Size- and Temperature-Dependent Intraband Optical Properties of Heavily n-Doped PbS Colloidal Quantum Dot Solid-State Films

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ABSTRACT: Steady-state access to intraband transitions in colloidal quantum dots (CQDs), *via* doping, permits exploitation of the electromagnetic spectrum at energies below the band gap. CQD intraband optoelectronics allows envisaging cheap mid- and long-wavelength infrared photodetectors and light-emitting devices, which today employ epitaxial materials. As intraband devices start to emerge, thorough studies of the basic properties of intraband transitions in different CQD materials are needed to guide technological research. In this work, we investigate the size and temperature dependence of the intraband transition in heavily n-doped PbS quantum dot (QD) films. In the studied QD size range (5–8 nm), the intraband energy spans from 209 to 151 meV. We measure the intraband absorption coefficient of heavily doped PbS QD films to be around $2 \times 10^4 \text{ cm}^{-1}$, proving that intraband absorption is as strong as interband absorption. We demonstrate a negative dependence of the intraband energy with temperature, in contrast to the positive dependence of the interband transition. Also opposite to the interband case, the temperature dependence of the intraband energy increases with decreasing size, going from $-29 \text{ } \mu\text{eV/K}$ to $-49 \text{ } \mu\text{eV/K}$ in the studied size range.

KEYWORDS: quantum dots, intraband, lead sulfide, absorption coefficient, temperature dependence

Quantum dots (QDs) are zero-dimensional solids that exhibit atomic-like electronic structures, with discrete electronic levels separated by a true zero density of states. The formidable control in size and composition of colloidal quantum dots (CQDs) has enabled experimental study of fundamental quantum physics as well as the utilization of these materials for a wide variety of applications in the fields of light emission¹ and detection,² photovoltaics,³ and field effect transistors.⁴ For semiconductor (SC) device engineering, one key advantage that CQDs offer compared to conventional bulk materials is band gap tunability. The band gap of CQDs can be increased from the value of their respective bulk counterpart in a controlled manner, by decreasing the size of the dots. This characteristic allows QDs of large band gap bulk SCs, such as cadmium chalcogenides, to be tuned in the entire range of visible light,⁵ QDs of low band gap SCs, such as lead chalcogenides, to span over the near and short-wave infrared (NIR and SWIR),⁶ and QDs of semimetals, such as mercury chalcogenides, to

span over the mid- and long-wave infrared (MWIR and LWIR).⁷

Over the last two decades, yet another degree of freedom in the band gap tunability of CQDs has been explored. By highly populating, *via* doping, either the conduction band (CB) with electrons or the valence band (VB) with holes, it is possible to access optically intraband transitions in those bands, as demonstrated for cadmium^{8,9} and lead chalcogenides.¹⁰ The emergence of intraband absorption is coupled to progressive bleaching of interband absorption, as the CB or VB becomes more populated. Intraband transitions, taking place between electronic states within a band, are less energetic than the

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conventionally exploited interband transitions and can even be smaller than the band gap of the bulk counterpart, thus allowing exploitation of part of the electromagnetic spectrum forbidden for a given bulk SC material. To give an example of its potential, fine-tuning of and access to intraband transitions in CQDs could lead to photodetectors and light sources in the MWIR and LWIR¹¹ made of relatively high bandgap, cheap, and nontoxic materials, replacing the current technology based on epitaxially grown HgCdTe, InGaAs and GaInSb.¹² Consequently, work in this field is becoming more and more intense, and steady-state probing of intraband transitions has already been achieved in several materials.¹³ However, until recently only mercury chalcogenide CQDs have exhibited stable high doping that allowed fabrication of intraband photodetectors.^{11,14,15} Recently, robust heavy doping has been demonstrated in PbS CQD films,¹⁶ enabling intraband absorption and photodetection in the MWIR and LWIR,¹⁷ at energies smaller than the PbS bulk band gap. At this point, studies of the basic properties of intraband transitions in CQDs are needed to guide the development of intraband-based devices and applications. In this work, we investigate the size and temperature dependence of intraband transitions in the CB of PbS CQDs. We report the intraband absorption coefficient of PbS QD films and discuss the size dependence of the oscillator strength of the first intraband transition in PbS QDs.

RESULTS AND DISCUSSION

PbS CQDs and Doped Films Used for the Study.

