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FIR Absorption in CdSe Quantum Dot Ensembles

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Absorption of far-infrared (FIR) radiation in very small CdSe crystallites (quantum dots, QDs) via excitation of confined dipolar vibrational modes was studied, both theoretically and experimentally. Spatial quantisation of optical phonons was analysed in the framework of a continuum model, which couples the phonon amplitude to the electrostatic potential via the Fröhlich interaction. The frequencies and oscillator strengths of the dipole-active optical vibration modes are presented calculated for a spherical QD, and for the first time for II–VI QDs these quantised modes were observed experimentally. Another effect studied in this work is the influence of the QD concentration on the FIR absorption of their ensemble. It is shown that the dipole–dipole interaction becomes very important in dense QD ensembles and leads to smearing of the structure in the CdSe phonon band as the QD concentration increases.

1. Introduction The optical properties of semiconductor quantum dot (QD) ensembles in the far-infrared (FIR) spectral region have received much less attention of researchers compared to those in the visible-to-ultraviolet one. This is despite the fact that FIR spectroscopy can probe confined optical phonons and eventually provide information about the electromagnetic interaction between QDs. Spatial quantisation of optical phonons in a spherical QD has been considered theoretically in [1, 2] within a continuum model, which includes phonon dispersion, the associated electric field and the coupling of transverse and longitudinal vibrations via boundary conditions. Some of the predictions of this theory have also been proved experimentally [3]. Nevertheless, the general belief is that the only FIR-active mode, in the phonon response region of a sphere made of a polar material, is the Fröhlich mode. Its frequency does not depend on the sphere radius and is given by

$$\omega_F = \left(\frac{\epsilon_s^\infty \omega_{LO}^2 + 2\epsilon_h \omega_{TO}^2}{\epsilon_s^\infty + 2\epsilon_h} \right)^{1/2}, \quad (1)$$

where ϵ_h is the host dielectric function, ϵ_s^∞ the QD high-frequency dielectric constant and ω_{LO} and ω_{TO} are the longitudinal and transverse optical phonon frequencies, respectively. This result follows from the classical consideration of Ref. [4], which neglects both phonon dispersion and mechanical confinement.

In this communication, we present results of our theoretical analysis, based on the model of [1, 2], for quantised dipolar vibration modes in a CdSe nanosphere. We show

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that its absorption spectrum contains a single mode centred at the Fröhlich frequency given by (1) only if the QD radius is sufficiently large. Our experimental results obtained on very small and highly monodisperse CdSe QDs clearly demonstrate the quantisation of the dipolar phonon modes. We also show the effect of increasing QD concentration on the structure of the FIR absorption band of a QD composite, and explain it by the dipole–dipole interaction between the dots.

2. Theoretical Background The key quantity which determines the FIR response of an ensemble of QDs is the polarisability α of a single sphere of radius R , $\alpha = \alpha_0 + \alpha_1$, where

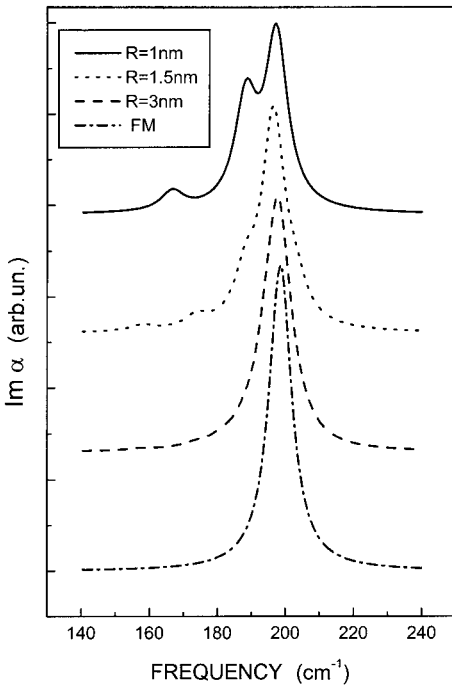
$$\alpha_0 = \frac{\epsilon_s^\infty - \epsilon_h}{\epsilon_s^\infty + 2\epsilon_h} R^3 \quad (2)$$

is a ‘background’ polarisability and

$$\alpha_1 = \frac{3\epsilon_s^\infty \epsilon_h}{(\epsilon_s^\infty + 2\epsilon_h)^2} (\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2) \sum_n \frac{B_n^2}{\omega_n^2 - \omega^2 - i\delta} \quad (3)$$

is determined by the dipolar phonon modes. In (3), n runs over different vibration eigenmodes with angular momentum $l = 1$, ω_n are their frequencies, and the oscillator strengths are given by

$$B_n = \int_0^R (u_r^{(n)} + 2u_\theta^{(n)}) r^2 dr, \quad (4)$$



where the eigenvectors $\mathbf{u}^{(n)}$ are normalised by the condition $\int_0^R (\mathbf{u}^{(n)})^2 r^2 dr = 1$. The eigenfrequencies and eigenvectors are obtained by solving the equations of motion, which include a phenomenological equation for the relative displacement of two ions in the unit cell and a Poisson equation coupling the electrostatic potential associated with a polar vibration to the phonon amplitude [1]. We chose rigid mechanical boundary conditions (the relative displacement vanishes at the sphere surface) and im-

