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Full Length Research Paper

Dependence of second order nonlinear susceptibility and efficiency on shape of CdS quantum dot

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This paper deals with the dependence of second order nonlinear susceptibility and second harmonic generation (SHG) efficiency on the shape of CdS quantum dot. A relation has been found between the electronic structure and second order nonlinear susceptibility. The effective mass approximation has been used to find the energy levels. We have considered both intra band and inter band near resonant transitions for SHG and theoretically investigated the SHG efficiency for different shapes of CdS quantum dot inspired by experiments conducted previously by Aktsipitrov (1995).

Key words: Second order nonlinear susceptibility; intraband transition, interband transition, SHG efficiency.

INTRODUCTION

Quantum dots are a unique class of semiconductors composed of periodic groups II-VI, III-V, IV-VI materials. Quantum dots can be of various shapes – cubical, spherical, ellipsoidal, pyramidal, dome, etc. The size and shape of these nanocrystals and the number of electrons they contain can be precisely controlled; a quantum dot can have anything from a single electron to a collection of several thousands. The unique linear and non linear optical properties of quantum dots have been attracting researchers' attention for many years. Second harmonic generation (SHG) is a nonlinear optical process in which photons interacting with nonlinear material are effectively combined to form new photons with twice the energy, and therefore twice the frequency and half the wavelength of the initial photons. SHG is sensitive to the electronic structure of the materials since it relies on optically induced transitions between electronic states or bands of the investigated medium (Ajoy and Lokanathan, 2004). The SHG efficiency depends on the second order nonlinear susceptibility. Quantum dots appear as promising candidates to achieve large non linear susceptibilities.The dipole matrix elements associated with quantum dot intraband transitions (also called intersublevel transitions) can be large (Brunhes et al., 1999) thus giving a high susceptibility.

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THEORY

We are basically concerned about the efficiency of the nanocrystal. Efficiency depends directly on square of second order nonlinear susceptibility, $\eta \propto \chi_{ijm}^{(2)^2}$ depends on the electronic structure of the bulk (Ajoy and Lokanathan, 2004). For a quantum dot, assuming that there is no E-K dependence and the state occupancy factor as $(E_{l'})=f(E_{l''})=0$ and $f(E_l)=1$, the expression can be simplified to:

$$\chi_{ijm}^{(2)} \propto \sum_{l,l'l''} M_i M_j M_m \left\{ \frac{\left(\frac{1}{E_{l'} - E_l - \hbar\omega + i\hbar\gamma_{l\to l'}} \right)}{E_{l''} - E_l - 2\hbar\omega + i\hbar\gamma_{l''\to l}} \right\}$$

Where $M_i = < \Psi_l \, | p_i \, | \Psi_{l'} >$ is the dipole matrix element between states l and l'. It is given as [2]

$$M_i = \int \Psi^* p_i \Psi \, dV$$

The integral is over all space but it can be restricted to the region where the initial and final wave functions are non-negligible. p_i is the dipole moment operator given by

$$p_i = e\sum_n x_n \sum_n y_n \sum_n z_n$$

where the summations are over the position of the electrons in the system. M_j and M_m account for the transitions for the other electronic levels involved. The electronic structure of the material enters through the eigen values E_l which depend on the electron indexed state.

$\gamma_{l\to l'}$ is the relaxation parameter associated with the transitions between the pertinently indexed states. In the absence of experimental data, the relaxation parameter for different intraband and interband transitions is taken constant and equal to 1meV. In the calculation, only the transitions from the ground state are considered since only the ground level is intentionally populated and hence the summation is not considered.

In order to investigate the second-order nonlinear susceptibility associated with the intraband and interband transitions, we have used a single-band effective-mass calculation to evaluate the energy of the confined levels as a function of the quantum dot size. Though the effective-mass approach exhibits some significant deviation from more sophisticated calculations, previous studies have shown that this single-band model provides a coherent interpretation of the experimentally observed intraband transitions. The inferences for interband transition have been drawn on similar lines.The value of effective mass of CdS is taken from the literature. We underline that the purpose of this paper is to provide a guideline to predict the size dependence of the second-order nonlinear susceptibilities in the cubical, spherical and elliptical quantum dots. An accurate description of the quantum-dot states and in particular of their energy would require a multiband k.p calculation or a pseudopotential calculation, which is beyond the scope of this paper.

