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Pressure-induced electronic coupling in CdSe semiconductor quantum dots

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While previous high-pressure optical and vibrational studies on CdSe quantum dots (QD's) have observed no evidence for size-dependent scaling laws in the experimental pressure behavior, we have found that low-pressure studies exhibit anomalous pressure dependencies that can be analyzed in two specific size regimes ($r<a_0$ and $r\sim a_0$, where r is the particle radius and a_0 is the Bohr radius). This corresponds to the limits of strong and weak confinement of the exciton for CdSe. By using photoluminescence and resonance Raman spectroscopies, we find optical and vibrational coefficients (82 meV GPa^{-1} and 3.51 cm^{-1} GPa^{-1}, respectively, for 22.5 Å radius dots) that significantly deviate from reported bulk values (37 meV GPa^{-1}) when $r<a_0$. At the largest QD sizes studied ($r=40$ Å), bulk-like pressure dependence is observed as expected. We believe the anomalous size dependent pressure behavior arises from changes in the nature of the electron-phonon (el-ph) coupling due to polaronic coupling in the QD lattice. Analyses of longitudinal optical mode Grüneisen parameters (γ_{LO}) show the expected el-ph coupling strengths derived from γ_{LO} agree well with calculated values for el-ph coupling strengths in CdSe QD's. An empirical pressure-dependent model is proposed which argues that polaronic decoupling occurs following a $1/r$ scaling law, which may be due to changes in el-ph coupling in these dimensionally restricted materials.

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I. INTRODUCTION

In semiconductor nanocrystals, or quantum dots (QD's), the size-dependent nature of the physical properties can give rise to systematic changes in the electron-phonon (el-ph) coupling and lattice covalency, particularly for materials in the strongly confined limit. Pressure tuning of electronic levels which are highly sensitive to the covalency and the magnitude of el-ph coupling in materials can be probed a combination of photoluminescence (PL) and vibrational analysis. Although theoretical studies of donor/acceptor (D/A) states in CdSe QD's predict changes in polaronic coupling between donor electronic levels and interior core electronic levels following a $1/r^2$ scaling law,[1–4] these scaling laws have not been previously observed on CdSe.[5–10] The observation of pressure coefficients for CdSe QD's in this manuscript can be classified in accord with two size regimes, strong ($r<a_0$) and moderate ($r\sim a_0$) confinement, and suggest donor state contributions to the photophysics of CdSe QD's may be important. In fact, as the radius of the crystallite approaches the Bohr radius (moderate confinement), the values of the pressure coefficients approach the bulk values as expected for materials in the quantum confined limit and are reflected experimentally in the photoluminescence (PL) and resonance Raman spectroscopy. This allows a scaling law to be generated for the pressure coefficients if the donor states are accounted for in these materials.

QD's are an ideal system to observe how pressure induced changes in electronic levels can be influenced by changes in el-ph, lattice covalency, and donor levels. Since the PL properties of CdSe are dominated by the $1S_{3/2}1S_e$ excitonic level (i.e., bright and dark excitons) delocalized over the entire particle, the pressure-dependent properties of the materials should approach the bulk value as r approaches a_0. Pressure-induced perturbation of the exchange coupling in these materials, as well as the excited state energies and the core lattice parameters allows pressure-dependent optical and vibrational spectroscopy to be used as a convenient probe of changes in the lattice ionicity with pressure and the underlying size-dependent coupling to donor levels for these materials.[11,12] Based on theoretical predictions, little to no pressure dependence ($dE^*/dp\sim 0$) is expected for the strongly confined limit (regime 1, $r<a_0$; ~30–40 % surface) and bulklike behavior should be observed as r approaches a_0, where $a_0=56$ Å in CdSe.[13] The lack of pressure dependence in the strongly confined regime arises from the strong coupling of defect levels in the QD to the core levels due to the strong confinement of the exciton wave function. This results in the excitonic levels being primarily perturbed by the particle size, and not the electron-hole (el-h) interactions. Extrapolating the model, QD's in the moderate to weakly confined limit ($r\geqslant a_0$) (regime 2: $r\geqslant a_0$; 20% and below surface) are expected to exhibit pressure dependent behavior modulated by the size-dependent contribution of polaron coupling to core levels which will be influenced by the magnitude of el-ph interactions in the QD lattice. In fact, optical studies on QD's under pressure have shown enhanced pressure response in InP, while in Si and CdSe no anomalous pressure dependence is observed.[5,6,10,12] The lack of enhanced pressure dependencies in these studies suggest the high-pressure behavior is dominated by structural modulations or pressure-induced lattice stress that lead to interband crossing rather than defect state coupling to the core electronic levels.[14]

