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Photoluminescence-Based Correlation of Semiconductor Electric Field Thickness with Adsorbate Hammett Substituent Constants. Adsorption of Aniline Derivatives onto Cadmium Selenide

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Abstract: Adsorption of ring-substituted aniline derivatives, presumably through the amino group, onto the (0001) face of single-crystal *n*-CdSe or *n*-CdS [CdS(e)] profoundly affects the semiconductor's photoluminescence (PL) by effecting charge transfer between surface states and the bulk semiconductor. The variations in PL intensity of etched samples are well fit by a dead-layer model, allowing estimation of the adduct-induced changes in depletion width. The magnitude of these changes can be molecularly tuned over nearly 1000 Å for moderately doped samples by the control of electron density at the coordination site, a parameter characterized by the Hammett substituent constant σ. In contrast, the affinity of the aniline derivatives for the CdS(e) surface, as estimated from the fit of concentration-dependent PL changes to the Langmuir adsorption isotherm model, is relatively insensitive to aniline substituent; equilibrium constants are $\sim 10^2$ M^{-1}. From variable-temperature experiments, the binding reaction for the *p*-OMe derivative of aniline is approximately thermoneutral and appears to be entropy driven. Temporal PL results support the presence of a broad distribution of recombination sites. PL decay curves are insensitive to adduct formation for the *p*-OMe and *p*-Me derivatives, suggesting that surface recombination velocity is not greatly affected by aniline adsorption. Variable incident light intensity studies, using the *p*-OMe derivative, are consistent with the notion of depletion width-driven PL changes. A model of orbital interactions occurring at the CdSe–aniline interface is proposed, in which interactions of the semiconductor surface with the aniline derivatives alter the occupancy of surface states by shifting their energy distribution relative to the band edges.

Introduction

We have recently investigated interfaces of semiconducting single-crystal, *n*-type CdS and CdSe [CdS(e)] with gases and with solutes in hydrocarbon solution using photoluminescence (PL) techniques.[1] The use of PL permits in situ characterization of these optically accessible interfaces without the need for electrical contacts: PL can be used to track changes in the depletion width (W) of the semiconductor resulting from molecular surface binding, to estimate equilibrium constants for these adducts, and to explore adduct-induced changes in the solid's carrier recombination kinetics. Moreover, exposure of the solid to families of compounds that bind weakly and reversibly permits analysis of the steric and electronic factors that control adduct formation with the surface and the resulting effect on the solid's electronic structure. These effects have been exploited in the design of a class of optically coupled chemical sensors.[1a,b]

The semiconductor interfaces described herein and elsewhere[1] differ in a fundamental way from semiconductor–metal and semiconductor–electrolyte interfaces. Specifically, unlike metals and electrolytes, the gases and hydrocarbon solutions do not serve as reservoirs of electrical charge that can be exchanged with the solid. Thus, charge transfer need not involve the external medium, but rather it will occur between the surface states and bulk of the semiconductor.[2] The nature of the surface states may be drastically altered by adsorption, leading to a corresponding change in the depletion region.[3] The key role that surface states play in defining the electronic properties of these and many other semiconductor-derived interfaces makes their chemical modification of both fundamental and practical interest.[4]

In this paper, we demonstrate control of the semiconductor's electric field thickness by electronic tuning through the noncoordinating portion of adsorbed molecules. Specifically, we use PL methods to show that adsorption of a series of meta- and para-substituted aniline derivatives onto single-crystal, *n*-CdS(e) substrates causes shifts in the depletion width that correlate with the adsorbates' Hammett substituent constants.[5,6] The magnitude and direction of the shifts are remarkable: The electric field thickness can be contracted *or* expanded over a total range of nearly a thousand angstroms for moderately doped semiconductors versus a toluene solvent reference. Complementing these experiments are time-resolved PL measurements that indicate the presence of a broad distribution of recombination centers: variable-temperature experiments that provide an estimate of the enthalpy and entropy of adduct formation; and variable-intensity experiments that illustrate how adduct formation affects the electric field thickness at different initial sizes of the depletion width. We also discuss possible interfacial orbital interactions that may account for our observations.