SPHERICAL QUANTUM DOT

A spherical quantum dot can be approximately described by an electron (of a certain effective mass) inside an infinitely deep spherically symmetric potential well of radius 'a' (Ajoy and Lokanathan,2004). The 3 dimensional time independent Schrödinger equation in spherical coordinates is solved under the following boundary condition V (r) = 0 , 0 ≤ r ≤ a
= ∞ , r > a

to get the energy levels $E_{n,l} = \frac{\hbar^2}{2m}\left(\frac{g_{l,n}}{a}\right)^2$ and the normalized wave functions

$$\Psi(r,\theta,\Phi) = N j_l\left(g_{l,n}\frac{r}{a}\right) Y_{lm}(\theta,\Phi)$$

Where $N = \left[\frac{2}{a^3[j_{l+1}(g_{l,n})]^2}\right]^{1/2}$

represents the normalization constant.

The near resonant transitions for an input excitation of 1.05 eV are found out for a 2.3 nm, 3.5 nm and 4 nm radius quantum dots. The states involved for 2.3 nm QD are 1s, 2s, $2p_x$, for 3.5 nm QD 1s, $2p_x$ and $3p_x$ and for 4 nm QD are 1s, 3s and 4s. The interband transitions have been found accordingly taking ideas from the work done in (Jun et al., 2005). The corresponding transition dipole moments are calculated by assuming the QD to contain a single electron at a unit distance along each axis. The simulations have been done guided by Akhlesh (2004) (Figures 1 to 4).

CUBICAL QUANTUM DOT

Similarly, a cubical quantum dot can be approximately described by an electron (of a certain effective mass) inside an infinitely deep potential well inside a cube of side L. The boundary condition is given as (Ajoy and Lokanathan, 2004):

V(x, y, z) = 0 for 0<x<L, 0<y<L, 0<z<L
= ∞ everywhere else

The 3 dimensional time independent Schrödinger equation in Cartesian coordinates is solved for the above boundary condition to get the energy levels as:

$$E_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)\ n_x, n_y, n_z = 1,2,3\ldots$$

and the normalized wave functions

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\frac{n_x\pi}{L}x\ \sin\frac{n_y\pi}{L}y\ \sin\frac{n_z\pi}{L}z$$

For a cubical quantum dot with infinite barriers, optical inter-sublevel transitions are only allowed between states with odd difference quantum numbers along the same axis (Akhlesh, 2004). The near resonant transitions for an input excitation of 1.05 eV are found out to be for 5.4, 5.5, 5.6, 5.7, 5.8 and 6 nm size quantum dots. The states involved for 5.4, 5.5, 5.6, 5.7 and 5.8 nm QD are 111, 114, and 144 and for 6 nm QD are 111, 124, 611 for 5.7 nm the transitions for the given input excitation are found to be closest to resonance. The corresponding Interband transitions have been evaluated. The corresponding transition dipole moments are calculated by assuming the QD to contain a single electron at a unit distance along each axis (Figures 5 to 8).

