Coherent Acoustic Phonons in a Semiconductor Quantum Dot

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Coherent acoustic phonons in PbS quantum dots are observed using femtosecond optical techniques. This is the first observation of coherent acoustic phonons in a semiconductor quantum dot; the phonons are generated through the deformation-potential coupling to the quantum-dot exciton. The acoustic modes are weakly damped, and we also find extremely weak coupling ($S \sim 0.01$) to the optical modes. These conclusions have important consequences for the vibronic nature of the exciton transition in the quantum dot and its dephasing.   [S0031-9007(97)04822-9]

The electronic and optical properties of semiconductor quantum dots (QD's) have attracted much attention recently due to their interesting physical properties and potential utility in applications. Exciton-phonon coupling is a crucial issue in nanocrystal physics, and this has motivated much of the previous work on the vibrational modes of quantum dots. The coupling to optical modes produces phonon sidebands in the optical transitions. Acoustic modes will also produce sidebands, but the net result of the coupling to numerous, heavily damped acoustic modes is an effective broadening of the zero-phonon line [1]. Therefore, coupling of quantum-dot excitons to acoustic phonons, which generally occurs via the deformation-potential interaction, sets a lower limit to the optical linewidth in QD's. In small dots this linewidth theoretically can be much larger than in the corresponding bulk material [2]. Thus, there is ample motivation to develop a more thorough and direct understanding of the deformation-potential coupling of excitons to acoustic phonons in QD's. The recent observation of ultranarrow luminescence lines from single QD's [3,4] adds to the interest in this problem.

Since the development of reliable sources of sub-100-fs optical pulses, researchers have been using these pulses to generate and monitor terahertz-frequency vibrations in materials. Coherent vibrations have been produced in molecules, semiconductors, insulators, and metals, as well as in artificial structures such as superlattices. (For a comprehensive review of this area, see Ref. [5].) Coherent optical phonons have been reported in QD's of CdSe [6], InP [7], and PbS [8].

The optical vibrational modes of QD's are typically underdamped, and couple strongly to the electronic states via the Fröhlich interaction [9,10]. The acoustic modes of QD's are typically overdamped [11,12], and in some cases are not observed in the Raman spectrum [9,10]. Despite the fact that the acoustic phonon spectrum of a quantum dot is theoretically discrete, there has been no previous report of coherent acoustic phonons in a semiconductor QD.

Because of their large Bohr radii and dispersive phonons, the lead salts offer unique opportunities for studying strong confinement of both charge carriers and phonons. The vibrational modes of PbS QD's in a polymer host are well characterized and understood theoretically [13]. Here we report the generation of coherent acoustic phonons in 3-nm PbS QD's. Short pulses resonant with the lowest exciton transition drive a weakly damped spheroidal acoustic mode via the deformation-potential coupling to the exciton. Interestingly, in the femtosecond experiments we observe only very weak coupling to an optical mode that is prominent in the (time-integrated) Raman spectrum. The implications of these findings for the exciton line shape will be discussed.

The vibrations of spherical elastic particles were first studied by Lamb [14]. Provided that the radius is not too small, the acoustic modes of a QD are accurately described by similar elastic continuum models [12]. Boundary conditions at the surface of the dot result in discrete torsional and spheroidal eigenmodes. The torsional modes are completely transverse, while the spheroidal modes have mixed longitudinal and transverse character. Confined acoustic vibrations have been observed in the low-frequency Raman-scattering spectra of $MgCr_2O_4$-$MgAl_2O_4$ and Cd(S,Se) nanocrystals [11,12]. The mode frequencies and their dependence on size agree well with calculations based on the continuum models.