Experimental Section

Materials and Methods. Single-crystal, vapor-grown, *c*-plates of *n*-CdS ($\sim$10 ppm Te-doped) and *n*-CdSe, resistivity $\sim$ 2 Ω·cm, were obtained from Cleveland Crystals. The crystals were etched in Br_2/MeOH (1:30 by volume; 5 s) or concentrated HCl (5 s; MeOH rinse),

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(1) (a) Meyer, G. J.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1988**, *110*, 4914. (b) Lisensky, G. C.; Meyer, G. J.; Ellis, A. B. *Anal. Chem.* **1988**, *60*, 2531. (c) Meyer, G. J.; Leung, L. K.; Yu, J. C.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1989**, *111*, 5146. (d) Murphy, C. J.; Ellis, A. B. *J. Phys. Chem.* **1990**, *94*, 3082. (e) Murphy, C. J. *J. Electrochem. Soc.* **1990**, *137*, C220. (f) Murphy, C. J.; Ellis, A. B. *Polyhedron.* In press. (g) Lisensky, G. C.; Penn, R. L.; Murphy, C. J.; Ellis, A. B. *Science (Washington, D.C.)* **1990**, *248*, 840.

(2) Many, A.; Goldstein, Y.; Glover, N. B. *Semiconductor Surfaces*; North-Holland: New York, 1971; pp 130–190.

(3) Williams, R. H. In *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1988; Vol. 5, Chapter 1.

(4) See, for example: (a) Parkinson, B. A.; Heller, A.; Miller, B. *J. Electrochem. Soc.* **1979**, *126*, 954. (b) Abrahams, I. L.; Tufts, B. J.; Lewis, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3472. (c) Yablonovitch, E.; Sandroff, C. J.; Bhat, R.; Gmitter, T. *Appl. Phys. Lett.* **1987**, *51*, 439.

(5) For a general discussion of Hammett plots, see: (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper & Row: New York, 1981; pp 130–145. (b) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191. (c) Wells, P. R. *Chem. Rev.* **1963**, *63*, 171. (d) Butler, A. R. *Chem. Br.* **1989**, *25*, 997.

(6) We note that electronic effects on semiconductor-mediated organic photoreactions have previously been investigated with Hammett plots: (a) Fox, M. A.; Chen, C.-C. *Tetrahedron Lett.* **1983**, *24*, 547. (b) Hasegawa, T.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1534. (c) Hasegawa, T.; de Mayo, P. *Langmuir* **1986**, *2*, 362.

0002-7863/90/1512-8344$02.50/0

revealing the shiny, Cd-rich (0001) face, which was excited in the PL experiments as previously described.[1a] In some experiments samples were cleaved parallel to the *c* axis with a razor blade. All the anilines (*p*-OMe, *m*-OMe, *p*-Me, *m*-Me, -H, *m*-CF_3, *m*-Cl, *p*-Cl, *m*-CN, *p*-CN, *N*-Me, *N*,*N*-Me_2) were at least 98% pure as purchased from Aldrich and were distilled in vacuo or sublimed before use. *n*-Butyric acid (Aldrich; 99+%) was used as received. Toluene (Baker) was purged with N_2. Solutions were prepared and stored in a N_2 glovebag, and used within 48 h.

Apparatus. The sample cell for room temperature experiments consisted of a 3- or 4-mL glass vessel having a Teflon stopcock at its bottom for liquid drainage; the semiconductor was glued with black epoxy to a glass rod and held in a Teflon adapter that served as a stopper for the cell. Glass syringes, inserted through a sidearm against positive N_2 pressure, were used to rinse the sample or fill the cell. Mounted samples were stored in toluene in a N_2 glovebag when not in use.

Steady-State Optical Measurements. The sample cell was fabricated, as above, from a 1.5-cm-diameter glass tube. Samples were excited with a Coherent Innova 90-5 Ar^+ laser (457.9 and 514.5 nm) or a Melles-Griot Model 80 He–Ne laser (632.8 nm), as previously described.[1a] PL intensity was continuously monitored at the PL band maximum (a recorder was used in time-base mode) as the solution was varied; at the resolution of the monochromator, ~3 nm, there was no change in the PL spectral distribution upon adsorption. The cell was drained and the PL recorded in pure toluene between each measurement in aniline solution. Laser intensities, changed both by altering laser power and by using neutral density filters, were measured with a Coherent Model 212 power meter and corrected for spectral sensitivity. In general, incident intensities of ~1 mW/cm^2 were used, except in experiments where the intensity dependence of adduct-induced PL changes was sought.

