

Observation of Coupled Vibrational Modes of a Semiconductor Nanocrystal

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Raman scattering and far-infrared absorption spectra of PbS nanocrystals with radii of 2 nm are presented. The experimental results are consistent with theoretical calculations which account correctly for the mechanical boundary conditions at the nanocrystal-host interface, and include the first observation of the mixed or coupled vibrational modes predicted by the theory.

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The electronic and optical properties of semiconductor nanocrystals, also known as quantum dots, have received considerable attention recently, while their vibrational properties have been less thoroughly studied. An accurate description of the vibrational modes of a nanocrystal is of fundamental interest, and is also required to understand the coupling of vibrational modes to electronic charge. The electron-phonon interaction is critical because it fundamentally limits the magnitude of the nonlinear response of a nanocrystal and hence its usefulness for applications such as optical switching.

A nanocrystal is defined as having the bulk crystal lattice, but localized electron and hole wave functions. In the simplest picture, size quantization of the phonons is neglected; the vibrational modes of a nanocrystal are the phonons of the bulk crystal. Multimode theories refine this approximation by confining the phonon wave function to the nanocrystal while retaining bulk dispersion relations [1]. More recent treatments use a classical dielectric model which couples the phonon amplitude to the electrostatic potential via the Fröhlich interaction, but still neglect phonon dispersion [2]. The application of spherical boundary conditions results in confined longitudinal and surface eigenmodes.

For an accurate treatment of materials with dispersive phonons, it is essential to satisfy the appropriate mechanical as well as electromagnetic boundary conditions. Recently, Roca, Trallero-Giner, and Cardona [3] developed a theory for the optical vibrational modes of a quantum dot and showed that correct boundary conditions demand the coupling of longitudinal and transverse modes. In the special case where the vibrational amplitude is completely confined to the nanocrystal, the modes can be classified as coupled or uncoupled. The uncoupled modes are purely transverse, have no associated electrostatic potential, and hence are not expected to be optically active. The coupled solutions have a mixed longitudinal and transverse character involving the mechanical amplitude and the electrostatic potential. Since they involve the electrostatic potential, the coupled modes should be optically active.

Here we report the observation of coupled vibrational modes of a quantum dot. The vibrational modes of PbS nanocrystals 2 nm in radius were studied with resonant Raman scattering and far-infrared absorption spectroscopy. The experimental observations are consistent with theoretical predictions [3,4] and cannot be accounted for by purely electromagnetic theories. This is the first experimental demonstration of the importance of the mechanical boundary conditions to the vibrational modes of semiconductor nanocrystals.

The consequences of correctly accounting for the mechanical boundary conditions will be most significant in the smallest nanocrystals of materials with dispersive phonons. Thus unambiguous observation of the coupled modes will be difficult. Chamberlain, Trallero-Giner, and Cardona showed theoretically that CdS nanocrystals with radii $R \lesssim 1.5$ nm will be needed to distinguish the coupled-mode frequencies from the bulk phonon frequencies [4]. In addition, the theory assumes a two-band parabolic model for the electronic states of the nanocrystal and therefore does not strictly apply to the II-VI compounds, with their valence band degeneracy. Figure 1 shows the

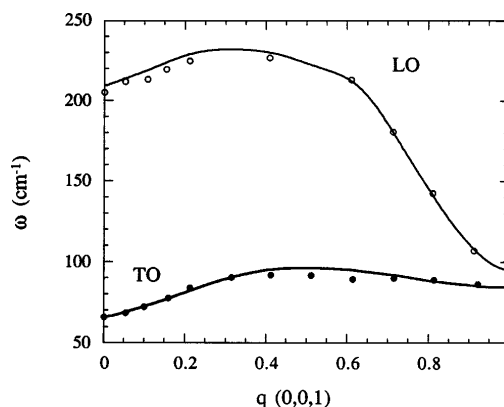


FIG. 1. Optical phonon dispersion in bulk PbS for the Γ -X direction of the Brillouin zone. The symbols are experimental data from [5], and the lines are a guide to the eye. The x axis is in units of $2\pi/a_0$, where a_0 is the lattice constant.

measured optical phonon dispersion of PbS [5]. The optical phonons are highly dispersive, and the longitudinal optic (LO) and transverse optic (TO) frequencies at the center of the Brillouin zone differ by a factor of 3. The dispersive phonons make the lead salts ideal for studies of phonon confinement. Quantum dots of PbS stabilized by poly(vinyl alcohol) (PVA) can be synthesized with radii of 2 nm and a narrow size distribution [6,7]. Furthermore, distinct exciton peaks in the absorption spectrum agree well with solutions of the Schrödinger equation assuming infinite potential wells and nondegenerate, parabolic conduction and valence bands [7]. Among materials which have been fabricated as nanocrystals to date, it appears that PbS is uniquely well suited to test the theory of vibrational modes of a semiconductor nanocrystal.

