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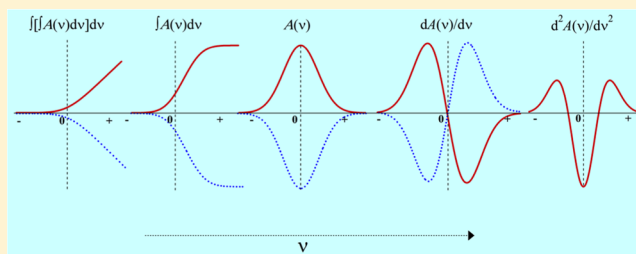
# Integral Method Analysis of Electroabsorption Spectra and Its Application to Quantum Dots of PbSe

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## S Supporting Information

**ABSTRACT:** The integral method is proposed to analyze the electroabsorption (E-A) spectra, since the change in the electric dipole moment and/or polarizability following absorption can be determined precisely and the bands buried under strong absorption bands can be confirmed. This method, where not only the observed E-A spectra but also each of their first and second integral spectra are fitted using the absorption and their derivative and integral spectra, has been successfully applied to the E-A spectra of semiconductor quantum dots of PbSe. In the results, one absorption band, which is not identified in the absorption spectrum because of the extremely weak intensity and also showing a remarkable blue shift in the presence of an electric field because of the large difference in polarizability between the ground state and the excited state, has been confirmed to be located between the first and second strong exciton bands. The size dependence of PbSe QDs of the peak position of the newly confirmed band as well as the magnitude of the change in electric dipole moment and polarizability following the absorption of each absorption band is also reported, based on the analysis by the integral method.



## 1. INTRODUCTION

External electric field effects on optical spectra or Stark effect spectra have been extensively used to investigate electronic structures and photoexcitation dynamics.<sup>1–5</sup> The electroabsorption (E-A) spectrum, that is, the field-induced change in absorption intensity as a function of wavelength or wavenumber, is useful for the determination of molecular parameters as well as the internal field in biological systems.<sup>6–8</sup> The change in the permanent electric dipole moment and polarizability following the electronic transition can be obtained from the E-A spectrum, with the fitting of the observed E-A spectra. A theory on the absorption of polarized light by an ensemble of mobile molecules was first developed by Liptay and co-workers.<sup>9</sup> Attempts were made to reproduce the observed E-A spectra by a linear combination of the zeroth, first, and second derivatives of the absorption spectra, and from the coefficient of each derivative component with which the observed E-A spectra can be reproduced, the change in physical parameters following photoexcitation can be determined. This analysis, which may be called the differential method, can be applied when absorption bands as well as the corresponding E-A bands can be well separated from each other. If the absorption bands cannot be separated from each other or the absorption band which corresponds to the observed E-A signals cannot be identified, then the differential method is unapplicable. Then, we propose another type of analysis of the E-A spectra, that is, integral method analysis, in which E-A spectra are integrated along their wavenumbers and the resulting spectra are simulated using both derivatives and integrals of the absorption spectra.

The integral method is applicable to any kind of molecular system and material. In the present study, special attention is paid to semiconductor quantum dots (QDs), which represent the ultimate in quantum-confined systems, and the integral method is applied to the E-A spectra of QDs of lead chalcogenide, i.e., PbSe, which is a direct band gap semiconductor with a small band gap. The application of QDs of PbSe may include a number of optoelectrical devices with near-infrared light and biological imaging.<sup>10–16</sup> In addition to possible device applications, the Stark effect can be used to prove the nature of the excited states of QDs. The E-A spectra of PbSe preliminarily reported in our previous paper were analyzed by using the derivatives of the whole absorption spectra with a focus on the first exciton band,<sup>17</sup> but advanced analysis is necessary to simulate the E-A spectra over the whole spectral region.