Figure 1 shows absorbance spectra of the PbS CQDs used in

Figure 1. Absorbance spectra, normalized to the maximum of the exciton peaks, of oleic-acid capped PbS CQDs dispersed in toluene. The QD diameter of the different solutions ranges between 5.2 and 9.0 nm.

this study, which evidence good control on the QD size (diameter) in the 5–9 nm range and low size dispersion. QD size has been obtained using the empirical model for oleic-acid capped QDs reported in ref 6 after fitting the exciton energy in the absorbance spectra.

After synthesis, we fabricated doped films following the method reported in ref 16. The films are spin-coated layer-by-layer on silicon substrates, exchanging the original oleic acid ligand with iodine. We use semi-insulating (lightly doped) silicon substrates throughout the whole study because the different measurements performed require transparency in the 1–12 μm range. After formation, the film is infiltrated and capped with alumina by atomic layer deposition, a method that has been proven to provide n-doping in PbSe¹⁸ and ZnO^{19,20}

QDs. The resulting PbS CQD films are heavily n-doped ($\sim 10^{19} \text{ cm}^{-3}$)¹⁶ and, consequently, exhibit steady-state intraband absorption in the CB.¹⁷ Figure 2b shows the first two interband

Figure 2. Interband absorption in heavily n-doped PbS CQD films. (a) Second-derivative analysis of the absorption spectrum. Vertical lines indicate the first three excitons. (b) Energy of the first two excitons, corresponding to lines 1 and 2 in (a) as a function of d . The lines are fits, as described in the main text. The inset illustrates the transitions of the first (red arrow) and second (blue arrows) excitons. Resulting from the n-doped character of the QDs, the measured E_2 originates exclusively from $1S_h-1P_e$ transitions and not from $1P_h-1S_e$ transitions.

excitons in the doped films as a function of the dot diameter, d , obtained *via* analysis of the absorption spectra, as shown in Figure 2a. Note that for some samples, E_2 could not be accurately fitted, hence the reduced number of data points for E_2 in Figure 2b. We found that the first exciton is red-shifted in the doped films as compared to the as-synthesized solutions (Supporting Figure S1). We used this exciton-shift fingerprint as well as the doping level of the samples (discussed later and shown in Figure 4d) to discard oxidation of the dots before or during film formation, thus guaranteeing proper sample quality for further quantitative studies. We found that the samples that showed signs of oxidation (slight blue-shift of the first exciton) also exhibited lower doping levels.

We have fitted the first exciton, E_1 ($1S_h-1S_e$), and the second exciton, E_2 ($1S_h-1P_e$), with eqs 1 and 2:

$$E_1 \text{ (eV)} = 0.41 + \frac{1.50}{d} + \frac{4.2}{d^2} \quad (1)$$

with a fit correlation coefficient, $R^2 > 0.99$.

$$E_2 \text{ (eV)} = 0.41 + \frac{3.09}{d} + \frac{1.4}{d^2} \quad (2)$$

with $R^2 > 0.99$.

The constant term 0.41 eV is the bulk band gap of PbS, E_g , at room temperature (RT). The size-dependent $1/d^2$ represents the confinement energy characteristic of particles

in a well under the effective mass approximation. The $1/d$ term is an empirical observation required to fit E_1 and E_2 , as it was the case in previous studies,^{6,21} indicating that corrections to this approximation are needed. In both transitions, the $1/d$ term is dominant over the quantum confinement one, as it is the case in as-synthesized PbS CQDs.⁶ In fact, for E_2 , data can be fitted without the $1/d^2$ term, in the $5 \text{ nm} < d < 8 \text{ nm}$ range, with $R^2 > 0.99$. However, the fact that the $1/d^2$ term of E_2 is almost negligible in this size range is not particular of doped dots. Cademartiri *et al.*²¹ showed that the second exciton in undoped PbS CQDs dispersed in solution deviates from the expected behavior for $d > 5 \text{ nm}$, which caused E_2 to not be fitted to an equation of the form of eq 1 in the 4–7 nm size range. Therefore, although we expect eq 1 to be valid for $d < 5 \text{ nm}$,^{6,21} we do not expect the same for eq 2.

