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# Higher excited electronic states in clusters of ZnSe, CdSe, and ZnS: Spin-orbit, vibronic, and relaxation phenomena

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Metal selenide clusters have been made and characterized, using the arrested precipitation colloidal technique. A comparison of sulfide and selenide spectra enables observation of the effect of changes in the highest occupied molecular orbitals upon cluster electronic properties. The first and second excited electronic states are both observed as a function of size in ZnSe clusters. The systematic dependence of the spectra lead to assignment of the higher state to a 1S-type hole based upon the split-off valence band. It is shown that the energy spectrum of discrete hole states is controlled by the spin-orbit energy and the isotropic hole mass in small, highly symmetrical clusters. This result contrasts with the heavy hole and light hole states observed for planar confinement. In  $\approx 20$  Å diameter ZnS clusters, there is a strong vibronic temperature dependence in the excited state spectra, while in clusters of smaller gap materials such vibronic effects are very minor. We conjecture that lifetime broadening is severe in clusters of small gap materials.

## INTRODUCTION

This paper is part of an extended experimental program on the size dependent development of bulk electronic properties in semiconductor clusters.<sup>1-6</sup> We use the recent discovery that certain liquid phase homogeneous precipitation reactions can be controlled to give colloids with narrow size distributions, and average diameters in the range  $\sim 15$ – $100$  Å ( $10^2$ – $10^4$  atoms).<sup>1-10</sup> ZnS and CdS crystallites made by this method have the same stoichiometry and crystal structure as the bulk material, but different optical (i.e., electronic) properties. It was concluded that these crystallites are *clusters* having hybrid electronic properties between the molecular and solid state limits.<sup>1</sup>

In all previous experimental work, only the lowest allowed, excited electronic state has been resolved. This state can be modeled using an elementary theory based upon Bloch molecular orbitals.<sup>11,12</sup> This model is physically applicable because electrons inside the cluster diffract off the nuclei in the same fashion as they do in the bulk material. Size dependence enters the model through imposition of boundary conditions at the crystallite surfaces

In semiconductors such as ZnSe, CdS, GaAs, etc., the conduction band is principally composed of S-type orbitals on metal atoms, while the valence band is composed of P-type functions on the Se, S, and As atoms. Thus in the previously studied series of sulfides with varying metal atoms, the effect of the conduction band on cluster properties was, in effect, investigated. Correspondingly, in a series like ZnS, ZnSe, and ZnTe the valence band undergoes systematic variation. It is for this reason that we extend these studies to selenides in this article.

The structure of the valence band in these semiconductor clusters is a rich, and previously unaddressed, quantum mechanical problem. While the conduction band is nondegenerate and almost isotropic, the valence band is threefold orbitally degenerate, shows significant spin-orbit splitting

due to the chalcogenide atom, and has an anisotropic effective mass tensor. In this manuscript we observe and analyze, for the first time, the *second* excited electronic state of  $\approx 20$  Å ZnS and ZnSe clusters. We demonstrate how this structure can be understood, in a simple way, starting with the quantum mechanics of the bulk valence bands.

We also report and discuss strong vibronic effects in the ZnS spectra, and discuss the general question of spectral widths and relaxation phenomena in semiconductor clusters. The coupling of cluster "exciton" excited states to vibrational modes has not been previously considered.

## EXPERIMENTAL ASPECTS

The technique of "arrested precipitation" has now become widespread,<sup>1-10,13,14</sup> and the phenomenological aspects that relate solvent, temperature, and precipitation technique to cluster size, and electronic spectra to cluster size, are moderately well understood. In general, the smallest clusters are made and stabilized by precipitation at low temperature in nonaqueous solvents. We describe five syntheses for CdSe and ZnSe:

ZnSe A: 2 cc of a  $9 \times 10^{-3}$  M  $\text{Zn}(\text{ClO}_4)_2$  methanol solution is injected into 100 cc of a stirred  $10^{-3}$  M  $\text{H}_2\text{Se}$  isopropanol solution under Ar. Both solutions are near  $-80^\circ\text{C}$ , and the colloid after injection is stored at  $-80^\circ\text{C}$ . The excess  $\text{H}_2\text{Se}$  is bubbled out with Ar after injection.

