Aside of size and shape, the strain induced by the mismatch of lattice parameters between core and shell in the nanocrystalline regime is an additional degree of freedom to engineer the electron energy levels. Herein, CdS/ZnS core/shell nanocrystals (NCs) with shell thickness up to four monolayers are studied. As a manifestation of strain, the low temperature radiative lifetime measurements indicate a reduction in Stokes shift from 36 meV for CdS to 5 meV for CdS/ZnS with four monolayers of overcoating. Concomitant cross-over of S- and P- symmetric hole levels is observed which can be understood in the framework of theoretical calculations predicting flipping the hierarchy of ground hole state by the strain in CdS NCs. Furthermore, a non-monotonic variation of higher energy levels in strained CdS NCs is discussed.

3.1 Introduction:

Chemically prepared semiconductor nanocrystals (NCs) facilitate control over size, shape, feasibility of doping and formation of core-shell nanostructures in quantum confinement regime [1–5]. Core-shell NCs are anticipated to attain higher photoluminescence (PL) yield and chemical robustness. Uniform growth of inorganic semiconductor layer on core semiconductor NC has not only improved [2,6–8] the PL efficiency but also allowed [9–13] manipulation of the discrete energy levels in multishell NCs called as wave function engineering. Lattice mismatched epitaxial shell formation can generate the interfacial defect levels which adversely affect the PL quantum yield. Strain induced modulations [10,14–16] on the optical properties of semiconductor NCs are conflicting. A forbidden gap is found to blue shift due to induced strain in NCs [17,18]. On the other hand in case of CdSe/CdTe, on generation of strain, reduction in the forbidden gap [19] is observed. Strain induced switchover of direct to indirect [20] as well as indirect to direct [21] bandgap is documented. Due to strain, band alignment of type I to type II core-shell structures, which is characterized by spatial separation of electron and hole is reported [10]. Similarly, change in band alignment from type II to type I is also observed [22]. Diverse strain-induced results dictate a need to probe implications of strain on the electronic and optical properties in further details. Core/shell and alloyed NCs are naturally suitable candidates for studying strain induced effects [23].

Even though, both CdSe and CdS have similar band structure, quantum size effects are profoundly examined in the prototypical system of CdSe due to the availability of highly luminescent and narrow size-distributed NCs. The state of art to prepare CdSe NCs with variety of shapes and luminescence efficiency comparable to that of dye molecules is now well developed. Band-edge emission process in CdSe is understood on the basis of a model [24] that explains exciton fine structure. The electron-hole exchange interaction, crystal field effects and other anisotropic factors lift [24–27] the degeneracy of band-edge exciton states. Consequently, the ground state of the exciton is an optically passive, spin forbidden dark state. On the formation of electron and hole pair, CdSe NCs rapidly relax from upper absorbing states to the dark state, which accounts for the long decay lifetime (about one microsecond at 10 K in contrast to few nanoseconds lifetime for bulk CdSe) and the size-dependent resonant Stokes shift. Value
of spin-orbit splitting is 0.07 eV in CdS while it is 0.42 eV in CdSe causing larger resonant Stokes shift in CdS, compared to CdSe. Yu et al. [28] have found a resonant Stokes shift of ~20-70 meV in CdS which is larger by four times in similar sized CdSe NCs.

Effect of strain on CdSe based core/shell NCs is addressed in the literature [6, 29–31]. The optical properties of CdSe/CdS quantum dots, tetrapods and nanorods are studied [29] by applying hydrostatic pressure. The emission and absorption features are observed to blue-shift or even split in two distinct peaks on strain generation. Similar results are observed [30] by forming thicker shells of CdS on CdSe (enhancing strain on CdSe NCs). Despite these reports, effect of strain on NCs is not comprehended well and the understanding is still in a rudimentary state. Further, strain induced behavior of other semiconductor nanostructures is still an open question. In an isolated report, strain induced effects are manifested [32] as the distinct polarization properties of CdS nanowires due to anisotropic response of A, B, and C excitons.