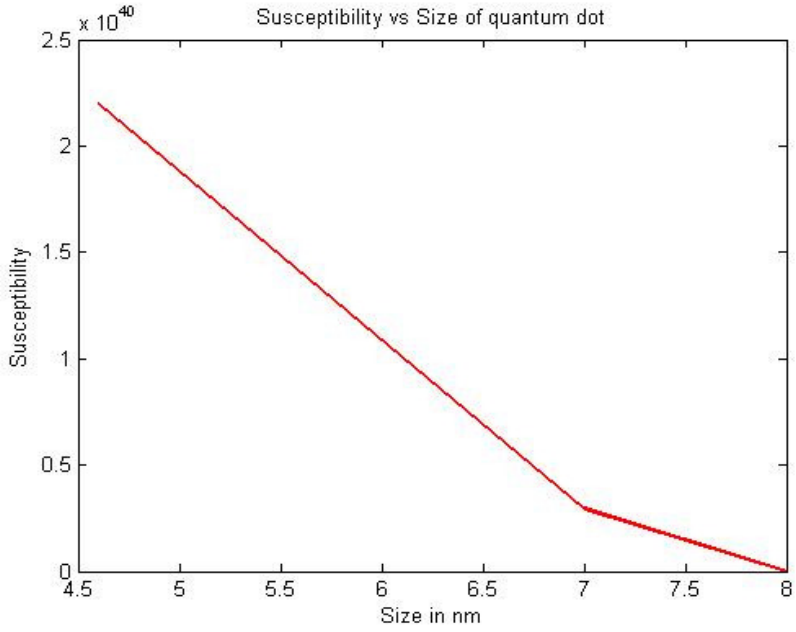

Figure 1. Susceptibility for a spherical CdS QD for intraband transition.

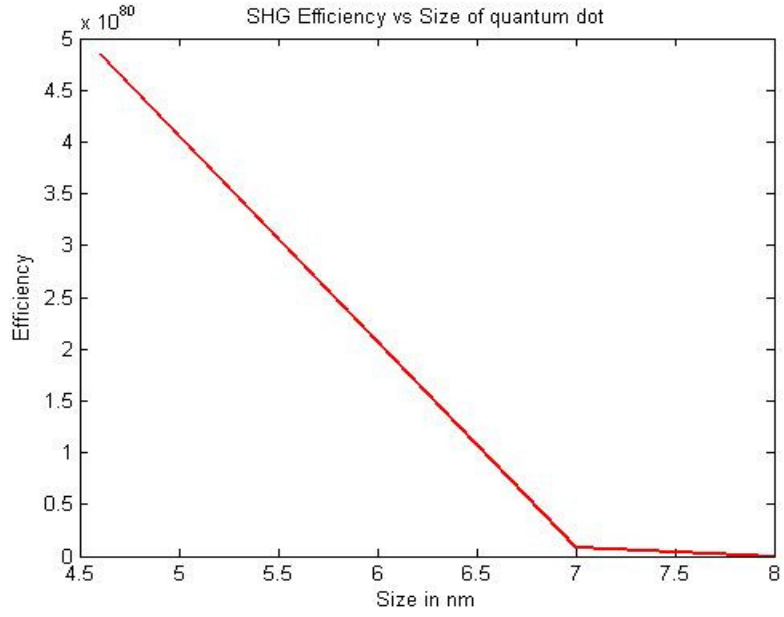

Figure 2. SHG efficiency for a spherical CdS QD for intraband transition.

ELLIPTICAL QUANTUM DOT

The time dependent Schrodinger Equation for an elliptical quantum dot is given by van den Broek and Peeters (2001):

$-\hbar^2/2m.\nabla^2\psi(x,y) + V(x,y)\,\psi(x,y) = E\,\psi(x,y)$

The energy spectrum has been optimized for simplified calculations as follows:

$E_{n,l} = \hbar^2/2m\, k_{n,l}^2(a/b)$

The zeroeth value of the Bessel function $k_{n,\,l}$ are pre-determined. The Energy Eigen values of the elliptical