ZnSe B: 2 cc of a  $9 \times 10^{-3}$  M  $\text{Zn}(\text{ClO}_4)_2$  methanol solution is injected into 100 cc of a stirred  $10^{-3}$  M  $\text{H}_2\text{Se}$  methanol solution, at room temperature, under Ar. The excess  $\text{H}_2\text{Se}$  is bubbled out with Ar after injection.

ZnSe C: 8 cc of a  $9 \times 10^{-3}$  M  $\text{Zn}(\text{ClO}_4)_2$  aqueous solution is injected into 100 cc of a stirred  $5 \times 10^{-3}$  M  $\text{H}_2\text{Se}$  in 2:1 ethylene glycol/water mixture, at room temperature, under Ar. The excess  $\text{H}_2\text{Se}$  is bubbled off with Ar.

CdSe A: As in ZnSe A, with the substitution of  $\text{Cd}(\text{ClO}_4)_2$ .

CdSe B: 10 cc of a  $9 \times 10^{-3}$  M  $\text{Cd}(\text{ClO}_4)_2$  aqueous solution is injected into 100 cc of a  $10^{-3}$  M  $\text{H}_2\text{Se}$  aqueous solu-

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tion containing 100 mg of polyvinyl alcohol (Aldrich #18463-2), at room temperature.

Examination of colloids by transmission electron microscopy at 50 000-fold enlargement shows "necklace" and "tree" fractal-like structures, similar to those that have been studied in metal colloid aggregation phenomena.<sup>15</sup> Examination of individual "particles" in these structures at 350 000-fold enlargement shows them to be tight, nearly symmetric clumps of smaller particles. Fragments of lattice plane images ( $\sim 20$ – $50$  Å size) are visible inside these clumps. These lattice plane images have the same structure as seen and analyzed earlier in cubic ZnS and CdS cluster precipitations.<sup>1-3</sup> We conclude that the selenide precipitations produces cubic zinc-blende tiny crystallites. We have not been able to stop the strong tendency of selenide colloids to tightly aggregate, and are not able to provide accurate size distributions. Nevertheless, the systematic change of spectra with technique, and comparison of selenide spectra with sulfide spectra of known crystallite size, allows us to be reasonably certain in correlating electronic spectra with size.

## OBSERVATIONS

### CdSe

CdSe has a bulk band gap near 1.74 eV ( $\approx 7100$  Å) at room temperature. The aqueous CdSe B colloid should have large particles based upon experience in similar  $S^{2-}$  systems. We see in Fig. 1 that the optical absorption begins near 700 nm and continues without structure at higher energies. This is the normal behavior for particles of diameter  $> 50$  Å, with near Bloch electronic states. In the CdSe A spectrum, however, the optical absorption begins near 400 nm and shows a plateau, or step (unresolved peak) near 380 nm. The CdSe A colloidal technique gives the smallest CdSe particles, by analogy with CdS results, and we see that, as in the CdS system, the small cluster spectra are far blue shifted from the bulk band gap. In this CdSe case, the observed shift from the bulk

band gap to the lowest crystallite excited state at  $\approx 380$  nm is 1.5 eV. The CdSe A spectra are independent of temperature down to  $-140$  °C in a frozen isopropanol glass. As in the CdS case, the lowest cluster excited electronic states are not clearly resolved.

### ZnSe

The bulk band gap of ZnSe is near 2.58 eV at room temperature ( $\approx 480$  nm). The small particle colloid ZnSe A, made at  $-80$  °C in isopropanol, shows an initial step at 290 nm in Fig. 2. This unresolved peak at  $\approx 290$  nm is blue shifted by 1.6 eV from the bulk band gap.

If this colloid is annealed at 0 °C for a few minutes, and then recooled to  $-80$  °C, the spectrum changes as shown. The integrated oscillator strength increases, and distinct peaks appear near 280 and 320 nm. Similar sharpening phenomena occur in ZnS colloids, where it is believed that annealing allows fusion of the smallest crystallites, and annealing of lattice defects within crystallites.

