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Electron–vibration coupling in semiconductor clusters studied by resonance Raman spectroscopy

A. P. Alivisatos,^{a)} T. D. Harris, P. J. Carroll, M. L. Steigerwald, and L. E. Brus
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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The resonance Raman spectrum of $45(+ - 3)$ Å diameter CdSe clusters was measured. The incident photons were resonant with the HOMO–LUMO transition in the clusters. At low temperature, one mode at 205 cm^{-1} is observed, as well as two overtones, with the integrated areas under these peaks in the ratio of 9:3:1. This mode is assigned as the longest wavelength longitudinal optical vibration of the cluster. The strength of the coupling between the lowest electronic excited state and the LO vibration is found to be 20 times weaker in these clusters than in the bulk solid. The CdSe cluster resonance Raman spectrum is shown to be consistent with the recently measured homogeneous cluster absorption spectrum.

INTRODUCTION

Semiconductor clusters comprised of hundreds to tens of thousands of atoms have attracted a great deal of attention ever since it was demonstrated that their electronic states depend strongly on size.¹ In the bulk solid, the diameter of the lowest electronic excited state, the exciton, is determined by the balance between the energy cost of localizing the electron and the hole on the one hand, and the energy gained by the Coulomb attraction between the electron and hole on the other. Exciton diameters range from hundreds to tens of Å, depending on the material. In clusters physically smaller than the bulk exciton diameter the increased kinetic energy from the confinement of the electron and the hole tends to blueshift the lowest excited state as R^{-2} , while the increased Coulomb attraction (due to increased electron–hole overlap) tends to redshift it as R^{-1} . In agreement with this picture, a net blueshift of the onset of the electronic absorption spectrum has been observed in clusters of many different semiconductors.

Compared to the electronic states, there is correspondingly little information available on the vibrational modes of these clusters. There is only one earlier brief report on the resonance Raman spectrum of CdS clusters in this size regime,² and two reports on much larger crystallites.^{3,4} This paucity of information is partly due to the fact that the bond length in these clusters is nearly the same as in the bulk solid,^{1,5} and therefore the force constants and vibrational frequencies ought to closely resemble those of the bulk. Nonetheless, the continuum of vibrational modes in the bulk solid will be transformed in finite clusters into a discrete series of states and the coupling of the vibrations to the electronic states and to the radiation field need not be the same in clusters as in the bulk solid.

In bulk cubic and hexagonal II–VI semiconductors, the free exciton is most strongly coupled to the long-wavelength optical phonons via the Frohlich interaction.⁶ In this effect, the displacement of the partially ionic nuclei is accompanied by a radial electric field extending over many unit cells, the potential of which is proportional to the amplitude of the

phonon. This electric field Coulombically couples to the exciton. As long as the effective mass of the electron and hole are different the coupling to the electron and to the hole, while opposite in sign, is not equal in magnitude, and therefore there is a net coupling. The strength of this exciton–phonon coupling is strongly peaked for those phonons whose wavelength matches the spatial extent of the exciton. This coupling is manifested in the resonance Raman spectrum in bulk II–VI semiconductors by a series of overtones of the LO phonon of the appropriate wave vector.⁷ Since the dispersion of the LO phonons is weak, the peaks which are observed occur at very nearly integer multiples of the $k = 0$ optical phonon frequency. In CdS, the most studied case, nine overtones of the LO phonon are observed.⁸ In CdSe at least four overtones are observed,⁹ with the intensity of the third overtone being equal to that of the second.

The highly delocalized excitonic states of bulk semiconductors couple mainly to optical vibrations with comparable wavelengths to the size of the exciton. Very short wavelength vibrations couple more weakly to the delocalized electronic states. In ever smaller clusters, this situation will change, and the coupling to short wavelength vibrations will come to dominate. As the electron and hole are confined into a smaller volume, the Frohlich coupling strength should be diminished, because the electric field caused by the vibration should be less effective in polarizing the exciton.¹⁰ Systematic trends in the electron–vibration coupling strengths with cluster size are of particular interest, because these coupling strengths can determine the shape and width of the electronic absorption spectrum of the cluster.¹⁰

In this paper we present measurements of the coupling between the lowest electronic excited state and longitudinal optical vibrations in CdSe clusters. The CdSe cluster samples under investigation are $45(+ - 3)$ Å in diameter.^{5,11} They occupy about one half the volume of the bulk CdSe exciton, and therefore show strong quantum confinement, with the lowest excited state occurring at 2.3 eV (540 nm), shifted 0.55 eV higher than the bulk exciton at 1.84 eV (670 nm). In order to investigate coupling of the lowest cluster electronic state to vibrations, the absorption and resonance Raman spectra need to be measured. This is not a simple matter, since the electronic spectra depend strongly on size,

^{a)} Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

and the best available samples contain a distribution (albeit narrow) of cluster sizes. In a recent paper we have demonstrated the use of transient photophysical hole burning to separate out the homogeneous and inhomogeneous contributions to the absorption spectrum of these samples.¹¹ The homogeneous absorption spectrum of the lowest cluster excited state derived in that experiment shows in it strong evidence for coupling to the optic and acoustic vibrations.