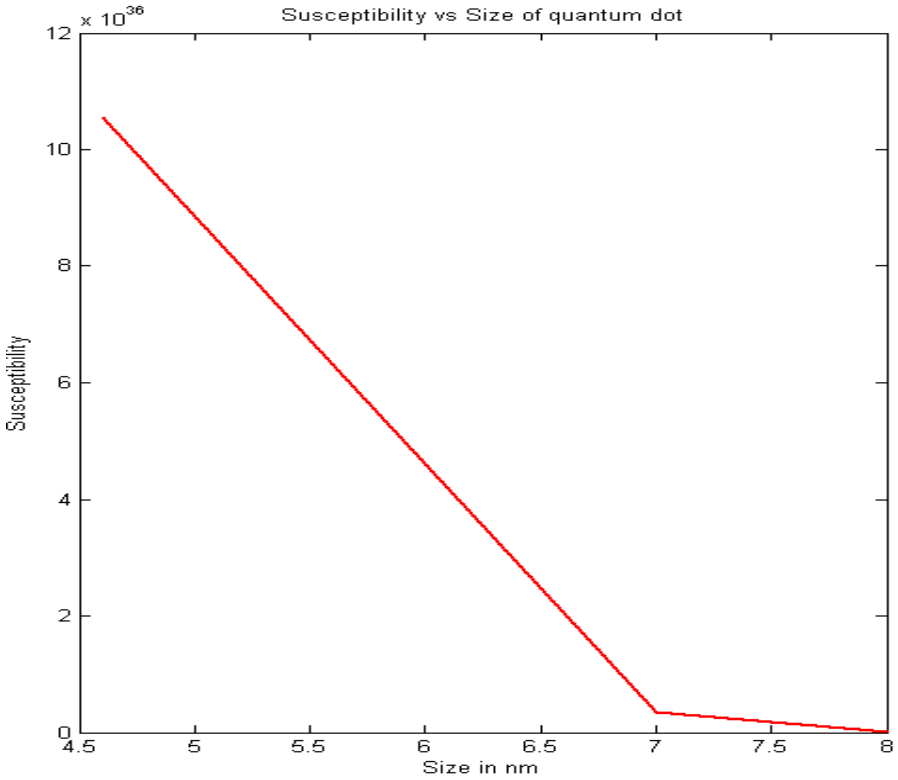

Figure 3. Susceptibility for a spherical CdS QD for interband transition

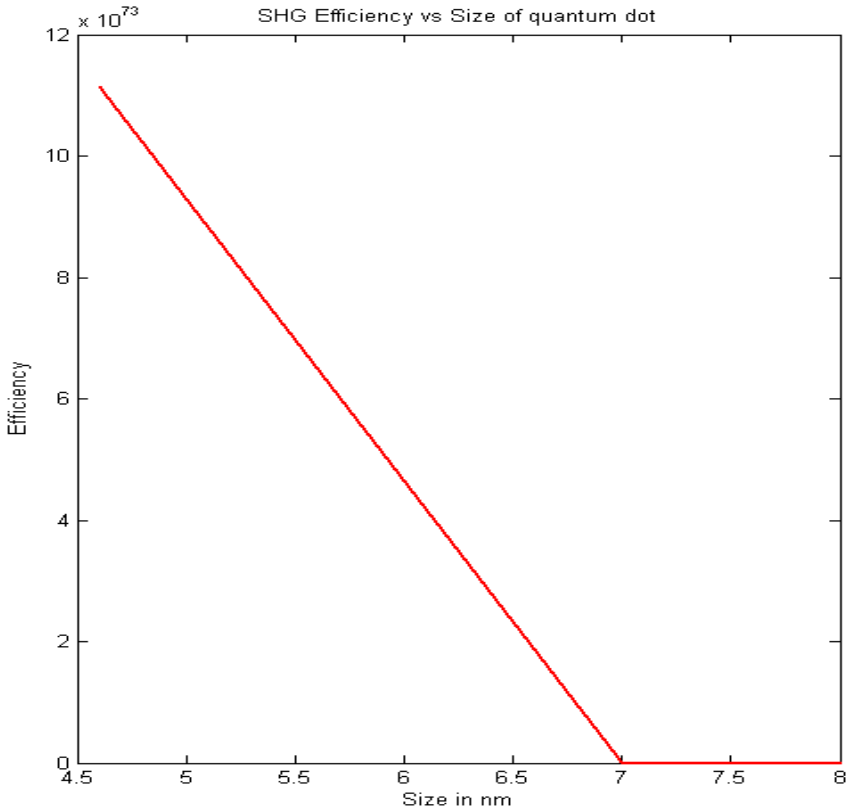

Figure 4. SHG efficiency for a spherical CdS QD for interband transition.

