

## Optical absorption spectra of lead iodide nanoclusters

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Optical absorption spectra of nanoclusters of lead iodide, synthesized by the colloidal technique, have been investigated. It is shown that the absorption peaks are due to different orders of interband transitions of a nominally single size of particles rather than the first-order transitions of a number of discrete sizes of particles, as reported earlier. The model used to explain the spectra of lead iodide has also been used to account for the optical absorption peaks of colloidal mercuric iodide and bismuth tri-iodide. [S0163-1829(98)01443-X]

### I. INTRODUCTION

Quantum-confined lead iodide ( $\text{PbI}_2$ ) nanoclusters have been under investigation for quite some time. Studies on photoluminescence,<sup>1</sup> Raman scattering,<sup>2</sup> photoconductivity, and electroluminescence<sup>3</sup> properties of the material have been reported. The basic idea is to use the natural layered structure of  $\text{PbI}_2$ ,<sup>4</sup> which is expected to facilitate the growth of zero-dimensional quantum-confined nanostructures. The size of the nanoclusters and the uniformity of the same are important factors in such studies. Since these nanoclusters are extremely small and are known to be unstable in air, it is difficult to measure the size directly. Efforts have been made to extract this information from the optical absorption spectra of  $\text{PbI}_2$  nanoclusters synthesized by the colloidal technique.<sup>5-8</sup>

Sandhoff *et al.*<sup>5</sup> observed three, two, and one peaks in the optical absorption spectra of colloidal  $\text{PbI}_2$  nanoclusters in acetonitrile, methanol, and water, respectively and attributed the peaks to crystallites having "magic numbers" of lateral dimensions grouped around 12, 18, and 29 Å having a thickness of about 7 Å. It was suggested that particles of all the three sizes were present in acetonitrile while the smaller two and the smallest size of particles were present in methanol and water, respectively. Transmission electron microscopy appeared to support the conclusions, but the results are not very conclusive since  $\text{PbI}_2$  nanoclusters are known to be unstable outside solution.<sup>2,8</sup> For similar  $\text{PbI}_2$  nanoclusters in 2-propanol, Micic *et al.*<sup>6</sup> reported particle-size distributions around 12, 16, and 25 Å of lateral dimension. It was, however, concluded that the absorption spectra could not be correlated with "magic number" particle sizes and the absorption peaks were attributed to oxidized iodine ions ( $\text{I}_3^-$ ) present in the solution. Roy and co-workers<sup>7,8</sup> generated  $\text{I}_3^-$  ions in a solution using a standard process<sup>9</sup> and recorded the absorption spectra in acetonitrile, methanol, and ethylene glycol, and compared them with the spectra of colloidal  $\text{PbI}_2$  solutions in the same solvents to confirm that the peaks observed in the spectra were due to  $\text{PbI}_2$  nanoclusters rather than due to  $\text{I}_3^-$  ions in the solution. They also determined the size of  $\text{PbI}_2$  nanoclusters to be 29, 18, and 12 Å in acetonitrile, 18 and 12 Å in methanol, and 12 Å in ethylene glycol and glycerol on the basis of optical absorption studies.

Raman scattering is expected to be a useful tool to find the size of nanoclusters in solution. To our knowledge, only

Tang *et al.*<sup>2</sup> reported such a measurement for  $\text{PbI}_2$  nanoclusters to show that the size was as small as 6 Å. The nanoclusters were, however, grown in zeolite supercages by a vapor diffusion method, and the size was controlled strongly by the inner radii of the cages. A study on the nanoclusters directly in the solvent would have been more useful in assessing the size.

In this paper we report room-temperature optical absorption spectra of colloidal nanoparticulate solutions of  $\text{PbI}_2$  in acetonitrile, deionized (DI) water, and methanol. It is shown that the peaks observed in the spectra are due to various orders of interband optical transitions of  $\text{PbI}_2$  nanoclusters of nominally the same lateral dimensions rather than due to first-order transitions of those of different discrete sizes. We show that the same model used for  $\text{PbI}_2$  also explains reported optical absorption spectra of nanoclusters of other layered semiconductors, like mercuric iodide ( $\text{HgI}_2$ ) (Ref. 6) and bismuth tri-iodide ( $\text{BiI}_3$ ).<sup>6,10</sup>

### II. SYNTHESIS OF $\text{PbI}_2$ NANOCCLUSERS, EXPERIMENTS, AND RESULTS

We synthesized  $\text{PbI}_2$  nanoclusters using the standard colloidal route<sup>5</sup> in three different solvents, acetonitrile, DI water, and methanol. 10 ml of aqueous solution of 0.01M lead nitrate was added to 250 ml of the solvent. The solution was then vigorously stirred while a 10 ml aqueous solution of 0.05M potassium iodide was added dropwise to synthesize colloidal  $\text{PbI}_2$ .