There is not a clear explanation for the peculiar size dependence of E_2 . Although it was a cause of controversy in the past, there is now a consensus that it corresponds to the $1S_h-1P_e$ and $1P_h-1S_e$ transitions.^{22,23} These two have very similar energies due to the almost identical electron and hole effective masses in PbS,²⁴ as indicated in the inset of Figure 2b. Both transitions should be forbidden by symmetry. However, it has been shown that parity selection rules are relaxed in PbS QDs, allowing optical absorption features that do not conserve parity.²² It has been discussed that breaking of the inversion symmetry of the wave function is needed to fully explain the optical absorption spectra of PbS QDs.²³ Ref 21 shows yet another higher-energy transition (seventh exciton) that exhibits a size dependence behavior similar to E_2 , with a sudden change in trend for $d > 5 \text{ nm}$, and discusses the possibility that this transition originates from a separate corner of the Brillouin zone. Here, we propose another explanation for the sudden change in the size dependence of E_2 . It has been reported that the morphology of PbS QDs changes with size, evolving from an octahedral shape, for $d < 3 \text{ nm}$, to a cuboctahedral shape, for $d > 4 \text{ nm}$.²⁵ Small QDs have Pb-rich (111) facets, whereas in larger dots, S-rich (100) facets emerge. We argue that the change in morphology in large dots, having exposed sulfur atoms, may contribute to the formation of new states that modify the energy of the second (and possibly the seventh) interband transition.

Size Dependence of the Intraband Transition. We have measured the absorption spectra of the intraband transitions in our films, A_{film} , by means of transmission and reflection measurements *via* Fourier transform infrared spectroscopy. Our samples consist of a thin film ($\sim 100 \text{ nm}$) of PbS QDs on top of a substrate ($\sim 300 \mu\text{m}$) of semi-insulating silicon, as sketched in Supporting Figure S2. A_{film} is defined as

$$A_{\text{film}} = 1 - R_{\text{meas}} - T_{\text{meas}} - A_{\text{subs}} \quad (3)$$

where R_{meas} and T_{meas} are the measured transmission and reflection, and A_{subs} is the absorption of the substrate, which was previously characterized through reflection and transmission measurements (see Supporting Figure S3). Figure 3a shows that the intraband transition shifts to higher energies as the dot size decreases, owing to increased quantum confinement. Sharp features at around 0.14 and 0.15 eV arise from the differences (such as the amount of SiO_2) in the reference silicon substrate and the substrate of each sample (see Supporting Figure S4). Below 0.13 eV, alumina contributes to absorption (Supporting Figure S5).

The size dependence of the intraband energy, E_{IB} , at RT is plotted in Figure 3b. We have fitted the results with eq 4:

Figure 3. (a) Intraband absorption spectra of QDs of different sizes normalized to the peak maxima. (b) Energy of the intraband transition, at RT, as a function of the dot diameter. Data are obtained as the central energies of Gaussian fits of absorption spectra such as those presented in (a). The error bars are estimates of the uncertainty in the fits ($\pm 3 \text{ meV}$). The red solid line corresponds to eq 4. The black dashed line represents the energy difference between the second and first excitons. (c) Second confinement energy ($E_2 - E_g$) divided by the first confinement energy ($E_1 - E_g$) as a function of the first confinement energy. E_2 ($1S_h-1P_e$) is obtained in two ways: directly from absorption spectra at RT ($\diamond$) and as E_{IB} ($1S_e-1P_e$) + E_1 ($1S_h-1S_e$) at RT ($\bullet$) and 98 K ($\star$).

$$E_{\text{IB}} (\text{eV}) = \frac{1.57}{d} - \frac{2.5}{d^2} \quad (4)$$

with $R^2 = 0.97$. The negative value of the $1/d^2$ term is expected, since we expect E_{IB} to be equal to $E_2 - E_1$ (see eqs 1 and 2). For comparison, we have plotted $E_2 - E_1$ in Figure 3b. These results support the fact that, for all studied samples, the absorption peaks analyzed correspond to intraband transitions. As it was the case for E_1 and E_2 , the $1/d$ term represents the dominant contribution to the size dependence of E_{IB} . This will be useful later on for the analysis of the temperature dependence of E_{IB} . As discussed previously, eq 2 is not valid for $d < 5 \text{ nm}$, therefore, eq 4 should not be valid either. We do not know whether eq 2 and, hence, eq 4 still hold for $d > 8.5$