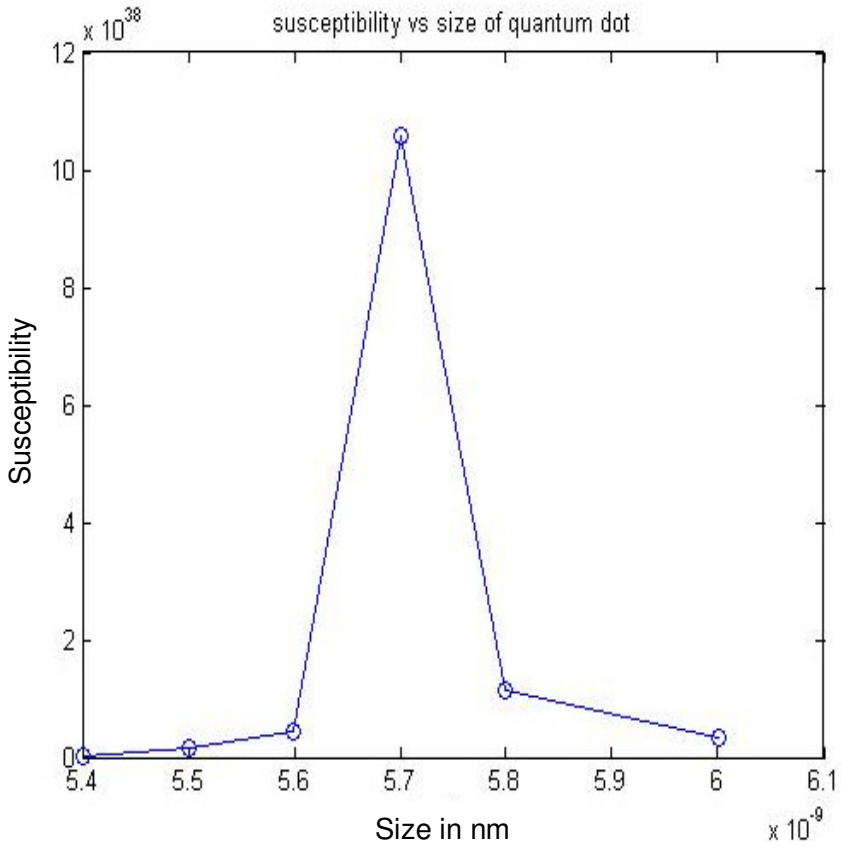

Figure 5. Susceptibility for a cubical CdS QD for Intraband transition.

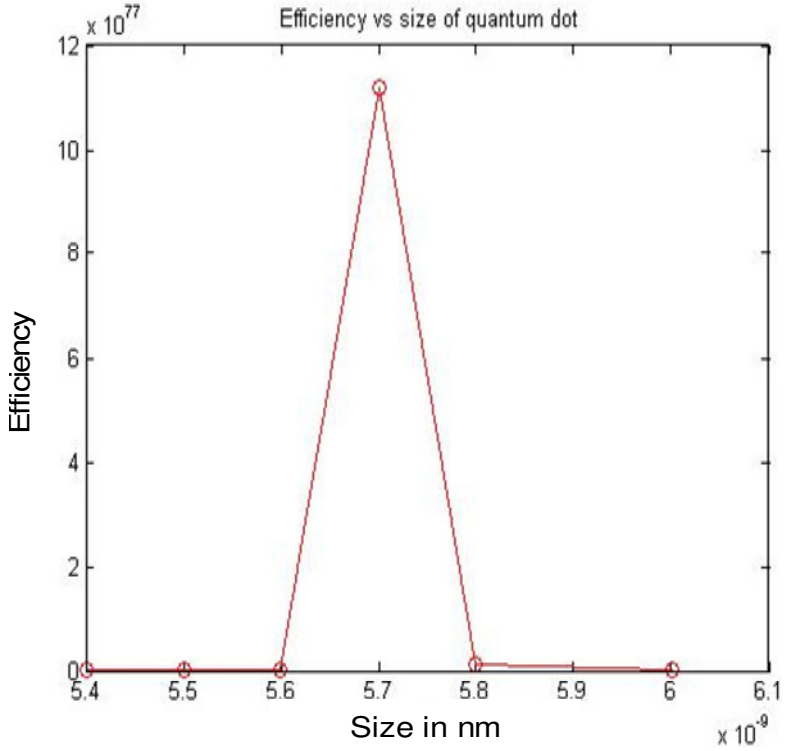

Figure 6. SHG efficiency for a cubical CdS QD for intraband transition.