The smaller spin-orbit coupling in CdS leads to larger resonant Stokes shift and hence forms an important class of materials. Herein, optical absorption and temperature dependent steady state photoluminescence (PL) studies reveal strain induced crossing of higher energy levels as well. The observations can be understood on the basis of reported [16] empirical tight binding method which predict that the strain exerted on CdS lattice can change the symmetry of the ground hole state. Radiative life time measurements from room temperature through 10 K concur with findings of steady state PL and absorption.

As a manifestation of strain, switching of ground state from heavy hole to light hole is observed [33] in case of self-assembled GaAs quantum dots. It may be worthwhile to note here that a size dependent changeover in hierarchy of S- and P- orbital hole levels is predicted [34] in CdS theoretically and later reconfirmed [35] experimentally. In the present work, we discuss the experimental manifestation of the crossing of energy levels in CdS NCs due to strain exerted by ZnS layers.
3.2 Results and discussion:

Here, for convenience, we call CdS core NCs as CdS-0, CdS with 2 ML of ZnS as CdS-2, CdS with 3 ML of ZnS as CdS-3, and CdS with 4ML ZnS shell as CdS-4 NCs. Figure 3.1 depicts HRTEM images and selected area diffraction (SAED) patterns of CdS-0 and CdS-4 NCs. Both CdS-0 and CdS-4 NCs are slightly prolate in shape and have size of 4.3 ± 1.5 nm, and 5.5 ± 1.3 nm respectively. The values of interplanar spacing $d$ are found out from HRTEM that confirm cubic zinc blende phase of CdS-0 and CdS-4 NCs. Lattice constant, $a$, deduced from (111) plane of CdS-0 (Figure 3.1 (a), (b)) and CdS-4 NCs (Figure 3.1 (d), (e)) is 5.89 ± 0.18 Å and 5.65 ± 0.06 Å respectively which amounts to the compression of lattice by ~ 4 %.

![HRTEM image](image)

**Figure 3.1.** (a) HRTEM image of CdS-0 NCs showing inter planar distance, (b) TEM image of CdS-0 NCs (c) electron diffraction (SAED) pattern of CdS-0 NCS, (d) HRTEM image of CdS-4 NCs with inter planar distance, (e) TEM image of CdS-4 NCs, (f) SAED pattern of CdS-4 NCs. Insets in (c) and (f) show size distribution.

Figure 3.1(c) and (f) show SAED pattern of CdS-0 and CdS-4 NCs respectively, which matches with the cubic zinc blende phase of CdS. The lattice constants evaluated from SAED pattern show 3.3 % contraction of CdS lattice on shell formation that is in agreement with the XRD data (Figure AI.1). The compressive strain is quantitatively
measured from x-ray diffraction (XRD) data by employing Williamson – Hall method [23,36,37]. The strain can be calculated using the equation:

\[ \beta \frac{\cos \theta}{\lambda} = \frac{1}{D} + \eta \frac{\sin \theta}{\lambda} \]  

3.1

where, \( \beta \) is the full width at half maximum (fwhm) of XRD peaks, \( \theta \) is the diffraction angle, \( \lambda \) is x-ray wavelength, \( D \) is the effective particle size, and \( \eta \) is the effective strain. The strain is calculated from the slope of the graph wherein \( \beta \cos \theta \) Vs \( 4 \sin \theta \) values are plotted (Figure A1.2) [23,37]. Values of strain observed by Williamson – Hall method are 2.2 % for CdS-0, 2.5 % for CdS-2, 3.7 % for CdS-3 and 4.1 % for CdS-4 NCs (Figure A1.2).