In this manuscript, we observe pressure dependence in the weakly confined regime approaching the reported bulk band edge pressure coefficient consistent with the lack of significant defect levels in the QD. Assuming donor state contributions to the delocalized excited state, a scaling law can be generated for the QD's in the moderate to weakly confined regime. We further observe that by correlating the small vibrational changes in the CdSe QD lattice $d\omega/dp$ and the changes in the excited state optical properties dE^*/dp, the density of state contributions from subgap D/A states to the

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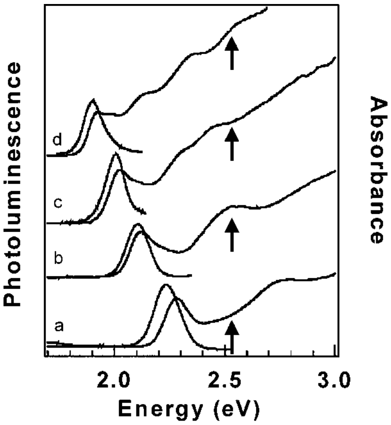

FIG. 1. Absorption and photoluminescence ($p=1$ atm; $T=298$ K) as a function of CdSe QD radius: (a) 19 Å, (b) 23 Å, (c) 30 Å, and (d) 43 Å. The PL spectra were obtained with 2.54 eV laser light; 80 mW power. The arrows mark where the PL and Raman spectra were excited in the pressure experiments.

core electronic levels induce polaronic defects which change with lattice covalency.

II. EXPERIMENTAL

CdSe QD's were prepared by standard lyothermal methods using a single source precursor route.[15] Crystallinity and size dispersity (5–6 %) of the materials are monitored by absorption, powder x-ray diffraction (pXRD), and transmission electron microscopy (TEM) analysis. Typical absorption and photoluminescence (298 K; 1 atm) are presented in Fig. 1.

The QD's were dispersed in *n*-hexane and put into a cylindrical optical-pressure cell (~110 μL). Use of *n*-hexane as the pressure transmitting medium in a liquid pressure optical cell[16] allows hydrostatic pressures up to 0.30 GPa (3.0 kbar) to be generated with minimal contributions from pressure-induced solvent effects based on the small degree of fractional compression of the solvent and the small change in dielectric constant in this pressure range for *n*-hexane.[17]

The luminescence and resonance Raman spectra (resonant with a high-energy $1P_h1P_e$ transition) were collected in backscattering configuration using the 2.54 eV line of an 10 W Spectra-Physics 2200 Ar-ion laser (488.0 nm, 80 mW power) as a pump source and collection of the spectra on a 0.5 M ARC single spectrograph (1800 lines mm^{-1}, blaze $=500$ nm) system coupled to a Princeton Instruments 512 $\times 512$ liquid nitrogen cooled charge coupled device (CCD) array. A holographic Notch filter (Kaiser optical) was used to reject the incident laser line.