In the ZnSe C colloid in Fig. 3, larger crystallites are expected and appear to be present, as judged by the initial broad peak near 390 nm. In the ZnSe B colloid, a spectrum similar to the ZnSe A spectrum is obtained, indicating smaller crystallite size. These two spectra in Fig. 3, as well as the annealed spectrum in Fig. 2, demonstrate a feature not apparent in the equivalent ZnS spectra—the presence of a second peak whose position is dependent upon size, at 340 nm in ZnSe C and 280 nm in ZnSe A and ZnSe B. We assign these higher transitions to the second excited state within each crystallite.

### ZnS

We have previously described the room temperature synthesis of  $\approx 21$  Å diameter ZnS crystallites in methanol (type "D" of Ref. 3). Figure 4 shows the spectra observed in a similar ZnS colloid made in a methanol/ethanol mixture,

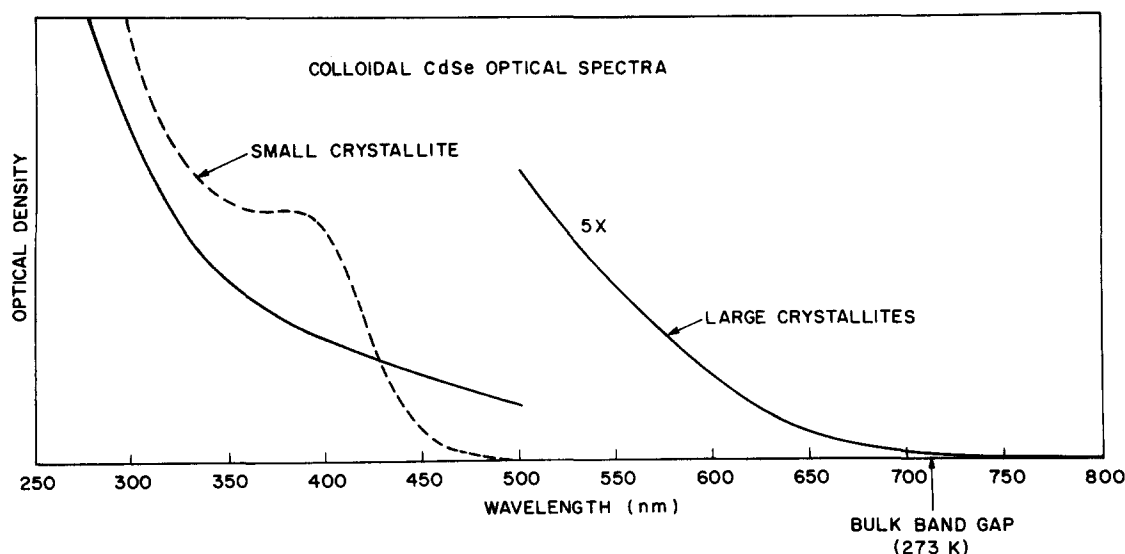


FIG. 1. CdSe colloidal absorption spectra. "Small" refers to CdSe A colloid at  $-80$  °C. "Large" refers to CdSe B colloid at 23 °C. The vertical scale for Large is expanded  $5\times$  500 nm. The mass of CdSe in the optical path is nominally the same in both spectra.

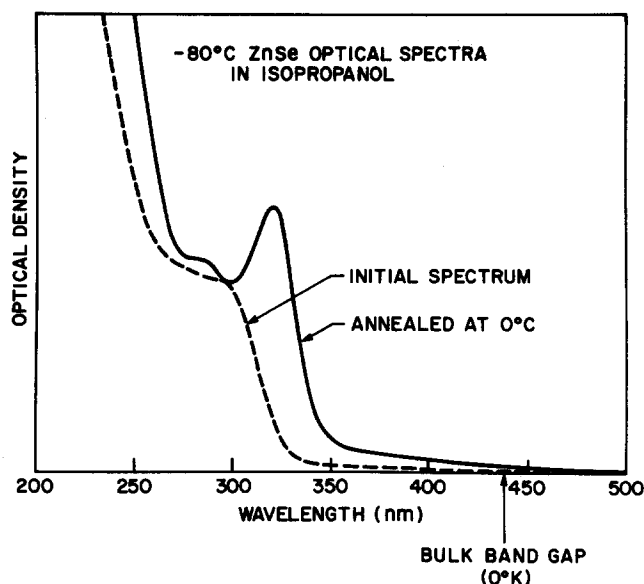


FIG. 2. ZnSe A colloidal optical spectra as described in the text.

