

Effect of excess charge on band energetics (optical absorption edge and carrier redox potentials) in small semiconductor particles

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J. Phys. Chem., **1989**, 93 (8), 3232-3237 • DOI: 10.1021/j100345a069

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counterion effects were observed for the photoionization of tetramethylbenzidine in micelles.³¹

Conclusions

This study shows that various structural parameters of the vesicles affect the photoionization yield of Chla in vesicles. An increased yield correlates with an increase of the hydration of the headgroups of the vesicle surfactants. A low transition temperature surfactant should improve the photoionization yield of Chla.

Vesicle destruction seems rather sensitive to alcohol addition and less sensitive to an increase of the ionic strength of the aqueous phase of the interface. Vesicle structure is largely retained upon rapid freezing, but some distortion probably occurs based on the weak effects of added DMSO or glycerol. Although a change

of the counterion may affect the hydration of vesicle headgroups, anionic vesicles destroy Chla and cationic vesicles only slightly increase the photoionization yield if Cl^- is substituted for Br^- .

Acknowledgment. This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, whom we gratefully acknowledge.

Registry No. Chla, 479-61-8; DPPC, 2644-64-6; DSPC, 67896-64-4; DOPC, 10015-85-7; DEPC, 52088-89-8; DPPG, 4537-77-3; DPPA, 19698-29-4; DMSO, 67-68-5; DMSO-*d*₆, 2206-27-1; NH_4^+ , 14798-03-9; Na, 7440-23-5; Cl^- , 16887-00-6; Br^- , 24959-67-9; KCl, 7447-40-7; NaCl, 7647-14-5; MgCl_2 , 7786-30-3; CdCl_2 , 10108-64-2; CsCl, 7647-17-8; CaCl_2 , 10043-52-4; 5-doxylstearic acid, 29545-48-0; 1-butanol, 71-36-3; 1-octanol, 111-87-5; glycerol, 56-81-5; glycerol-*d*₅, 62502-71-0.

Effect of Excess Charge on Band Energetics (Optical Absorption Edge and Carrier Redox Potentials) in Small Semiconductor Particles

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A theoretical model, based on the "Burstein shift", is proposed to explain the absorption edge shift and the existence of electron energies (reducing powers) greater than that of the conduction band edge, E_c , for small semiconductor particles in photochemical systems. In this model, photoinduced high electron concentrations in the semiconductor particles raise the Fermi level, E_f , into the conduction band, so that the semiconductor becomes degenerate. Under these conditions the energy necessary to excite electrons optically from the valence band into the conduction band will be larger than the minimum separation between the bands (the width of the forbidden energy gap, E_g) because of momentum conservation. This causes an absorption edge shift and produces electrons at energy E_f (above E_c), making possible electron transfers to a collector electrode or to oxidants with potentials negative of E_c , when particles are strongly irradiated.

Introduction

In this paper we address the behavior of small semiconductor particles under irradiation and discuss the origin of the shifts in the absorption edge and the energies of photogenerated electrons compared to those of the bulk semiconductor. We propose a model to describe the Fermi level shift for these particles under irradiation or charging and describe how this shift affects photoinduced electron-transfer reactions. The reversible photocharging of monomolecular layers of CdS is demonstrated, and results on the electrochemical characterization of WO_3 particles are interpreted with this model.

Photoreactions at small semiconductor particles have been under investigation since the late 1970s because of possible practical applications and also as a fundamental probe of photolytic and electron-transfer reactions at interfaces.^{1,2} While the broad aspects of the photoreactions at particles can be understood from studies of photoelectrochemistry at bulk single-crystal semiconductor electrodes, the particles differ in a number of ways from bulk materials. For example, photogenerated electrons (e^-) can have energies that are different from those of the conduction band edge (E_c) of the bulk semiconductor in contact with the same solution.³ The energies (i.e., reduction potentials) of the photogenerated electrons on particles can be measured by collecting them either with an oxidant in solution, detecting the reduced form spectroscopically⁴ or electrochemically,^{5,6} or directly with an inert collector electrode immersed in an irradiated suspension.^{3,7-9} One of the advantages of the latter technique is that the potential of the collector electrode can be adjusted relative to the redox potentials or Fermi level of electrons in the semiconductor particles. These

studies have shown that the Fermi level of electrons in particles is a function of the irradiation intensity (the potential becoming more negative as the photon flux increases) and that the potential can be considerably more negative than that predicted from E_c of the bulk semiconductor. This "photocharging" of the semiconductor particles can promote reactions that occur at potentials more negative than E_c . Other effects of this photocharging in semiconductor systems have also been observed recently. When CdS particles were subjected to a 10- μs photoflash, there was a blue shift in the absorption edge of the semiconductor.¹⁰ There is evidence to support the assumption that excess electrons on the semiconductor particles are involved in this blue shift.^{10,11} Although there has been some discussion of this phenomenon, no