Figure 4. Absorption coefficients in heavily n-doped PbS CQD films. (a) Absorption coefficient spectra measured in PbS QD thin films for QDs of different sizes. (b) Peak values of the intraband (red circles) and interband (blue rhombus) absorption coefficients. Values are obtained by fitting the absorption spectra to Gaussians. The error bars account for the error propagation of the uncertainty in film thickness (see Supporting Table S1) and the absorption measurements (5%, estimated). (c) Integrated absorption coefficients. Values are obtained by integration of the fitted Gaussians. (d) Measured occupancy factor of $1S_e$. (e) The maximum attainable value of $\bar{\alpha}$, $\bar{\alpha}_{\text{max}}$, and oscillator strength per volume of the intraband and interband absorption. The line is a power law fit. (f) Oscillator strength per QD of the intraband absorption.

nm. We know, however, that E_{IB} should get progressively closer to zero as the quantum confinement gets weaker. For dot diameters close to the exciton Bohr radius, a_{B} , of PbS (~ 20 nm), the nanocrystals are in the weak confinement regime and E_{IB} should approach zero.

In the framework of the effective mass approximation, the normalized confinement energy of the different interband transitions (confinement energy of exciton i , $E_i - E_g$, divided by the confinement energy of the first exciton, $E_1 - E_g$) should be independent of $E_1 - E_g$.¹⁰ Figure 3c plots the normalized confinement energy of the second intraband transition. We have used two set of values for E_2 , those obtained directly from absorption measurements (Figure 2b) and values obtained as $E_1 + E_{\text{IB}}$ (Figures 2b and 3b). As expected, both sets of values yield very similar results. However, instead of a size-independent value, we observe a linear decrease of the normalized confinement energy of the second exciton for $E_1 - E_g$ in the 0.25–0.45 eV range ($8 \text{ nm} > d > 5 \text{ nm}$). This behavior matches the one reported for undoped PbS CQDs dispersed in solution,²¹ where $(E_2 - E_g)/(E_1 - E_g) \approx 1.39$ for $E_1 - E_g > 0.45 \text{ eV}$ ($d < 5 \text{ nm}$) and increases for smaller confinement energies (larger dots). We ascribe this behavior to the fact that both E_1 and E_2 have a predominant $1/d$ contribution over the $1/d^2$ confinement energy term, as discussed in the previous section.

Figure 3c also shows measurements of $(E_2 - E_g)/(E_1 - E_g)$ at 98 K. To calculate E_g at low temperatures, we used 320 $\mu\text{eV/K}$ as the temperature dependence of the bulk PbS band gap.²⁶ The low-temperature values of normalized confinement energies match closely the values at RT, indicating that E_1 and E_2 at low temperatures follow similar size dependences to

those shown in Figure 2b. The impact of temperature on the intraband transition will be studied later on.

Absorption Coefficient of Doped PbS QD Films.

Characterizing the intrinsic absorption intensity of a semiconductor is crucial both for its use in practical applications and for theoretical studies. We have performed absorption measurements such as those shown in Figure 3a to calculate the absorption coefficient of our films (see Methods). Figure 4a shows some of the measured absorption coefficient spectra of the intraband region. The peak values of α for the $1S_e$ – $1P_e$ transition are plotted in Figure 4b as a function of d . The α peak values and other relevant parameters of the results presented in Figure 4 are compiled in Supporting Table S1. For comparison, α for the interband ($1S_h$ – $1S_e$) transition in the same samples is also plotted in Figure 4b. Note that in these absorption measurements, we have not been able to measure the interband transitions for all samples, and the reason is two-fold: For the samples with smaller QDs, the exciton energy falls out of the detector range. For the samples with larger QDs, the interband absorption peak is almost completely bleached ($1S_e$ almost completely filled). The measured interband absorption coefficient in these heavily doped samples is around $0.5 \times 10^4 \text{ cm}^{-1}$. From this value, we can estimate what the interband absorption coefficient would be in undoped samples. The interband absorption peak in the doped samples has been bleached to about a quarter of its value prior to doping (Supporting Figure S6). Therefore, the interband absorption coefficient for undoped or lightly doped films would be in the order of $2 \times 10^4 \text{ cm}^{-1}$, similar to the measured value of the intraband absorption coefficient and

close to values previously reported for undoped PbS QDs measured in solution.²⁷

To make a better comparison between absorption intensity in different films, Figure 4c shows the values of α integrated over the intraband (or interband) absorption range, $\bar{\alpha}$. Integration over the whole spectrum of the transition corrects for the impact on α peak values of differences in full width half maxima (fwhm, see Supporting Table S1) of the absorption spectra. We ascribe the differences on fwhm to different size distribution in the synthesized nanoparticles.