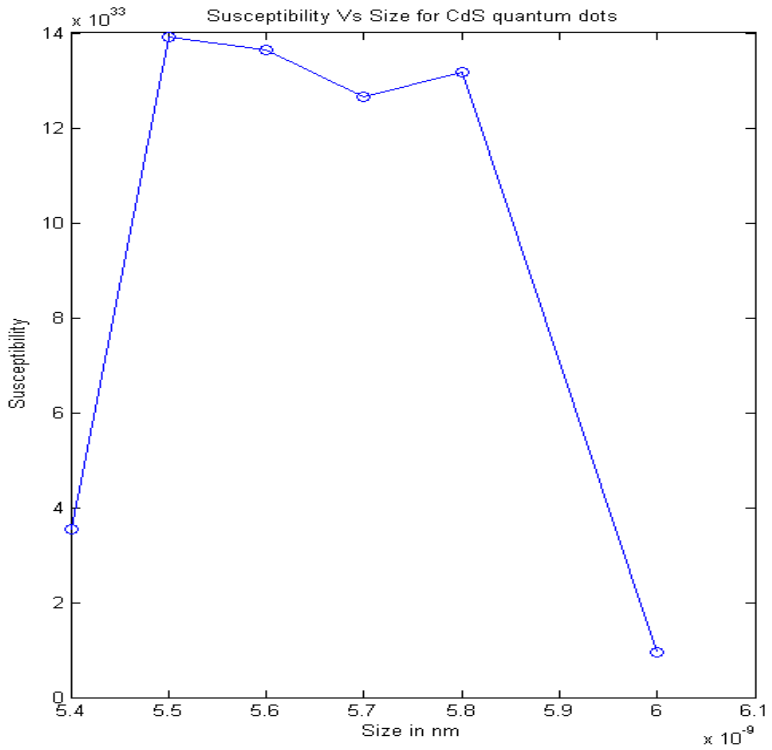

Figure 7. Susceptibility for a cubical CdS QD for interband transition.

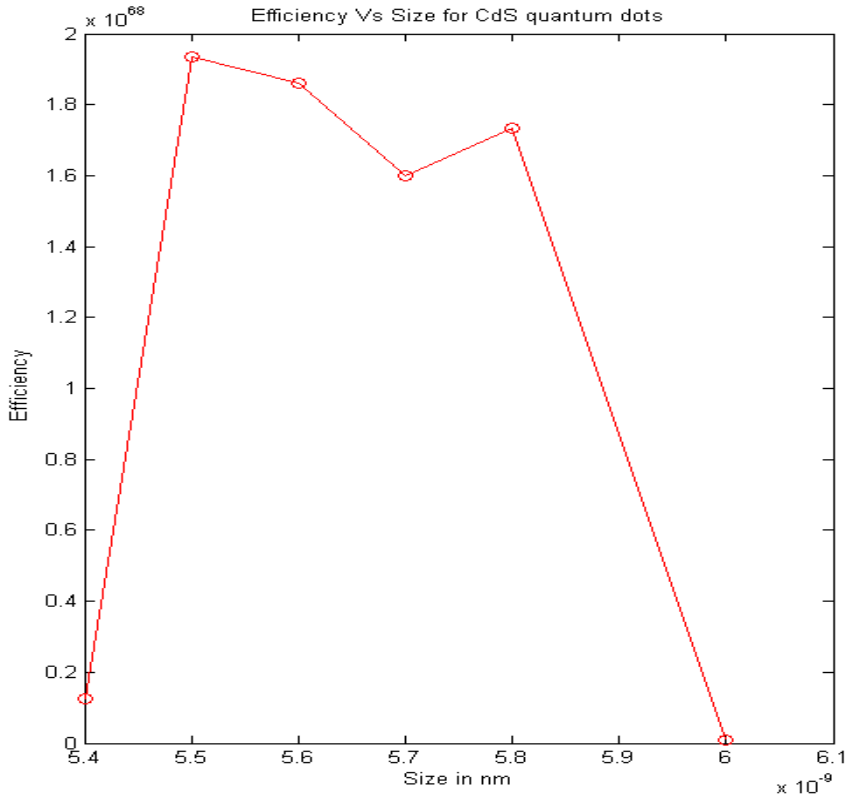

Figure 8. SHG efficiency for a cubical CdS QD for interband transition.