Time-Resolved Optical Measurements. The sample cell was fabricated, as above, from a 1.0-cm square quartz cuvette. An average power of ~100 or ~275 mW, depending on laser configuration, of 587-nm excitation was provided by a Coherent Antares Nd:YAG laser system, as previously described.[7] The beam was focused to ~1- or ~0.2-mm-diameter points on the crystal, yielding maximum outputs ranging from ~10^{18} to 10^{20} photons cm^{-3}/pulse. Neutral density filters were used to reduce the laser intensity. Time-correlated single-photon counting was employed to measure the PL decay profiles.[8] The instrument response function was ~60 ps. Fits of data were performed to the Kohlrausch form, using a modification of the program CURFIT by Bevington.[9] The PL decay curves were iteratively reconvoluted from the instrument response function.

Variable-Temperature Studies. A 15-cm-long 14/20 Liebig condenser, modified with both a Teflon stopcock at the base for liquid drainage and an inlet above the water jacket for solution injection, served as the sample cell. Temperature control (±0.5 °C) between −30 and 60 °C was provided by a GCA Precision R20 circulating bath that pumped 95% ethanol through the cell's water jacket. Mounted semiconductor samples were inserted through a Teflon adapter that served as a stopper for this cell. The temperature of the solutions in which the semiconductor was immersed was monitored by a calibrated temperature transducer (Analog Devices, AD590), mounted at the end of the sample glass rod. Solutions were placed in the temperature bath for at least 15 min to thermally equilibrate and were then introduced through the sidearm of the cell against positive N_2 pressure. Samples were excited with the Ar^+ laser. In order to clear the frost that developed at low temperature, a stream of dinitrogen was trained on the area of the cell that was illuminated.

Results and Discussion

Dead-Layer Model. We have estimated adsorption-induced changes in the depletion width, *W*, of *n*-type CdS(e) by steady-state PL measurements through use of a dead-layer model. The model assumes that a region of thickness *D*, on the order of the depletion width, is nonemissive, or "dead" insofar as PL is concerned, because the photogenerated electron-hole pairs are swept apart by the electric field and cannot recombine to yield PL.[10]

The quantitative form of the dead-layer model that we employ for CdS(e)/aniline interfaces is given by eq 1, where PL_{ref} is the

$$PL_{ref}/PL_x = \exp(-\alpha' \Delta D) \qquad (1)$$

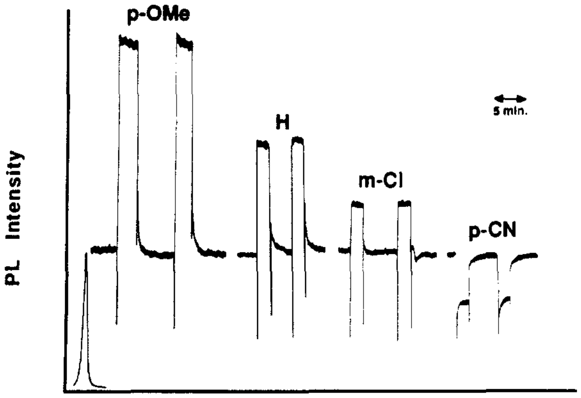

Figure 1. Relative changes in PL intensity at 720 nm (the PL spectrum is superimposed in the lower left corner to show the baseline) resulting from alternating exposure of an etched *n*-CdSe sample to toluene (initial and alternate response for each derivative) and to a ~0.2 M solution of the indicated aniline derivative in toluene. Downward spikes are caused by the draining of the sample cell when changing solutions. The sample was excited with 457.9-nm light.

PL intensity in a toluene reference solvent; PL_x is the PL intensity in a toluene solution of an aniline derivative; $\alpha' = (\alpha + \beta)$ is the absorptivity of the semiconductor, corrected for self-absorption; and $\Delta D = (D_{ref} - D_x)$ is the difference in the dead-layer thickness in passing from pure solvent to aniline solution. Operationally, we check for applicability of the model by use of different interrogating excitation wavelengths: eq 1 predicts different PL ratios but a constant value for ΔD as absorptivity is varied.