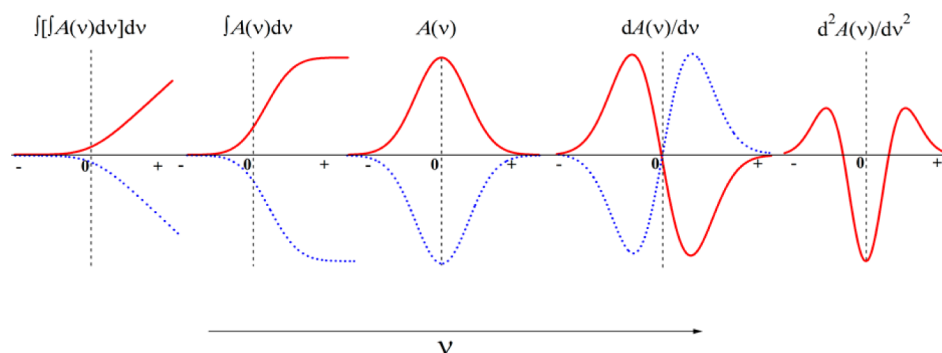
## 2. THEORETICAL BACKGROUND OF THE INTEGRAL METHOD ANALYSIS

When an electric field ( $F$ ) is applied to molecules, each energy level is shifted by  $-\mu F - \alpha F^2/2$ , depending on the electric dipole moment ( $\mu$ ) and the molecular polarizability ( $\alpha$ ) of the state concerned, due to the so-called Stark shift. As a result, the optical transition energy is shifted by  $\Delta E (= -\Delta\mu F - \Delta\alpha F^2/2)$ , where  $\Delta\mu$  and  $\Delta\alpha$  are the differences in electric dipole moment and molecular polarizability, respectively, between the ground

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**Figure 1.** Spectral shape of the integral and derivative of the Gaussian absorption profile. The second integral, first integral, zeroth integral (zeroth derivative), first derivative, and second derivative spectra (from left to right).

state (g) and excited state (e), i.e.,  $\Delta\mu = \mu_e - \mu_g$  and  $\Delta\alpha = \alpha_e - \alpha_g$ . According to the theory of electric field effects on optical spectra, the field-induced change in absorption intensity at wavenumber  $\nu$ , i.e.,  $\Delta A(\nu)$ , is given by a linear combination of the zeroth, first, and second derivatives of the absorption spectra  $A(\nu)$ :<sup>1,9,18</sup>

$$\Delta A(\nu) = (fF)^2 \left[ A_\chi A(\nu) + B_\chi \nu \frac{d}{d\nu} \left( \frac{A(\nu)}{\nu} \right) + C_\chi \nu \frac{d^2}{d\nu^2} \left( \frac{A(\nu)}{\nu} \right) \right] \quad (1)$$

Here  $f$  is the internal field factor, and  $F = |F|$ . E-A spectra depend on the angle between the direction of  $F$  and the polarization direction of the electric vector of the absorbed light, i.e.,  $\chi$ . In an immobilized and randomly distributed system,  $A_\chi$  originates from the change in transition moment induced by electric fields. With the magic angle  $\chi$ , i.e.,  $54.7^\circ$ ,  $B_\chi$  and  $C_\chi$  are given as follows:

$$B_\chi = \frac{\Delta\bar{\alpha}}{2hc}, \quad C_\chi = \frac{|\Delta\mu|^2}{6h^2c^2} \quad (2)$$

$\Delta\bar{\alpha}$  denotes the trace of  $\Delta\alpha$ , i.e.,  $\Delta\bar{\alpha} = (1/3)\text{Tr}(\Delta\alpha)$ .

If the E-A spectra are given by a sum of the zeroth, first, and second derivatives of  $A(\nu)$ , the integral of the E-A spectra along the wavenumber is approximately given as follows:

$$\int \Delta A(\nu) d\nu \cong (fF)^2 \left\{ A_\chi \int A(\nu) d\nu + B_\chi A(\nu) + C_\chi \frac{dA(\nu)}{d\nu} \right\} \quad (3)$$

On the right-hand side, the first term shows a monotonic increase or decrease, depending on the sign of  $A_\chi$ , as a function of wavenumber, the second term shows the spectral shape given by the absorption spectrum, and the third term shows the spectral shape given by the first derivative of the absorption spectrum. A further integral of the first integral, that is, the second integral of the E-A spectra along the wavenumber, is given as follows:

$$\int \left\{ \int \Delta A(\nu) d\nu \right\} d\nu \cong (fF)^2 \left[ A_\chi \int \left\{ \int A(\nu) d\nu \right\} d\nu + B_\chi \int A(\nu) d\nu + C_\chi A(\nu) \right] \quad (4)$$

The first and second terms on the right-hand side show a monotonic increase or decrease, depending on the sign of  $A_\chi$  and  $B_\chi$ , while the third term shows a spectral shape which is the same as the absorption spectrum.