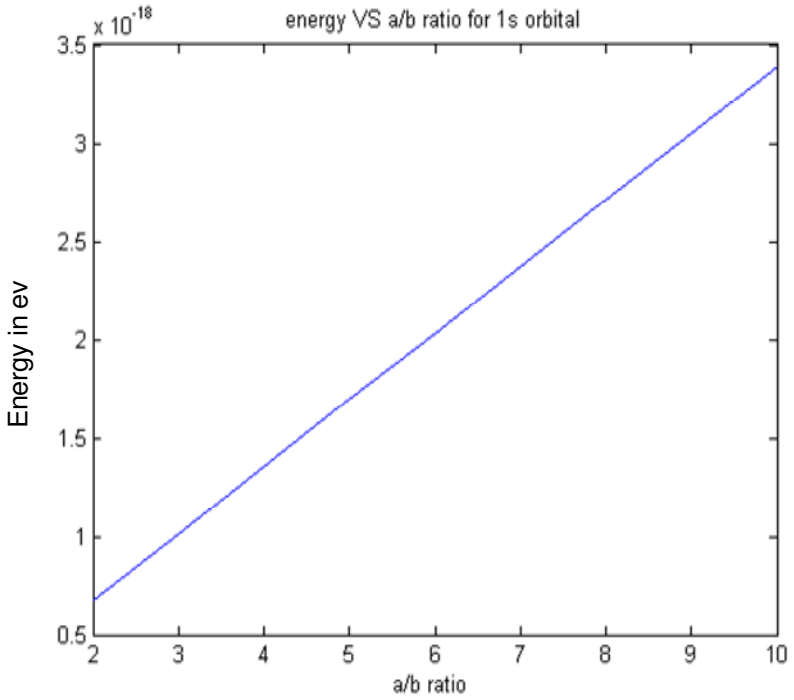

Figure 9. Energy variation of Elliptical quantum dot with a/b.

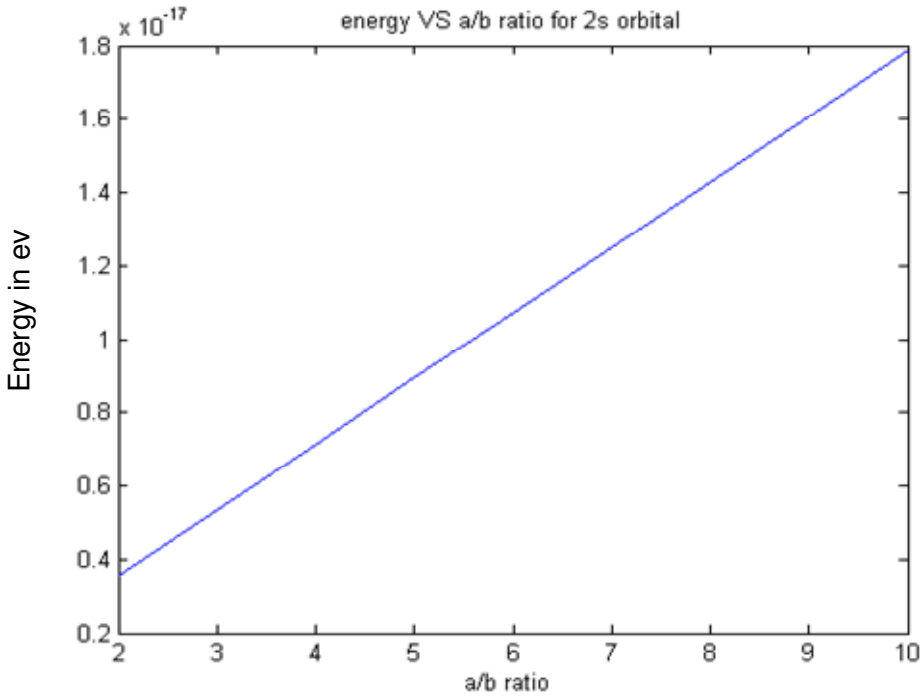

Figure 10. Energy variation of Elliptical quantum dot in 2s orbital.

quantum dots as a function of the a/b that is, the semi major to semi minor axis ratio is calculated and a graph plotted (Figures 9 and 10) (Table 1).