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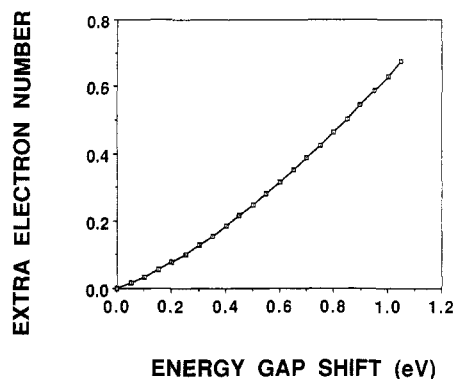


Figure 2. Dependence of the energy gap shift on number of extra electrons in CdS semiconductor particle (diameter 15 Å).

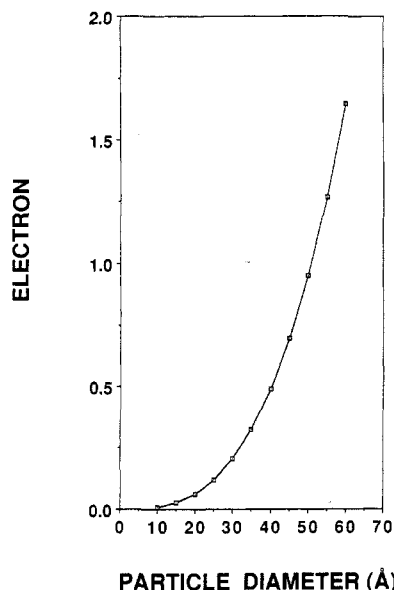


Figure 3. Dependence of n_{crit} , the critical number of electrons per particle for $(|E_f - E_c| = 4kT_e)$, on the particle diameter, for CdS, for $T_e = 300$ K, $m_e = 0.21m_0$, $m_h = 0.80m_0$.

E_m is located just at the bottom of the conduction band, i.e., where the Burstein shift is zero (so that $E_f - E_c = 4kT_e$). This occurs at an electron concentration, n_{crit} , of about $1.5 \times 10^{19}/\text{cm}^3$ calculated from eq 4. For n-type CdS, $E_{g,opt} \approx E_g$ when $n < n_{crit}$, and will be approximately equal to $E_g + 1.26(E_f - E_c - 0.1)$ when $n > n_{crit}$.

Usually, it is not easy to observe experimentally such an energy gap shift in large single-crystal semiconductors, since a much larger number of charge carriers is needed to make them degenerate, and the absorption by free charge carriers would, in general, mask the intrinsic absorption edge. For very small semiconductor particles, e.g., those used in colloidal photochemical systems, however, a significant energy gap shift should be obtained by adding only a few extra electrons to the particles. Figure 2 shows the dependence of the energy gap shift on additional number of electrons in spherical CdS particles with a diameter of 15 Å, as calculated from eq 4 and 5. Note that only 0.1 additional electron density (which corresponds to about $7 \times 10^{19} \text{ cm}^{-3}$) can lead to a 0.25-eV shift. As further illustrations of this effect, Figures 3 and 4 show the dependence of n_{crit} on CdS particle diameter and the predicted energy gap shift for particles with an effective extra electron number of 0.58 (interfacial chemical processes could probably produce a fractional number of electrons, as discussed later). We define the extra electron number as number of electrons per particle above that corresponding to n_{crit} .