which allows cooling to 77 K in the optically transparent glass.<sup>4</sup> There is a strong blue shift and modest sharpening of the spectra upon cooling. At 77 K, a second peak on the high energy side of the principle peak is partially resolved; at 293 K the second peak is not resolved, but contributes to a modestly asymmetric shape for the principal peak. The reversible temperature dependence observed here is the strongest yet reported in cluster electronic spectroscopy.

## DISCUSSION AND ANALYSIS

### Higher excited electronic states

In the smallest clusters of ZnS and ZnSe we see the same pattern: a resolved, strong transition for the cluster lowest excited state, and a second, weaker transition at higher ener-

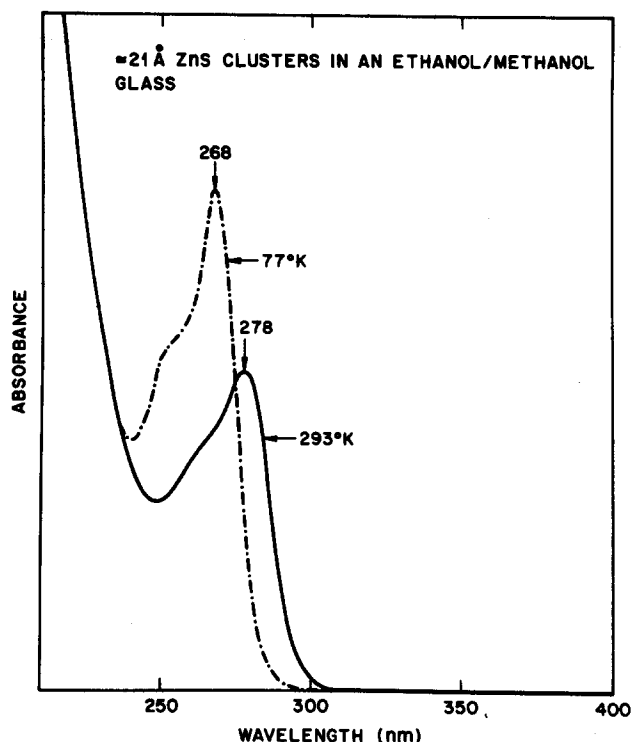


FIG. 4. Temperature dependence of  $\approx 21$  Å diameter ZnS colloidal optical spectra, in a mixed ethanol/methanol solvent.

gy. The splitting is  $\approx 1800$   $\text{cm}^{-1}$  in ZnS and  $\approx 4000$   $\text{cm}^{-1}$  in ZnSe. Figure 3 shows that this splitting at low resolution is *not* increasing with decreasing ZnSe cluster size. This result indicates that the two transitions do not involve different spatial confinement quantum numbers,<sup>16</sup> or two different effective masses. We are led to consider a purely electronic splitting. We now briefly review the bulk band structure<sup>17,18</sup> of these materials, in order to provide the framework for assignment of these cluster transitions.

The bulk band structure is schematically illustrated on the left-hand side of Fig. 5. The valence band is sixfold degenerate, counting both spin and orbital angular momentum. At  $k = 0$ , the spin-orbit interaction splits the band into