The effects of confinement on the vibrational modes of QD's of IV-VI materials are dramatic owing to the dispersive phonons and unusual dielectric properties of the bulk materials. The vibrational modes of PbS QD's in a polymer host were determined using resonant-Raman and far-infrared absorption spectroscopies [13]. The results of those experiments agree with theoretical calculations of the optical vibrational modes that account for the mechanical and electrostatic boundary conditions [15,16]. The Raman-scattering spectrum of PbS QD's of diameter 3 nm is shown in Fig. 1(a). The broad peak at $\sim$215 cm^{-1} is assigned to the lowest-order optical mode with angular momentum $\ell = 0$. This mode is purely radial and has eigenfunctions similar to the $\ell = 0$ longitudinal-optical (LO) vibrational modes obtained using dielectric theories [9,17]. The sharp peak at
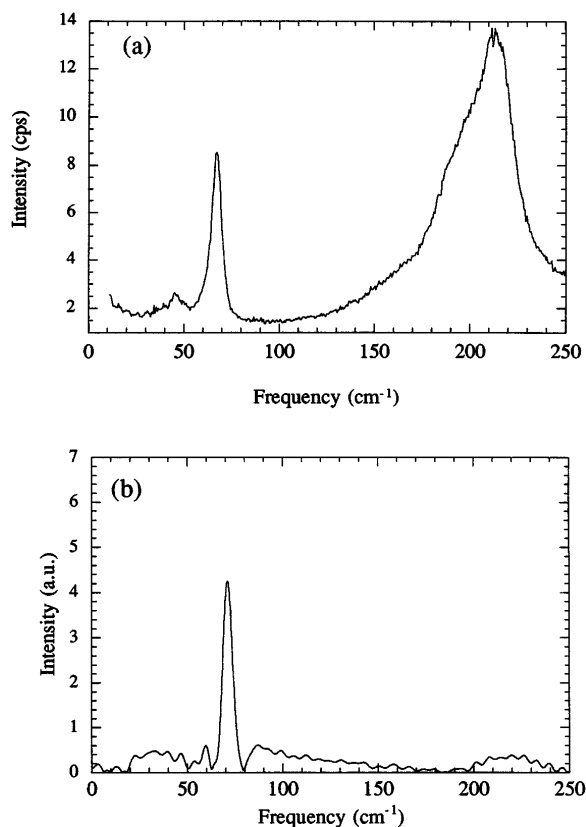
FIG. 1.   Comparison of Raman-scattering and time-domain results. (a) First-order Raman-scattering spectrum of 3-nm PbS nanocrystals recorded at 4.2 K with excitation at 584 nm. Similar spectra were obtained for excitation wavelengths between 580 and 630 nm and temperatures between 4 and 300 K. (b) Fourier-transform amplitude of the time-domain trace shown in Fig. 2. The spectrum has been divided by the power spectrum of the laser pulse to account for the effect of the finite pulse duration.

~ 70 cm^{-1} is due to the lowest-order spheroidal acoustic mode with $\ell = 0$. Briefly, we reach this conclusion based on the magnitude and polarization properties of the peak and the agreement with the theoretical frequency $\omega_a = 68$ cm^{-1} [13]. There is also a small but reproducible peak at 45 cm^{-1} due to the lowest-order spheroidal acoustic mode with $\ell = 2$.

Here we are primarily interested in the spheroidal acoustic mode with $\ell = 0$. Based on the Raman spectrum, it should be possible to drive it impulsively with pulses shorter than ~ 150 fs. With ~ 50-fs pulses the optical mode will also be excited, so a superposition of the two modes is expected.

Measurements were performed on PbS QD's synthesized in an aqueous solution of poly(vinyl alcohol) (PVA) following the procedure in Ref. [18] and subsequently dried into thin films. X-ray scattering confirms the sodium-chloride crystal structure with the bulk PbS lattice constant. The nanocrystal size is 3 nm, with a variation of $\pm 4\%$ [19].

Time-domain data were obtained by measuring saturated absorption in a standard pump-probe setup. Pulses from a Ti:sapphire regenerative amplifier were used to pump an optical parametric amplifier [20], the output of which was frequency-doubled to produce 50-fs pulses, wavelength-tunable across the lowest exciton transition at 600 nm. At the sample the excitation pulses had intensities of $5-10$ GW/cm^2. The absorption of PbS nanocrystals in poly(vinyl alcohol) can be permanently bleached by strong illumination, so the experiments were done with low pulse energies (~ 10 nJ) to avoid any bleaching effects. We were particularly careful to ensure that measurements were made on fresh material and that no permanent photoinduced changes occurred during the acquisition of each experimental trace.