Experimental Section

CdS layers were deposited on quartz slides by treating Langmuir-Blodgett layers of cadmium arachidate with H_2S , as de-

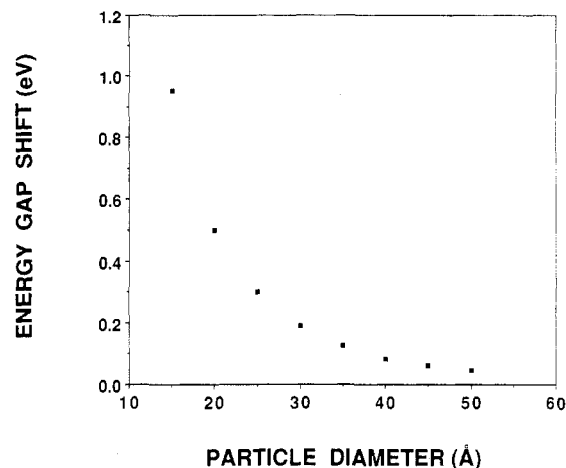


Figure 4. Increase in energy gap ($E_{g,opt} - E_g$) as a function of particle diameter for CdS with an extra electron number of 0.58 $e^-/\text{particle}$. CdS parameters as in Figure 3.

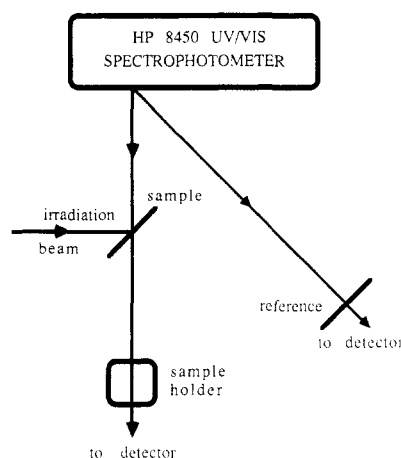


Figure 5. Schematic diagram of apparatus for absorbance measurements on CdS thin film array (sample). Irradiation beam was with a 1000-W quartz tungsten-halogen lamp.

scribed elsewhere.²⁴ The absorption spectra of the films were measured with an HP Model 8450 UV/VIS spectrophotometer (Hewlett-Packard, Palo Alto, CA) over the range 200–800 nm in 1 s. The procedure for obtaining spectra of the films under irradiation with a second, high-intensity light source utilized the arrangement shown in Figure 5. After a measurement of the sample in the usual sample position without additional irradiation and with a blank quartz slide as reference, the sample was moved to the new position, shown in Figure 5. The location of the sample and the angle between the sample surface and the incident beam were carefully adjusted until the spectrum obtained in this position was the same as that found previously. A 1000-W quartz tungsten-halogen lamp (ca. 150 mW/cm^2 for wavelengths below 530 nm) was used as the light source. The source was alternately turned on and off to obtain absorption spectra with and without additional irradiation. To reduce possible reflection or scattering effects, only a small (ca. 5 mm diameter) irradiation spot impinged on the sample surface. After the measurements, the sample was replaced by a quartz slide in the same position and alignment as the sample slide. Irradiation of the quartz slide showed only base line in the absorption spectrum, suggesting the absence of any light-scattering effects.

Results and Discussion

Photoinduced Absorption Edge Shift in Colloidal CdS. A small (30 Å) shift to higher energies in the absorption edge occurred when samples of colloidal CdS were subjected to a 10- μs

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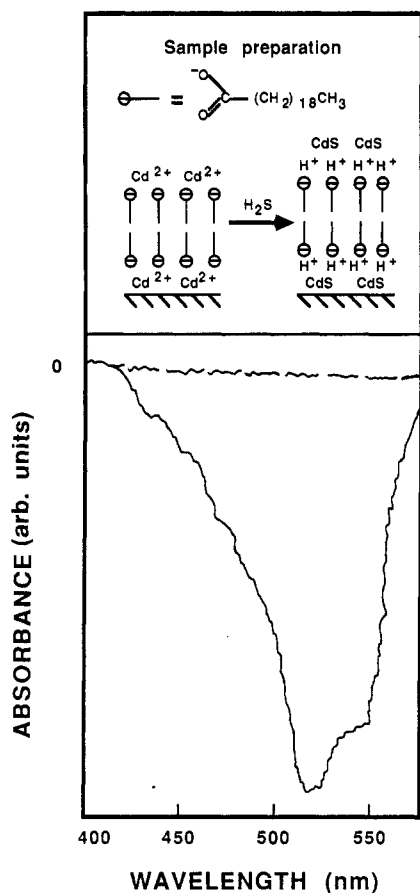