The absorption band given by a Gaussian shape, its first and second derivatives, and its first and second integrals are shown in Figure 1. In the differential method analysis, all of the absorption bands must be known at the beginning. In the integral method analysis, on the other hand, the first integral

and the second integral of the observed E-A spectra are taken, besides the E-A spectra. Then, the first integral of the E-A spectrum is simulated by a linear combination of the zeroth and first derivatives and the first integral of the absorption spectrum, and the second integral of the E-A spectrum is simulated by a linear combination of the zeroth derivative and the first and second integrals of the absorption spectrum. Coefficients  $A_\chi$  and  $B_\chi$  can take both positive and negative values, while coefficient  $C_\chi$  can take only positive values (eq 2). In the integral method, therefore, all of the observed spectra that include the E-A spectrum and its first and second integral spectra must be fitted with the same coefficients of  $A_\chi$ ,  $B_\chi$ , and  $C_\chi$ . The absorption band which gives a large contribution of the second derivative component in the E-A spectrum is deduced as a peak in the second integral of the E-A spectrum (eq 4). If the Stark shift is very large, then the absorption band can be identified, even when the absorption intensity is negligibly weak. Thus, the advantage of the analysis by the integral method is that the absorption bands can be confirmed even when the absorption intensity is too weak to be detected. Another advantage of the integral method is the increase in the parameters with which extremely precise simulation can be done for the observed E-A spectra.

In the differential method, the observed E-A spectra are just simulated by using the zeroth, first, and second derivatives of the absorption spectrum, and an accidental agreement between observed and simulated spectra cannot be checked. In the integral method, on the other hand, the observed E-A spectrum and its first and second integrals are compared to the simulated spectra step by step using the derivatives and integrals, and the possibility of accidental agreement between the observed and simulated spectra can be drastically reduced.

### 3. EXPERIMENTAL SECTION

PbSe nanocrystalline QDs were synthesized by a non-coordinating solvent method.<sup>19</sup> PbSe QDs with different sizes were prepared by varying the reaction time. The X-ray diffraction (XRD) patterns were measured with a Rigaku-Dmax 2500 diffractometer with Cu K $\alpha$  radiation at a wavelength of 0.15405 nm. The sizes of the QDs were determined from the microscopy images with a scanning transmission electron microscope (Hitachi HD-2000 STEM).

A chloroform solution of a mixture of PbSe QDs and poly(methyl methacrylate) (PMMA) was poured on an indium–tin oxide (ITO)-coated quartz substrate, and a thin PMMA film was prepared by a spin-coating technique. A semitransparent aluminum (Al) film was prepared on the

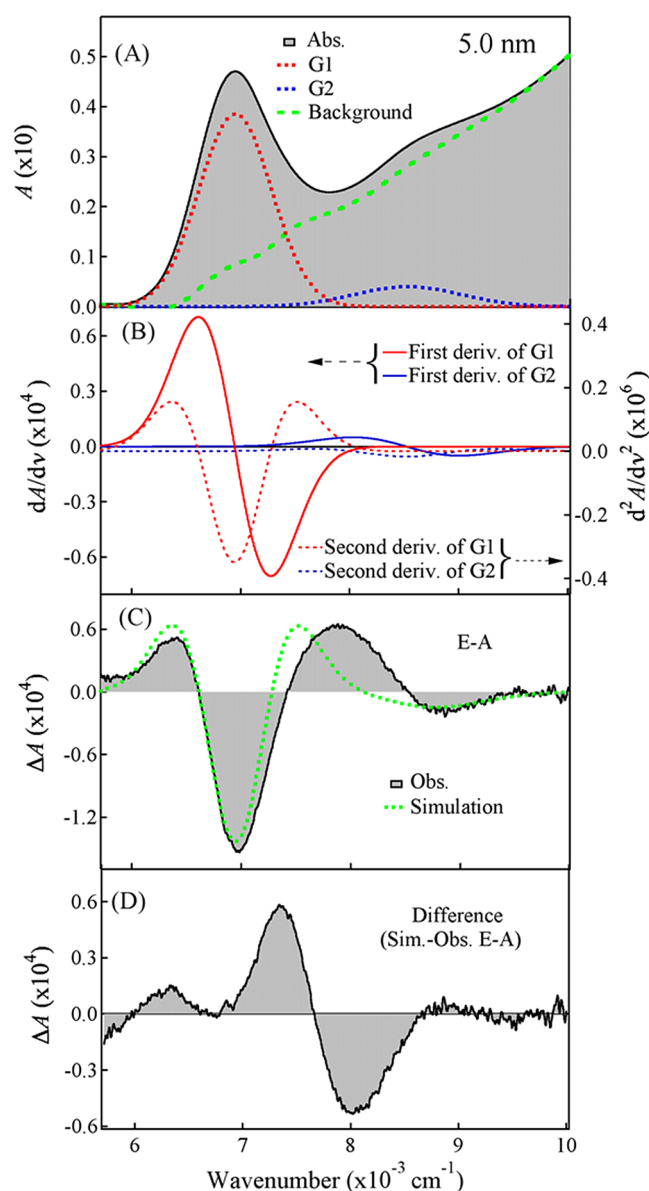
PMMA film using a vacuum vapor deposition technique. The thickness of the polymer film was typically  $0.5\ \mu\text{m}$ . The ITO and Al films were used as electrodes to apply sinusoidal voltage at 1 kHz. A field-induced change in the transmission intensity of the sample film was detected with a lock-in amplifier at the second harmonic of the modulation frequency (Jasco, EMV-100), and the direct-current component of the transmission intensity was simultaneously measured. The strength of the electric field was determined from the applied voltage divided by the thickness of the PMMA film. On the basis of the results, E-A spectra were obtained at room temperature.<sup>17</sup> The angle between the direction of the applied electric field and the electric vector of the excitation light was set to be  $54.7^\circ$  (magic angle) in the E-A measurements.