The transient response of the QD's is shown in Fig. 2. The differential transmission of the probe pulse $\Delta T/T$ is plotted versus the time delay between the pump and probe pulses. The damped oscillation due to the $\ell = 0$ acoustic mode is clearly evident, superimposed on the absorption bleaching due to saturation of the exciton. The bleaching recovers as the exciton population decays, probably into defect states. The Fourier transform of the time-domain data is divided by the pulse spectrum to account for the filtering of the finite spectral width and the result is shown in Fig. 1(b) for comparison to the Raman scattering spectrum. The lowest exciton transition of lead-salt QD's is well approximated as a two-level system coupled to a vibrational mode, and in that case the Fourier transform of the time-domain data should be identical to the Raman-scattering spectrum [5]. The 70-cm^{-1} frequency and the damping of the acoustic mode agree well with those measured by Raman scattering. On the other hand, the $\ell = 0$ optical mode is barely observable in the Fourier transform amplitude or through
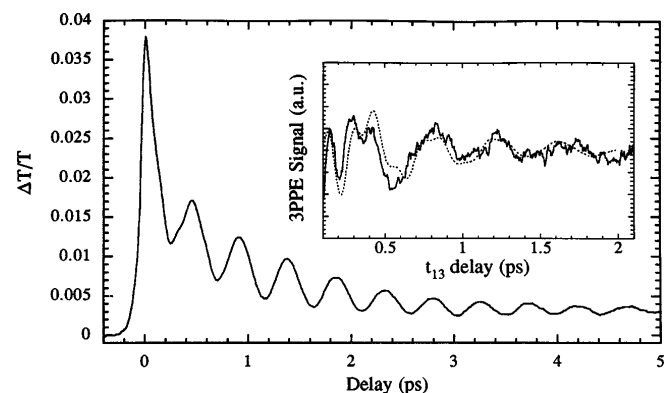

FIG. 2.   The main figure shows a transient saturated-absorption signal. The inset shows a three pulse photon echo signal as a function of delay between the first and third pulses, the delay for which the signal best exhibits the consequences of exciton-phonon coupling. The solid line is experimental data and the dotted line is a theoretical fit using the standard analysis as in Ref. [6]. The exponential decay due to recovery of the exciton population has been subtracted.

its effect on the shape of the first few cycles of the time-domain trace; this will be explained below.

In similar experiments on PbS QD's, Machol *et al.* previously reported the observation of coherent oscillations with a frequency of 90 cm^{-1} [8]. This frequency matches the frequency of a coupled optical mode with $\ell = 1$, which is not Raman active. We have not observed the 90-cm^{-1} oscillation in an extensive series of nonlinear-absorption and four-wave-mixing experiments that includes the results described here. We cannot resolve this discrepancy with certainty, but we did demonstrate that some photobleaching of the PbS/PVA samples is required to produce the induced-absorption signals observed by Machol *et al.* Thus, the appearance of the coupled mode may be peculiar to the photobleached sample.

The interaction of electrons with acoustic phonons arises primarily from deformation-potential and piezo-electric coupling. PbS is not piezoelectric. Takagahara has shown that even in piezoelectric materials the deformation-potential coupling should dominate in small QD's [2]. We calculated the coupling strength using the exciton wave functions of Ref. [19] and the results are shown in Fig. 3 for several values of the difference between the electron and hole deformation potentials $(D_e - D_h)$. The Huang-Rhys parameter S (equal to the interaction energy in units of the phonon energy) is a measure of the exciton-phonon coupling strength. For the 3-nm QD's studied here, $S_{\text{acoustic}} \sim 0.01 - 0.1$ for reasonable values of $D_e - D_h$.

The weak damping of the spheroidal acoustic mode facilitates its observation. To our knowledge there is no treatment of the damping of the vibrational modes of a QD, although it is plausible that there are fewer relaxation pathways in smaller QD's. We find that the width of the Raman peak increases by less than 5% between 4 and 300 K. This suggests that the dominant damping mechanism does not involve other phonons, i.e., that the
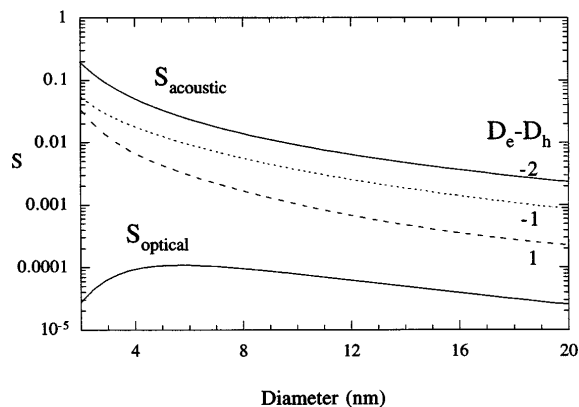
vibration may be damped by radiating energy into the host. The lack of host vibrational modes in the vicinity of the acoustic mode frequency may contribute to the observed narrow linewidth, although there is no obvious reason why PbS should be fundamentally different from other QD's in polymer hosts. The density of acoustic modes in the PbS QD's is somewhat lower than that in QD's studied previously, which contributes to isolating the observed spheroidal mode.