Figure 6. Difference spectra of CdS thin film array prepared from a Langmuir-Blodgett film containing seven cadmium arachidate layers (producing four CdS monolayers on treatment with H_2S as shown in inset) (—) with and (---) without irradiation from tungsten-halogen lamp.

photoflash ($\lambda > 300$ nm), with a resulting sharp decrease in absorbance in the 450–500-nm region.¹⁰ A transient difference spectrum was obtained 10 ms after the photoflash for N_2 -purged CdS at room temperature. This cannot be explained by photodecomposition or photocorrosion of the CdS semiconductor particles during the photoflash process, since the change in the absorption spectrum was reversible. This can be interpreted in terms of the above model by a photoflash-induced increase in the concentration of electrons in the conduction band to populate levels above E_c and give rise to an absorption edge shift to shorter wavelengths. After the photoflash, the photoinduced electrons in the conduction band recombine with holes in the valence band or are transferred to a species in solution. When the electron concentration becomes sufficiently low, the degenerate CdS returns to a nondegenerate state, with the original absorption spectrum of CdS. As predicted from this model, the rate of recovery in the spectrum was reduced considerably and the dark relaxation took more than 10^5 s¹⁰ when CdS colloids were irradiated in the presence of 10^{-2} M cysteine, which acts as an electron donor to photogenerated holes in CdS.^{25,26} In this case, holes in the valence band are captured by cysteine, and the photoinduced electron in the conduction band can only relax through slow electron-transfer processes, e.g., with water molecules. The irradiated CdS semiconductor particles remain degenerate longer than in the absence of a sacrificial donor. Similarly, the rate of recovery in the spectrum was accelerated when electron acceptors such as O_2 and MV^{2+} were present in systems of CdS and cysteine.¹⁰ MV^{2+} is known to absorb on CdS particles^{27,28} and can intercept direct

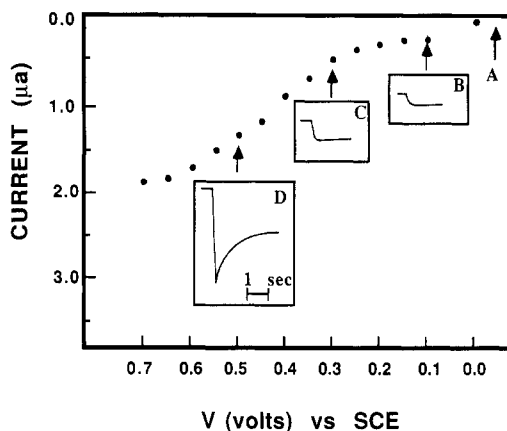


Figure 7. Steady-state photocurrents vs electrode potential for WO_3 /tartrate at pH 2.3. The insets are transients obtained at those potentials (after Leland and Bard^{9b}).

electron-hole recombination. No shift in absorption edge could be detected when only CdS and MV^{2+} were present and MV^{++} was generated within the photoflash ($10 \mu\text{s}$) for all concentrations of MV^{2+} ($>10^{-6}$ M).¹⁰ Since the photoinduced electrons can be transferred rapidly from CdS particles to MV^{2+} , forming MV^{++} , the semiconductor cannot become degenerate, and no Burstein shift is expected. These results have been extended and confirmed by Henglein et al.¹¹ Related observations with CdS in a Nafion film²⁸ can be explained in a similar way.

Photoinduced Shift in CdS Films. A similar, steady state, effect can be observed with irradiated very thin (monomolecular) films of CdS. Four monolayers of CdS were deposited on a quartz slide by treatment of organized films of cadmium arachidate prepared on a Langmuir-Blodgett trough with H_2S , as described elsewhere.²⁴ The absorption spectrum of the film was obtained in the configuration shown in Figure 5. Absorption spectra in Figure 6 show the effect of irradiation of the film in air with a 1000-W quartz tungsten-halogen lamp as described in the Experimental Section. Before irradiation the spectrum shows a blue shift from the bulk CdS absorption edge because of the small size of the CdS particles in the film, as discussed elsewhere.²⁴ With irradiation a bleaching is observed, which corresponds to a further blue shift. Again, we ascribe this to accumulation of electrons in the conduction band. Note that the two curves in Figure 6 differ only in the absorption edge region, as expected from the proposed model. Note also that when the irradiated beam was extinguished, the spectrum returned to the original one. The spectrum could be reversibly switched between the two states a number of times, indicating that the observed shift was not caused by irreversible degradation of the CdS.