Figure 3.2 shows optical absorption and PL spectra of CdS-0 and CdS-4 NCs at room temperature. Optical absorption features appear at 408 nm (3.04 eV) and 425 nm (2.92 eV), while the second excited state (indicated by * in Figure 3.2) is visible at 373 nm (3.32 eV) and 368 nm (3.37 eV) for CdS-0 and CdS-4 NCs respectively. The first excitonic feature arises due to \( 1S_h-1S_e \) transition. On the other hand, the second excitonic feature, in case of CdS, is from \( 1P_h-1P_e \) transition [16,34].

![Figure 3.2](image)

**Figure 3.2.** Optical absorption and PL spectra of (a) CdS-0 and (b) CdS-4 NCs recorded at room temperature. * indicates excited state transition. Insets show the defect levels for the corresponding NCs.
It is noteworthy that the first excitonic feature (band edge absorption) red shifts whereas the second excitonic feature blue shifts on shell formation. Concomitant red-shift of 0.11 eV in band edge PL emission is observed in CdS-4 (2.84 eV) compared to CdS-0 (2.95 eV) at room temperature. As anticipated, the quantum efficiency of CdS-0 NCs increases from 12 % to 42 % on ZnS shell formation. Moreover, the defect emission observable in CdS-0 at ~ 2.3 eV, diminishes on the shell formation (Figure 3.2 insets). The observed defect emission at lower energy presumably originates from surface states [38]. Appearance of defect related broad band due to partial passivation of CdS NCs is theoretically addressed [39] and agrees well with the experimental works.

In general, the first excitonic feature, of the optical absorption, is explored to study the quantum confinement effect. Recently, the power of second excitonic state to elucidate the quantum size effects is appreciated [40]. In the complex core/shell nano-heterostructures, the first excitonic feature provides the information about electron-hole wave function overlap while the second excitonic feature reports the localization of electron and hole. However, this method provides the information only for NCs without interfacial strain. As is evident from above discussion on structural data, our NCs have strain at the interface. Even though the charge carrier localization in strained NCs cannot be predicted, the intrinsic information of the wave function overlap can always be deduced. The oscillator strength is a measure of [40] wave function overlap and can be estimated from the area under the absorption feature. The oscillator strength is estimated as described by Smith et al. [40].
Figure 3.3. Background subtracted absorption spectra of (a) CdS-0 and (b) CdS-4 NCs.

In Figure 3.3, we show background corrected, room temperature optical absorption spectra of (a) CdS-0 and (b) CdS-4 NCs. Interestingly, on background correction; one can unambiguously locate the peak position of second excitonic feature. Intensity of the second absorption feature increases on shell formation. On 4 ML ZnS cladding, the ratio of oscillator strength of the first transition to second transition is 0.21, while that for CdS-0 is 0.56. A substantial increase in second transition oscillator strength as compared to first transition is observed on shell formation. The tight binding calculations on strained CdS/ZnS core/shell structure is reported by Díaz et al. [16]. These calculations predict that due to strain in CdS/ZnS core/shell structure, $S$-type hole wave function is localized [16] near the interface, whereas $S$-type electron wave function has a maximum amplitude at the center, resulting in the smaller overlap which reduces the oscillator strength of the first excitonic feature. On the other hand $P$-type hole wave function is centralized in the core region yielding higher overlap that results into the higher value of the oscillator strength of the second excitonic feature. Our data provides the direct experimental proof for these calculations.