#### 4. RESULTS AND DISCUSSION

Absorption and E-A spectra of PbSe QDs having a diameter of 5.0 nm observed in a PMMA film are shown in Figure 2. The E-A signal intensity of PbSe QDs in a PMMA film is proportional to the square of the applied electric field, as expected from eq 1. Two bands are clearly observed in the absorption spectrum with peaks at  $\sim 6950$  and  $\sim 8500\ \text{cm}^{-1}$ , respectively, which are denoted as G1 and G2 bands. They can be assigned to the exciton bands in PbSe QDs.<sup>20,21</sup>

At first, the E-A spectra were analyzed with the differential method. As shown in Figure 2, the absorption spectrum of PbSe with a diameter of 5.0 nm in the region from  $5800$  to  $10\ 000\ \text{cm}^{-1}$  is regarded as a superposition of two exciton bands (G1 and G2) and the broad background whose intensity increases monotonically with increasing excitation energy. Then, the absorption spectrum was decomposed to these three bands by assuming that both G1 and G2 have a Gaussian profile (Figure 2). The fact that the E-A spectrum at around G1 is similar to the second derivative of the G1 band and that the minimum position of the E-A spectrum at around G2 is very close to the minimum position of the second derivative spectrum of G2 suggests that the E-A spectrum originates from  $|\Delta\mu|$  following the transition to these exciton states. The E-A signal intensity in the higher-wavenumber region is very weak in the observed E-A spectra, suggesting that the contribution of the broad background is negligibly small. Then, the E-A spectrum was attempted to be fitted by the derivative spectra of G1 and G2. In the analysis, each absorption band was treated independently so that the final Stark signal was taken as a sum of the E-A spectrum of each band. In both bands, the main contribution to the E-A spectra is the second-derivative component. The zeroth-derivative component may not be necessary in the simulation of G1, indicating that the transition moment to the first exciton state is not affected by electric fields. For the G2 band, a small contribution of the zeroth- and first-derivative components has been considered in Figure 2.

Apparently, the E-A spectrum is reproduced by a linear combination of the derivative components of both bands (Figure 2C). However, a careful look shows that the fitting is unsatisfactory in the region between the G1 and G2 bands. In order to quantify the unsatisfactory matching, the difference between the E-A spectrum simulated by the differential method and the observed E-A spectrum is shown in Figure 2D. Even when the contribution of the broad background is considered, a reliable fitting could not be obtained. This is true not only in PbSe QDs with a diameter of 5.0 nm but also in other sizes of PbSe QDs examined in the present study. In all cases, the satisfied fitting could not be obtained in the region between G1