Inherent in the dead-layer model are several assumptions and limitations. First, *D* may not be equal to *W*, although both have shown the same trend with applied voltage in semiconductor–metal and semiconductor–electrolyte junctions.[11,12] Second, PL is a nonequilibrium measurement: Photoexcitation can alter the depletion width from its dark equilibrium value. It is thus important to emphasize that *ΔD corresponds to dead-layer differences induced by adsorption relative to a reference state that is also under the same intensity of illumination.* Of course, low light intensities best approximate the dark equilibrium situation, and most of the studies described herein have been conducted with weak illumination (~1 mW/cm^2). Finally, we note that the dead-layer model is a special case of a more general expression for the PL intensity that includes the surface recombination velocity *S* as a parameter.[13] Reduction of the general expression to eq 1 occurs if *S* is either insensitive to adsorption or relatively large in both ambients ($S \gg L_p/\tau_p$ and $\alpha L_p^2/\tau_p$, where L_p is the minority carrier (hole) diffusion length and τ_p is the hole lifetime).

Dead-Layer Results. Upon ultrabandgap excitation, the band edge PL of CdSe ($E_g \sim 1.7$ eV; $\lambda_{max} \sim 720$ nm) and CdS ($E_g \sim 2.4$ eV; $\lambda_{max} \sim 510$ nm) is reversibly changed by the addition of ring-substituted aniline derivatives to the toluene solvent in which the semiconductor is immersed; at the low resolution employed, only the PL intensity and not the spectral distribution is affected by adduct formation. We have focused on meta and para substituents to minimize the steric effects on surface binding. Like other amines,[1a,g] aniline causes an enhancement in PL intensity relative to solvent. Qualitatively, meta and para substituents that can deliver additional electron density enhance this effect, as shown in Figure 1 for the *p*-OMe derivative. Figure 1 also shows that a strong electron-withdrawing substituent, *p*-CN,[14] can actually cause a decrease in PL intensity relative to the reference value for this sample.

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(7) Leung, L. K.; Meyer, G. J.; Lisensky, G. C.; Ellis, A. B. *J. Phys. Chem.* **1990**, *94*, 1214.

(8) O'Connor, D. Z.; Phillips, D. In *Time-Correlated Single Photon Counting*; Academic Press: New York, 1985.

(9) Bevington, P. R. In *Data Reduction and Error Analysis for Physical Sciences*; McGraw-Hill: New York, 1969.

(10) Ellis, A. B. In *Chemistry and Structure at Interfaces: New Laser and Optical Techniques*; Hall, R. B., Ellis, A. B., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Chapter 6.

(11) Hollingsworth, R. E.; Sites, J. R. *J. Appl. Phys.* **1982**, *53*, 5357.

(12) Burk, A. A., Jr.; Johnson, P. B.; Hobson, W. S.; Ellis, A. B. *J. Appl. Phys.* **1986**, *59*, 1621.

(13) Mettler, K. *J. Appl. Phys.* **1977**, *12*, 75.

(14) Since acetonitrile, cyanopyridines, and benzonitrile did not perturb the CdSe PL intensity relative to a toluene ambient (up to ~30% v/v), we presume that *m*- and *p*-cyanoaniline, like the other aniline derivatives, bind through the amino group.

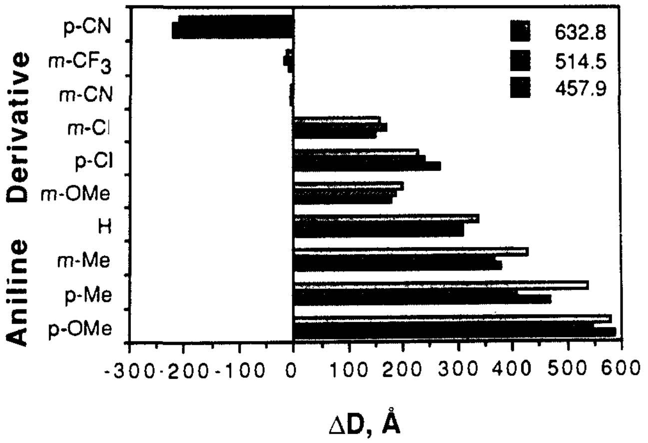

Figure 2. Maximum values of ΔD, ±10%, for a single CdSe sample with each of the aniline derivatives examined, calculated with eq 1 of the text. Typical aniline concentrations needed to produce the maximum PL changes were ~0.2 M. Excitation wavelengths in nm are shown in the legend. Penetration depths ($1/\alpha$ of 570, 740, and 1500 Å at 457.9, 514.5, and 632.8 nm, respectively) and the correction for self-absorption (β = 1.2×10^4 cm^{-1}) were obtained from ref 15. Positive values of ΔD correspond to a contraction in the dead-layer thickness with aniline adsorption and negative values to an expansion.