In our QD films, α and $\bar{\alpha}$ are influenced by factors extrinsic to the QDs, such as the packing density of the films (or the volume fraction occupied by the QDs) and the presence of a surrounding medium (alumina) imposed by the doping procedure, which alters the effective dielectric function of the film.²⁷ For fundamental studies that require comparison with theory, the oscillator strength is a more adequate parameter. The oscillator strength is an intrinsic property of materials related to the probability of an electronic quantum transition upon the presence of a resonant electromagnetic field. The integrated absorption coefficient of the QD film is directly related to the oscillator strength per volume, f_v .²⁸ The oscillator strength per particle, f_{QD} , instead, determines the radiative lifetime. Because we ignore the dielectric constant of our material in the energy range of our study as well as the exact volume fraction occupied by the QDs in the films, we cannot know precisely the intrinsic absorption coefficient of the QD material, and consequently, we cannot make a quantitative study of the oscillator strength of our particles. However, under the assumption that the film packing density and dielectric constant are similar in all samples, we are able to evaluate in qualitative terms the dependence of f_{QD} with d . In doing so, the doping level of our samples needs to be determined. PbS QDs can accommodate up to 8 electrons in the $1S_e$ state.²⁴ Therefore, we define the $1S_e$ occupancy factor $\emptyset = \frac{n_{QD}}{8}$, where n_{QD} is the average doping level of the QDs in the film (measured in electrons per QD, see Methods). Figure 4d shows the measured $\emptyset$ as a function of d . It shows a higher occupancy in larger dots. Note that the phenomenological observation of increased doping in larger sized QDs has been previously reported in other CQD materials, such as CdSe²⁹ and HgSe.¹⁴ In the doping method employed in this work, the increasing doping with size seems to be strongly related to the size-dependent presence of exposed sulfur sites to undergo halide substitution,¹⁶ which in turn leads the Fermi level to approach and cross the $1S_e$ state. Whereas the oscillator strength defines the probability of a quantum absorption process to take place, the occupancy of the initial and final states has to be additionally considered to calculate the absorption coefficient.³⁰ Thus, looking at the intraband transition, in undoped PbS QDs (empty $1S_e$) $\bar{\alpha} = 0$, because the initial state is empty, whereas $f_{QD} \neq 0$, because it is independent of the occupancy of the initial and final states. Therefore, for a proper comparison of the oscillator strength in different samples, $\bar{\alpha}$ has to be corrected by $\emptyset$. Let us call $\bar{\alpha}_{max}$ the maximum attainable value of $\bar{\alpha}$. For intraband transitions, $\bar{\alpha}$ will be maximum at $\emptyset = 1$, whereas for interband transitions, $\bar{\alpha}$ will be maximum at $\emptyset = 0$. Hence, we define $\bar{\alpha}_{max} = \bar{\alpha}/\emptyset$ for intraband transitions and $\bar{\alpha}_{max} = \bar{\alpha}/(1 - \emptyset)$ for interband transitions. This correction allows us to relate directly the measured $\bar{\alpha}$ to f_v , as shown in Figure 4e. Note that, implicitly, we are assuming that, resulting from Fermi–Dirac statistics,

the $1P_e$ state is mostly empty at RT for all samples, given $E_{IB} > 0.15$ eV (Supporting Figure S7). The results show that the oscillator strength of the intraband transition is in the same order and even higher than that of the interband transition. For the intraband case, we have fitted f_v to a power law equation, resulting in an exponent value of -2.7 and $R^2 = 0.98$. f_{QD} is obtained as $f_{QD} = f_v \times V$, where V is the volume of a QD of diameter d . Figure 4f plots the size dependence of f_{QD} , assuming the QDs to be spherical.