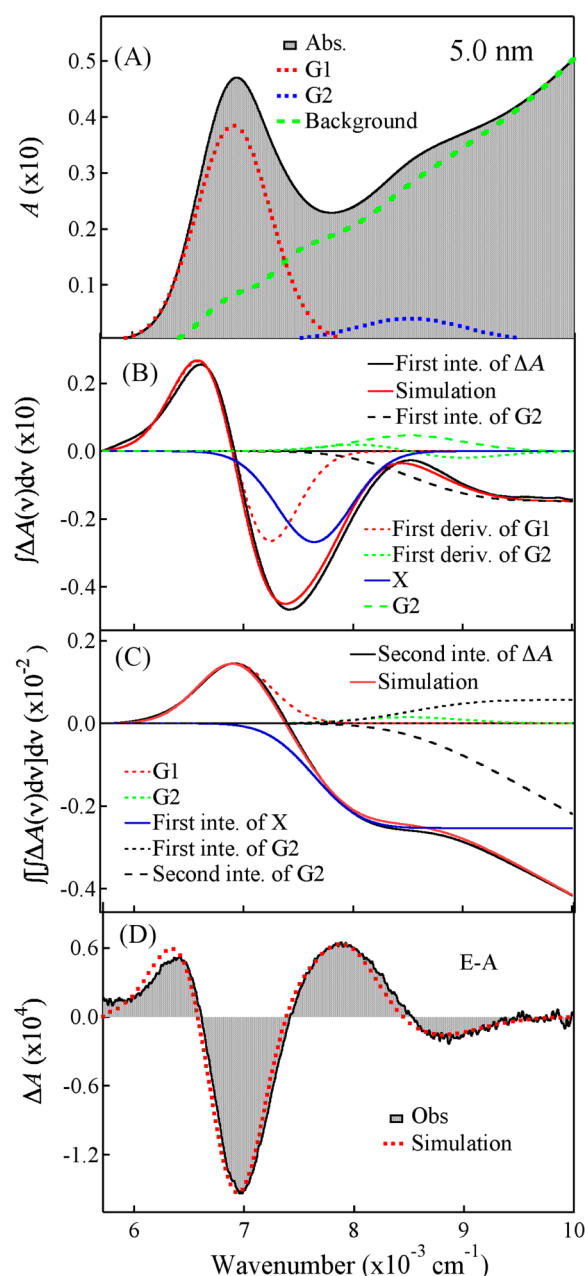


**Figure 2.** Differential method analysis of the E-A spectra of PbSe QDs with a diameter of 5.0 nm in a PMMA film. (A) Absorption spectrum (shaded line) of PbSe QDs and its decomposition to bands G1 and G2 having the Gaussian profile and the remainder, which were used for simulation. (B) First and second derivative spectra of G1 and G2. (C) E-A spectrum (shaded line) at a field strength of  $0.5\ \text{MV cm}^{-1}$  and the simulated spectrum (dotted line) derived using the differential method. (D) Difference between the simulated E-A spectrum and the observed spectrum shown in (C).

and G2 using the differential method. As the origin of the disagreement between the simulated spectrum and the observed E-A spectrum, two possibilities can be considered: (1) an absorption band which is not observed at zero field newly appears in the presence of electric fields; (2) very weak absorption bands which are not identified in the absorption spectrum at zero field show a large electric field effect on the absorption spectrum, that is, the presence of the large Stark shift of the extremely weak absorption band.

When weak absorption bands give large Stark shifts, the integral method is useful in analyzing the E-A spectra. Then, the first integral and the second integral of the observed E-A spectrum were taken. The results are shown in Figure 3B,C. As





**Figure 3.** Integral method analysis of the E-A spectra of PbSe QDs with a diameter of 5.0 nm in a PMMA film. (A) Absorption spectrum (shaded line) and G1 and G2 bands having the Gaussian profile and the remainder. (B) The first integral of the E-A spectrum (black solid line), simulated spectrum (red solid line), and the following spectral contribution to the simulated spectrum: the first derivative of G1 (red dotted line), the G2 band (green broken line), the first derivative of G2 (green dotted line), the first integral of G2 (black broken line), and the X band (blue solid line). (C) The second integral of the E-A spectrum (black solid line), simulated spectrum (red solid line), and the following spectral contribution to the simulated spectrum: G1 band (red dotted line), G2 band (green dotted line), the first integral of G2 (black dotted line), the second integral of G2 (black broken line), and the first integral of the X band (blue solid line). (D) E-A spectrum (shaded line) at a field strength of  $0.5 \text{ MV cm}^{-1}$  and the simulated spectrum (red dotted line) derived using the integral method.

already mentioned, the second integral of the E-A spectrum which gives the second derivative of the absorption spectrum