The resonance Raman spectrum of the same clusters ought to provide complimentary information to the absorption spectrum. This complementarity has been studied in detail in large molecules, where the theory of resonance Raman scattering in large molecules has been extensively developed. In strongly allowed molecular transitions mode intensities in the resonance Raman spectrum are related to excited state geometry and bond length changes via Franck-Condon factors in the Albrecht A term.¹² These lines in the spectra are due to totally symmetric modes. The effects of homogeneous and inhomogeneous broadening on molecular resonance Raman spectra have been investigated.¹³ The finite size of the clusters under investigation here renders the continua of electronic and vibrational states of the bulk discrete, and therefore the cluster can be said to more closely resemble a very large molecule rather than an infinite solid. The same phenomena are involved in the resonance Raman scattering in semiconductor clusters as in large molecules, the only difference being the mechanism by which the electronic and vibrational states are coupled.

The similarity between large molecules and the CdSe clusters is particularly strong regarding the influence of inhomogeneous broadening on the resonance Raman spectrum. A given incident photon energy is resonant with the electronic transition of only one subset of the clusters. The total Raman scattering spectrum is a sum of independent contributions from across the inhomogeneous distribution, with the contribution falling off as the cluster transition frequency is further away from the incident photon energy.

OFFSET HARMONIC OSCILLATOR MODEL OF ELECTRON-VIBRATION COUPLING

In an infinite system, the distortion of the lattice around the exciton is properly treated as a superposition of displacements of the different wave vector phonons of the lattice (assuming the optical mode is nearly dispersionless). Alternatively, the distortion of the lattice can be represented as a displacement along a single harmonic normal mode coordinate.^{7,14,15} This simple phenomenological model naturally allows a connection to be made between the resonance Raman scattering in the infinite solid and in the finite cluster or molecular limit. The potential in the ground electronic state E_i and the excited state E_j are given by¹⁶

$$E_i = \frac{1}{2} M \omega_{LO}^2 Q^2, \quad (1)$$

$$E_j = E_{ij} - \sqrt{2} \Delta \hbar \omega_{LO} \left(\frac{M \omega_{LO}}{h} \right)^{1/2} Q + \frac{1}{2} M \omega_{LO}^2 Q^2, \quad (2)$$

where Q is the normal mode coordinate, and Δ is the displacement of the harmonic oscillator in the excited state, normalized to the zero point motion. The vibrational states are harmonic oscillator wave functions, and the overlap

between ground and excited state wave functions is given by

$$\langle n|m \rangle = \left(\frac{n!}{m!} \right)^{1/2} \exp \left(-\frac{1}{2} \Delta^2 \right) \Delta^{n-m} L_m^{n-m}(\Delta^2), \quad (3)$$

where L denotes the appropriate associated Laguerre polynomial. Merlin *et al.* have shown that the dimensionless displacement Δ for the Frohlich interaction in a bulk solid is given by¹⁵

$$\Delta = 1.97 \frac{e^2}{a_0 \hbar \omega_{LO}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{1}{w} \times \int_{x=0}^w x^4 (2+x^2)^2 (1+x^2)^{-4} dx, \quad (4)$$

where a_0 is the lattice constant, and

$$w = (3\pi^2)^{1/3} \frac{a_0}{a_b}, \quad (5)$$

and a_b is the exciton Bohr radius. The Raman cross section for an n -phonon process at low temperature is then given by (Albrecht A term)

$$|R^n(\omega)|^2 = \mu^4 \left| \sum_{m=0}^{\infty} \frac{\langle n|m \rangle \langle m|0 \rangle}{E_{ij} + \hbar \omega_{LO} - \hbar \omega + i\Gamma} \right|^2, \quad (6)$$

where μ is the electronic transition dipole moment, $\hbar \omega$ is the incident photon energy, m denotes the intermediate vibrational level in the excited state, and Γ is the homogeneous linewidth, due to T_1 , T_2 , and low frequency modes.¹³ Using Eq. (3) and (6), it can be seen that the value of Δ for a given system can be determined by measuring the ratio of the integrated intensities of the various overtones observed. Table I shows the calculated values of Δ for the Wurtzite (hexagonal) forms of CdS and CdSe, obtained using Eq. (4). These calculated values of Δ are consistent with the intensity ratios of the multiphonon Raman spectra that have been observed in these materials. In the case of CdSe, Gross *et al.*⁹ have measured the ratio of the second to the third overtone to be 1, which would correspond to $\Delta = 3.6$.