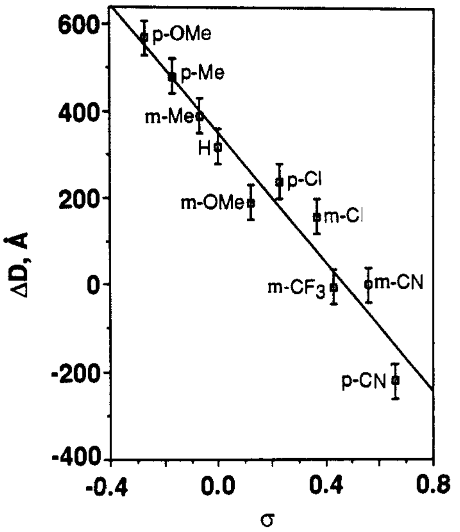

Figure 3. Plot of the maximum ΔD value (Figure 2 data; the average of the values obtained by using three excitation wavelengths was used) obtained for each aniline derivative vs its Hammett substituent constant σ, which was obtained from ref 5a. The correlation coefficient of the least-squares best line is −0.98.

The PL changes are reversible and concentration dependent, saturating by ~0.2 M. The maximum changes in PL intensity correspond to the maximum shift in dead-layer thickness induced by aniline adsorption (eq 1). Values of α' were obtained from the literature.[15] Figure 2 shows that a constant ΔD value is obtained for each aniline derivative by using three excitation wavelengths, agreeing with the prediction of the simple dead-layer model.

A good linear correlation is found between maximum ΔD values and the corresponding Hammett substituent constants (Figure 3) over ranges of ~800 Å in ΔD and 1.0 in σ. The linearity of the plot is consistent with the electronic origin of the PL changes and also implies that the nature of the reaction, presumably coordination by the amino group to surface Cd^{2+} sites, is unchanged by these ring substitutions.[5] NMR shifts of the amino protons also track linearly with σ in nonpolar solvents to produce a sign change.[16]

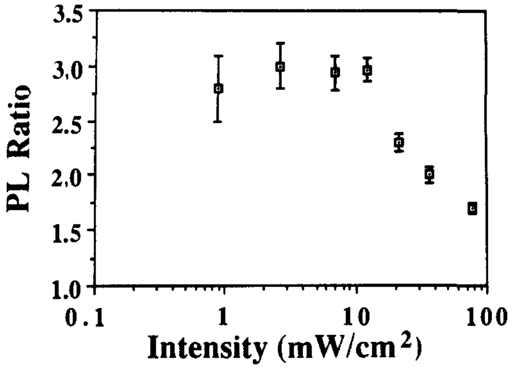

Figure 4. Dependence of the maximum PL intensity ratio (PL intensity in 0.2 M *p*-methoxyaniline solution divided by the PL intensity in toluene reference solvent) on the incident light intensity for one *n*-CdSe sample. The excitation wavelength was 514.5 nm. Data were taken in random order.

Two applications of the Hammett methodology are molecular and surface comparisons. For example, *N*-methylaniline yields a ΔD value at saturation that is equivalent to that obtained with the most electron-releasing, ring-substituted derivative, *p*-methoxyaniline. Use of different surfaces resulted in Hammett plots with different slopes: A comparably conductive sample of CdS, for example, was less susceptible to electronic tuning, yielding aniline-induced ΔD contractions that only ranged from 600 to 100 Å over the same spread of σ values shown in Figure 3. Use of cleaved CdSe samples yielded PL changes that did not fit the dead-layer model but, for 457.9-nm excitation, did qualitatively track the Hammett parameter.