Optical absorption spectra of the solutions were obtained at room temperature by the Shimadzu 3101PC UV-visible spectrophotometer at 2 nm resolution in the wavelength range of 600–190 nm by recording values of  $\log_{10}(1/T)$  where  $T$  was the transmittance. Spectra were taken with the corresponding solvent put in an identical quartz glass cuvette as the reference to eliminate any baseline contribution from the solvent. Absorption spectra of the solvents were recorded separately also to ensure that the solvents did not have any absorption peak in the range of the study. Nanoparticulate solutions were systematically diluted to study the concentration dependence of the absorption spectra, particularly for solutions in acetonitrile and DI water since these are the least and the most polar solvents,<sup>5</sup> respectively.

Figures 1, 2, and 3 show absorption spectra of  $\text{PbI}_2$  nanoclusters in acetonitrile, water, and methanol, respectively for

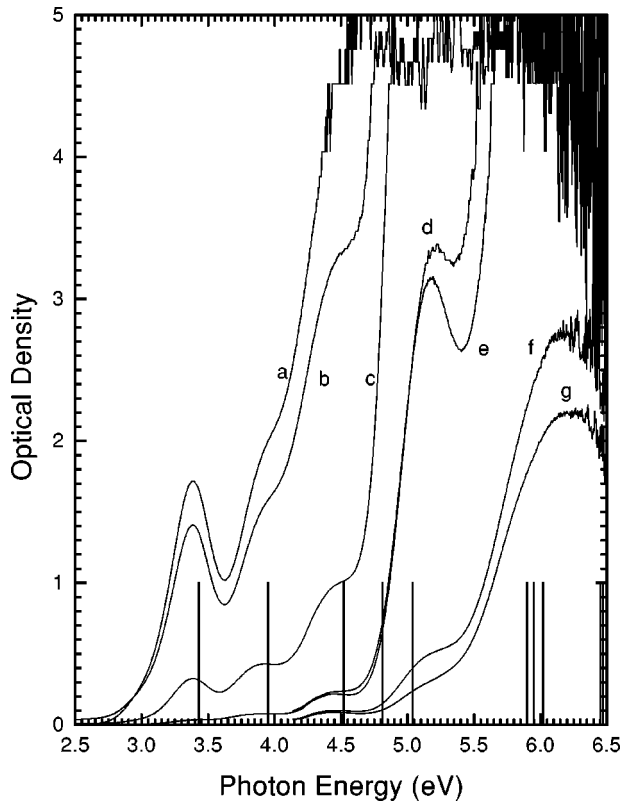


FIG. 1. Optical absorption spectra of  $\text{PbI}_2$  nanoclusters in acetonitrile. Curves labeled  $a-g$  are for decreasing concentrations of the colloidal dispersion. The sample for curve  $g$  is approximately 2000 times dilute compared to that for curve  $a$ . Vertical lines of unit length mark calculated absorption energies of nanoclusters having  $a=1.25$  nm.

different concentrations of the solutions. There are five peaks in the case of acetonitrile, one shoulder and two peaks for water, and two peaks for methanol. It is noted that in all cases, low-energy peaks are more prominent in spectra of concentrated solutions while high-energy peaks appear in sufficiently dilute solutions only. Similar observations were made earlier<sup>6</sup> also. Fluctuations at the high-energy ends of the spectra shown in Figs. 1–3 occur because transmitted light reaching the detector is attenuated to the latter's noise level unless the solution is adequately dilute. This emphasizes the importance of attaining a suitable level of dilution, which may be nominally 1000 times of the original solution, in revealing the complete absorption spectrum. The first peaks in Figs. 1, 2, and 3 are located at 3.38, 4.1, and 3.45 eV, respectively. The first peak in acetonitrile is in good agreement with reported observations.<sup>5,8</sup> The first peaks observed in water and methanol were not reported earlier. The first peak observed at 3.45 eV in methanol, however, compares well with the lowest-energy peak observed at 3.46 eV in a similar solvent, 2-propanol.<sup>6</sup> All the peaks, along with those observed by other workers, are listed in Table I.