EXPERIMENTAL AND RESULTS

The preparation and characterization of the CdSe cluster samples used in these experiments has been described in detail elsewhere.⁵ The clusters were prepared by arrested precipitation in reverse micelles with subsequent derivatization of the surface Se atoms with either alkyl or phenyl

TABLE I. Parameters for CdS and CdSe, used to calculate Δ with Eq. (4). Shown here are the effective masses of the electron and hole, the lattice constant, the low and high frequency dielectric constant, the free exciton Bohr radius, the LO phonon frequency, the Frohlich coupling parameter, and the calculated value of Δ . The parameters were obtained from Ref. 10.

Property	CdS	CdSe
m_e	0.18	0.13
m_h	0.51	0.45
a_0 (Å)	5.82	6.05
ϵ_∞	5.3	6.1
ϵ_0	8.7	9.3
a_b (Å)	21.6	32.3
ω_{LO} (cm ⁻¹)	305	210
Δ	3.07	2.93

groups. This derivatization permits the isolation of the clusters from the micellar medium, and makes the clusters stable against dissolution or aggregation. It also makes the clusters soluble in hydrophobic solvents and polymer films. These samples have been characterized by numerous techniques. Transmission electron microscope images of the clusters show that they are spherical (aspect ratio less than 1.2:1), with a mean diameter of 45 Å. Both TEM and x-ray powder diffraction show that the interior of the clusters is crystalline with the lattice constant of bulk, cubic CdSe (6.05 Å). The pressure dependence of the electronic absorption edge and of the LO vibrational frequency have been measured, and agree well with the values for bulk hexagonal CdSe.¹⁷ This evidence supports the point of view that the lattice properties of the clusters are the same as those of bulk CdSe (cubic or hexagonal).

X-ray fluorescence and scanning Auger show that the surface layer is Se rich, leading to an overall stoichiometry in the clusters of Se about 1.2: Cd 1. The surface of the clusters is neutral and not charged. This conclusion is supported by the fact that the clusters are only soluble in hydrophobic solvents. In addition, in the Se 77 NMR, two peaks are observed, one associated with the bulk and one with the surface Se.¹⁸ The chemical shift for both of these peaks is very close to that expected for neutral Se in the interior of cubic or hexagonal CdSe, and far from the value expected for ionic Se. Since the clusters surface is prepared with a neutral, organometallic source of Se, it is reasonable that the surface should be neutral.

The electronic absorption spectrum of the clusters differs significantly from the bulk, showing substantial quantum confinement effects, and has been investigated in detail in our recent hole-burning paper.¹¹ The major conclusions from that paper are: (1) The total electronic absorption spectrum of the sample at low temperature in a polystyrene film consists of a sum of contributions from clusters of different sizes. The width of this inhomogeneous distribution is 1000 cm⁻¹ (this depends on the sample, of course), which corresponds to 6 Å FWHM size distribution, in a simple quantum confinement model. (2) The homogeneous contribution of the lowest electronic excited state to the absorption spectrum consists of a peak with 140 cm⁻¹ FWHM, followed by a sideband shifted 200 cm⁻¹ higher in energy, and with a total integrated area that is one half the area of the main peak. (3) The 140 cm⁻¹ peak broadens with increasing temperature above 5 K. This width of this peak must therefore be at least partially due to coupling between the electronic excited state and low-frequency acoustic vibrations in the cluster.