The absorption strength of interband transitions has been studied for different semiconductor nanocrystals by measuring the absorption coefficient, the molar extinction coefficient, or the absorption cross section.^{6,21,31–37} Early calculations of the strength of interband transitions suggested that f_{QD} for E_1 should be independent of the dot size, so long as the dots are in the strong confinement regime.²⁸ More recently, it was pointed out that further theoretical studies, going beyond the effective mass approximation, are needed to explain the experimental results obtained for different materials.²⁷ Fewer studies are reported on interband transitions. Ref 14 calculates a linear dependence with size of the oscillator strength of the interband transition in HgSe QDs. Some theoretical works have calculated the oscillator strength of intraband transitions for QDs of different materials.^{30,38,39} However, because of the particularities of each study, none of these works can be directly related to our case. Our results indicate that the oscillator strength per particle of the intraband transition in PbS QDs has a weak dependence on d in the studied size range. We hope that this work will motivate theoretical studies of the oscillator strength of intraband transitions in lead chalcogenide QD materials.

Temperature Dependence of the Intraband Transition. Analysis of the temperature dependence of the interband and intraband transitions is also fundamental for the development of theoretical models that can predict the optical properties of CQD materials as well as in their applications to light emitters and photodetectors. The temperature dependence of the interband transition in cadmium and lead chalcogenide CQDs has been extensively analyzed.^{37,40–45} In the case of PbS, Olkhovets *et al.*⁴⁰ showed that E_1 is nearly independent of temperature in small dots ($d < 4$ nm), as expected for atomic-like energy levels. As the dots get larger, E_1 has an increasing positive dependence with temperature, approaching the temperature dependence of bulk PbS as quantum confinement is reduced. Different theoretical models have been used to explain the experimental results, taking into account the impact of lattice expansion,⁴⁰ electron–phonon (el–ph) interactions,^{40,41,43} and effective mass.⁴⁴ From these works, it is concluded that el–ph interactions play a predominant role in the temperature dependence of E_1 .

We have measured the intraband absorption in our heavily doped samples in the temperature range of 98–298 K (see Methods). Figure 5a,b shows measurements for two samples with different dot sizes. The first noticeable feature is the red-shift of E_{IB} as temperature increases, conversely to the reported blue-shift of E_1 in undoped PbS CQDs.⁴⁰ A similar effect was reported for HgSe QDs.¹⁴ The positive dependence of E_1 with temperature is preserved in doped QDs, as shown in Figure 5c. Another interesting aspect is the apparent increase in intraband absorption intensity upon sample cooling. We think that this is an intrinsic property of the material, not due to a variation of $\emptyset$ with temperature, since the doping level of the dots has been

Figure 5. Intraband absorption spectrum at different temperatures of highly n-doped PbS CQDs films with QD diameter (a) 6.5 nm and (b) 8.4 nm. The two spikes at around 0.14 eV are due to the temperature variation of the SiO₂ absorption peak (see Methods). (c) Interband absorption spectrum at different temperatures of the same sample as in (a). (d) Temperature dependence of the interband (●) and intraband (■) transitions in heavily n-doped PbS CQD films on silicon substrate. For comparison, the case of interband transitions in lightly n-doped films is also shown (○). Broken lines are guides to the eye. The solid red line is a fit to C/d , where C is a constant.

shown to be constant in the 80–300 K range.¹⁷ The increase of intraband absorption intensity at low temperatures is in line with previous reports of increased absorption cross section of the interband transition at low temperatures in PbS CQDs.⁴² Finally, by comparing Figure 5a,b, it can be appreciated that the energy shift of the intraband transition is stronger for smaller dots, as opposed to what has been found for the interband case.

In order to do a quantitative analysis of the temperature dependence of the intraband and interband transitions, we have identified the energies E_1 and E_{IB} at different temperatures, as described previously. In addition, we have measured samples with light n-type doping ($\Phi \ll 1$, see Methods) in which there are no signs of interband bleaching or intraband absorption. An example of temperature dependence for such samples is shown in Supporting Figure S8. For E_1 and E_{IB} , we have calculated the respective coefficients of energy variation with temperature, $\partial E_1/\partial T$ and $\partial E_{IB}/\partial T$, as the slopes of linear fits to the measured data (Supporting Figure S9). Although the temperature dependence of E_1 is not linear in the whole 0–300 K range,^{42,43} the use of a linear dependence is generally accepted as a valid approximation in the 100–300 K range.^{40,42} Our results show that a linear dependence is also a good approximation for the intraband transition in that temperature range.