### III. DISCUSSION

Attempts were made previously to explain similar spectra by a model based on the effective mass approximation (EMA), where the  $\text{PbI}_2$  clusters were taken as infinitely deep three-dimensional rectangular potential wells.<sup>5,6</sup> However,

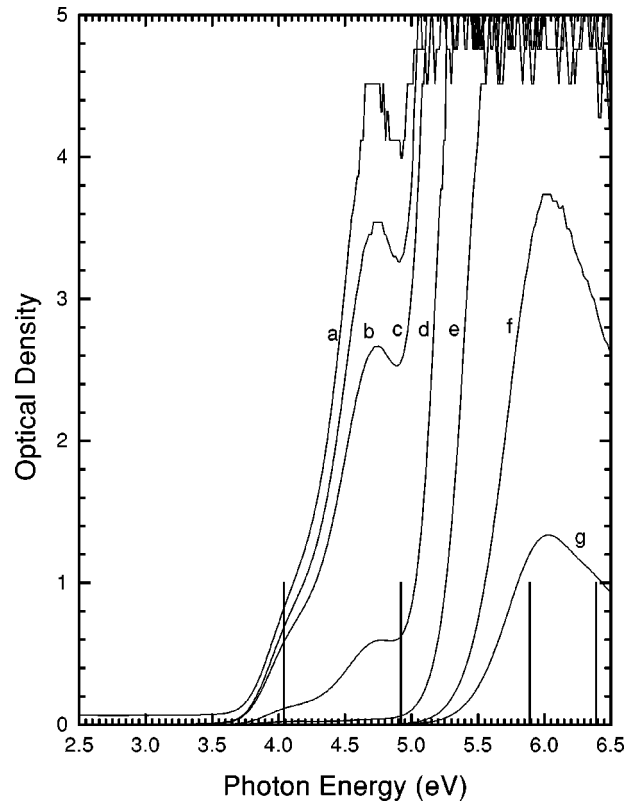


FIG. 2. Optical absorption spectra of  $\text{PbI}_2$  nanoclusters in DI water. Curves labeled  $a-g$  are for decreasing concentrations of the colloidal dispersion. The sample for curve  $g$  is approximately 2000 times dilute compared to that for curve  $a$ . Vertical lines of unit length mark calculated absorption energies of nanoclusters having  $a=0.96$  nm.

$\text{PbI}_2$  has a hexagonal layered structure and nanocrystals of the material are expected to retain the morphological symmetry of the bulk material.<sup>11</sup> We, therefore, model a  $\text{PbI}_2$  nanocluster as an infinitely deep right-circular cylindrical potential well of radius  $a$  and length  $l$ . Using the EMA, the optical absorption energies, of such a quantum dot (QD) in the strong confinement limit, are obtained following Nag and Gangopadhyay<sup>12</sup> as

$$E_{m,s,n} = E_g + \frac{\pi^2 \hbar^2}{2\mu_{\perp} a^2} \left[ \left( \frac{\rho_{ms}}{\pi} \right)^2 + \left( \frac{a}{l} \right)^2 \left( \frac{\mu_{\perp}}{\mu_{\parallel}} \right) n^2 \right]. \quad (1)$$

Here  $E_g$  is the bulk band gap,  $\mu_{\parallel}$  and  $\mu_{\perp}$  are reduced carrier effective masses scaled by the free-electron mass in the directions parallel and perpendicular to the  $c$  axis, respectively, in the material. The quantity  $\rho_{ms}$  is the  $s$ th zero of the Bessel function  $J_m(\rho)$  of order  $m$ , and the quantum number  $n$  takes integral values. Since the morphological symmetry of a nanocluster is assumed to be the same as that of the bulk material, the value of  $(a/l)$  in Eq. (1) is equated to the bulk ratio  $(a_B/c)$ , where  $a_B$  and  $c$  are the lattice parameters of the bulk material in the directions perpendicular and parallel to the  $c$  axis, respectively. The material parameters of  $\text{PbI}_2$  used in our calculations are<sup>13</sup>  $E_g = 2.55$  eV,  $a_B = 4.557$  Å,  $c = 6.979$  Å,  $m_{e\parallel}^* = 1.25$ ,  $m_{e\perp}^* = 0.25$ ,  $m_{h\parallel}^*$ ,  $m_{h\perp}^* = 1.1$ .