Intensity Effects. If high incident light intensity reduces the pre-adsorption value of D, the adduct-induced reductions in D should become smaller than they are at low intensity. We have investigated the intensity dependence of the PL ratio using 514.5-nm light. Figure 4 illustrates the maximum PL ratio measured for the *p*-OMe derivative and reveals it to be constant between ~1 and 10 mW/cm^2. As the intensity increases beyond this point, the PL ratio is indeed reduced, consistent with a pre-adsorption state with a smaller electric field thickness. For *n*-butyric acid, a compound that gives substantial PL decreases on all CdSe samples tested, the opposite effect can be observed: at high incident light intensities, the PL decreases are more pronounced. This is consistent with the notion that band flattening at high intensity enables adsorbates that expand the dead layer to produce larger values of ΔD relative to those obtained at low intensity.

Adduct Thermodynamics. Equilibrium constants for adduct formation between the adsorbate and the semiconductor surface can be estimated from the concentration dependence of the PL changes by using the Langmuir adsorption isotherm model. The assumptions of the model are the following: (1) the solid contains a fixed number of adsorption sites, and, at any temperature and concentration, a fraction θ of these are occupied at equilibrium; (2) each site holds one adsorbed molecule; (3) the heat of adsorption is the same for all sites and is independent of θ; and (4) there are no intermolecular interactions between adsorbed molecules. The quantitative form of the model is given by eq 2,[17]

$$\theta = KC/(1 + KC) \text{ or } 1/\theta = 1 + 1/(KC) \qquad (2)$$

where θ is the fractional surface coverage, K is the equilibrium constant, and C is the solution concentration of the adsorbate; a double-reciprocal plot of θ^{-1} vs C^{-1} should be linear with a slope equal to K^{-1}. We assume that maximum PL changes correspond to maximum surface coverage (θ = 1). If we take θ to be the fractional change in ΔD (vide infra), which from eq 1 is proportional to ln (PL_x/PL_{ref}), we obtain eq 3, where PL_{ref}, PL_{sat},

$$\theta = \ln [PL_x/PL_{ref}]/\ln [PL_{sat}/PL_{ref}] \qquad (3)$$

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(15) Absorptivities for CdSe are found in: Parsons, R. B.; Wardzynski, W.; Yoffe, A. D. *Proc. R. Soc. London, A* **1961**, *262*, 120. The absorptivity for CdS at 457.9 nm was extrapolated from data in: Dutton, D. *Phys. Rev.* **1958**, *112*, 785.

(16) Dyall, L. K. *Aust. J. Chem.* **1964**, *17*, 419.

(17) Moore, W. J. *Physical Chemistry*, 4th ed.; Prentice-Hall: Englewood Cliffs, NJ, 1972; p 497.

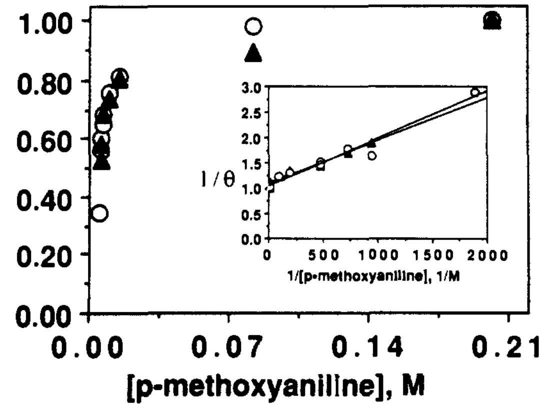

Figure 5. Plots of the fractional surface coverage θ, defined by eq 3, vs *p*-methoxyaniline concentration at −30 °C (open circles) and at +38 °C (triangles). The double-reciprocal plots are shown as insets; linearity implies that the fits to the Langmuir model are good for both cases. Values of K, calculated from eq 2, were 1200 ± 200 M^{-1} at −30 °C and 1300 ± 200 M^{-1} at +38 °C. The sample was excited with 457.9-nm light.

and PL_x correspond to the reference ($\theta = 0$), saturated ($\theta = 1$), and intermediate PL intensities.[18]

Our data are well fit by the Langmuir adsorption isotherm model. Values of K are ~70 to 210 M^{-1} for most of the anilines, with random distribution across the Hammett series; only the *p*-OMe derivative had a substantially different value of K, ~1000 M^{-1}. We have also examined the effect of methyl substitution at the amino group: the *N*-methyl derivative displayed a lower adduct formation constant of ~20 M^{-1} at 295 K, and for *N,N*-dimethylaniline the constant was too small to measure, perhaps reflecting increasing steric constraints. The low values of K reflect the weak nature of the interaction between the surface binding sites and the aniline derivatives.