The measured temperature dependence coefficients are plotted in Figure 5d as a function of the dot diameter. As anticipated, the temperature dependence of the intraband transition is negative and is stronger for smaller dots. These results can be qualitatively explained by considering only el-ph coupling effects, which, as mentioned before, are dominant in the temperature dependence of E_1 in undoped PbS QDs. The contribution of el-ph coupling to the temperature

dependence of interband transitions in PbS QDs is smaller for higher energies.⁴⁰ Thus, the temperature dependence of E_2 is expected to be weaker than that of E_1 . Since $E_{IB} = E_2 - E_1$, it follows that $\partial E_{IB}/\partial T < 0$. In addition, since the energy difference between E_2 and E_1 is larger for smaller dots, $\partial E_{IB}/\partial T$ should increase (in magnitude) as the dot size is reduced.

In our lightly doped films, the values of $\partial E_1/\partial T$ are similar to those previously reported for undoped QDs.⁴⁰ Upon heavy doping, $\partial E_1/\partial T$ is reduced. The difference in $\partial E_1/\partial T$ between the heavily doped and lightly doped samples increases with dot size and, hence, with Φ (see Figure 4). For samples with $d = 5$ nm ($\Phi \sim 0.1$), both values are very close. We deduce that upon occupation of 1S_e, the el-ph interaction is modified, resulting in a reduced contribution to the temperature dependence of E_1 .

Next, we analyze the size dependence of $\partial E_{IB}/\partial T$ on the basis of empirical results discussed above. We know, through eqs 1 and 2, that at RT both E_1 and E_2 are dominated by the $1/d$ term. In addition, Figure 3 indicates that this behavior is maintained at low temperatures. It follows that $\partial E_{IB}/\partial T$ will have a $1/d$ dependence with size. Figure 5 shows a fit ($R^2 = 0.96$) of the measured data to C/d , where C is a constant. For large values of d , $\partial E_{IB}/\partial T$ tends to zero, since $E_{IB} \rightarrow 0$ because of the relaxation of the quantum confinement as $d \rightarrow a_B$.

CONCLUSIONS

We have performed size- and temperature-dependent optical studies of the intraband transition in densely packed films of PbS QDs, thus providing valuable data that can be directly used in device design and engineering. The absorption coefficient of the intraband transition is in the order of the absorption coefficient of the interband transition (10^4 cm⁻¹). This result implies that thin-film PbS intraband optoelectronics can be envisaged. Additionally, dots with semioccupied 1S_e (only partially bleached interband) exhibit strong absorption in both interband and intraband transitions. These dual-band strong absorbers may be interesting for multigap optoelectronic devices such as intermediate band solar cells,⁴⁶ which currently experience a major setback related to weak absorption.⁴⁷

Our measurements reveal absorption in the first intraband transition (1S_e–1P_e). However, absorption at more energetic intraband transitions (from 1S_e to higher levels such as 1D_e, 2S_e, and 1F_e)²² could not be detected (Supporting Figure S10), likely because these transitions are either forbidden or much weaker than the first intraband transition in the studied size range. Our results further indicate that the oscillator strength per particle of the intraband transition has a weak dependence on the dot size.

METHODS

PbS Colloidal QD Synthesis. PbS QDs synthesis was adapted from a previously reported multi-injection procedure.⁴⁸ Briefly, a mixture of lead oxide (PbO), 1-octadecene (ODE), and oleic acid was degassed overnight at 90 °C under vacuum. After degassing, the solution was placed under Ar atmosphere, and a specific reaction temperature was set. A solution of hexamethyldisilathiane ((TMS)₂S) in ODE was quickly injected. After 6 min, a second solution of (TMS)₂S in ODE was dropwise injected in a rate of 0.75 mL/min. After this second injection, heating was stopped, and the solution was let to naturally cool down to room temperature. QDs were purified three times by precipitation with acetone and ethanol and redispersed in anhydrous toluene. Finally, the concentration was adjusted to 30

mg/mL, and the solution was bubbled with N₂. Depending on the reaction parameters, PbS QDs of different sizes were synthesized.