The theoretical framework given by Roca, Trallero-Giner, and Cardona must be extended slightly for PbS nanocrystals. Analytic solutions for the vibrational modes of a semiconductor heterostructure are only possible for quadratic dispersion relations of the form $\omega \sim q^2$ [8]. As Fig. 1 shows, however, the phonon dispersion in PbS cannot be modeled accurately without additional terms in the dispersion relations. We obtained good fits to the measured dispersion by including linear terms in the dispersion relations. Analytical expressions for the wave vectors of the longitudinal and transverse phonon components were obtained by Roca, Trallero-Giner, and Cardona [3] by imposing the condition that the phonon amplitude vanishes at the nanocrystal/host interface. We modified the secular equations for the phonon wave vectors given in [3] and [4] to account for the linear term in the dispersion relations, and the vibrational frequencies were finally calculated from the resulting wave vectors.

The frequencies of the first five phonon modes with angular momentum $\ell_p = 0$ are shown in Fig. 2(a). These modes are purely radial, and the frequencies approach the zone-center frequency $\omega_L = 209 \text{ cm}^{-1}$ at large radii. Figure 2(b) shows the frequencies of the $\ell_p = 1$ coupled modes. The TO components tend to $\omega_T = 65 \text{ cm}^{-1}$, and again the LO components tend to ω_L in the limit of large radii. The band of closely spaced solutions between 70 and 95 cm^{-1} is due to modes with both confined LO and TO components. For PbS in PVA, the frequency of the electrostatic surface mode with $\ell_p = 1$, also known as the Fröhlich mode, occurs at 188 cm^{-1} . The interaction of the Fröhlich mode with the confined LO modes causes the bending at $\sim 190 \text{ cm}^{-1}$ [4].

From our calculations we can predict the Raman and infrared spectra of 2 nm PbS quantum dots. In Raman scattering via the Fröhlich interaction, the observable phonon modes are limited to $\ell_p = 0$ for excitation resonant with the $1s$ - $1s$ electronic transition [4]. The calculated Raman cross section is dominated by a peak at $\sim 228 \text{ cm}^{-1}$ arising from the lowest order $\ell_p = 0$ phonon mode, which is a factor of 100 larger than peaks due to higher-order modes. In general, phonons with $\ell_p = 1$

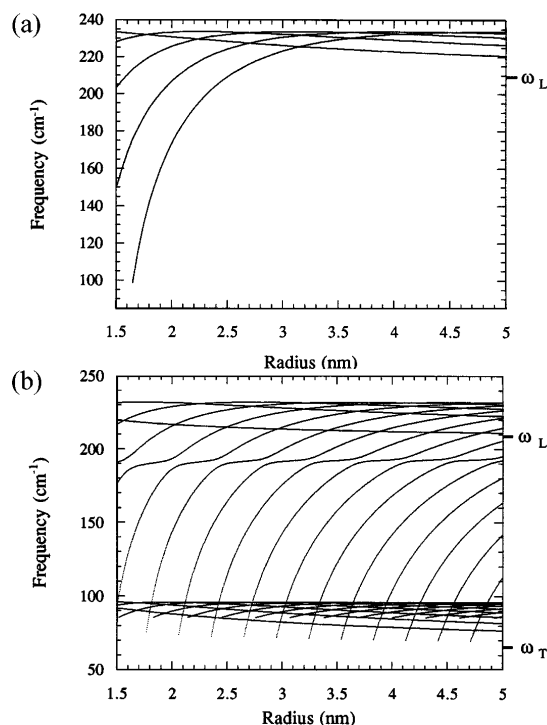


FIG. 2. (a) Frequencies of the five lowest-order coupled modes with $\ell_p = 0$ for varying radius. (b) Frequencies of the coupled modes with $\ell_p = 1$.

should be infrared active [3,4]. The $\ell_p = 1$ modes with frequencies between 70 and 95 cm^{-1} contain low-order TO components and should thus absorb strongly in the far infrared [9].