In fact, the calculations indicate that [16,41,42] $P$-type symmetry of hole ground state for smaller-size CdS NCs changes to $S$-type symmetric hole state above a critical size. Irrespective of size, the electronic ground state is $S$-type. The underlying reason for
the characteristic trend lies in the small spin-orbit coupling in CdS NCs. The crossover of hole states is also possible in other II-VI semiconductors. Due to the smaller value of spin-orbit coupling, the hole level mixing takes place and crossover is visible for larger CdS NCs compared to CdSe \[28,35\]. Theoretical studies \[16\] predict the similar changeover of hierarchy of electronic energy levels of CdS by lattice strain. As evident from Figure 3.3, the first absorption feature red shifts and the second feature blue shifts. The red shift of the first excitonic feature indicates a reduction in the gap between S type electron and hole states. The blue shift in the second optical absorption feature indicates increase in gap between the P type electron and hole states. Furthermore, the electronic energy levels are relatively immune to change in shape and size, while the hole energy states are sensitively altered \[16,28,34,35\]. The reduction in gap of S type energy states thus imply that the 1S hole levels are shifting up in energy. However, the increased gap between P states shows lowering energy of P type hole state. As the hole ground state in CdS has a P type symmetry, these findings indicate shifting of hole energy levels due to shell induced strain. The present result supports the anticipated lowering of P hole level with respect to S hole level as a manifestation of induced strain on the lattice.
Figure 3.4. (a) Photoluminescence spectra of CdS-0, (b) CdS-4 NCs at 10 K with excitation energy 3.3 eV (375 nm), (c) Photoluminescence excitation spectra of CdS-0 recorded by holding the emission energy at 2.99 eV constant and (d) CdS-4 NCs (emission energy at 2.89 eV) at 10 K along with fitted Gaussian peaks (blue lines). Inset for (d) shows schematic of transition energies.

The effect of size as well as strain on the energy level can further be probed using PLE spectroscopy at low temperature (at 10 K). Figure 3.4(a) and (b) depict normalized PL spectra of CdS-0 and CdS-4 NCs at 10 K with excitation wavelength of 375 nm (3.3 eV). In CdS-0 NCs, the defect emission substantially increases at 10 K as compared to RT. The observation of surface and interfacial traps at low temperature is reported recently [38,43,44]. Midgap states respond to temperature and its intensity increases with decrease in temperature. A feeble defect emission is also observable for CdS-4 NCs. However, the intensity of band edge emission is predominant with respect to the defect level emission for CdS-4 NCs. Appearance of defect level emission of CdS-4 NCs indicates that interfacial defects are present, albeit weaker in the number. These interfacial defects could be induced by ZnS shell formation.

PLE spectra of CdS-0 (Figure 3.4(c)) and CdS-4 NCs (Figure 3.4(d)) at 10 K are analyzed to understand the energy level structure. The transitions in PLE spectra are labeled as $E_1$, $E_2$, $E_3$, and $E_4$ for $1S_{3/2}^h-1S_e^e$, $1S_{1/2}^h-1S_e^e$, $1P_{3/2}^h-1P_e^e$, and $1P_{1/2}^h-1P_e^e$. 

49
respectively. Transition energies as a function of size of CdS NCs are obtained [45] using size selective PLE measurements and are presented in Table 3.1.

<table>
<thead>
<tr>
<th>size (nm)</th>
<th>emission energy (eV)</th>
<th>E₁(eV) 1S₃/₂ -1Sₑ</th>
<th>E₂(eV) 1S₁/₂ -1Sₑ</th>
<th>E₃(eV) 1P₃/₂ -1Pₑ</th>
<th>E₄(eV) 1P₁/₂ -1Pₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.75</td>
<td>2.99</td>
<td>3.017(± 0.006)</td>
<td>3.103(± 0.007)</td>
<td>3.308(± 0.001)</td>
<td>3.416(± 0.014)</td>
</tr>
<tr>
<td>3.35</td>
<td>3.02</td>
<td>3.108(± 0.007)</td>
<td>3.180(± 0.014)</td>
<td>3.326(± 0.000)</td>
<td>3.424(± 0.003)</td>
</tr>
<tr>
<td>3.01</td>
<td>3.1</td>
<td>3.199(± 0.007)</td>
<td>3.243(± 0.035)</td>
<td>3.454(± 0.018)</td>
<td>3.684(± 0.008)</td>
</tr>
<tr>
<td>2.87</td>
<td>3.14</td>
<td>3.238(± 0.021)</td>
<td>3.312(± 0.013)</td>
<td>3.545(± 0.023)</td>
<td>3.651(± 0.017)</td>
</tr>
<tr>
<td>3.75**</td>
<td>2.89</td>
<td>2.926(± 0.002)</td>
<td>2.974(± 0.001)</td>
<td>3.324(± 0.000)</td>
<td>3.489(± 0.048)</td>
</tr>
</tbody>
</table>