ANALYSIS

On analysis of the approximate values of SHG efficiency

Table 1. Energy eigen values (in eV) of elliptical quantum dot w.r.t a/b.

Orbitals \ a/b ratio	2	4	6	8	10
1s	$1.6951e^{-018}$	$8.4755e^{-020}$	$5.6503e^{-020}$	$4.2378e^{-020}$	$3.3902e^{-020}$
2s	$8.931e^{-019}$	$4.4657e^{-019}$	$2.9771e^{-019}$	$2.2328e^{-019}$	$1.7863e^{-019}$
2p	$1.4426e^{-018}$	$7.2132e^{-019}$	$4.8088e^{-019}$	$3.6066e^{-019}$	$2.8853e^{-019}$
3p	$3.0337e^{-018}$	$1.5168e^{-018}$	$1.0112e^{-018}$	$7.5842e^{-019}$	$6.0673e^{-019}$
3d	$3.9575e^{-018}$	$1.9788e^{-018}$	$1.3192e^{-018}$	$9.8938e^{-019}$	$7.9151e^{-019}$
4s	$4.0754e^{-018}$	$2.0377e^{-018}$	$1.3585e^{-018}$	$1.0188e^{-018}$	$8.1507e^{-019}$
4p	$5.2033e^{-018}$	$2.6016e^{-018}$	$1.7344e^{-018}$	$1.3008e^{-018}$	$1.0407e^{-018}$
4d	$6.416e^{-018}$	$3.2084e^{-018}$	$2.1389e^{-018}$	$1.6042e^{-018}$	$1.2834e^{-018}$

obtained for spherical and cubical CdS quantum dot for the given input excitation, it is found that the cubical quantum dot has a higher efficiency than the spherical one. This may be accounted due to the greater electron confinement in a Cubical quantum dot. The Interband transition is found to exhibit a higher efficiency as compared to intraband. No conclusion can be made definitely for elliptical quantum dots under the given assumptions. But it is seen from the graphs obtained that the energy (in ev) increase with the increase in the (a/b) ratio.

DISCUSSION

The enhancement of the quadratic response (efficiency) upon decrease in the particle size amounts to 6 orders for metal particles (taking Silver) and 5 orders for semi conductor (taking CdSe) (Aktsipitrov et al., 1995).This experiment has laid the foundation for this theoretical work. However we have proposed to incorporate the effect of crystal sizes and shapes. For a cubical quantum dot with infinite barriers, inter-sublevel transitions are only allowed between states with odd difference quantum numbers along the same axes. So the near resonant transitions are only obtained for a small range of sizes. This is unlike the case of spherical quantum dot where near resonant transitions can be obtained for a wider range.

The volume confinement for a cubical quantum dot is more than that for a spherical quantum dot. Thus for the same size the transition dipole moment for a cubical nanocrystal is greater than that for a spherical quantum dot. This gives a higher susceptibility and efficiency from a cubical quantum dot. The elliptical dots show an increase in the energy with an increase in the (a/b) ratio. However, in the absence of concrete experimental data, no comparison could be made between the elliptical with the cubical or spherical. The interband transitions have been found to be more efficient than the corresponding intraband transition. This may be accounted due to the greater amount of energy released during emission when the particle makes an interband transition.

We have only compared the susceptibility and SHG efficiency values for quantum dots of different shapes. No exact values have been found. More certain parameter values will be required for finding the exact values of susceptibility and efficiency. Also during interband transitions losses and scattering phenomenon have been neglected. Only ideal conditions have been assumed where the quantum dot emits out the same energy as it has absorbed during a transition.

NOMENCLATURE

χ: Second order nonlinear susceptibilty
η: Efficiency of SHG
l: Index for ground state
l': Index for first excited state
l'': Index for second excited state
M_i: Transition dipole moment between states l and l'
M_j: Transition dipole moment between states l' and l''
M_m: Transition dipole moment between states l'' and l
$f(E_l)$: State occupancy factor (suffix denotes the state)
$\gamma_{l\text{-}l'}$: Relaxation parameter(suffix denotes the transition states)
E_l: Energy value of ground state
$\hbar\omega$: Input excitation energy (eV)
j_l: Spherical Bessel function
$g_{l,n}$: Zeros of spherical Bessel function

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