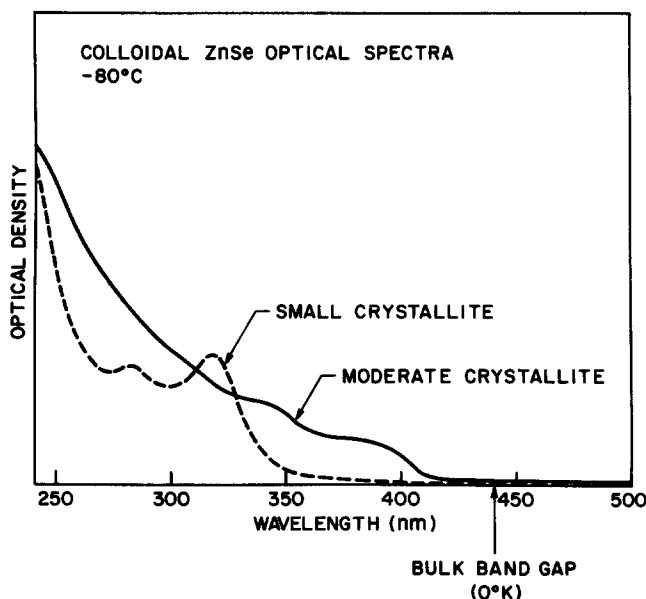


FIG. 3. ZnSe B ("small") and ZnSe C ("moderate") colloidal optical spectra. The ZnSe mass in the optical path is nominally the same in both spectra.

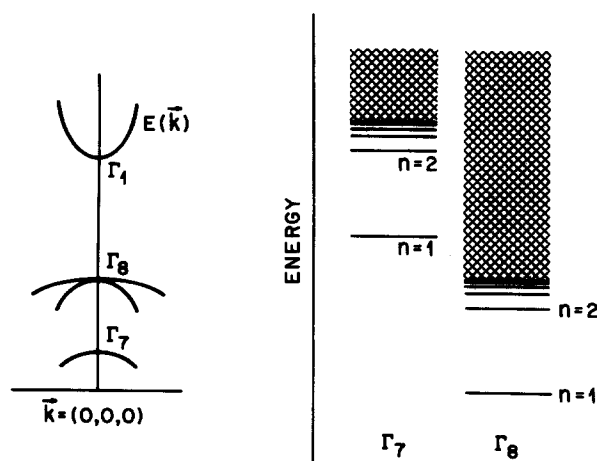


FIG. 5. Schematic diagram of valence and conduction bands of zinc-blende crystals near the band gap (adapted from Ref. 18). The right-hand side shows the schematic exciton structure on a much expanded energy scale.

an upper fourfold degenerate  $\Gamma_8$  component, and a lower twofold degenerate  $\Gamma_7$  component. The conduction band  $\Gamma_1$  is also twofold degenerate. The resulting bound electron-hole states ("excitons") in bulk crystals are shown on the right-hand side, following the analysis of Baldereschi and Lipari.<sup>18</sup> There are two nearly Rydberg series of very weakly bound, near-hydrogenic states that converge to the  $\Gamma_7 \rightarrow \Gamma_1$  and  $\Gamma_8 \rightarrow \Gamma_1$  band gaps. In the ZnSe 1S exciton, the hydrogenic electron and hole kinetic energies are only  $\simeq 0.02$  and  $\simeq 0.005$  eV, while  $\Delta_{so} = 0.43$  eV.<sup>19</sup>

The crystal has  $T_d$  symmetry, and the Bloch molecular orbitals are almost spherically symmetric. The exciton states are not quite spherically symmetric because the hole effective mass is not quite isotropic. The anisotropic terms have  $D(L=2)$  symmetry, and mix 1S with 3D, 4D, etc., within and across the Rydberg series. The mixing is small because the anisotropic (off-diagonal) hole effective masses are much larger than the combined isotropic hole and electron masses.

Most of the oscillator strength in absorption is carried by transitions to 1S and  $1S_\Delta$ , with relative intensity  $1:\sqrt{2}$ .<sup>17</sup> Two discrete states are seen in absorption with splitting almost exactly  $\Delta_{so}$ .

It is remarkable that the lowest two discrete states in our smallest ZnSe crystallites have the appearance of the 1S and  $1S_\Delta$  bulk excitons. There is a large  $\sim 1.1$  eV shift to higher energy; nevertheless, there are still two states with similar relative oscillator strengths and absolute spacing  $\Delta_{so}$ .