The vibrational modes were studied experimentally using resonance Raman and far-infrared absorption spectroscopies. We synthesized PbS nanocrystals in an aqueous solution of PVA following the procedure described in [6] and subsequently dried the colloid into thin films [7]. We determined the particle size from images taken with a scanning transmission electron microscope and by comparing the calculated and measured optical absorption spectra. Both approaches yield an average radius of 2 nm, with a variation of $\pm 5\%$. The lowest-energy peak in the absorption spectrum occurs at 600 nm and is attributed to the $1s$ - $1s$ exciton transition on the basis of agreement with the transition wavelength calculated for particles of 2 nm radius. We recorded the Raman spectra in backscattering geometry (with a Dilor model xy spectrometer) using a tunable dye laser and a HeNe laser for excitation. Spectra were recorded at 4.2 and 300 K with a resolution of 2.5 cm^{-1} , for various excitation wavelengths across the $1s$ - $1s$ exciton resonance. A typical spectrum is shown in Fig. 3. There is a large peak at 217 cm^{-1} , which is a shift of 8 cm^{-1} from the bulk value. This peak has a reproducible shoulder at 190 cm^{-1} . We also observe an intense, narrow peak at

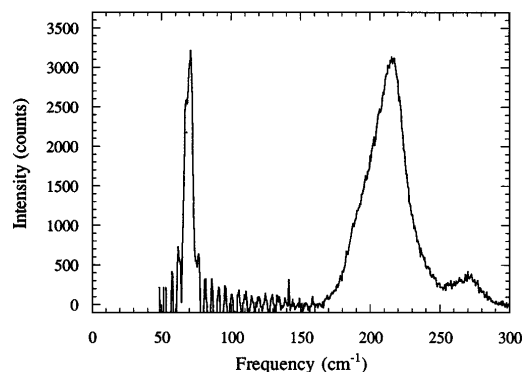


FIG. 3. Resonant Raman spectrum of 2 nm PbS nanocrystals recorded at 4.2 K with excitation at 581 nm. Similar spectra were obtained for other excitation wavelengths resonant with $1s$ - $1s$ exciton.

68 cm^{-1} and a small peak at 272 cm^{-1} . We measured the far-infrared absorption with a Bruker Fourier-transform infrared spectrometer, and the spectrum was found to be independent of temperature between 15 and 300 K. A broad peak centered at 90 cm^{-1} dominates the spectrum, as shown in Fig. 4. There is also a smaller peak at 275 cm^{-1} . The Raman and infrared spectra of PVA were recorded to ensure that any observed features were not due to the host material. A preliminary far-infrared spectrum was reported previously [7], and the 90 cm^{-1} peak was tentatively attributed to a confined TO mode.

The calculations correctly predict the key features of the Raman and far-infrared spectra. We assign the peak in the Raman spectrum at 217 cm^{-1} to the first-order phonon mode with $\ell_p = 0$ on the basis of its energy and polarization. The observed peak is within $\sim 10\text{ cm}^{-1}$ of the predicted value, which is reasonable given the assumption of a spherically symmetric Brillouin zone. Also, the scattered light is polarized parallel to the incident light, indicating that it is scattered by a spherical ($\ell_p = 0$) mode [3]. The broad peak in the far-infrared spectrum at 90 cm^{-1} is due to coupled modes with $\ell_p =$

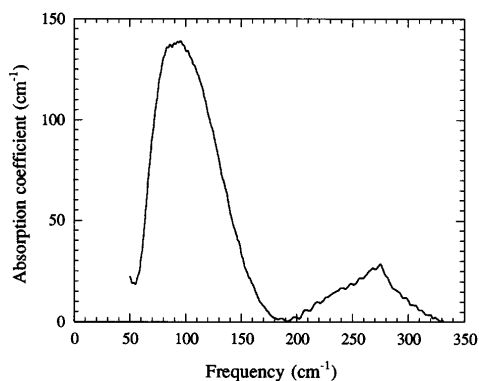


FIG. 4. Room-temperature far-infrared absorption spectrum of PbS nanocrystals.

1. Many coupled-mode solutions exist between 85 and 95 cm^{-1} , and these may contribute to the width of the peak. The feature at 190 cm^{-1} in the Raman spectrum may be related to surface modes, while the peaks at 68 and 272 cm^{-1} in the Raman spectrum and the peak at 275 cm^{-1} in the far-infrared spectrum are not accounted for by the theory; all of these will be discussed below.

The infrared spectrum is crucial to our interpretation. The electromagnetic theory of spherical particles [9] predicts strong absorption by surface modes at $\sim 190\text{ cm}^{-1}$, and fails to predict the observed absorption at $\sim 90\text{ cm}^{-1}$. Multimode phonon models [1] simply impose confinement on the bulk LO and TO phonons. We were able to find a phonon envelope function (the choice is arbitrary) which accounts for the peak in the Raman spectrum at 217 cm^{-1} , but an infrared absorption peak is then expected at 68 cm^{-1} due to the confined TO mode. Alternately, by choosing the envelope function to produce infrared absorption at 90 cm^{-1} , a Raman peak at 230 cm^{-1} is expected. Only the rigorous treatment including the correct boundary conditions accounts consistently for both the Raman and infrared spectra. The agreement between theory and experiment also implies that the mechanical vibrational amplitude is approximately zero at the PbS/PVA interface, as is reasonably expected given the difference between the structures, and therefore the vibrational modes, of the two materials.