Photoinduced Fermi Level Shifts in Semiconductor Particles and Effect on Electron-Transfer Reactions. Electron transfer from irradiated TiO_2 particles to methylviologen, MV^{2+} , to form MV^{++} would not occur if E_c of the semiconductor was lower than the redox potential of the $\text{MV}^{2+}/\text{MV}^{++}$ couple. This would be the case at $\text{pH} < 11$, if the particles showed the same E_c as bulk TiO_2 . This process, however, could be realized when semiconductor particles were illuminated.⁵ The concept of a quasi-Fermi level was adopted to explain this phenomenon, since the density of excess electrons generated by the light increases as the holes are scavenged, and the Fermi level then shifts to that corresponding to a sufficiently negative potential to drive the reduction of MV^{2+} .⁵

From the model proposed here, the Fermi level is shifted into the conduction band (i.e., the semiconductor becomes degenerate) when the electron concentration becomes sufficiently high, so that a redox system whose potential is negative of E_c would be reducible. This has been observed for direct electron transfer from particles to a collector electrode, as shown in Figure 7.^{9b} In this experiment, a Pt electrode serving as an electron collector, whose

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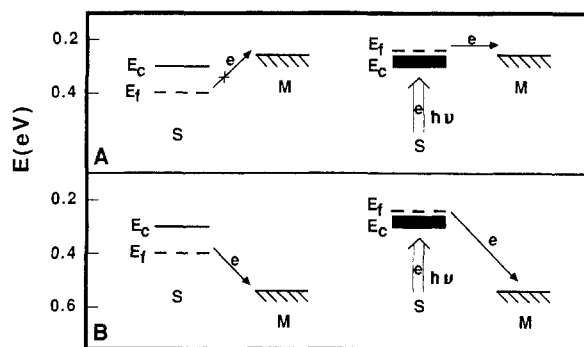


Figure 8. Schematic diagram of the photoinduced electron transfer from WO_3 semiconductor to Pt metal collector under different potentials.

potential could be adjusted with respect to E_f of the semiconductor particles, was employed with tungsten trioxide semiconductor particles irradiated by high-intensity light with a 2.5-kW ozone-free Xe lamp. With the addition of tartrate, an irreversible hole scavenger, to the solution, electrons accumulated in the particles, and, as a result, a direct electron transfer from WO_3 to the Pt collector held at 0.1 V vs SCE at pH 2.3 was observed. This potential is about 0.04 V negative of the E_c of bulk WO_3 (Figure 7).

The model presented in this paper can also be used to explain the shape of the photocurrent-time transients as a function of potential^{9b} as shown in the insets of Figure 7. Three different situations are considered: (a) When the collector electrode is held appreciably negative of E_c , no electron transfer from semiconductor particles to metal collector occurs, even under irradiation, and no photocurrent is observed. (b) When the electrode is held negative of the Fermi level of the semiconductor but near the conduction band edge, no electron transfer occurs from the semiconductor to the collector in the dark under equilibrium conditions. However, irradiation of the semiconductor particles raises the Fermi level into the conduction band and promotes electron transfer to the electrode, especially when a high-intensity light is employed and a hole scavenger is presented, as shown in Figure 8A. As expected, the steady-state photocurrents observed were small and a short induction period was needed for the semiconductor particles to accumulate electrons, as seen in photocurrent transient B in Figure 7 at lower potentials. (c) When the collector was held positive of the Fermi level of the semiconductor particles, electron transfer from semiconductor to the metal electrode is thermodynamically spontaneous. A relatively large steady-state photocurrent with a peak-shaped transient is observed. Initially, when the semiconductor particles in the dark contact the metal collector, electron transfer to the collector should be observed. An energy barrier will be created gradually at the interface, accompanying the electron flow to the metal electrode, and the rate of electron transfer should slow down as the interfacial energy barrier grows. The transient photocurrent curve at higher potentials in Figure 7 represents such a process. The interfacial characteristics should be that of a metal-semiconductor contact, since a layer of particles adhering to the electrode surfaces has been observed and this layer dominated the photoinduced electron transfer at higher potentials.^{9b} Interestingly, two different electron-transfer processes as proposed in Figure 8 can be distinguished in Figure 7; the steady-state photocurrent curve clearly shows two different regions with the critical point at about 0.3 V vs SCE besides the apparent difference in transient photocurrent curves in these two regions. In the lower potential region, the steady-state photocurrent increased very slowly with increasing potential because the potentials of metal electron collector were negative vs the Fermi level of the semiconductor particles. On the other hand, the photocurrent-voltage characteristics follow the Tafel relationship in the higher potential region as discussed previously.⁹ Note, however, that the photocurrent transients observed with TiO_2 and Fe_2O_3 do not show these effects, so that other factors (e.g., relative kinetics of interfacial charge transfer processes) must also be important.