The observed absorption energies of  $\text{PbI}_2$  nanoclusters in a particular solvent are correlated to the theoretical model in

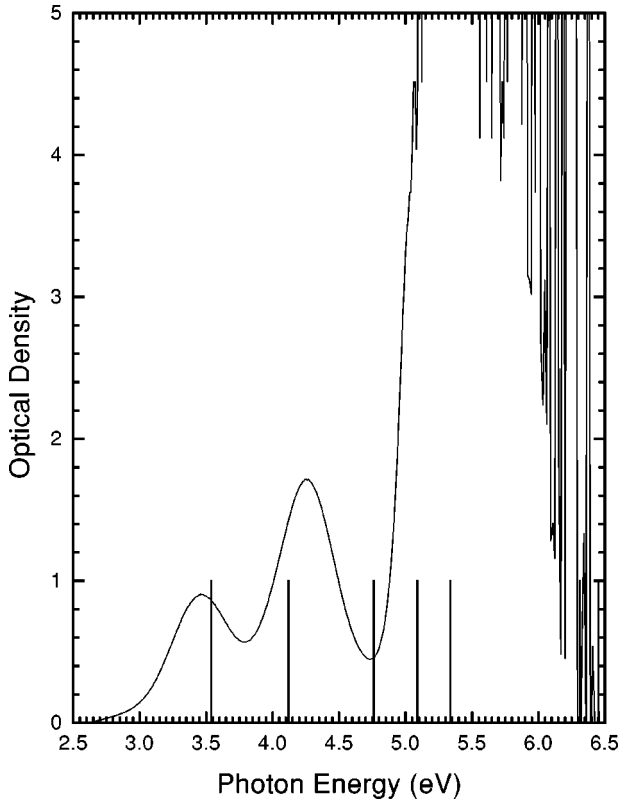


FIG. 3. A typical optical absorption spectrum of  $\text{PbI}_2$  nanoclusters in methanol. Vertical lines of unit length mark calculated absorption energies of nanoclusters having  $a=1.18$  nm.

the following way. The lowest-energy absorption peak is assigned to the first-order transition for  $m=0$ ,  $s=1$ ,  $n=1$  and the radius  $a$  of the nanocluster is calculated from Eq. (1). Successively higher-energy peaks are then assigned to probable higher-order transitions, and corresponding values of  $a$  are calculated. Results obtained for  $\text{PbI}_2$  nanoclusters in acetonitrile, DI water, methanol, and 2-propanol are listed in Table I. The nominal value of radius  $a$  is found to be around 1 nm. For nanoclusters in water, the value of  $a$  calculated for the first-order transition is likely to have some errors since this transition is very weak and the peak position is not very clear. Otherwise, small variations in the calculated values of  $a$  for a particular solvent are likely due to the choice of the same values of effective masses over a wide range of energy. The overall agreement in values of  $a$  across solvents and laboratories is significant and is unlikely to be a coincidence. We suggest that this indicates that the multiple peaks are due to higher-order transitions of the same size of nanoclusters rather than due to first-order transitions of a number of discrete sizes of particles. A closer look reveals that the mean value of  $a$  decreases as the solvent is changed from acetonitrile ( $a \approx 1.25$  nm) to water ( $a \approx 0.96$  nm) through methanol ( $a \approx 1.18$  nm) and 2-propanol ( $a \approx 1.15$  nm), where the polarity of the solvent is increasing in the same sequence. We note this to be somewhat similar to the observation that nanoclusters having smaller lateral dimensions are present in a more polar solvent.<sup>5</sup> The difference is, we do not find the absence of nanoclusters of one or two larger discrete sizes in a more polar solvent, but see the reduction in the mean size of the nanoclusters in monodisperse colloidal solutions. The magnitude of  $a$  also ensures that the condition of strong con-

TABLE I. Absorption peaks of  $\text{PbI}_2$  nanoclusters in different solvents, the assigned orders of transition, and the corresponding calculated values of the lateral dimension.