Fig. 1. Imaginary part of the QD polarisability calculated according to Eqs. (2)–(4) for CdSe spheres of different radii. Dash-dotted curve corresponds to the Fröhlich mode (FM), which is independent of the radius

Table 1
Material parameters used in the calculations

parameter	value
bending parameters (cm ⁻² Å ²):	
LO phonon band	2.8 × 10 ⁴
TO phonon band	-1.8 × 10 ³
ω _{LO} (cm ⁻¹)	211
ω _{TO} (cm ⁻¹)	169
damping (cm ⁻¹)	8
ε _s [∞]	6.2
ε _h	1.5

posed the condition of continuity of the potential and electrical induction across the surface.

Some of the calculated results are presented in Fig. 1 (the parameters used are listed in Table 1), from which it can be seen that for very small ($R = 1$ nm) QDs the imaginary part of the polarisability has a multimodal structure. When the QD size increases this structure disappears and a single resonance near the Fröhlich frequency is observed.

Let us turn to the QD concentration effect on the ensemble FIR response. The dipole–dipole interaction in small particle composites has been studied by many authors (see [5] for a review), however, quantum-size effects were not considered. An approach allowing for a strong dependence of the single sphere polarisability on its radius was proposed in [6], but it works only in the low-concentration limit. Here, we adopt the classical Bruggeman approach (original reference can be found in [5]), which is a kind of coherent potential approximation. It is known [7] that, for a strong perturbation (of the dielectric function), such an approximation works well if the concentration of inclusions is not small. A step necessary to incorporate the quantum-size effects in the Bruggeman formula consists of the following. According to the classical definition, the polarisability of a sphere possessing a dielectric function ϵ_s is given by (2) with ϵ_s^∞ replaced by ϵ_s . Let us formally introduce such an ϵ_s for a QD, which would lead to the correct expression for the polarisability given by (2) to (4). This gives

$$\epsilon_s = \epsilon_s^\infty \frac{1 + \frac{8\pi}{3} \alpha_1 / (R^3 \epsilon_s^\infty)}{1 - \frac{4\pi}{3} \alpha_1 / (R^3 \epsilon_h)}. \tag{5}$$

An effective dielectric function ϵ^* of the QD ensemble is then defined by the Bruggeman formula

$$f \frac{\epsilon_s - \epsilon^*}{\epsilon^* + \frac{1}{3}(\epsilon_s - \epsilon^*)} + (1 - f) \frac{\epsilon_h - \epsilon^*}{\epsilon^* + \frac{1}{3}(\epsilon_h - \epsilon^*)} = 0, \tag{6}$$

where f is the volume fraction of QDs.

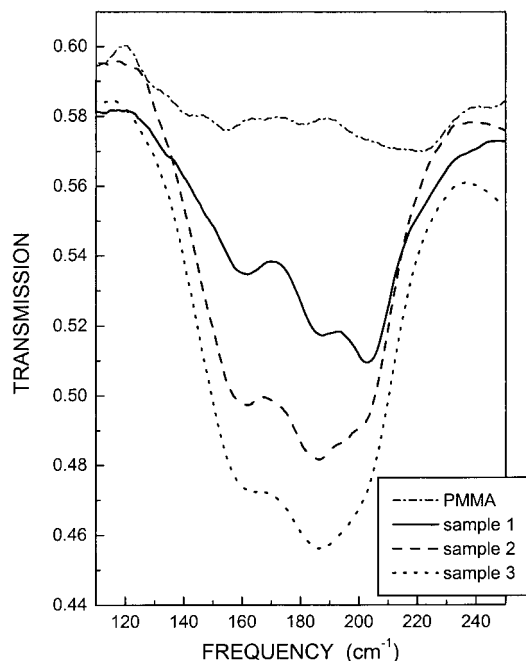
3. Experiment We chose CdSe QDs prepared via a wet-chemical route for checking the theoretical predictions outlined in the previous section. Details of the synthesis pro-

cedure can be found in [8]. Highly monodisperse CdSe nanocrystallites were produced in the form of a colloidal solution in pyridine. They were deposited on silicon substrates as composite films containing isolated QDs (in different concentrations) dispersed in a polymethyl-methacrylate (PMMA) matrix and matrix-free (MF) films consisting of solely QDs. The QD volume fraction for the MF films was estimated to be 30–35%.

The optical absorption spectrum of the QD colloidal solution consisted of a number of quite narrow peaks corresponding to quantised electron-hole states. Using the effective mass approximation (EMA), we obtained a value of $R = 1.6$ nm for the mean particle radius from the position of the first peak ($\lambda_1 = 410$ nm). EMA is known to overestimate the blue shift produced by the quantum confinement, so the actual QD size can be somewhat smaller. Nevertheless, by modelling the optical absorption spectra of the most dilute CdSe/PMMA film (see [9] for details of the modelling procedure) we were convinced that the size dispersion does not exceed 3% of the QD mean size.