What is the theoretical effect of size quantization on the degenerate valence band in Fig. 5? This problem was studied some time ago for one-dimensional quantization in the excited electronic states of  $\simeq 100$  Å semiconductor slabs.<sup>20,21</sup> In this case the split-off valence band  $\Gamma_7$  gives rise to one series of discrete hole states. The degenerate  $\Gamma_8$  band is split and quantized because the slab shape symmetry is lower than the  $T_d$  unit cell symmetry. There are two series of quantized hole states labeled "heavy holes" and "light holes." Their effective masses, governing the dependence of energy on size, are

$$m_h = \frac{m_0}{\gamma_1 - 2\gamma_2}, \quad (1)$$

$$m_{ll} = \frac{m_0}{\gamma_1 + 2\gamma_2}, \quad (2)$$

where  $m_0$  is the free electron mass and  $\gamma_1, \gamma_2$  are the Luttinger band shape parameters. The two hole masses are quite different (0.81  $m_0$  and 0.27  $m_0$  for ZnSe).

This size effect problem is strongly dependent on crystallite geometry. We outline the following treatment for three-dimensional spherical confinement: First, recall that the quantized states for an isotropic effective mass are simply the "particle in a sphere" eigenstates.<sup>12</sup> Their relative spacing rapidly increases with decreasing radius. The anisotropy of the hole kinetic energy mixes and splits such states. Therefore, consider a zero order basis of six series of particle-in-a-sphere functions with spherical harmonic angular factors  $Y_{LM}$ ; a fourfold degenerate series beginning at the top of  $\Gamma_8$ , and a twofold degenerate series beginning at  $\Gamma_7$ . Following

Baldereschi and Lipari,<sup>18</sup> the hole kinetic energy Hamiltonian can be written

$$\hat{H}_h = \hat{H}_s + \hat{H}_D, \quad (3)$$

where  $\hat{H}_s$  is diagonal in  $Y_{LM}$ :

$$\hat{H}_s = \begin{Bmatrix} \hat{K} & 0 & 0 & 0 & 0 & 0 \\ 0 & \hat{K} & 0 & 0 & 0 & 0 \\ 0 & 0 & \hat{K} & 0 & 0 & 0 \\ 0 & 0 & 0 & \hat{K} & 0 & 0 \\ 0 & 0 & 0 & 0 & \hat{K} + \Delta & 0 \\ 0 & 0 & 0 & 0 & 0 & \hat{K} + \Delta \end{Bmatrix}, \quad (4)$$

where

$$\hat{K} = -\frac{\hbar^2}{2m_i} \nabla^2$$

and  $\Delta$  is the spin-orbit energy.  $m_i$  is the isotropic hole mass defined as

$$m_i = m_0/\gamma_1. \quad (5)$$

The zero order states are split and mixed by  $\hat{H}_D$ , which has diagonal and off-diagonal elements, all of  $L=2$  symmetry.

Consider the  $1S(\Gamma_7)$  and  $1S(\Gamma_8)$  zero order states.  $\hat{H}_D$  does not shift or split either state, in first order perturbation theory.  $1S(\Gamma_8)$  is also not split in second order perturbation theory, but does couple with  $1S(\Gamma_7)$ , rather weakly, through states of  $D$  symmetry. Inspection of the level structure in the figure shows that the  $\Gamma_8$  1D state will come into resonance with the  $\Gamma_7$  1S state for cluster radius

$$R \simeq \frac{\sqrt{11.1\hbar^2}}{m_i \Delta} \simeq 20 \text{ Å for ZnSe.}$$

At this diameter there may be significant mixing. For smaller clusters 1D shifts away, and the two 1S states should remain relatively pure.

