IR-active vibrational modes of CdTe, CdSe, and CdTe/CdSe colloidal quantum dot ensembles

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Abstract. The frequencies of the vibrational modes of CdTe and CdSe quantum dots and CdTe/CdSe core/shell nanoparticles prepared by the colloidal chemistry method are determined using IR transmission and IR reflection spectroscopy. The experimental IR transmission spectrum of CdTe and CdSe nanocrystals exhibits a broad minimum located between the frequencies of the transverse (TO) and longitudinal (LO) optical phonons of bulk CdTe and CdSe crystals. The frequencies of the modes for ensembles of CdTe and CdSe quantum dots are considerably shifted toward lower frequencies as compared to those calculated for single quantum dots. This is explained by the dipole-dipole interaction between quantum dots. The frequencies of modes for the structures with core/shell nanoparticles differ little from the calculated frequencies. This suggests a weakening of the interaction in these structures due to the enhancement of dielectric screening.

1. Introduction

Quantum dots (QDs) are attracting considerable interest owing to the specific properties they possess that differ from those of bulk materials, as well as to their obvious application potential. QDs can be prepared by a variety of methods. The methods most widely used at present are based on the self-organization phenomenon. These are the methods of molecular beam epitaxy and colloid chemistry. The letter method can be employed to synthesize microcrystals a few nanometers in diameter. The band gap and luminescence energy of this nanocrystals (QDs) vary with their size. By using various chemical methods, it is possible to prepare colloidal solutions of almost spherical semiconductor nanoparticles with a controlled size [1-3].

Currently, QD structures have been primarily studied using structural and photoluminescence methods. Lattice spectroscopy has been invoked much less frequently. Lattice spectroscopy provides additional valuable information on characteristics important for physics of QDs, such as the elastic stresses, interfaces, shape, composition, and structure of QDs and their interaction with one another.

In this work we investigated the IR transmission and reflection spectra of structures with CdTe and CdSe single-layer and CdTe/CdSe double-layer QDs.
2. Samples
CdTe and CdSe colloidal nanocrystals stabilized by oleic acid were prepared by pulsed nucleation in a high-boiling solvent following a procedure similar to that employed in [3]. Thin film samples for spectroscopic studies were prepared by depositing a few drops of the QD solution in hexane on single-crystal silicon or gallium arsenide substrate, followed by drying in air. According to profilometric measurements the film thickness was of the order of 1 μm.

Transmission electron microscopic studies [3] revealed that the nanoparticles in these films are close to densely packed spheres. The diameter of the CdTe and CdSe nanocrystals as derived from photoluminescence energies [3-7] is of 3-4 nm.

The transmission and reflection measurements were conducted in the spectral range 50–500 cm⁻¹ on a Bruker IFS66V/S Fourier-transform spectrometer with a resolution of 1.5 cm⁻¹ at 300 K. The samples were prepared in the form of thin films consisting of CdTe, CdSe, and CdTe/CdSe nanoparticles (3-4 nm in size) immersed in oleic acid. The films were deposited on the GaAs and Si substrates and had a rough dull surface. The transmission spectra were measured on films deposited on the Si substrate, because silicon is transparent in the range 50 – 400 cm⁻¹.

3. Experiment and Discussion
Figure 1 shows the transmission spectra of a film with CdTe nanocrystals of 4.2 nm in diameter (curve b) and a Si substrate (curve a) at room temperature. The transmission spectrum exhibits a broad minimum located between the frequencies of the transverse (TO = 140 cm⁻¹) and longitudinal (LO = 170 cm⁻¹) optical phonons of bulk CdTe crystals. The transmission band is centered at 152 cm⁻¹. The transmission spectrum of a film with CdSe nanocrystals is shown in figure 2a. A broad transmission minimum is observed between the frequencies of the TO (170cm⁻¹) and LO (210 cm⁻¹) phonons of bulk CdSe crystals and corresponds to 190 cm⁻¹. We also studied nanoparticles consisting of a core and a shell. The cores were CdTe nanocrystals of 4 nm in diameter, and the shell were 1-2 nm thick CdSe layers. The transmission spectrum of a film with these nanoparticles is presented in figure 2b. The spectrum has two minima at 151.2 and 188 cm⁻¹.