We studied the FIR absorption of two CdSe/PMMA films of different QD concentration (approximately 5% and 25%, respectively) and one MF film. Let us emphasize that all three films were prepared from the same colloidal solution. Thicknesses of the films were between 300 and 700 nm. Transmission spectra were taken at room temperature using a Bruker IFS66V FTIR spectrometer. We also checked that the PMMA matrix does not produce any significant absorption in the spectral region of interest.

4. Discussion The transmission spectra given in Fig. 2 show the quantisation of the dipole-active lattice vibrations confined in very small QDs. Three quantised phonon modes are clearly seen for the most dilute film ($f = 0.05$). To reproduce this in theoretical calculations we had to take the QD radius as low as 1 nm (see Fig. 3). However, this number mainly depends on the bending parameter of the bulk LO-phonon band.



There is no experimental data regarding this parameter, so, we took a value obtained by scaling CdS dispersion curves onto the frequency range characteristic of CdSe. Thus, we do not think this is a serious disagreement between the theory and experiment.

As we have mentioned earlier, the structure in the absorption band resulting from the quantum confinement of phonons disappears with an in-

Fig. 2. Experimental FIR absorption spectra for three films with different CdSe QD volume fraction: (1) $f = 5\%$ of CdSe in PMMA, (2) $f = 25\%$ of CdSe in PMMA, (3) MF film. Also shown is the spectrum of the PMMA matrix

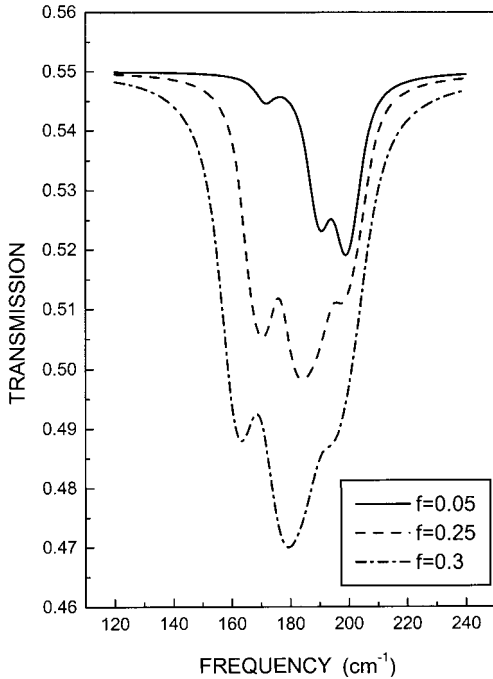


Fig. 3. Transmission spectra of composite films calculated for different filling fractions of CdSe QDs using formulas (5) and (6) for ϵ^* and the single QD polarisability from Eqs. (1)–(3). A Gaussian distribution of the sphere radii with $\langle R \rangle = 1$ nm and $\sigma R / \langle R \rangle = 2\%$ was assumed. The thickness for the $f = 0.05$ film was taken two times as that for the other two films (300 nm)

nificant absorption. Accordingly, the QD polarisability becomes practically independent of the size. On the contrary, for $R \approx 1$ nm the frequencies of the (few) confined modes change considerably with R , so, it is essential to have one-size QDs to observe the spatial quantisation effect.

Our experimental results (Fig. 2) also show the importance of the interaction between QDs. As the QD concentration increases, the structure in the absorption band is smoothed out. At the same time, there is some ‘intensity transfer’ from higher to lower frequency modes. We have been able to model this effect using Eqs. (2)–(6) (see Fig. 3). For low f , the dipole–dipole interaction between the well separated dots is just a perturbation leading to a broadening of the absorption peaks, as predicted by the modified Maxwell-Garnett theory [6]. For dense ensembles, there are fluctuational QD arrangements, which produce low-frequency resonances corresponding to the condition

$$\text{Re} \left[\frac{4\pi}{3} a_1 / (R^3 \epsilon_h) \right] = 1.$$

Accordingly, the centre of the absorption band shifts towards the bulk TO-phonon frequency.

In conclusion, we considered spatial quantisation of optical phonons in CdSe spherical QDs and proposed a generalisation of the Bruggeman formalism for the effective dielectric function of a composite containing very small QDs whose polarisability has a resonant dependence on the QD size. For the first time for II–VI QDs, the quantised dipolar modes were observed experimentally. Also, we demonstrated the effects of increasing QD concentration on the ensemble absorption and explained them in terms of the dipole–dipole interaction between the QDs.

crease of the QD size (Fig. 1). This is why just a single absorption peak near the Fröhlich frequency is normally observed for II–VI QDs (see, for example [10]). It should be emphasized that the Fröhlich mode is not an eigenmode of this problem considering the boundary conditions taken. The number of dipolar modes grows as the QD size increases. However, only those eigenmodes whose frequencies are close to ω_F produce sig-

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