The resonance Raman spectra of the clusters were obtained using a cw dye laser containing coumarin 535 pumped by the 477 nm argon ion laser line, or occasionally directly with lines from the ion laser. Typical incident powers were in the 1 to 20 mW range. The Raman scattered light was wavelength selected using a SPEX Triplemate, and the spectra were recorded with a Photometrics CCD camera. Three types of measurements were performed. In the first set, the CdSe cluster Raman spectra were measured at 1.6 K. In these experiments, clusters surface derivatized with phenyl

were homogeneously dispersed in a polystyrene film. 1–5 mg of CdSe clusters were dissolved in 1 ml pyridine, and to this solution 300 mg of polystyrene beads (Aldrich, Stock No. 18,247-7) were added. Once this mixture was homogeneous, a film was cast from the solution by evaporation of the pyridine. The films were then cooled to 1.6 K in a liquid helium immersion cryostat. The resonance Raman spectrum of the clusters at low temperature is shown in Fig. 1. The spectrum shows three peaks, at 205, 408, and 610 cm⁻¹, with progressively smaller intensity. The rising background is due to fluorescence of the clusters. The integrated areas under the peaks are in the ratio 9:3:1.

In a second set of experiments, the resonance Raman spectra of clusters surface derivatized with iso-octyl groups and dissolved homogeneously in benzene were measured at room temperature. In these spectra a single mode is observed at 205 cm⁻¹. The frequency of this mode was the same for clusters derivatized with phenyl groups and dissolved in pyridine. The resonance Raman excitation spectrum was measured for these samples, using the 605.6 cm⁻¹ mode of benzene as an internal standard (Fig. 2). Note that the resonance Raman spectrum rises and falls in a region where the cluster absorption spectrum is monotonically increasing, and that the FWHM of the excitation spectrum is 2000 cm⁻¹.

In a third set of experiments, the temperature dependence of the Raman spectra of the phenyl-capped clusters were measured in a glass consisting of 6 parts water, 3 parts pyridine, and 1 part ethylene glycol. The spectra did not shift with temperature, and the 15 cm⁻¹ width of the peak at 205 cm⁻¹ did not depend on temperature between 5 and 95 K. The frequency of this mode appeared to shift only 2 cm⁻¹ to lower energy, significantly less than the width of the line, when the exciting radiation was tuned from 5287 to 4880 Å. An effort to observe Raman scattering from the acoustic vibrations of the cluster in the 20 to 80 cm⁻¹ region was not successful.

DISCUSSION

The close similarity between the bulk and cluster lattice constants leads us to expect the force constants for the vibra-

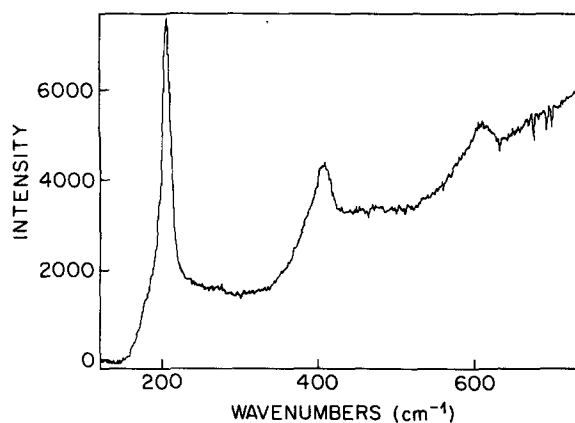


FIG. 1. The resonance Raman spectrum of 45 Å diameter CdSe clusters obtained using the 5145 Å argon ion laser line. The cluster surface atoms have been derivatized with phenyl groups. The clusters were homogeneously dispersed in a polystyrene film and were at 1.6 K.

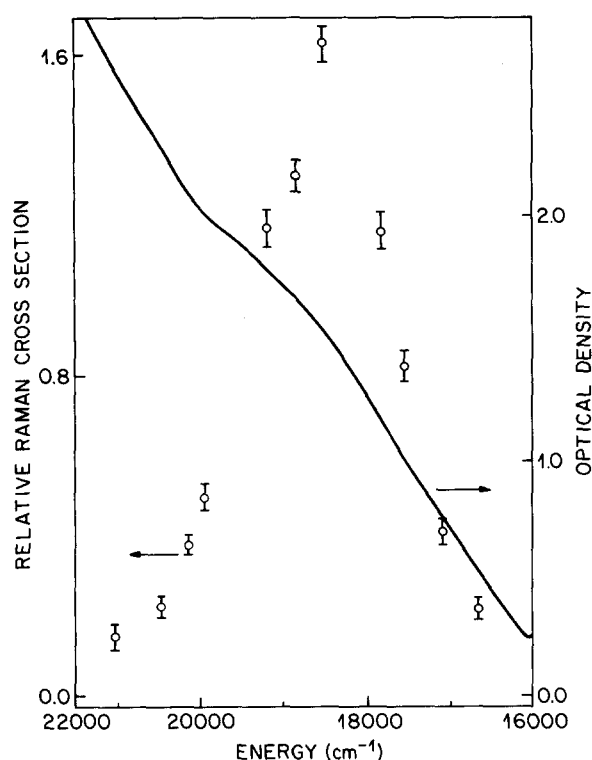


FIG. 2. The resonance Raman excitation spectrum of the 205 cm^{-1} mode of the CdSe clusters, obtained at room temperature. The cluster surface atoms were derivatized with iso-octyl groups in this case. The clusters were dissolved in benzene, and the 605.6 cm^{-1} mode was used as an internal reference.