**Table 3.1:** PLE peak positions for CdS-0 NCs at 10 K probed for different sizes. The last row is for CdS-4 sample. *Sizes are calculated based on semi-empirical formula [46]

\[
D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29
\]

**Size of CdS-0 core NCs of CdS-4 sample**

Difference between various energy levels is found by subtracting the transition energies. For example, difference between emission energy and E₁ represents the energy difference between 1S₃/₂ and 1P₃/₂ hole levels. The separation between energy levels is summarized in Table 3.2. In case of CdS NCs, the lowest excitonic hole level (HOMO) is 1P₃/₂, whereas the lowest excitonic electron level (LUMO) is 1Sₑ [34]. The transition from 1P₃/₂ to 1Sₑ is very weak due to the disparity in symmetry of involved states. [34]

As a result, the first absorption feature is due to the 1S₃/₂-1Sₑ [34] transition, while the emitting transition is 1Sₑ-1P₃/₂ [34], which invariably leads to the larger resonant Stokes shift for CdS NCs. With increasing size, energy difference between 1P₃/₂ and 1S₃/₂ levels diminishes, and eventually cross each other to have 1S₃/₂ as a ground hole state at a critical size [28,35,41].
Table 3.2: Separation between hole energy levels for varying sizes of CdS-0 NCs. The last row is for CdS-4 sample. *Sizes are calculated based on semi-empirical formula [46]

\[ D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29 \]

**Size of CdS-0 core NC of CdS-4 sample

Schematic of size dependent hierarchy of energy level is depicted in Figure 3.5(a), while the effect of strain on the energy level hierarchy is presented in Figure 3.5 (b). Figure 3.5(c) depicts separation of hole energy levels as a function of size and ZnS cladding. The separation between the energy levels on shell formation is shown by the dotted rectangle. Hollow triangles in Figure 3.5(c) represent energy separation between 1P_{3/2}^h and 1P_{1/2}^h which varies weakly with size of NCs. Similarly hollow squares represent the separation between 1S_{3/2}^h and 1S_{1/2}^h hole energy levels, which is also weakly size-dependent. The separation between S (1S_{3/2}^h and 1S_{1/2}^h) and P (1P_{3/2}^h and 1P_{1/2}^h) levels varies in a subtle fashion with the size. Larger hole effective mass leads to weak size dependence of these energy levels.

However, if one looks at the separation between S and P levels, the behavior is complex. The lower panel of Figure 3.5(c), shows the variation in separation of S and P levels, where solid triangles represent the separation between 1S_{1/2}^h and 1P_{1/2}^h and solid squares represent separation between 1S_{3/2}^h and 1P_{1/2}^h. The separation between 1S_{1/2}^h and 1P_{1/2}^h levels reduces with increasing size, whereas the separation between 1S_{3/2}^h and 1P_{1/2}^h increases with the size. The reduction in gap between 1S_{1/2}^h and 1P_{1/2}^h implies