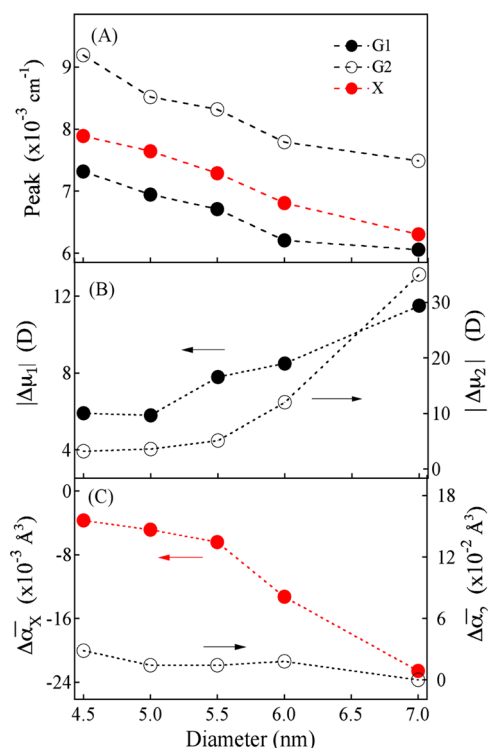
should show the spectrum whose shape is the same as the absorption spectrum. When the second integral of the E-A spectrum is watched from this point of view, two peaks which correspond to G1 and G2 are clearly seen in Figure 3C, in agreement with the conclusion that the E-A spectra of G1 and G2 are mainly given by the second derivative of the absorption spectrum. The absence of the peak other than the ones corresponding to G1 and G2 in the second integral spectrum indicates that it is not necessary to consider another absorption band which gives the second derivative of the absorption spectrum. The fact that the value of the second integral in the region between G1 and G2 is far from zero suggests that the first derivative and/or zeroth derivative of the weak unknown absorption band must be considered in the observed E-A spectrum. It is unlikely that the zeroth-derivative component of the unknown absorption band exists in the region between G1 and G2 and the first derivative component of the weak unknown absorption band appears to be observed in the E-A spectrum. In fact, the difference between the observed E-A spectrum and the spectrum simulated with the second derivative of G1 and G2 is similar in shape to the first derivative of the Gaussian profile (Figure 2D), suggesting the presence of the first derivative spectrum of the weak unknown absorption band in the E-A spectra.

As shown in eq 3, the first integral of the E-A spectrum should be given by a linear combination of the zeroth and first derivatives of the absorption bands if the zeroth-derivative component is negligible in the E-A spectra. The analysis by the differential method and the second integral of the E-A spectrum indicates that G1 and G2 give the first-derivative component of the absorption spectrum in the first integral of the E-A spectrum, and the magnitude of  $\Delta\mu$  was determined to be 5.8 and 3.6 D for G1 and G2, respectively. Then, the first-derivative component of G1 and G2 was subtracted from the first integral of the E-A spectrum. In the result, the absorption band whose shape is similar to the Gaussian profile has been deduced from the first integral spectrum, as shown in Figure 3B, indicating that the weak unknown absorption band which shows a large value of  $\Delta\bar{\alpha}$  following absorption is located between G1 and G2. Hereafter, this band is represented as the X band. As far as we know, this is the first report for the X band. Since this band cannot be identified in the absorption spectrum, the exact value of  $\Delta\bar{\alpha}$  cannot be determined. By assuming that the peak intensity of this absorption band is 1/10 of the observed intensity,  $\Delta\bar{\alpha}$  is estimated to be  $-4855 \text{ \AA}^3$  following the absorption of the X band. Note that the negative sign indicates the decrease in the polarizability following absorption, i.e., the field-induced blue shift of the absorption spectrum. Actually, the absorption intensity of the X band may be less than 1/10 of the observed intensity. Accordingly, the magnitude of  $\Delta\bar{\alpha}$  evaluated in the present study for the X band may be the lower limit. The E-A spectrum simulated with the second derivative of absorption bands G1 and G2 and with the first derivative of the X band is well fitted to the observed E-A spectrum over the whole spectral region. Actually, the small contribution of the zeroth- and first-derivative components of the absorption spectrum is considered for G2 for the better fitting of the E-A spectrum (Figure 3D). By following the representation of the electronic states given in refs 20 and 21, we can assign the X band to the transition from  $(j, \pi) = (1/2, 1)$  to  $(1/2 \text{ or } 3/2, 1)$  or from  $(j, \pi) = (1/2 \text{ or } 3/2, -1)$  to  $(1/2, -1)$ , which is forbidden in the isotropic approximation. Here,  $j$  and  $\pi$  represent the total angular momentum and the parity of the electronic state,

respectively. These transitions may be partially allowed owing to strong anisotropy of the energy bands of bulk PbSe.<sup>22</sup>