The lack of correlation of K values with the Hammett parameter prompted us to estimate the enthalpy and entropy of formation for the aniline–surface bond by determining K as a function of temperature. For the adduct of *p*-methoxyaniline with CdSe, K is invariant within experimental error over a temperature range of −30 to +60 °C, as illustrated for two temperatures in Figure 5. This result implies that the reaction is nearly thermoneutral and is driven by an entropy change of ~+14 e.u. This result is surprising, given the negative entropy changes that might be expected to accompany simple adsorption of molecules onto a surface.[19] A similar positive entropy change has been reported previously, however, for adsorption of pyridine onto CdS.[20] In our system, an overall positive entropic change could result from loss of aggregation in solution,[21] from release of adventitious impurities from the surface to solution, or possibly from the effects of charge transfer from localized surface states to the semiconductor bulk. Given the effect of intensity on PL ratio, we examined the intensity dependence of K for the *p*-OMe derivative at 295 K. Within experimental error, no variation was observed for incident intensities ranging from ~1 to 100 mW/cm^2.

Time-Resolved Experiments. A major assumption of the dead-layer model is that the surface recombination velocity, S, is either very high in both toluene solvent and aniline solution or unaffected by the solution environment.[13] Temporal PL experiments were therefore undertaken to seek evidence for adduct-induced changes in recombination kinetics.

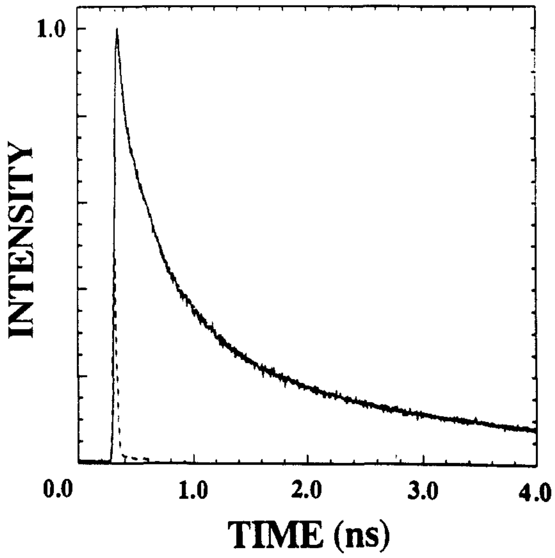

Figure 6. Luminescence decay from etched CdSe in toluene with 587-nm excitation at an estimated average power of 1.25 mW. The dashed curve is the instrument response function. The fit to the Kohlrausch equation (eq 4) is plotted through the data. The fit parameters are $\beta = 0.30$ and $\tau = 150$ ps.

The PL decay curves of *n*-CdSe are nonexponential (Figure 6) and are well fit by the two-parameter Kohlrausch equation (eq 4).[7] The parameter β ($0 < \beta < 1$) has been related to a distribution of exponential decay times that are serially linked (β increases as the distribution of decay times becomes more homogeneous), and the parameter τ, the lifetime, represents the peak of the distribution. For etched CdS(e) samples, a distribution of linked relaxation times might be expected for the likely scenario, in the presence or absence of aniline derivatives, that a variety of recombination sites having different decay times is present.

$$I(t) = I_0 \exp[-(t/\tau)^{\beta}] \qquad (4)$$

We find that the luminescent decay profiles for etched CdSe in toluene are unaffected by *p*-methoxyaniline adsorption. This is the case both at moderate intensity and also at high intensity (~10^{20} photons cm^{-3}/pulse), where the bands should be more nearly flat.[7,22] Although the decay profiles are insensitive to aniline adsorption, the absolute PL intensity (counts) for aniline adsorption is larger than that found in toluene, in agreement with the steady-state results. Fitting our decay data to eq 4 yields typical β and τ values of 0.30 and 150 ps, respectively. The low value of β is indicative of a broad distribution of recombination sites.

The fact that the decay profiles are insensitive to aniline adsorption implies that either S is unchanged by adsorption or our technique is unable to detect changes in S that may be occurring. However, we note that we can detect significant changes in decay profiles with cleaved CdSe samples (for one sample, β and τ were 0.38 and 270 ps, respectively, in toluene, and 0.46 and 1150 ps in *p*-methoxyaniline solution at 1.25 mW incident power), whose steady-state PL changes do *not* fit the dead-layer model.