Solvent	Absorption peaks (eV)	Quantum numbers $n, s, n$	Calculated radius $a$ (nm)
Acetonitrile <sup>a</sup>	3.38	0, 1, 1	1.28
	3.86	0, 1, 2	1.29
	4.48	1, 1, 1	1.25
	5.19	1, 1, 2	1.21
	6.20	1, 1, 3	1.20
Acetonitrile <sup>b</sup>	3.42	0, 1, 1	1.26
	3.95	0, 1, 2	1.25
	4.80	0, 1, 3	1.25
Acetonitrile <sup>c</sup>	3.4	0, 1, 1	1.27
	4.0	0, 1, 2	1.23
	4.8	0, 1, 3	1.25
Water <sup>a</sup>	4.1	0, 1, 1	0.94
	4.75	0, 1, 2	1.00
	6.02	1, 1, 1	0.93
Water <sup>b</sup>	3.95	0, 1, 2	1.25
	4.80	0, 1, 3	1.25
Methanol <sup>a</sup>	3.45	0, 1, 1	1.23
	4.25	0, 1, 2	1.13
Methanol <sup>b</sup>	3.95	0, 1, 2	1.25
	4.80	0, 1, 3	1.25
	5.34	0, 1, 3	1.13
2-propanol <sup>d</sup>	3.46	0, 1, 1	1.22
	4.28	0, 1, 2	1.12
	5.34	0, 1, 3	1.13

<sup>a</sup>Present work.

<sup>b</sup>Reference 5.

<sup>c</sup>Reference 8.

<sup>d</sup>Reference 6.

finement,  $a < 2r_B$ ,<sup>14</sup> or even  $a < 1.5r_B$ ,<sup>15</sup> is valid since exciton Bohr radius  $r_B$  in  $\text{PbI}_2$  is about 1.9 nm.<sup>16</sup>

We calculate the optical absorption spectrum of quantum-confined  $\text{PbI}_2$  QD's to correlate the increasing strengths of absorption peaks observed with increasing photon energy to relative strengths of various orders of interband optical transitions of these QD's. The absorption coefficient,  $\alpha_d$  of a QD is given by<sup>17</sup>

$$\alpha_d = \frac{\omega}{n_0 c} \text{Im}(\chi_d), \quad (2)$$

where  $\omega$  is the angular frequency of the incident light,  $n_0$  is the refractive index of the host material in which the dot is embedded,  $c$  is the velocity of light in free space, and  $\text{Im}(\chi_d)$  is the imaginary part of the electric susceptibility of the QD. For a system of identical cylindrical QD's,<sup>18</sup>

$$\chi_d = \frac{N_0 e^2}{\omega^2 \epsilon_0 m_0} \left[ \frac{2|P_{cv}|^2}{m_0} \left\{ \sum_{m,s,n} g(m,s,n) \times \left( \frac{1}{E_{m,s,n} - \hbar\omega - i\Gamma} + \frac{1}{E_{m,s,n} + \hbar\omega + i\Gamma} \right) \right\} - 1 \right]. \quad (3)$$