This analysis predicts two low lying 1S type hole states, split by  $\Delta$ , in small clusters. The  $\Gamma_8$  1S state remains degenerate through second order. Both states shift together to higher energy via the isotropic hole mass [Eq. (5)], and not the light or heavy hole mass. These states are observed via allowed transitions terminating on the 1S electron state in Fig. 6. We assign our two resolved transitions to these two expected 1S type transitions. The allowed  $1P \rightarrow 1P$  type transitions should be considerably further blue shifted, as appears to be the case experimentally.<sup>16</sup>

In ZnSe clusters the splitting between the two transitions is  $\simeq 0.4$  eV, essentially equal to the ZnSe bulk spin-orbit splitting 0.43 eV. In ZnS the splitting is, as expected, smaller  $\simeq 0.22$  eV. However, it is larger than the ZnS bulk spin-orbit splitting 0.07 eV. As the spin-orbit energy becomes small, the interactions neglected in zero order become more important. It would be interesting to carry out the complete diagonalization of  $\hat{H}_h$  for small  $\Delta$  to find the predicted splitting for spherical crystallites. More realistically, an accurate calculation would be sensitive to the presently unknown, exact crystallite shape.

This simple treatment also shows how spectra potentially provide shape information as well as dimension information. Spectra such as we observe for ZnSe imply highly symmetric compact clusters. Correspondingly, spectra showing

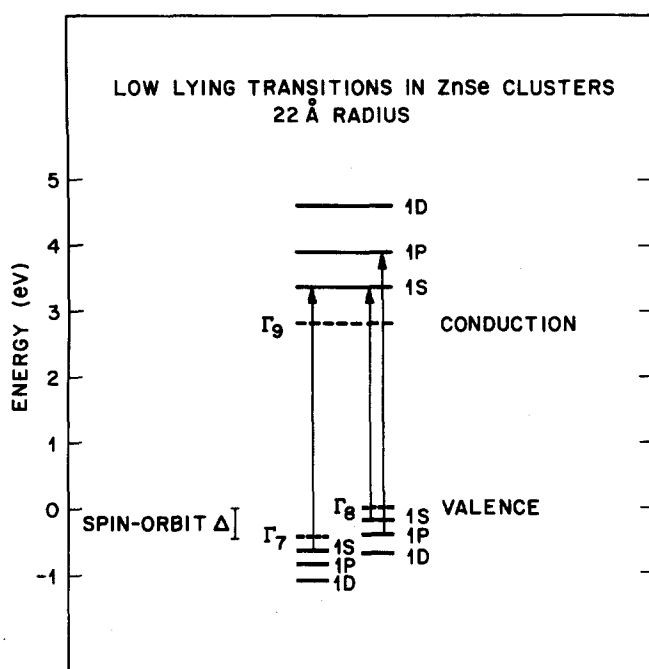


FIG. 6. Calculated zero order, discrete molecular orbitals, and allowed electronic transitions for a spherical ZnSe cluster of 44 Å diameter. Only one of the two possible 1P type transitions is drawn in. Dotted lines show bulk band edge positions. In the text and in Fig. 5, the conduction band is labeled  $\Gamma_9$ .

the well known light and heavy hole pattern<sup>21</sup> would indicate platelet cluster shape.

### Vibronic thermal effects

The temperature dependent absorption spectra in ZnS can be empirically fit as the sum of two Gaussians with parameters in Table I. The two transitions shift  $\approx 1200 \text{ cm}^{-1}$  to higher energy at 77 K, while preserving their relative intensity and  $\approx 1800 \text{ cm}^{-1}$  splitting.

This remarkably large, reversible shift with temperature indicates (a) that the electronic transition is strongly coupled to cluster vibrations, and (b) the cluster normal modes are appreciably different in the excited electronic state. The two electronic transitions we observe are unresolved superpositions of vibronic transitions. In the absence of resolved vibronic lines, it does not seem worthwhile to attempt a detailed model of the potential energy curve shapes.

Thermal broadening has been previously observed for the lowest excited electronic states of thin GaAs semiconductor sheets.<sup>22</sup> Here it is thought that the transition couples most strongly with LO type phonons via the Fröhlich interaction. In partially ionic zinc-blende and Wurtzite lattice materials (GaAs, ZnSe, CdS, etc.) LO phonons have the

TABLE I. Parameters in the fitting of the Fig. 4 ZnS cluster absorption spectra to the sum of two Gaussians.  $E_1, E_2$ , and  $\sigma$  are the two peak positions and width in  $\text{cm}^{-1}$ .  $I_1/I_2$  is the ratio of peak intensities.