Role of Charging in $E_{g,\text{opt}}$ of Q Particles. While size effects may be of importance in determining the band gap shift ($\Delta E = |E_{g,\text{opt}} - E_g|$) in small semiconductor particles compared to the bulk material, effects of excess charge on the particles, even when not intentionally introduced, may also play a role. As described above in the theoretical section, only a small number of excess electrons, Δn , need exist in a small particle to produce a sufficient electron density, n , to cause degeneracy and a finite ΔE . Thus for a spherical particle of radius, R , and volume, V , n is given by

$$n = \Delta n/V = \Delta n/(4\pi R^3/3) \quad (7)$$

and, from eq 4 and 5

$$\Delta E = [1 + (m_e/m_h)] [(h^2/2m_e)(9/32\pi^2)^{2/3}(\Delta n^{2/3}/R^2) - 4kT_e] \quad (8)$$

The presence of such charging effects may account for the poor quantitative agreement found in the past in relating ΔE to R based on eq 1. Moreover, for particles small enough to show this effect, the spectrum might be expected to show discrete absorption transitions corresponding to quantized energy levels.¹⁴ Discrete transitions have not been observed in most of the studies of colloidal semiconductor particles that did show obvious blue shifts, such as TiO_2 ,²⁹ ZnO ,³⁰ FeS_2 ,³¹ and PbS ,^{12e,13d,32} this has generally been ascribed to a lack of uniformity in the sizes of the particles used in these studies. Discrete peaks have been seen with PbI_2 , HgI_2 , and BiI_3 ; these have been interpreted in terms of "magic numbers",^{12d,16a,33,34a,b} discrete excited-state transitions with uniform small particles,³⁵ and "chemical effects",^{12c,36} respectively. If charging effects are of importance in determining the ΔE of colloidal semiconductors, then the actual particle size needed for the observation of Q-particle effects would be much smaller than those previously reported. PbS colloids show no evidence of structure in absorption spectra with PbS particles of radii 10–15 Å^{12e,13d,32} (considered as the typical region for observing a quantum size effect). More recently, however, studies on PbS in polymers suggested that discrete transitions could be observed in extremely small particles ($R < 6.5$ Å).^{16d}

Since the amount of excess charge needed to produce a finite ΔE in a small particle is tiny (e.g., the numbers of excess electrons corresponding to n_{crit} in CdS particles are 0.008, 0.025, 1.3, and 1.7 electrons for diameters of 10, 15, 55, and 60 Å, respectively), several processes for the origin of excess charge are possible. (1) As shown above, irradiation in the presence of a sacrificial donor can lead to charging. (2) An electron donor (reductant) present in solution with an E° corresponding to an energy above E_c could inject charge into the particle. (3) Adventitious impurities present during formation of the colloids could act as dopants. (4) Adsorbed species (e.g., anions) could partially transfer charge into the semiconductor particle. Note that the absorption edge shift to shorter wavelengths observed by the addition of electrons to colloidal CdS particles with the shift being more significant for smaller particles ($R \sim 15$ Å) compared to larger ones,¹¹ is consistent with the model proposed here. Finally, we note that although the discussion in this paper has primarily been concerned with the effects of excess electrons in the conduction band (or degeneracy in n-type materials), exactly parallel effects will occur for excess holes in the valence band and degenerate p-type materials. These excess hole effects might be more difficult to observe

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in practice, since they would often lead to decomposition of the semiconductor material.³⁷

The model proposed in this paper provides a new and simple approach to the estimation of energy gap shifts in small colloidal particles containing excess charge or dopants. The model can be considered only an approximate one for very small particles containing few (or fractional numbers of) electrons or dopants, since the analogy with a heavily doped bulk semiconductor is only a rough one. For very small particles the simple bulk parabolic band picture loses its validity, and Coulombic interactions of e^- and h^+ , an increasing importance of surface atoms and states, and the onset of discrete energy levels rather than bands will be significant.

