{K\rho^2 f_6(\alpha/n)^3\pi^4\hbar^2P^6S(E)g_l}{(\hbar\omega)^9V(R)\phi^{-1}}, \tag{4}$$

where K is a phenomenological constant of the order of 10 to 100 incorporating bulk material effects not taken into account by the perturbation theory, ρ is the Maxwell-Garnett local-field correction, which can be very large at a resonance of photon absorption,[13] α is the fine-structure constant, n is the index of refraction of the dot, $V(R)$ is the volume of a microdot, f_6 is a constant on the order of unity,[13] P is the Kane momentum parameter (which is almost material independent), $g_l=2(2l+1)$ is the degeneracy, $S(E)$ is the Lorentzian line shape factor ($\approx 1/\Delta E$ at resonance), ϕ is the volume concentration of dots in the sample, and ω is the incident light frequency. Equation (4) can be averaged over a known distribution of particle sizes.

Table 1 shows the resonant three-photon transitions for the three types of dots studied in this experiment. It is important to note that in all cases, there is at least one three-photon resonance. In the 5.2-nm dots, there is also a one- and two-photon resonance. However, because of the strong saturable absorption, the one-photon transition is suppressed in the region of intensity where the three-photon absorption is measurable, and the two-photon effect contributes along with the saturable absorption to the total third-order process, characterized by β. The same type of effect is apparent in the 2.4-nm dots, where the one-photon absorption is relatively weak, and there is also a two-photon resonance as well as the three-photon resonance. The existence of one- and two-photon resonances along with a three-photon resonance can enhance the three-photon absorption, since it is possible for one or two photons to make a resonant intermediate transition in the three-photon absorption process involving both interband and intraband transitions. This effect can contribute to the large three-photon absorption for the 5.2-nm dots. For example, in the 5.2-nm dots, the 4D(h)$-$6S(e) resonance can proceed via 4D(h)$-$4P(h)$+$4P(h)$-$4P(e), which is a two-

Table 1 Electronic resonance structure of CdSe quantum dots.

Size (nm)	Trans. order [E(eV)]	Transition	Resonance energy (eV)
5.2	1γ (2.33)	2S(h)→2S(e)	2.3
5.2	2γ (4.66)	4D(h)→4P(e)	4.64
5.2	3γ (7.0)	5P(h)→5F(e)	7.07
5.2	3γ (7.0)	5G(h)→5D(e)	6.99
5.2	3γ (7.0)	4D(h)→6S(e)	7.1
2.4	1γ (2.33)	1S(h)→1S(e)	2.39
2.4	2γ (4.66)	2P(h)→2S(e)	4.63
2.4	3γ (7.0)	1F(h)→1H(e)	6.93
2.4	3γ (7.0)	1I(h)→1G(e)	6.78
1.9	3γ (7.0)	1F(h)→1F(e)	6.91
1.9	3γ (7.0)	1D(h)→1S(e)	6.90

photon resonance, followed by 4P(e)−6S(e), which completes the three-photon resonance. This yields an enhancement factor of $(E_\gamma/\Delta E)^2$ over a nonintermediate resonant transition, which can be several orders of magnitude and can contribute to the large three-photon absorption observed for the 5.2-nm dots. For the 1.9-nm dots, there are no one- or two-photon resonances. The one-photon absorption is suppressed due to saturation at the intensity where the three-photon absorption is measurable. Estimates of the three-photon absorption coefficient for bulk materials are at least two orders of magnitude less than the three-photon absorption coefficient observed in this experiment.[12] However, such differences have been observed,[2,4,5] and could here be from a combination of resonant enhancements to the electronic nonlinearities, as well as other types of nonlinearities not explored by the current model.

Using Eq. (4), with $\rho \approx 10$, the interband contribution is estimated at the 1F(h)→1F(e) resonances for the 1.9-nm dot to be of the order of 1.0 cm^3/GW^2. Correcting for the volume concentration of dots reduces this to the 0.1-cm^3/GW^2 range. However, including intraband contributions to this resonance, which are at least of the same order of magnitude as the interband transitions, can provide another one or two orders of magnitude, bringing the result for γ closer to the measurements. Whether more accurate calculations using more terms and including additional sources of nonlinearities can produce results closer to the measured result is the subject of ongoing work. A primary goal of the future development will be the ability to engineer high-quality, multiphoton absorbers with properties even superior to those seen here for the 1.9-nm dots.

In conclusion, we have identified extremely strong, size-dependent three-photon absorption in quantum dot samples. To maximize the effective nonlinearities available for practical applications, we performed the studies in the nanosecond regime to access more than simply electronic nonlinearities. We have developed a six-band model to analyze and predict the nonlinear absorption features of the dots based on material composition and size. One important potential application of the multiphoton absorption being explored in composite samples is nonlinear lithography.[9,10] The ability to design dot-based composites with specific nonlinear absorption characteristics using our model could provide a major advance in that field. Continuing studies are also exploring the refractive nonlinear properties of the dots, the nonlinearities of the composites, and the ability to engineer samples with desired properties based on our model.

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