III. POLARONIC EFFECTS ON PRESSURE INDUCED OPTICAL PROPERTIES

In nanoscale condensed phase QD's, defect levels may arise from surface states and can play a significant role in the electronic nature of these materials. In fact, the influence of surface state perturbation on core electronic levels for QD's has been observed to influence the el-*h* trapping rates with a decrease in trapping rates at defect centers as the particle size increases.[18] In analogy to bulk materials, polarons at the surface of a QD can be treated as defect levels in the electronic band structure. Based on the size dependence of the surface-to-volume (S:V) ratio in QD's, the degree of coupling of polarons and core levels should track the density of states of these subgap levels.[1,19] This allows the total energy of a quantum dot to be expressed as a core electronic term with a perturbation term for the polaron state as suggested by Efros *et al.*,

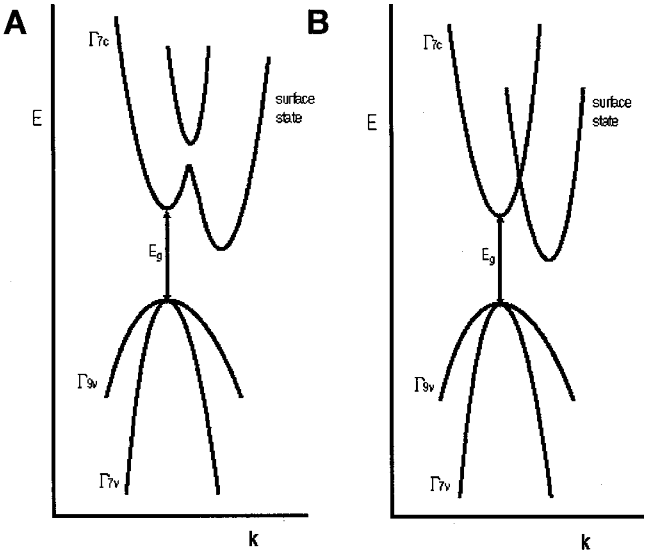

FIG. 2. Schematic band diagrams illustrating the extreme limits of polaron-core coupling seen in QD's. (A) illustrates the strongly confined limit, where polaronic coupling is largest, and induces a perturbation to the total QD energy. (B) illustrates the bulk limit, where polaronic coupling is minimal.

$$E_{\text{total}}=\frac{\hbar^2\pi^2}{2m_e r^2}-\frac{e^2}{\varepsilon r}f\left(\frac{d}{r}\right), \tag{1}$$

where m_e is the electron mass, ε is the crystal dielectric constant, r is the particle radius, d is the donor position in the crystal, and $f(x)=1-\sin(2\pi x)/(2\pi x)+\mathrm{Cin}(2\pi)-\mathrm{Cin}(2\pi x)$ [$\mathrm{Cin}(x)$ is a cosine integral and varies from $f(0)\sim 2.4$ to $f(1)\sim 1$].[1] This equation predicts the magnitude of the perturbation term should increase as the polaron states are localized on the interior of the dot. The perturbation term should also scale with the density of defects and the level of el-ph interactions in the QD material. In a QD, the el-ph terms scale with the dot size.[20]

Small changes in the bulk modulus ($B_o'=11$) in the low-pressure range (<1 GPa) for wurtizte CdSe indicate that structural effects on the PL should be minimal.[6] The magnitude of the pressure induced shifts in the PL are expected to track the contribution of the core-polaron interaction, modulated by subtle changes in the lattice covalency with confinement, size, and pressure. For strongly confined systems (regime 1), the electronic wave function is delocalized over the whole crystal volume, indicating complete coupling of the interior crystal states to the exterior polaronic defect states [Fig. 2(a)] and can be represented in terms of a nonadiabatic surface in which the tunneling barrier for coupling is small.[1]

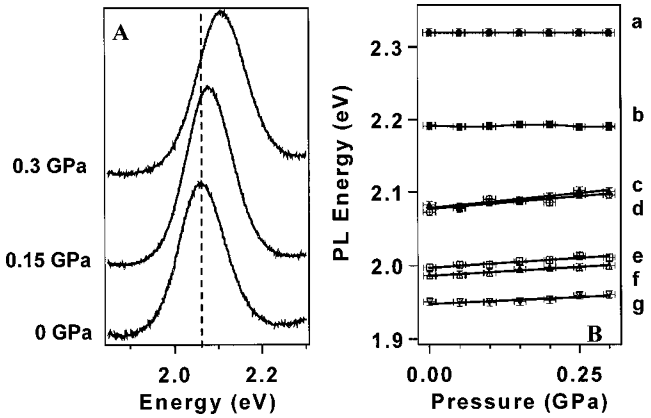

FIG. 3. Pressure-dependent photoluminescence spectra as a function of (A) pressure (for a 22.5 Å particle) and (B) CdSe QD radius: (a) 14 Å, (b) 20 Å, (c) 22.5 Å, (d) 27.5 Å, (e) 30 Å, (f) 35 Å, and (g) 40 Å. The spectra were obtained with 2.54 eV laser light; 10 mW power; 298 ± 2 K.