The presence of the electric dipole moment in the excited state of CdSe QDs was suggested in CdSe QDs by a possible resonance between localized surface and interior states, based on the E-A spectra which has a shape similar to that of the second derivative of the absorption spectra.<sup>23</sup> However, nearly identical Stark spectra of CdSe QDs was interpreted in terms of the mixing between the allowed state and dark state without considering the polar state in CdSe QDs.<sup>24</sup> In the case of PbSe QDs, there is no indication of the field-induced change in absorption intensity of the X band, suggesting that it is unnecessary to consider the field-induced mixing between the lowest state, to which the optical transition gives the strong G1 band, and the nearby dark state, to which the anisotropy-induced transition gives the weak X band. Therefore, it appears that the excited states reached by the absorption of bands G1 and G2 have remarkable charge-separated character. Only the first-derivative component of the absorption spectrum is dominant in the E-A spectrum of the X band, probably because  $\Delta\bar{\alpha}$  following the absorption of this band is extremely large in comparison to the change in the electric dipole moment. Absorption and E-A spectra of PbSe QDs with different average sizes were obtained.<sup>17</sup> Similar to other QD systems, absorption spectra of PbSe QDs exhibit a blue shift as the diameter decreases. The lowest-energy exciton bands (Figure 2 and Supporting Information) demonstrate tuning from  $6.05 \times 10^3 \text{ cm}^{-1}$  (1653 nm) to  $7.32 \times 10^3 \text{ cm}^{-1}$  (1366 nm), which corresponds to diameters of 7.0–4.5 nm. The E-A spectra of PbSe QDs having these diameters are also reproduced well by considering G1, G2, and X bands. The results of the integral method analysis of the E-A spectra of PbSe QDs having diameters of 4.5, 5.5, 6.0, and 7.0 nm are shown in Supporting Information. Coefficients  $A_{\chi}$ ,  $B_{\chi}$ , and  $C_{\chi}$  which reproduce the observed E-A spectrum and its first and second integrals are given in Table S1 in Supporting Information. The magnitude of  $\Delta\mu$  determined from the second-derivative components for G1 and G2, i.e.,  $|\Delta\mu_1|$  and  $|\Delta\mu_2|$ , and the magnitude of  $\Delta\bar{\alpha}$  determined from the first-derivative component for X and G2, i.e.,  $\Delta\bar{\alpha}_X$  and  $\Delta\bar{\alpha}_2$ , are also shown in Table S2 in Supporting Information. Plots of  $|\Delta\mu_1|$  and  $|\Delta\mu_2|$  and plots of  $\Delta\bar{\alpha}_X$  and  $\Delta\bar{\alpha}_2$  are shown in Figure 4, together with the plots of the peak position of the G1, G2, and X bands, as a function of the diameter of QDs. The differential method and the integral method are the same in the sense that the ultimate purpose is to determine coefficients  $A_{\chi}$ ,  $B_{\chi}$ , and  $C_{\chi}$  which reproduce the observed E-A spectrum in both analyses. As mentioned above, however, the integral method is much more powerful in determining the coefficients precisely.

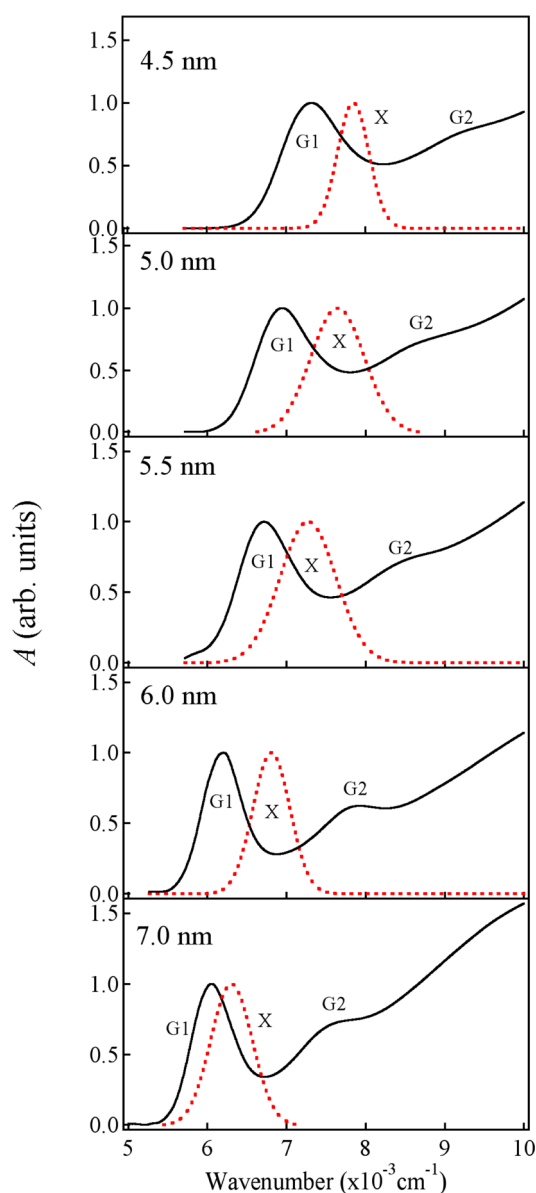
The spectral shape of the X band obtained from the integral method analysis for different sizes of PbSe QDs is shown in Figure 5, together with the absorption spectrum. Note that the absorption intensity of the first exciton band is normalized to unity in every case. All of the bands of G1, G2, and X show a red shift as the size increases. As shown in Figure 4,  $|\Delta\mu_1|$  and  $|\Delta\mu_2|$  of PbSe QDs have a tendency that both increase with increasing particle size;  $|\Delta\mu_1|$  increases from  $\sim 6$  to 11.5 D, while  $|\Delta\mu_2|$  increases from  $\sim 3$  to 35 D with the increase in size from 4.5 to 7.0 nm.  $\Delta\alpha$  of the X band also becomes larger, that is,  $\Delta\bar{\alpha}$  changes monotonically from  $-3700$  to  $-22\,560 \text{ \AA}^3$ , as the size increases from 4.5 to 7.0 nm. The magnitudes of both  $|\Delta\mu_1|$  and  $|\Delta\mu_2|$  increase nearly monotonically with the increase in size (Figure 4B). Because the electrical dipole moment is