tions to be very similar in the two cases. This point of view is confirmed by the resonance Raman measurements we have presented here, in which the vibrational frequency which is observed, 205 cm^{-1} , is near the bulk CdSe longitudinal phonon frequency of 210 cm^{-1} .⁹ We therefore conclude that the observed vibration is the longest wavelength totally symmetric longitudinal optical vibration the cluster will support. Simple theory for the lowest electronic states, based on $1S$ orbitals, also indicates that this vibrational mode will couple most strongly.¹¹

The electronic absorption spectrum, measured with hole burning, provides an independent measurement of the coupling between the HOMO–LUMO and the LO vibration.¹¹ Using the results of the hole-burning experiment we can determine all the parameters which are needed in order to predict the shape of the optical vibration resonance Raman spectrum using the offset harmonic oscillator model. In the hole-burning experiment it was demonstrated that the homogeneous cluster absorption spectrum consists of a HOMO–LUMO peak 140 cm^{-1} broad, and a phonon sideband approximately one half the integrated intensity of the zero-phonon line, and shifted 5 nm , or about 200 cm^{-1} to higher energy. This phonon sideband is attributed to the same longitudinal optical vibration which is observed in the resonance Raman. The sideband is followed by continuum absorption to higher energy. Within the offset harmonic oscillator model Δ of Eq. (3) must be 0.7 in order for the ratio of the absorption into the first overtone to be half the value for the zero phonon line.

The width which appears in the denominator of Eq. (6) is set to 140 cm^{-1} , the width of the zero-optical-phonon line measured by hole burning. The width of this line is probably due to coupling to the acoustic vibrations of the cluster. This conclusion is bolstered by the temperature dependence of the width of the line.¹¹ No Raman peaks are observed, however, at the low frequencies where these modes are expected to occur. This may be because of the difficulty of isolating the scattered laser light, or because the acoustic modes of the cluster coincide with low frequency modes of the surrounding matrix, and hence are severely broadened. In terms of the resonance Raman, this is analogous to the large molecule case,^{19,20} where a Franck–Condon progression in a very low frequency mode determines the excitation spectrum width for the high frequency resonance Raman modes.

Using these parameters and Eqs. (3) and (6) the intensity of the various overtones in the resonance Raman spectrum of a single (homogeneous) cluster is now determined for any given value of the incident photon frequency. The sample upon which the experiment is performed, however, contains a distribution of cluster sizes, and the homogeneous spectrum shifts depending on the cluster size. The total cluster absorption spectrum is the integral of the homogeneous cluster absorption spectrum over the inhomogeneous distribution. The inhomogeneous distribution is a Gaussian with a width of $750\text{--}2000\text{ cm}^{-1}$, depending on the sample.¹¹ This has important implications for the resonance Raman scattering. For any given incident photon frequency the sample contains some clusters which are exactly on resonance, and some which are far from resonance, with each cluster independently contributing to the total Raman scattering intensity. The effects of inhomogeneous broadening on molecular resonance Raman spectra are similar.¹³ This effect is readily taken into account by assuming that the vibrational frequency is constant across the inhomogeneous distribution, and integrating the cross section for scattering over the distribution of HOMO–LUMO transition frequencies E_0 :

$$|R''(\omega)|^2 = \int_{E_0} |R''(\omega, E_0)|^2 G(E_0) dE_0, \quad (7)$$

where $G(E_0)$ is the Gaussian distribution of HOMO–LUMO transition frequencies. When this integration is performed, for $\Delta = 0.7$ and $\Gamma = 140\text{ cm}^{-1}$, the ratio of the intensities of the first three lines in the Raman spectrum is $9:3:1$, in close agreement with the experimentally measured values.