The theory of [3] and [4] offers two possible explanations for the shoulder in the Raman spectrum at $\sim 190\text{ cm}^{-1}$. The shoulder frequency is close to that of the fourth-lowest eigenmode with $\ell_p = 0$ [Fig. 2(a)]. As mentioned above, the contributions of higher-order modes are negligible for the spherical electron and hole wave functions of the PbS nanocrystal. However, the $1s$ - $1s$ exciton decays with a lifetime of 5 ps, presumably into a trap or defect state [7]. A calculation of the Raman cross section shows that the peak at 190 cm^{-1} is enhanced to within an order of magnitude of the intensity of the peak at 217 cm^{-1} when one charge carrier is trapped at the surface of the nanocrystal. Thus the shoulder at $\sim 190\text{ cm}^{-1}$ could be due to the fourth-lowest eigenmode with $\ell_p = 0$. An alternate explanation for the shoulder is Raman scattering from the surface components of modes with $\ell_p \geq 1$, which would occur if the spherical symmetry were broken (by trapped charge, for example). Because of the large difference between the dielectric constants of PbS and PVA, the surface-mode contributions will be pinned at $\sim 190\text{ cm}^{-1}$ for all angular momenta. Studies with varying particle size should answer this question, since the coupled-mode frequencies depend on particle size, while the electromagnetic surface-mode frequencies are independent of particle size.

The theory of [3] and [4] does not apply to all of the features of the Raman and infrared spectra. The narrow spike at 68 cm^{-1} occurs close to ω_T . However, we assign the peak to a spheroidal acoustic mode [10,11] with $\ell_p = 0$ for the following reasons: (1) the $\ell_p = 0$ acoustic

modes should be Raman active, while the transverse modes are forbidden [3,11]; (2) the estimated vibrational mode frequency, $\omega_a = 48 \text{ cm}^{-1}$, is in reasonable agreement with experiment; (3) the Raman cross section calculated for scattering via the deformation potential interaction is similar to that calculated for optical-mode scattering by the polar interaction [10], in agreement with experiment; (4) the 68 cm^{-1} mode scatters light with a polarization parallel to the incident light, indicating it is a spherical ($\ell_p = 0$) mode [3,11]; and (5) the narrow linewidth is consistent with the weaker damping of an acoustic mode compared to a transverse-optical mode. Finally, the peaks in the Raman and infrared spectra at $\sim 275 \text{ cm}^{-1}$ are above any lattice frequency and close to the sum of the frequencies of the $\ell_p = 0$ acoustic mode and the $\ell_p = 0$ coupled optical mode. Therefore we tentatively ascribe the peaks at $\sim 275 \text{ cm}^{-1}$ to two-phonon processes. The treatment of [3] and [4] considers only one-phonon Raman scattering from optical modes, and so is not expected to account for all of the features that we observe.

A more systematic comparison of theory and experiment will be interesting but will require variation of the nanocrystal radius and/or Raman scattering studies with the excitation resonant with higher excited states. The fabrication of PbS quantum dots with well-controlled but variable particle size in a polymer host has not been reported. Also, Raman spectroscopy resonant with higher electronic states of 2 nm PbS nanocrystals will require ultraviolet excitation and detection. Monodispersed PbS quantum dots with controllable particle size (radius $\geq 3 \text{ nm}$) have been fabricated in an oxide glass host [12]. We measured the far-infrared absorption of oxide-glass samples with nanocrystal radii between 3 and 8 nm, but were unable to obtain any information about the nanocrystals because the host is opaque in this region [13]. In these samples the $1s$ - $1s$ transition occurs at wavelengths longer than $\sim 1.2 \mu\text{m}$, making Raman studies difficult. However, the same modes which are observed in Raman scattering resonant with the $1s$ - $1s$ exciton should be observable with the incident light resonant with the $1p$ - $1p$ transition [4]. We recorded the Raman spectrum of PbS nanocrystals of 3 nm radius with the excitation resonant with the $1p$ - $1p$ electronic state, which occurs at 570 nm. A peak is observed at 230 cm^{-1} , close to the predicted

value of 225 cm^{-1} for the lowest-order coupled mode with $\ell_p = 0$. To our knowledge this is the first observation of Raman scattering resonant with a clearly identified higher excited state of a nanocrystal.

In conclusion, coupled optical phonon modes of PbS nanocrystals have been observed using resonant Raman and far-infrared spectroscopies. These measurements agree with theoretical predictions and thereby confirm the influence of electrostatic and mechanical boundary conditions on the vibrational modes of semiconductor nanocrystals. Future studies will address the coupling of these modes to excitons.

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