**Figure 4.** Plots of the physical parameters of PbSe QDs as a function of diameter. (A) Plots of the peak positions of G1, G2, and X. (B) Plots of  $|\Delta\mu_1|$  and  $|\Delta\mu_2|$ . (C) Plots of  $\Delta\bar{\alpha}_X$  and  $\Delta\bar{\alpha}_2$ .

proportional to the distance between the positive and negative charges, these results suggest that the photogenerated electron and hole are separated and move further apart as the particle becomes larger. The steep increase in  $|\Delta\mu_2|$  with increasing size, in comparison to  $|\Delta\mu_1|$ , is probably ascribed to the difference in the electronic states related to the G1 and G2 bands; the G1 band is assigned to the transition from  $(j, \pi) = (1/2, 1)$  to  $(1/2, -1)$ , and the G2 band is assigned to the transition from  $(1/2 \text{ or } 3/2, -1)$  to  $(1/2 \text{ or } 3/2, 1)$ .<sup>20,21</sup> The energy level of  $(1/2 \text{ or } 3/2, 1)$  reached by the G2 band has higher energy, and the wave function having a higher energy may couple with the localized surface state more efficiently as the size increases. This enhancement of the coupling may lead to the increase in charge separation and the steeper increase in  $|\Delta\mu|$ . Note that the zeroth and first derivatives of the absorption spectrum were necessary to reproduce the E-A spectra of G2 except for the QDs with a diameter of 7.0 nm. The contribution of these components is shown in Table S1 in Supporting Information.

There is no doubt that the X band shows a very large change in polarizability following absorption, whereas G1 and G2 show large changes in the electric dipole moment. The fact that the X band shows a blue shift in the presence of an electric field indicates that molecular polarizability in the excited state is much smaller than that in the ground state for any size of QDs. At the moment, the exact value of polarizability cannot be obtained since the present E-A spectra just give information about the change in the electric dipole moment or polarizability following absorption. In nanocrystalline materials, the presence of the large permanent dipole moment in the ground state has been reported.<sup>25</sup> In the present results, the magnitude of  $\Delta\mu$  of PbSe QDs may correspond to the increase in the electric dipole moment following photoexcitation. It should be noted that the magnitude of the polarizability of each PbSe QD in the ground



**Figure 5.** X band newly found for the PbSe QDs. The observed absorption spectra (solid line) and the absorption spectra of the X bands (red dotted line) derived with the integral method for different diameters from 4.5 to 7.0 nm.

state must be larger than the absolute value of  $\Delta\bar{\alpha}$  given in Table S1 in Supporting Information.

## 5. CONCLUSIONS

The integral method has been proposed for the analysis of the E-A spectra. In the present study, the E-A spectra of PbSe in the near-infrared region with a size in the range of 4.5–7.0 nm in diameter have been successfully analyzed by this method. In the spectral region above the first exciton band G1, one hidden band whose E-A spectrum is similar in shape to the first derivative of the absorption spectrum is newly confirmed, and the large change in molecular polarizability following the excitation of this band has been evaluated. The peak position of the newly confirmed band as well as other bands shows a blue shift with decreasing size of QDs, and the magnitude of the change both in the electric dipole moment following the absorption of G1 and G2 and in the molecular polarizability

following the absorption of the newly confirmed bands increases nearly monotonically with increasing size of the QDs. The integral method is applicable to any kind of molecular systems and materials. It should be stressed that the integral method analysis should be also applied to reconfirm the validity of the differential method analysis, even when it seems that the E-A spectra can be analyzed by the differential method since the absorption bands are well separated from each other.

## ■ ASSOCIATED CONTENT

### Supporting Information

Additional experimental data and analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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