The enormous width (2000 cm^{-1}) of the cluster resonance Raman excitation spectrum can be readily understood when the hole-burning experiments are taken into account. The excitation spectrum rises and falls with the distribution of HOMO–LUMO transition frequencies, and the width of this spectrum reflects the inhomogeneous, not the homogeneous, width. This also explains why there is only one peak in the excitation spectrum, instead of two which are normally observed (one for in-going and one for out-going resonance). It is interesting to note that no Raman scattering is observed when the laser is resonant with higher lying excited states of the cluster. Presumably this is due to lifetime effects, with Γ much larger for the higher states.

The experimental evidence, from the absorption and the resonance Raman spectrum is fully consistent, and demonstrates that the strength of the coupling to the long wavelength longitudinal optical vibrations is substantially weaker in 45 Å diameter CdSe clusters than in bulk CdSe. Within the offset harmonic oscillator model, the energy of the electronic excited state is decreased by the coupling to the vibrations by an amount $\sqrt{2}\Delta^2\hbar\omega$. Thus a change of Δ from 3 to 0.7 in going from bulk to cluster represents a 20-fold decrease in this coupling energy.

What is the reason for this diminished coupling strength? There are four issues which will be considered. While many of the II–VI semiconductors, including CdSe, can be obtained in either form (depending on the detailed kinetics of the crystallization), hexagonal CdSe is much more common than cubic, and almost all the available data is for the hexagonal form.²¹ On the other hand, every known method of preparing II–VI clusters yields the cubic modification.¹ Could the difference in coupling strength be an artifact of comparing clusters with the cubic crystal structure to hexagonal bulk? This is very unlikely. In ZnS, the one case where measurements are available for both structures in the bulk, the strength of the Frohlich coupling to the bulk exciton is not different in the two structures.²² In addition, the frequency of the LO vibration, and even the anharmonicity of the vibration, in the cubic clusters, are very close to the values for bulk hexagonal CdSe.¹⁷

Since it is the electric field induced by the lattice vibration that is responsible for the Frohlich coupling to the electronic states, the coupling strength could be influenced by the presence of static charges on the surface atoms of the clusters. The preponderance of evidence suggests that in the particles under investigation here, the surface is not charged. This evidence includes the solubility of the particles in hydrophobic, but not in hydrophilic solvents, and the NMR.¹⁸ If there were a net field due to the presence of charged atoms on the surface, this field would be radial. The electric field which accompanies the vibrations is also radial, pointing in towards the center of the cluster during one half of the vibration, and outwards during the other half. Thus the polarization of the electrons would be enhanced during half the cycle, but diminished by an equal amount in the other half, with no net effect on the total electron–vibration coupling energy.

The density of vibrational states is much smaller in the clusters than in the bulk. The structural deformation of the lattice which accompanies electronic excitation is therefore distributed over many more modes in the bulk solid than in the cluster. This does not affect the total energy of the coupling between the lattice and the vibrations. While the coupling to any given mode is weaker in the bulk solid, this is exactly compensated for by the increased number of modes.

Schmitt-Rink, Miller, and Chemla have discussed the most plausible mechanism for the reduced coupling.¹⁰ The sign of the Frohlich interaction is opposite for the electron and the hole. In the extreme limit of quantum confinement, where the cluster diameter is much smaller than the bulk exciton diameter, the kinetic energy term completely dominates, the wave functions of the electron and hole are equal

everywhere, and the Frohlich coupling vanishes. In the bulk solid, where the Coulomb attraction binds the electron and hole together, the difference in effective masses between the electron and hole means that they will have different wave functions, and there will be a net coupling. This is equivalent to saying that the strength of the Frohlich coupling depends on the polarizability of the electronic excited state, and this polarizability becomes smaller in smaller clusters. While the reduced coupling cannot be definitely assigned to this mechanism without further measurements, it seems to be by far the most reasonable.

SUMMARY AND CONCLUSIONS

The HOMO–LUMO electronic transition in 45 Å CdSe semiconductor clusters is coupled to longitudinal optical vibrations of the cluster, apparently via the Frohlich interaction. This coupling has been measured in absorption and in resonance Raman and the two measurements are consistent. The strength of the coupling is 20 times weaker in these clusters compared to the bulk solid. This reduction in coupling strength is consistent with the increased overlap of the electron and hole when there is substantial quantum confinement. It would be of great interest to relate these measurements of the resonance Raman spectrum to the correlation energy of the electron and hole in the first excited state, as a function of crystallite size. The resonance Raman excitation spectrum of the clusters shows that only the first electronic excited state is coupled to this LO mode. No peaks in the resonance Raman spectrum are observed for incident photon energies higher than the HOMO–LUMO transition, supporting the conclusion that the higher electronic states are severely homogeneously broadened.

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