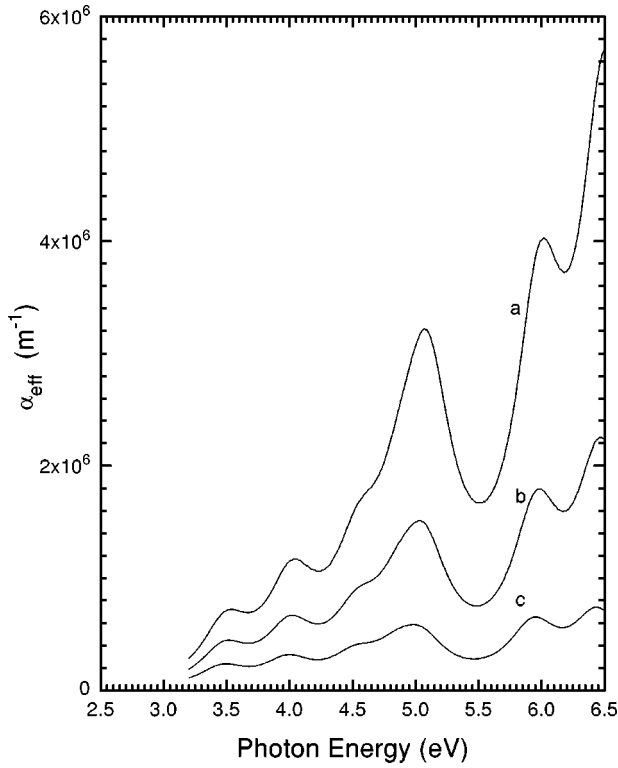


FIG. 4. Typical calculated optical absorption spectra of cylindrical  $\text{PbI}_2$  quantum dots dispersed in acetonitrile for the volume fraction parameter, (a)  $p=0.1$ , (b) 0.05, and (c) 0.025.

Here  $P_{cv}$  is the momentum matrix element for interband transition in the bulk QD material, calculated using the standard expression,<sup>19</sup>

$$|P_{cv}|^2 = \frac{m_0^2 E_g (E_g + \Delta)}{3m_e^* (E_g + 2\Delta/3)}; \quad (4)$$

$N_0$  is the number density of electrons available for transition in a QD;  $g(m, s, n)$  is the possible degeneracy of the energy level  $E_{m, s, n}$ ;  $\Gamma$  is the phenomenological broadening parameter, and all other symbols have usual significance. The absorption coefficient evaluated using Eqs. (2) and (3) does not include the effect of the polarization field produced by neighboring QD's on a given dot. The effective dielectric constant  $\epsilon_{\text{eff}}$  of an ensemble of QD's dispersed randomly in a dielectric host medium is given by<sup>20</sup>

$$\epsilon_{\text{eff}}(\omega) = \epsilon_h \left[ \frac{\epsilon_d(1+2p) + 2\epsilon_h(1-p)}{\epsilon_d(1-p) + \epsilon_h(2+p)} \right], \quad (5)$$

when this collective effect is considered. Here  $\epsilon_d = 1 + \chi_d$  and  $\epsilon_h$  are the average dielectric constants of the host material. It is assumed that the absorption of the host is negligibly small in the frequency range of interest. The parameter  $p$  is the volume fraction of the QD's, defined as the product of the number density of the QD's,  $D_0$ , and the volume of a QD,  $V_0$ . The effective absorption coefficient  $\epsilon_{\text{eff}}$  of the host material containing a dispersion of QD's is then obtained from a relation similar to Eq. (2) with  $\chi_d$  replaced by  $\chi_{\text{eff}}$ , calculated back from Eq. (5).

In a typical calculation  $\Gamma$  has been chosen to be  $0.2E_a$ , where  $E_a$  is the prefactor of the quantity in parentheses in

TABLE II. Absorption peaks of  $\text{HgI}_2$  and  $\text{BiI}_3$  nanoclusters in different solvents, the assigned orders of transition, and the corresponding calculated values of the lateral dimension.

Material	Solvent	Absorption peaks (eV)	Quantum numbers $n, s, n$	Calculated radius $a$ (nm)
$\text{HgI}_2^{\text{a}}$	2-propanol <sup>b</sup>	3.49	0, 1, 1	1.01
		4.07	0, 1, 2	1.02
		4.81	0, 1, 3	1.07
$\text{BiI}_3^{\text{c}}$	Acetonitrile <sup>b</sup>	2.58	0, 1, 1	1.42
		3.35	0, 1, 2	1.06
		3.82	0, 1, 3	1.08
	Acetonitrile <sup>d</sup>	4.35	1, 1, 1	1.09
		5.28	0, 1, 4	0.95
		2.67	0, 1, 1	1.31
		3.46	0, 1, 2	1.02
		4.31	1, 1, 1	1.09

<sup>a</sup> $E_g = 2.14$  eV,  $a_B = 4.357$  Å,  $c = 12.36$  Å,  $m_{e\parallel}^* = 0.25$ ,  $m_{e\perp}^* = 0.29$ ,  $m_{h\parallel}^* = 1.72$ ,  $m_{h\perp}^* = 0.56$  (Ref. 13).

<sup>b</sup>Reference 6.

<sup>c</sup> $E_g = 2.0$  eV,  $a_B = 7.51$  Å,  $c = 20.71$  Å (Ref. 13),  $m_e^* = 0.55$ ,  $m_{h\parallel}^* = 1.67$ ,  $m_{h\perp}^* = 0.35$  (Ref. 6).