<table>
<thead>
<tr>
<th>size (nm)</th>
<th>emission energy (eV)</th>
<th>separation between 1S_{3/2}^h and 1S_{1/2}^h (eV)</th>
<th>separation between 1P_{3/2}^h and 1P_{1/2}^h (eV)</th>
<th>separation between 1S_{3/2}^h and 1P_{1/2}^h (eV)</th>
<th>separation between 1S_{1/2}^h and 1P_{1/2}^h (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.75</td>
<td>2.99</td>
<td>0.086</td>
<td>0.108</td>
<td>0.081</td>
<td>0.003</td>
</tr>
<tr>
<td>3.35</td>
<td>3.02</td>
<td>0.072</td>
<td>0.098</td>
<td>0.01</td>
<td>0.062</td>
</tr>
<tr>
<td>3.01</td>
<td>3.1</td>
<td>0.07</td>
<td>0.1</td>
<td>0.011</td>
<td>0.07</td>
</tr>
<tr>
<td>2.87</td>
<td>3.14</td>
<td>0.074</td>
<td>0.106</td>
<td>0.008</td>
<td>0.066</td>
</tr>
<tr>
<td>3.75**</td>
<td>2.89</td>
<td>0.048</td>
<td>0.165</td>
<td>0.129</td>
<td>(-0.081)</td>
</tr>
</tbody>
</table>
these levels are pulled closer to each other, and increased gap between $1S^h_{3/2}$ and $1P^h_{1/2}$ implies the levels are pushed apart from each other.

Figure 3.5. (a) Energy level diagram for CdS-0 NCs with the highest size and the lowest size (deduced from PLE), (b) for CdS-0 and CdS-4 NCs, (c) change in the hole energy levels with size and on shell formation (marked with dotted box).

From Figure 3.5(a) it is clear that for smaller NCs the ground hole level is $1P^h_{3/2}$, the next level is $1S^h_{3/2}$ which is followed by $1P^h_{1/2}$, and $1S^h_{1/2}$. This shows that both $S$ type levels are shifting up in energy with increase in size. In other words, the hole state with $S$-symmetry increases in energy, and that with $P$-symmetry decreases in energy. This is in agreement with the previous reports [34,41] which say that the first two hole ($1S^h_{3/2}$ and $1P^h_{3/2}$) levels cross each other as size is reduced. In the present work, the change in excited hole levels, along with the change in well documented ground hole state, as a function of size is mapped. The difference in electronic states is calculated from the PLE data by taking difference between $E^e_3$ and emission energy. The separation between $1S^e$ lowest electronic state and $1P^e$ the first excited electronic state is found to increase monotonically with the reduction in size in accordance with quantum confinement effect.
The effect of strain on ground hole state is elaborated in the literature [16,42]. Here, we observe that inducing strain by over coating CdS NCs by ZnS shell drastically affects energies of second and higher excited states. The energy level separations in case of CdS-4 NCs are deduced from PLE spectra and are presented in Figure 3.5(c) in dotted region. This behavior is quite complex, compared to size induced change in the energy levels which shows a weak size dependence. Size has a negligible effect on separation between S levels (or P levels). The plot clearly indicates that on shell formation S levels are coming closer to each other, whereas, P levels are going away from each other. From the lower panel of Figure 3.5(c) it is clear that on shell formation, difference between $1S_{1/2}^h$ and $1P_{1/2}^h$ decreases on the other hand the separation between $1S_{3/2}^h$ and $1P_{1/2}^h$ increases. This lead to the conclusion that $1P_{1/2}^h$ level is shifting down in energy. It is worthwhile to note that the difference between $1S_{1/2}^h$ and $1P_{1/2}^h$ is negative (Table 3.2) indicating that the two levels are crossing each other. The up shifting of $1S_{3/2}^h$ and down shifting of $1P_{1/2}^h$ levels explain the reduced separation of $1S_{3/2}^h$-$1S_{1/2}^h$ and increased separation of $1P_{3/2}^h$ and $1P_{1/2}^h$. In literature the change in hierarchy of the ground ($1S_{3/2}^h$ and $1P_{3/2}^h$) hole levels is predicted. Here, we have demonstrated that the deeper lying $1S_{1/2}^h$ and $1P_{1/2}^h$ levels are also crossing over due to induced strain. However, the hierarchy of the ground $1P_{3/2}^h$ and $1S_{3/2}^h$ hole level is difficult to explain using the current data. Moreover, as one of these levels ($1S_{3/2}^h$ and $1P_{3/2}^h$) is involved in emission process, the hierarchy can easily be explained using temperature dependent TRPL measurements.