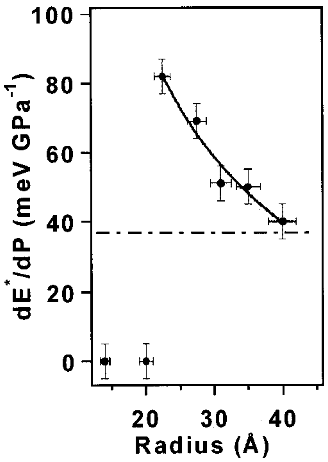

FIG. 4. Size-dependent excited state pressure coefficients as a function of CdSe QD radius. Note the break between 20 and 22.5 Å explained by strong confinement properties of the QD (see text). The dashed line refers to the bulk CdSe pressure coefficient of 37 meV GPa^{-1} (Ref. 23).

We expect little to no pressure dependence in this regime due to the magnitude of the el-h confinement in this size regime and the small barrier for core-polaron interactions. Similar models have been used to explain pressure dependent donor states contributions in bulk semiconductors and inorganic materials.[21,22] In the moderately to weakly confined regime (regime 2), the electronic wave function decreases rapidly at the crystal surface, which gives rise to a classical electronic barrier between the two states [Fig. 2(b)]. This results in weakly coupled interactions between the D/A states and the core levels. Deviations from bulk-like behavior in this regime can arise from perturbation of the el-ph coupling in these dimensionally restricted materials.

Selected pressure dependent optical spectra for a 22.5 Å radius particle are shown in Fig. 3(a). The most striking feature of the pressure dependent PL data [Fig. 3(b)] is the lack of pressure response below 22.5 Å radius ($dE^*/dp = 0$ meV GPa^{-1}), in agreement with regime 2 behavior for the 14 and 20 Å radius QD. At 22.5 Å radius and above, the PL pressure coefficients exhibit strong pressure dependence as seen in Table I, which follows the expected behavior for systems in regime 1. Interestingly, the excited state pressure coefficients in regime 1 when $2r > a_0$ approach the reported absorption pressure coefficients (37 meV GPa^{-1}) rather than the reported PL pressure coefficients (58 meV GPa^{-1}).[23,24] This observation suggests either STE or defect levels in bulk CdSe may contribute to the larger observed PL pressure coefficient in comparison to that of the absorption value. Coupled to the shift of the PL, the full width at half maximum (FWHM) for the PL band increases approximately 30% (~125 to ~185 meV). This is similar to high-pressure studies on InP QD's (Ref. 14) and is most likely due to population distribution effects rather than size dispersity effects as it occurs in all samples studied. The pressure induced changes in the PL of the CdSe QD's may arise from either a core structural reconstruction or from coupling to localized lattice defects, as has been observed previously in metal nanoparticles.[20] Based on the small shifts in the bulk modulus for CdSe with pressure and the observation of little participation of structural perturbations in high-pressure optical studies of CdSe, structural reconstruction is most likely a minimal contributor to the observed pressure-dependent PL behavior in this study.[6,9] This suggests that the observed PL properties may arise from D/A state coupling as theoretically predicted.[1]

TABLE I. Excited state pressure coefficients of CdSe QD's at room temperature (298 ± 2 K).

QD radius (Å)	dE^*/dp (meV GPa^{-1})
14	0
20	0
22.5	82
27.5	69
30	51
35	50
40	40
bulk	37[a]
	58[b]

[a] Ref. 24.

[b] Ref. 25.