<sup>d</sup>Reference 10.

Eq. (1), and  $p=0.1, 0.05$ , and  $0.025$  for increasingly dilute solutions. The parameter  $N_0$  is the product of  $D_0$  and  $\nu$ , the number of electrons available for a transition per QD. In order to estimate the value of  $\nu$ , we note that the topmost and the next six lower valence bands of  $\text{PbI}_2$  are populated by two electrons belonging to the  $6s$  orbital of the lead atom and five electrons of the  $5p$  orbital of each iodine atom,<sup>4</sup> respectively. Thus, in a hexagonal  $\text{PbI}_2$  QD consisting of six lead and 12 iodine atoms,<sup>11</sup>  $\nu$  is expected to be 12 and 60 for transitions involving the topmost and the lower valence bands, respectively. It has been observed that the topmost valence band gets exhausted around 4 eV (Ref. 4) in bulk  $\text{PbI}_2$ . It is, therefore, reasonable to take  $\nu=12$  up to a transition energy of  $(4 \text{ eV} + E_{0,1,1} - E_g)$  in a  $\text{PbI}_2$  QD and  $\nu=60$  for higher energies. The factor  $E_{0,1,1} - E_g$  accounts for the shift due to quantum confinement.

Typical calculated spectra of  $\alpha_{\text{eff}}$  of  $\text{PbI}_2$  nanoclusters in acetonitrile ( $n_0 = 1.34423$ ) (Ref. 21) are shown in Fig. 4. It is evident that the strengths of transitions get enhanced with increasing energy, which is the trend observed experimentally. Such enhancement in the strength of transitions is attributed to the increase in the number of electrons participating in the transitions, and to the collective effect. The latter causes slight blueshift also of the absorption energies. Strengths may increase further if higher-energy levels have larger degeneracy as in the cases of cubic and spherical QD's. In our case, this accidental degeneracy is resolved, and  $g(m, s, n) = 1$ . While comparing the relative magnitudes of absorption peaks observed experimentally with those calculated, it must be kept in mind that the EMA gives poor results with increasing energy. This is a probable reason why calculated strengths of higher-order transitions are not as large as those of the experimentally observed ones, particularly above 5 eV.

We applied the model discussed above to nanoclusters of

other layered semiconductors, like  $\text{HgI}_2$  and  $\text{BiI}_3$ . The optical absorption peaks observed by other workers and the results obtained from our calculations are listed in Table II. It is interesting to note that the calculated values of  $a$  for different orders of transition agree very well with one another for each material. We find that the value of  $a$  obtained for the first-order transition ( $m=0, s=1, n=1$ ) in nanoclusters of  $\text{BiI}_3$  is considerably larger compared to those obtained for higher-order transitions. However, from the published spectra<sup>6,10</sup> we see that the peak positions are not clearly identifiable, which is likely to be the source of this discrepancy.

#### IV. CONCLUSIONS

We have modeled colloidal  $\text{PbI}_2$  nanoclusters by right circular-cylindrical potential wells of finite length and infinite depth, and have shown that peaks observed in the optical absorption spectra are due to different orders of transition of nominally one single size of particles rather than to first-order transitions of various discrete sizes of particles. For this, a study of the absorption spectra of solutions of systematically varying concentration is found to be essential to obtain a complete spectrum because low- and high-energy

peaks are pronounced in relatively concentrated and dilute solutions, respectively. The same theoretical model has been extended to account for absorption peaks of colloidal  $\text{HgI}_2$  and  $\text{BiI}_3$  with similar conclusions. It appears that the colloidal route adopted for synthesizing the nanoclusters is capable of producing monodisperse solutions, which is an interesting area to investigate further. Very recently, Peng *et al.*<sup>22</sup> have reported ‘‘focusing’’ of size distributions of III-V and II-VI semiconductor nanocrystals grown by the colloidal method. They have shown that then growth of selected sizes of nanocrystals is preferred by the growth kinetics. Although  $\text{PbI}_2$  is a IV-VII material, the work of Peng *et al.*, in a way, supports our idea. Our conclusion is of course limited by the fact that the size of the nanoclusters was not measured by a direct method, which is difficult in a colloidal dispersion.

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