The relative couplings of the electronic states to acoustic and optical modes determines the intrinsic QD lineshape and so deserves some discussion. The time-integrated Raman spectrum (fundamental and overtones) implies that the coupling to the $\ell = 0$ optical mode is large ($S_{\text{optical}} \sim 0.7$) and much larger than the coupling to the $\ell = 0$ acoustic mode [21]. This would imply that the optical mode should appear as a large-amplitude oscillation in the first picosecond of the time-domain trace. However, it is barely observable in the time-resolved experiment. Briefly, we suggest the following explanation [21] for this discrepancy. Trapped charge builds up on the QD's during the steady-state Raman measurements, producing local electric fields. In the presence of trapped charge, the coupling of excitons to polar phonons increases by at least an order of magnitude [17,21]. A measurement that is performed before either charge carrier is trapped (which occurs in picoseconds) should detect the intrinsic coupling to optical phonons. This is expected to be very weak in PbS QD's (S_{optical} in Fig. 3). Thus, the femtosecond time-resolved experiments are sensitive only to the weak coupling of the intrinsic wave function to the optical phonons. The coupling to acoustic modes is not essentially electromagnetic, and so should not be distorted by the trapped charge and associated fields. The trapped charge decays in less than the 1 ms between pulses, so each pair of pump and probe pulses encounters unexcited material.

The generation of coherent acoustic phonons and the absence of coherent optical phonons contrast sharply with previous studies of CdSe and InP QD's [6,7], suggesting major differences in the exciton-phonon coupling between IV-VI and II-VI or III-V materials. Quantitative exciton-phonon couplings cannot be inferred from saturated-absorption data. To obtain the exciton-phonon couplings, we performed three-pulse photon echo (3PPE) measurements, in which the vibrations modulate the electronic polarization. From those measurements (Fig. 2, inset) we infer $S_{\text{acoustic}} = 0.1$ and $S_{\text{optical}} = 0.01$. The relative strengths are consistent with the ratio of the intensities in the Fourier transform of the saturated-absorption data [Fig. 1(b)]. The magnitude of S_{acoustic} is also consistent with the lack of a strong overtone of the acoustic mode in the Raman spectrum, and agrees with the calculated value of S_{acoustic} for reasonable values of $(D_e - D_h)$.

The occurrence of a small number of underdamped acoustic modes has profound implications for the

FIG. 3. Calculated values of the Huang-Rhys factor S for the coupling of the lowest exciton to the spheroidal acoustic mode. $D_e - D_h$ has units of eV. S is the interaction energy in units of the phonon energy. The polar coupling to the optical mode with $\ell = 0$ is also shown.

homogeneous line shape of a QD. Underdamped optical modes produce sidebands. In principle, acoustic modes also produce sidebands that will be observed in the time domain as a coherent modulation or beat of the electronic polarization. However, a quasicontinuum of overdamped acoustic modes will produce an irreversible decay of the dipole coherence and contribute to an effective broadening of the zero-phonon line. This is the case in previous investigations of the exciton dephasing in CdSe and InP QD's [6,7]. The acoustic modes were not observed experimentally; the quasicontinuum of acoustic modes (heat bath) was modeled as a single mode. It is interesting to try to connect the observation of coherent acoustic phonons with the narrow ($\sim$100 μeV) luminescence linewidths of single CdSe QD's [3]. Empedocles *et al.* conclude that coupling to acoustic modes is negligible [3], but it is impossible to estimate the coupling with any accuracy without knowing the frequency of the mode. When the acoustic modes are underdamped, the homogeneous linewidth of the zero-phonon line is not determined by the envelope of phonon sidebands, but by energy fluctuations induced by multiphonon processes or eventually the decay of the exciton population. Thus strong coupling to acoustic modes does not necessarily imply rapid dephasing and a broad homogeneous line. In previous studies of the absorbing transition, strong coupling to a few modes broadens the Franck-Condon envelope, and the zero-phonon line is lost. The results presented here indicate that in the strong-confinement limit the vibronic transitions are in fact recovered. Measurements of the exciton dipole dephasing will be very interesting but require better sensitivity and time resolution than the experiments described here.

A systematic study of the acoustic modes of PbS QD's with variable nanocrystal size will also be valuable. The fabrication of monodisperse PbS quantum dots with variable particle size in a polymer host has not been reported. Saturated absorption measurements of monodisperse PbS quantum dots with controllable particle size (diameter $\geq$4 nm) in an oxide glass host show no evidence of coherent phonons. 3PPE measurements are in progress and should provide the magnitude of the exciton-phonon coupling in these samples.

In conclusion, we observe coherent spheroidal acoustic phonons in PbS QD's. The underdamped acoustic mode appears as a phonon sideband, rather than contributing to the width of the zero-phonon line of the exciton transition. Thus, first-order coupling to the acoustic mode does not contribute to irreversible dephasing of the exciton in these QD's.

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