n-Doped PbS QD Film Fabrication. PbS CQD films were deposited using a layer-by-layer spin-coating process under ambient conditions at 2500 rpm. For each layer, the CQD solution was deposited on semi-insulating (10–20 Ω·cm) double-polished Si. Solid-state ligand exchange was performed by flooding the surface with 1-ethyl-3-methylimidazolium iodide in methanol (EMIL, 7 mg/mL) 30 s before spin-coating dry at 2500 rpm. Two washes with methanol were used to remove unbound ligands. After film formation, samples are lightly n-doped.¹⁶ Heavy n-doping is achieved by infiltrating and capping the films with alumina (Al₂O₃) via atomic layer deposition, following an already reported method.¹⁶

Measurement of the QD Doping Level. We employed a previously reported method to measure n_{QD} in our samples.¹⁶ n_{QD} is extracted from the bleaching of the first exciton absorption peak upon heavy doping. Absorption was measured ambient conditions, using a Cary 5000 UV–vis-NIR spectrometer. If we define I_1 and I_2 as the integrated absorption strength of the first excitonic transition of the lightly doped and heavily doped samples, respectively, then $n_{\text{QD}} = 8(1 - I_2/I_1)$. For related figures, see ref 16.

Room-Temperature Absorption Measurements. Absorption of the thin films, A_{film} , was obtained (see eq 3) by means of reflection and transmission measurements, using a Cary 600 FTIR with microscope. The bench of the FTIR was purged with nitrogen gas to minimize the impact of atmospheric absorption in the measurements.

Calculation of the Absorption Coefficient, α . For the simple case of a thin slab of homogeneous material, α can be calculated by taking into consideration the multiple internal reflections that occur at the front and back air/sample interfaces, which increase the effective optical path.⁴⁹ When the thin-film is deposited on a substrate, reflections taking place at every interface (refractive-index change), as well as absorption in the substrate, must be taken into account. For this case, α can also be analytically calculated assuming $at \ll 1$,⁵⁰ where t is the thickness of the thin film. However, in all cases the refractive index of the sample or, alternatively, the fraction of reflected light in a single air/sample interface must be known. Because of the wavelength range in our study (5–9 μm), it was not possible for us to measure either of these values. Hence, we have calculated α using a simple model described by eq 8:

$$A_{\text{int}} = 1 - e^{-\alpha t} \quad (8)$$

where $A_{\text{int}} = A_{\text{film}}/(1 - R_{\text{meas}})$. A_{film} is the measured absorption of the thin film, and R_{meas} is the measured reflectance (see eq 3). A_{int} represents the intrinsic absorption of the film—irrespective of the external medium—taking into account only the light that enters the film. To verify the validity of our model, we calculated α for samples of the same QDs but having different film thickness (Supporting Figure S11). The small difference in α among the different samples discards strong multiple-reflection effects in our measurements. The uncertainty in the determination of α can be explained in terms of errors propagated from the thickness and absorption measurements.

Temperature-Dependent Absorption Measurements. Absorption was obtained as $1 - \text{transmission}$. Temperature variable transmission measurements were made under vacuum, using a Cary 610 FTIR with microscope coupled to a liquid-nitrogen cooled, temperature-controllable Linkam HFS350EV-PB4 stage equipped with ZnSe windows. For all samples, the temperature change was done at a controlled rate (3 K/min). After reaching the temperature set point, temperature was stabilized 5 min prior to performing the measurements.

A bare-silicon substrate was used as a background sample. The same background, measured at RT, was used to determine the transmission of the samples at all temperatures. Low-temperature measurements exhibit a double-peak feature centered at 0.136 eV. This feature is due to the temperature-dependent energy shift of the SiO₂ absorption in the samples, which is not corrected by the RT background.

Determination of Sample Thickness. The thicknesses of the samples used in absorption measurement were measured using a KLA-Tencor Alpha-Step IQ Surface Profiler.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.0c02033>.

Example of thin-film absorption measurements, validation of the absorption model, bleach of exciton upon doping, fits of temperature dependence of interband and intraband transitions, absorption spectrum of silicon substrate and alumina, energy shift of the first exciton in doped QDs, relevant parameters of the intraband samples analyzed (PDF)

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Author Contributions

I.R. designed the experiments and analyzed the results. I.R., B.K., and M.P. performed the absorption measurements. M.D. synthesized the QDs. I.R. and O.Ö. fabricated the samples. I.R. and G.K. wrote the manuscript with input from all authors. G.K. designed the experiments and supervised the work.

Notes

The authors declare no competing financial interest.

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