Using the models developed for metal nanoparticles,[18,25] a semiquantitative understanding of the observed pressure-dependent tuning of the PL in CdSe QD's can be gained. In Fig. 4, a plot of dE^*/dp vs QD radius (r) fits to a phenomenological equation [Eq. (2)], which scales with the particle size

$$\frac{\partial E_{\mathrm{obs}}}{\partial p} = ar + \frac{b}{r}. \tag{2}$$

r is the particle radius, a is a scalar which is proportional to $[(dE/dp)_{\mathrm{core}}][1/a_0]$, $1/b$ can be regarded as an effective electron scattering term that occurs from a highly localized polaronic type defect on the nanoparticle surface,[20] and $(dE/dp)_{\mathrm{core}}$ is the bulk pressure coefficient. The scattering

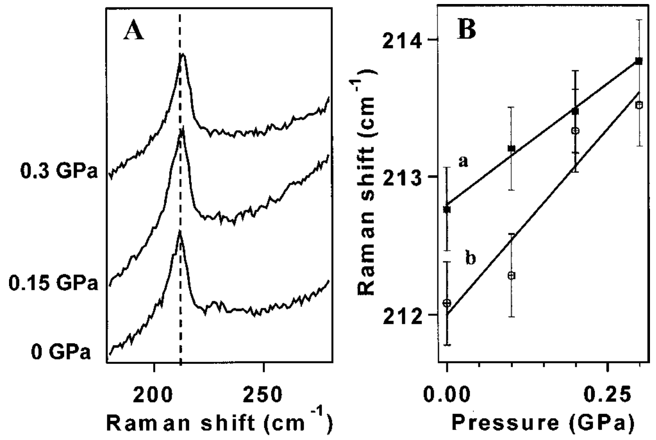

FIG. 5. Pressure-dependent resonance Raman as a function of (A) pressure (for a 30 Å radius particle) and (B) CdSe QD radius: (a) 20 Å and (b) 35 Å. The spectra were obtained with 2.54 eV laser light; 80 mW power; 298±2 K.

term $1/b$ may be inversely related to the effective polaron length in these materials.[18] The expression in Eq. (2) indicates that the pressure coefficient will deviate from bulk values at small particle sizes due to contribution from b and deviations from bulk values will be minimized at larger particle sizes as $r \rightarrow a_0$. This is consistent with the observation of the PL properties of the QD being modulated by a localized polaronic defect, which tend to decouple from the core levels at higher pressure for systems at the limit of $r < a_0$. Evidence for a highly delocalized polaron can be gained by inspection of the pressure-dependent resonance Raman spectra.

IV. SIZE-DEPENDENT ELECTRON-PHONON COUPLING IN CdSe QD's

The magnitude of the perturbation to the core excitonic properties will depend both on the defect type and depth, and the contribution from the materials' core el-ph coupling. The degree of el-ph interactions in the condensed phase is reflected in the ionicity of the material and can be analyzed by calculation of the mode Grüneisen parameters (γ_i). The γ_i parameter can be analyzed by probing the pressure-dependent shifts in the vibrational parameters of the core levels.[26] As lattice covalency increases, the magnitude of el-ph interactions leads to an increase in the contribution of defect perturbations of the excitonic levels.

Resonance Raman experiments allow the direct analysis of el-ph interactions in materials by probing the cross section for coupling between the vibrational and electronic levels of a system.[27–29] In the resonance condition, excitation of a $1P_h 1P_e$ transition at 2.54 eV in CdSe allows the longitudinal optical (LO) phonon modes coupled to the excited state to be probed. Pressure dependent resonance Raman experiments below the structural phase transition in CdSe QD's exhibit a pressure-dependent shift in the core LO phonon and an apparent loss of intensity of the defect (polaron) localized vibration for CdSe [Fig. 5(a)]. The fundamental LO mode for CdSe is observed at ~210 cm^{-1} with a shoulder to lower frequency. Analysis of the asymmetry of the $\mathbf{k}=0$ LO phonon mode in CdSe QD's has been previously assigned as arising from a localized defect LO mode which couples to the excited state properties of the QD.[20] As reported previously, this allows the observed phonon to be deconvoluted as a contribution of core (~210 cm^{-1}) and defect (polaron) (~190 cm^{-1}) modes.[20] Overtone modes in this experiment are obscured by photoluminescence from the sample and pressure cell interference. Size-dependent hardening of the LO phonon with pressure is observed for CdSe as seen in Fig. 5(b). The observed vibrational pressure coefficients ($d\omega_{\mathrm{LO}}/dp$) are plotted in Table II and calculated from Fig. 5(b) using a least squares fit to the data [Eq. (3)],