In Figure 3.6, we compare PL lifetime curves of CdS-0, CdS-2, CdS-3 and CdS-4 NCs at room temperature (RT) and at 8 K (LT). For CdS-0, CdS-2 and CdS-3 NCs, PL decay curves are biexponential, whereas decay curve on cladding shell of four ML is single exponential. Values of room temperature lifetime for CdS-0, CdS-2, CdS-3, and CdS-4 are given in Table 3.3.
Table 3.3: Lifetimes of core and core/shell NCs at room temperature (300 K) and low temperature (8 K).

Fast component of lifetime is usually attributed [47] to internal core states, while slow component is related [48] to surface traps. With thicker shells on CdS NCs, the surface traps are passivated, giving the mono exponential lifetime. The slower component does not show temperature dependence. Moreover, as this component is from surface states, only faster lifetime component is considered for further analysis. The lifetime reduces from 16 ns (RT) to 10.2 ns (LT) in case of CdS-0 NCs whereas, for CdS-2 NCs the lifetimes are 11 ns (RT) and 8.5 ns (LT).

![Image of PL Intensity vs Time graphs for CdS and CdS/ZnS NCs at 300 K and 8 K](image)

**Figure 3.6.** Room temperature (300 K) and low temperature (8 K) radiative lifetime curves of CdS-0, CdS-2, CdS-3 and CdS-4 NCs.

It has been reported earlier [28,35] that at room temperature, CdS NCs with size of 2.2 nm or above show relatively long lifetime as emission is from optically forbidden
transition (between \(S\) electron and \(P\) hole levels) which would be thermally populated, besides optically allowed transition. On lowering the temperature, only optically allowed energy levels (\(S\)-type symmetric hole and \(S\)-type symmetric electron) would be populated, as they are at lower energy. At low temperature, the emission is from optically allowed transition (optically forbidden levels (\(P\)-type symmetric hole) are not populated and hence do not contribute in the emission), yielding the shorter lifetime [35]. This is evident from Table 3.3. Prolonged lifetime is observed for CdS-3 NCs at low temperature (13 ns) as compared to room temperature (7 ns). Further, on cladding 4 ML ZnS, PL lifetimes are 13.2 ns (LT) and 7 ns (RT). Temperature dependence of radiative lifetime is different for CdS-0 compared to CdS-3 and CdS-4 NCs. Opposite trend of lifetimes in case of CdS-3 and CdS-4 NCs is due to the fact that shell formation reverts transition from optically allowed to forbidden. In short, hierarchy of \(P\) hole levels and \(S\) hole levels changes, affecting the lifetimes of the NCs [35,49].

The experimental observations can be further understood with the help of a model [35] based on the transitions between \(S\)-symmetric electrons and \(S\)- and \(P\)-type hole levels which are closely spaced. The model assumes that the optically forbidden state lies below optically active state with separation between the two levels being \(\Delta\) [50]. The decay rate, \(\Gamma = \tau^{-1}\), using Boltzmann statistics can be given as:

\[
\Gamma = \frac{\Gamma_1 + \Gamma_2 e^{-\Delta/k_BT}}{1 + e^{-\Delta/k_BT}}
\] 3.2

A thermal distribution of excitons within these two levels is considered. \(\Gamma_1\) and \(\Gamma_2\) are decay rates of optically forbidden and optically allowed states respectively and are derived from fitting temperature dependent lifetime using Equation 3.2. In Figure 3.7 (a) solid lines depict curve representing Equation 3.2. From fitting, it is observed that the separation, \(\Delta\) between the two levels decreases with shell formation (36 meV for CdS-0 and 5 meV for CdS-4 NCs). The energy difference between \(S\)-type and \(P\)-type symmetric hole states is as small as 5 meV due to the strain generated in the lattice. Such a small energy difference would tend to mix the hole levels and re-distribute [35] the oscillator strength.