The reflection spectra were measured using films with CdTe and CdSe nanocrystals deposited on GaAs substrate. The reflection spectra of the GaAs substrate exhibits a pronounced reflection band at ω = 273 cm⁻¹ without features in the range of lattice vibrations of CdTe and CdSe nanocrystals. The features observed in the lattice reflection spectra and their interpretation for the film/substrate were discussed in [8]. In our case light reflection from the colloidal film is partially diffuse in character due to the complex surface morphology of the film. It makes difficult to perform the dispersion analysis of the reflection spectra with sufficient accuracy. An analysis similar to that described in [8] yielded ω = 146 cm⁻¹ for the vibration frequency of CdTe nanocrystals. This frequency is lower than the frequency of 152 cm⁻¹ determined from the transmission spectra.

Now we consider the experimental results obtained. IR radiation interacts with dipole vibrational modes of the nanocrystals. The frequencies of these modes can be derived from the continuity conditions for the (quasi)electrostatic potential and the induction component normal to the surface (assumed to be spherical). Expanding the potentials inside and outside the quantum dot surface in spherical harmonics leads to the following expression for the frequencies of so-called Frohlich modes [4]:

\[ \omega_F = \omega_{0i} \sqrt{\left( l^2 + \varepsilon_m + l \varepsilon_{0i}\right) / \left( l^2 + l \varepsilon_m + \varepsilon_{\infty i}\right)} \]  

(1)

where \( l \) is the number of the harmonic and \( \varepsilon_m \) is the permittivity of the matrix material. The constants \( \omega_{0i} = \omega_{TO}, \varepsilon_{0i}, \) and \( \varepsilon_{\infty i} \) characterize the dielectric function of the nanocrystal (quantum dot) material, that is,

\[ \varepsilon(\omega) = \varepsilon_{\infty i} + \left( \varepsilon_{0i} - \varepsilon_{\infty i}\right) / \left[ 1 - (\omega / \omega_{0i})^2 \right] \]  

(2)
In order to obtain the frequencies of the vibrational modes of CdTe/CdSe double-layer QD it is necessary to apply the above boundary conditions to the two QD surfaces. As a result, we find the following equation:

\[
[l \varepsilon_i(\omega) + (l+1)\varepsilon_e(\omega)][l \varepsilon_i(\omega) + (l+1)\varepsilon_m] - \rho l (l+1)[\varepsilon_i(\omega) - \varepsilon_e(\omega)][\varepsilon_m - \varepsilon_e(\omega)] = 0
\]

Here function \(\varepsilon_i(\omega)\) coinciding with expression (2) characterizes the material of the QD core and the function \(\varepsilon_e(\omega)\) characterizing the shell material is determined from expression (2) through the replacements \(i \rightarrow e\) and \(\rho = (R_i/R_e)^{2l+1}\), where \(R_i\) is the core radius and \(R_e\) is the radius of the QD shell. Equation (3) is a cubic equation with respect to \(\omega^2\) \((\omega \neq \omega_{0i}, \omega_{0e})\). All solutions of Eq. (3), except those with \(l = 0\), depend on the parameter \(\rho\). Using the constants \(\varepsilon_i\) (10.3 for CdTe, 8.6 for CdSe) \(\varepsilon_e\) (6.9 for CdTe, 6 for CdSe) and the value \(\varepsilon_m = 2.5\) for the oleic acid, at \(l = 1\), we obtain from (1) frequencies of 158.7 and 194.9 cm\(^{-1}\) for the Frohlich modes of CdTe and CdSe single-layer QDs, respectively. Note that these frequencies are noticeably higher than frequencies of 152 and 190 cm\(^{-1}\) corresponding to transmission minima.

The calculated frequencies of the vibrational modes with \(l = 1\) for CdTe/CdSe double-layer QD in oleic acid as a function of the parameter \(\rho\) are plotted in figure 3. For the ratio \(R_i/R_e = 2/3\), we obtain frequencies 149.1, 188.1, and 206.1 cm\(^{-1}\). In this case, the first two frequencies fit very closely to the experimental frequencies. The third high-frequency mode couples only weakly to IR radiation, because the electric field of this mode is concentrated within a narrow layer of the QD shell. This mode is not observed in experiment.