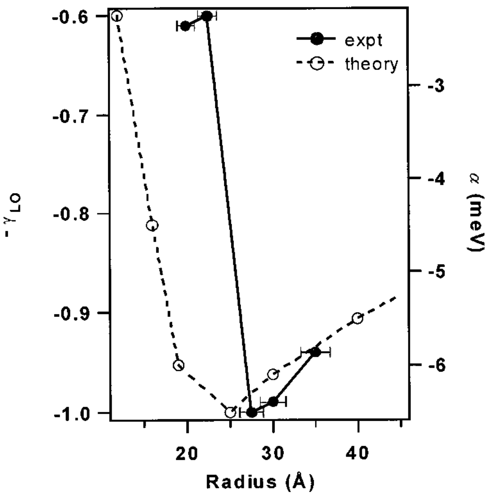

FIG. 6. Correlation of LO mode Grüneisen parameters (γ_{LO}) and values of the electron-phonon coupling strength α (in units of meV) calculated in Ref. 4 as a function of CdSe QD radius. The values for γ_{LO} are plotted as $-\gamma_{\mathrm{LO}}$ to emphasize the correlation of γ_{LO} with α. The lines are guide to the eyes.

$$\omega = \omega_{\mathrm{LO}} + \alpha p, \tag{3}$$

where ω_{LO} is the ambient pressure LO phonon frequency, α is the vibrational pressure coefficient, and p is pressure in GPa. Based on the calculated vibrational pressure coefficients, the LO mode Grüneisen parameters[30] exhibit two specific size regimes for CdSe ($r \leqslant 22.5$ Å and $r \geqslant 28$ Å), which correlate with calculations for el-ph coupling strengths in CdSe QD's by Melnikov and Fowler (Fig. 6).[4] More importantly, the observation of size-dependent Grüneisen parameters show that there is a distinct increase in lattice covalency (and therefore decrease in el-ph coupling strength) in the strongly confined regime. This provides further evidence that deviations in el-ph interactions exist in this regime, which may give rise to polaronic-type defects, and therefore the observed anomalies seen in the PL experiments.

A more direct method to analyze el-ph interactions is to evaluate the pressure dependencies of the LO mode integrated intensities. Although pressure induced changes in the optical cross sections may perturb the resonance enhancement of the Raman experiment, evaluation of the mode intensity ratios of the core LO and polaron defect LO are useful. In our experiments, coupled to the changes in the LO

TABLE II. Pressure dependence of the CdSe LO phonon at room temperature (298 ± 2 K). The values of the mode frequency ω_{LO}, α, and LO mode Grüneisen parameter γ_{LO} were extrapolated at ambient conditions.

QD radius (Å)	ω_{LO} (cm^{-1})	α (cm^{-1} GPa^{-1})	γ_{LO}
20	212.8	3.51	0.61
22.5	212.4	3.43	0.60
27.5	212.4	6.12	1.00
30	211.7	5.65	0.99
35	212.0	5.37	0.94

mode with pressure, the localized polaron LO mode exhibits significant loss in the integrated intensity at pressures exceeding 0.1–0.15 GPa. The observed sharp drop in intensity of this mode is consistent with a first order ‘‘electronic phase transition’’ arising from a change in the el-ph coupling between the core and defect states, due to a decrease in resonance between the polaron and core levels resulting in state decoupling. The loss of polaron coupling to core levels may explain the observation of break in linearity at higher pressures arising from complete defect decoupling and bulklike behavior, as observed in previous high-pressure studies.[6,12,14] The lack of mode hardening of the polaron mode with applied pressure implies an effective mode Grüneisen parameter of zero and is consistent with a strongly localized polaronic state in these materials where el-el interactions are dominated by el-ph interactions, as predicted in the PL pressure-dependent optical properties.