	$E_1$	$E_2$	$I_1/I_2$	$\sigma$
293 K	36 000	37 800	5/2	1000
77 K	37 300	39 100	5/2	800

interesting property that vibrational oscillation creates long range electric fields  $\vec{E}$  extending over many unit cells. These fields interact with electrons and holes via Coulomb forces, thus providing a vibronic interaction mechanism (Fröhlich interaction) that is not nominally present in conventional molecules.

In bulk cubic ZnS crystals, the extrapolated band edge (i.e., band gap) shifts red with increasing temperature due to this same vibronic effect.<sup>23</sup> The shift between 77 and 293 K is  $\approx 1200 \text{ cm}^{-1}$ , essentially the same as observed in our  $\approx 20 \text{ Å}$  crystallites.

The form of LO phonons present in small spherical crystallites has been considered in explicit detail, and numerical calculations have been performed of the average internal electric fields present as a function of temperature.<sup>24,25</sup> The form and magnitude of various possible vibronic interactions have not been explicitly analyzed, however. Remarkably the long-range Fröhlich interaction between electrons and LO phonons should be absent if both electron and hole are in the same spatial wave function.<sup>26</sup> This is the case if both are in 1S wave functions. Thus it appears that the vibronic interaction mechanisms in  $\sim 20 \text{ Å}$  ZnS crystallites are not the same as in the bulk, even though the magnitudes of vibronic shifts are similar. This problem needs further experimental work.

### Relaxation and "resonances"

Of all published semiconductor cluster electronic absorption spectra known to us, the  $\approx 21 \text{ Å}$  ZnS clusters in Fig. 4 have the smallest exciton experimental linewidth ( $\approx 800 \text{ cm}^{-1}$  at 77 K), and the largest vibronic temperature dependence. This vibronic effect indicates that the excited state lives long enough for the cluster to relax to a new Franck-Condon structure. This time is at least on the order of a couple of vibrational periods—perhaps  $10^{-13} \text{ s}$ . On the other hand, the absence of exciton fluorescence in any case where clusters are made by liquid phase relaxation processes indicates that excitons in general do not live as long as  $10^{-9} \text{ s}$ . Fluorescence is a useful probe of lifetime because the fluorescence should be fully allowed with radiative lifetimes  $\approx 10^{-9} \text{ s}$ .<sup>12</sup>

Broad transitions and unresolved steps, such as shown for ZnSe and CdSe in Figs. 1–3, are more typically observed for semiconductor clusters. These broad electronic transitions show almost no temperature dependence, unlike Fig. 4. There appears to be a correlation between bulk band gap and cluster electronic transition width, in that small band gap materials show extreme broadening. ZnS, with relatively narrow widths, is the largest band gap material examined in cluster form to our knowledge. In all these colloids there is an inhomogeneous width due to size distributions. Nevertheless, the distribution widths are not appreciably larger in smaller band gap materials. This observation suggests that there is some sort of relaxation rate energy gap law contributing to the observed widths. Large  $S_0 \rightarrow S_1$  gap clusters would tend to show less lifetime broadening. We conjecture that, in the smaller clusters ( $< 50 \text{ Å}$ ) of low band gap materials, exciton lifetimes are  $\leq 10^{-13} \text{ s}$  because of ultrafast relaxation into lower lying states—surface states and perhaps

internal point defects. The luminescence of  $\simeq 22$  and  $\simeq 38$  Å CdS clusters is entirely due to trapped electrons and holes (i.e., not the exciton states seen in absorption), strongly coupled to lattice phonons.<sup>5</sup>

If the homogeneous relaxation linewidth is really as large as suggested, then these exciton states might best be termed "resonances." The situation is somewhat analogous to the higher singlet states of small molecules, which are often severely broadened by vibronic coupling to lower singlets. Conversely, if a way could be found to make surface passivated (i.e., bonded), defect free clusters, then sharper exciton spectra should be observed.

## ACKNOWLEDGMENTS

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