4. Conclusion

Therefore, we can conclude that the experimental mode frequencies of double-layer core/shell QDs very nearly coincide with the theoretical values, whereas the experimental mode frequencies of single-layer QDs are substantially lower those predicted by theory. These differences can be associated with the coupling between the vibrations of different QDs. Let us estimate the coupling between the vibrational modes of QDs. This can be done using the interpolation expression relating the vibrational frequencies of single \(\omega_i\) and coupled \(\omega_i'\) QDs:

\[
\omega_i'^2 = \omega_i^2 + x(\omega_i^2 - \omega_F^2)
\]

where \(x\) \((0 \leq x \leq 1)\) is the volume fraction occupied by the QD material and \(i = TO\) and \(LO\) phonons. Since precise determination of \(x\) from experimental data is difficult, we will solve the inverse problem and find the volume fraction \(x\) from the frequencies \(\omega_i'\) and \(\omega_F\). By assuming that \(\omega_F' = 152.0\) cm\(^{-1}\),

**Figure 2.** IR transmission spectra of:
(a) the Si substrate
(b) a film with CdTe nanocrystals

**Figure 1.** IR transmission spectra of (a) film with CdSe nanocrystals and (b) a film with CdTe/CdSe core/shell nanoparticles.
ω_F = 158.7 cm⁻¹, and ω_i = ω_TO = 140.0 cm⁻¹ for the CdTe QDs, we obtain x = 0.37. By using ω_F’ = 190.0 cm⁻¹, ω_F = 194.9 cm⁻¹, and ω_i = ω_TO = 175 cm⁻¹ for CdSe QDs, we find x = 0.27. Note, that both volume fractions x are smaller than the volume fraction x_c = 0.74 corresponding to closely packed spheres. Taking into account that χ/χ_c = (R/R_c)³, where R_c is the QD radius corresponding to dense packing of spheres, the average gap between the quantum dots can be estimated from the expression 
\[ d = 2(R_c - R) = 2R\left(\frac{x}{x_c}\right)^{1/3} - 1 \]. Assuming R = 2 nm for CdTe QDs and R = 1.5 nm for CdSe QDs, we obtain for the gaps d = 1.03 and 1.19 nm, respectively. Therefore, we arrive at reasonable values of x and d. These parameters are in a good agreement with that determined from the sample density measurements.

The closeness between the calculated and experimental frequencies of the modes in double-layer QDs (core/shell) can be explained by the relatively weak coupling between the vibrations of such QDs. The coupling weakens in this case due to the screening of the electric field associated with the vibrations of one QD component (core) by high permittivity (as compared to that of the oleic acid) of the other component (shell) and vice versa.

**Figure 3.** Calculated frequencies of IR-active modes of CdTe/CdSe core/shell nanoparticles.

Thus, a comparison of the experimental vibrational frequencies of single-layer QDs with those calculated for single QD suggested the conclusion that such QDs are coupled to a considerable extent. The frequency shift resulting from this coupling were used to estimate the gaps between the QDs. The coupling between double-layer QDs is screened substantially. The vibrational modes of double-layer QDs were calculated with due regard for their dependence on the ratio of the layer radii.

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**References**

[1] Alivisatos A P 1996 *J. Chem. Phys.* **100** 13226
[2] Artemyev M V, Bibik A I, Gurinovich L I, Gaponenko S V and Woggon U 1999 *Phys. Rev.* B **60** 1504
[3] Vasiliev R B, Dorofeev S G, Dirin D N, Belov D A, and Kuznetsova T A 2004 *Mendeleev Commun.* **14** 169
[4] Ruppin R and Englman R 1970 *Rep. Prog. Phys.* **33** 149
[5] Didenko Yuri T and Suslick Kenneth S J 2005 *Am. Chem. Soc.* **127** 12196
[6] Peng X, Wickham J and Alivisatos A P 1998 *J. Am. Chem. Soc.* **120** 5343
[7] Yu W W, Wang Y A and Peng X 2003 *Chem. Mater.* **15** 4300
[8] Vodop'yanov L K, Kozyrev S P and Sadof'ev Yu G 1999 *Fiz. Tverd. Tela* **41** 982; 1999 *Phys. Solid State* **41** 893