V. DISCUSSION

Analysis of the CdSe size-dependent Grüneisen parameters calculated from the pressure dependent vibrational properties in Fig. 6 and Table II suggests a significant level of perturbation exists in the lattice for QD’s in the strongly confined limit ($r \leqslant a_0$). We note that these observed anomalies leading to the observed perturbations are not a function of pressure induced melting events (e.g., the organic surfactant), as only ~0.5 meV (~0.05 kJ mol^{-1}) of energy is generated from the application of these modest pressures. As seen in Fig. 6, above 56 Å ($r=28$ Å), as the particles go from the strongly to the moderately confined limit, the QD’s begin to approach the bulk value for γ_{LO}. As the particle size is decreased, the value for γ_{LO} reaches a maximum, which indicates a fairly ionic lattice. This increase in ionicity should lead to an increase in el-ph coupling, and this assessment is verified by calculations on CdSe QD’s by Melnikov and Fowler who show the el-ph interaction energy minimizes at $r\sim25$ Å.[4] As the particle size is decreased ($r<25$ Å), Melnikov and Fowler find that the el-ph energy again begins to rise, indicating destabilization of the coupling strength. This correlates with the observed size dependence in γ_{LO}. At small particle sizes, we observe a large decrease in γ_{LO} which indicates an increase in lattice covalecy and a corresponding decrease in the el-ph coupling strength. The shift in the magnitude of γ_{LO} correlates with the size dependence observed in the PL spectroscopy, suggesting the perturbation most likely arises from a modulation of the level of el-ph coupling in these materials as a function of size, which correlates with the degree of defect-core level coupling in the PL spectroscopy. The enhanced coupling in regime *I* materials may arise from the strong mixing of the core and defect atoms due to a large ratio of surface to volume (~40%) atoms in the nanocrystal. The lack of pressure behavior in this regime may also be attributed to quantum-mechanical effects, as the el-*h* exchange interaction in this size range is comparable to kT (25 meV) therefore causing the emitting state to consist primarily from the ±2 exciton state, which may show a different pressure response than the thermally averaged $\pm1^L$, 0^L, and ±2 emitting states. Interestingly, this breakpoint in γ_{LO} and in the observed dE^*/dp arises at the breakpoint for the contribution of the kinetic energy term in the particle-in-the-box model for the size-dependent absorption,[31] as well as the size-regime for thermodynamic stabilization of these materials arising from chain interactions that govern the QD surface.[32] More importantly, the size dependence of the pressure coefficients tend to extrapolate to the bulk absorption pressure coefficient which implies that our large QD’s are highly crystalline with little defects and the excited state of these materials favor a delocalized model, as proposed by Efros and co-workers.[1]

VI. CONCLUSIONS

As predicted, QD’s exhibit two pressure-dependent regimes for polaron coupling to core levels. As witnessed in previous high pressure experiments, the application of extreme pressures tend to decouple the polaron, and the materials exhibit pressure dependencies analogous to their bulk counterparts. The interpretation of our results suggests that low pressures are needed to probe these polaronic interactions and to observe size-dependent scaling laws related the optical properties of the QD. The adiabaticity of a quantum dot band structure can be thought of in terms of a strongly crossing and avoiding model and scales as a phenomenological expression related linearly with the bulk pressure properties and inversely with the surface properties, as expected for a system with a S:V ratio that scales as $1/r$ (Fig. 2). The pressure coefficient trends for the PL and vibrational terms indicate the largest tuning of the electronic levels at low pressure arise for QD’s approaching the size of the Bohr exciton radius. The increase of lattice covalency, measured from the size dependent Grüneisen parameters, provides evidence that the polaron arises from increased el-ph interactions in these materials. Further studies into the pressure tuning other II-VI and III-V materials are underway to test the models proposed in this manuscript.

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