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(38) The recent paper by Kamat, P. V.; Dimitrijević, N. M.; Fessenden, R. W. *J. Phys. Chem.* **1988**, *92*, 2324 on In_2S_3 colloids mentions this effect for photobleaching but does not suggest a quantitative model.

Conclusions

We have proposed a model to describe charging effects on energy level shifts in semiconductor particles. High electron concentrations created, for example, by strong irradiation to the particles can cause the semiconductor to become degenerate and raise the Fermi level into the conduction band. As a result, the energy necessary to excite electrons optically from the valence to the conduction band will be larger than the width of the forbidden energy gap, and thus, such particles will show an absorption edge shift toward the blue compared to the bulk semiconductor material. This charging will also affect the energies of photo-generated conduction band electrons and hence affect electron-transfer processes at irradiated particles and the measured potential for collection of such charges with an electrode or solution species.

Acknowledgment. The support of this research by the National Science Foundation (CHE8304666) is gratefully acknowledged. We thank E. S. Smotkin for sample preparation.

Chemisorption on Metals: The Method of Moments Point of View

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We show that the interaction of two adatoms, V_n , mediated by a semimetallic graphite surface is oscillatory as a function of the number of sites between the two chemisorbed species. The discussion is based on a method of moments expansion of the density of states of the locally perturbed system. In model calculations properly sized clusters or periodic clusters can be chosen by requiring the separation of the adsorbates to be large enough to separate all adatoms in one unit cell from the other unit cells by at least 4–5 intact sites in all directions. The results show a close connection between site preferences for a second adspecies and substitutional preferences in delocalized π -electron systems.

Interaction between chemisorbed species on metals, semimetals, and other systems with delocalized electrons contains an indirect component which decays slowly with distance. These long-range interactions are the solid-state analogues of the well-known rules of substitutional preferences for alternant hydrocarbons.¹

Friedel² has shown that in a metal a local perturbation causes an oscillatory decreasing potential

$$V(r) \sim \cos(2k_F r) / (2k_F r)^3$$

where k_F is the Fermi wave vector.

In conjugated hydrocarbons quite similar oscillations of charge densities and bond orders occur in response to a local perturbation. For instance Gutman³ has shown that, if two centers are connected by only one path (series of bonds), then a perturbation at the first center causes a charge polarization at the other one. The sign of these charges alternate with a rapidly decreasing amplitude as the separation between the two sites increases.

Due to the oscillatory charge distribution resulting from perturbation of one site, there has to be a nonbonded indirect interaction between two such perturbations: one expects a long-range oscillatory component due to the interaction of the two Friedel oscillations aroused by the two perturbations, e.g., the chemisorption of two H atoms on graphite. Unfortunately, no analytical results exist for a general molecule or surface such as the ones mentioned above for one path chains.³

Recently LaFemina and Lowe⁴ have studied hydrogen atomic chemisorption on graphite at low coverages using the energy band formalism, which is based on periodic boundary conditions. They

have considered a unit cell of 18 C atoms and two hydrogens, absorbed at a site indicated by * on Figure 1, and a second one at either of the sites specifically indicated. Since the unit cell is repeated in two directions in this periodic model, the interaction of the chemisorbed species is complicated by the presence of other hydrogens in adjacent cells. For example, for γ -chemisorption (as pointed out in ref 4), a starred atom in a neighboring cell is separated by two empty sites while the starred one inside the cell is separated by four empty sites. As a result, such calculations based on periodic boundary conditions should include many more sites to obtain a clear picture concerning the "bare" interaction between two adspecies.

The purpose of this paper is to present a new approach, based on the method of moments, with the aim to understand the nature of nonbonded adspecies-adspecies interactions mediated through the delocalized electrons of a surface.

We first review the moment's expansion of the energy expression for an extended system as perturbed by one or more chemisorbed species. The new formula so derived (eq 8) expresses the energy change in terms of the change in the number of electrons and in terms of changes in the moments, the latter being local if the perturbation is local. A test example is given demonstrating the favorable convergence of the method with respect to the size of the cluster going into the evaluation of the moments. Subsequently, the problem of two hydrogen atoms chemisorbed on graphite is analyzed by using a simple Hückel Hamiltonian. The

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