Dependence of shell thickness on transition rates is plotted in Figure 3.7 (b). It indicates reduction in \(\Gamma_1\) and improvement in \(\Gamma_2\) with increase in shell thickness (Figure 3.7(b)). The figure also shows a crossover in \(\Gamma_1\) and \(\Gamma_2\). The crossover is understood in
terms of change in the hierarchy of hole energy levels with increase in cladding. For CdS NCs, \( \Gamma_1 \) (ground state transition) is less than \( \Gamma_2 \) (excited state transition), which is a signature of forbidden ground state transition, which involves \( P \)-type hole levels [35]. Further, cladding three or four ML of ZnS, lead to the higher value of \( \Gamma_1 \) than \( \Gamma_2 \). This shows that for higher shell thickness, ground state transition is allowed with \( S \)-symmetry holes.

![Figure 3.7](image)

**Figure 3.7.** (a) Change in decay time of CdS-0, CdS-2, CdS-3 and CdS-4 NCs with temperature. Solid lines represent the best fit to the experimental data by equation 3.2. (b) Decay rate (\( \Gamma \)) with increase in shell ML. \( \Gamma_1 \), and \( \Gamma_2 \) are transition rates of ground and first excited levels respectively.

Using PLE data we have already proved that the deep lying \( 1S_{1/2}^h \) and \( 1P_{1/2}^h \) energy levels are crossing each other. Here using temperature dependent TRPL, we have demonstrated that the induced strain alters the ground state from \( 1P_{3/2}^h \) to \( 1S_{3/2}^h \). According to the tight binding model [16], strain at the interface causes localization of \( S \) type charge carriers near the interface [16] thus making \( S \) symmetry state the hole ground state. On the other hand the \( P \) type holes are accumulated in the core of CdS [16]. This accumulation of charges away from the core and at the center of core causes the change in the energy of these charge carriers, effectively changing the energy hierarchy of ground state [16]. We infer that this localization of \( S \) type charge carriers is responsible for the change in hierarchy of \( S \) type and \( P \) type energy levels in the NCs. Our results provide direct experimental proof to these theoretical calculations.
3.3 Conclusions:

In conclusion, we have studied implications of strain on the first and higher excited states of CdS NCs indicating redistribution of the oscillator strength which is a signature for variation in symmetry of energy levels. The separation between $1S_{3/2}^h$ and $1S_{1/2}^h$ reduces while the separation between $1P_{3/2}^h$ and $1P_{1/2}^h$ increases on the shell formation. With increase in size of CdS NCs, the separation between $1S_{3/2}^h$ and $1P_{3/2}^h$ reduces, however the separation in $P$ levels or $S$ levels is insensitive to size. Over coating CdS NCs with 4 ML ZnS, the Stokes shift (separation between $1S_{3/2}^h$ and $1P_{3/2}^h$ hole levels) decreases. TRPL measurements show reduction in resonant Stokes shift from 36 meV to 5 meV as a consequence of lattice strain. Moreover, TRPL measurements clearly reveal crossover between ground and first excited hole level. This finding is in accordance with the theoretical prediction. Previous reports showed that the ground state hierarchy can be tuned by size. Here, we have provided an experimental proof for change in the hierarchy of the energy level with introduction of interfacial strain. The induced strain not only changes the hierarchy of the ground hole state, but also affects the excited hole states in such a way that they cross each other. Core/shell NCs are often preferred to obtain higher quantum yield. However, strain induced on core NC can be a detrimental factor which affects the radiative lifetime and hence the quantum yield. This work also states the importance of strain on engineering the electron energy levels in semiconductor NCs.
Chapter 3: Strain-induced hierarchy...

References