An Interfacial Orbital Interaction Model. For the (0001) face of *n*-CdS(e), we can envision coordinatively unsaturated surface Cd ions serving as electron acceptors, thereby trapping negative charge at the surface to produce a positively charged depletion region. Quantitatively, the relationship between the surface charge and the depletion width of doped semiconductors can be derived

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(18) Good fits to the Langmuir model can also be obtained by equating θ to the fractional PL change, $\theta = (PL_x - PL_{ref})/(PL_{sat} - PL_{ref})$.[1] Equation 3, which can be rewritten as $\ln [1 + (PL_x - PL_{ref})/PL_{ref}]/\ln [1 + (PL_{sat} - PL_{ref})/PL_{ref}]$, reduces to this expression when the overall PL change is small, since under that condition $\ln (1 + x)$ is approximately equal to x. In comparing equilibrium constants derived by using the two definitions of θ, the same order of magnitude for K and relative trends between sets of K values are preserved within families of compounds. The fits to the Langmuir model are very good with either choice of θ, except in cases where the PL enhancements are very large, when eq 3 provides superior fits. Our treatment should be regarded as approximate because we do not have absolute coverages that would directly relate ΔD to the number of adsorbed molecules.

(19) Atkins, P. W. *Physical Chemistry*, 2nd ed.; Freeman: New York, 1982; p 1016.

(20) Maidanovskaya, L. G.; Terpugova, A. F.; Plotnikova, V. P. *Russ. J. Phys. Chem.* **1968**, *42*, 429.

(21) Lady, J. H.; Whetsel, K. B. *J. Phys. Chem.* **1964**, *68*, 1001.

(22) (a) Evenor, M.; Gottesfeld, S.; Harzion, Z.; Huppert, D.; Feldberg, S. W. *J. Phys. Chem.* **1984**, *88*, 6213. (b) Gottesfeld, S. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 362.

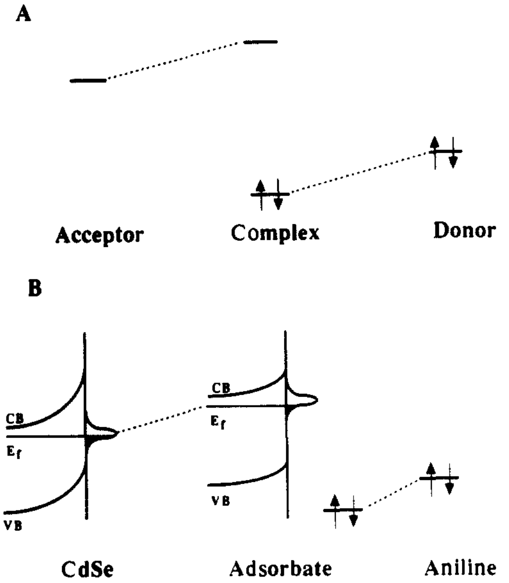

Figure 7. (A) Molecular orbital formation involving a donor–acceptor pair; the donor's HOMO is slightly stabilized by the interaction, while the acceptor's LUMO is slightly destabilized. (B) The analogous orbital picture for the interaction of *n*-CdSe surface states with an aniline donor. The surface state energies are pictured as a distribution about the Fermi level, E_f. Shaded portions of the distribution correspond to occupied surface states. The donor's HOMO is slightly stabilized, while the surface state energies are slightly raised in energy relative to the conduction band edge. The positions of the Fermi level, conduction band edge (CB), and valence band edge (VB) are not directly measurable from our PL data.

from electrostatic principles. Following Smith's treatment,[23] the total negative surface charge of $-eN_s$ per unit area (N_s is the number of available surface sites, per unit area, below the Fermi level; e is the electron charge) at equilibrium is balanced by the exposed ionized impurity charge of eN_d (N_d is the donor concentration for the uniformly doped *n*-type semiconductors employed herein) times the depletion width W (eq 5). This is a

$$N_s = N_d W \tag{5}$$

consequence of the charge neutrality required by Gauss' law: the electric field flux lines must terminate in the interior of the semiconductor.

The energetic distribution and electronic occupany of surface states may be altered by adsorption.[3] With respect to surface adduct formation, eq 5 predicts that adsorbates that cause a change in surface charge will proportionately change the depletion width. Since our PL data fit the Langmuir adsorption isotherm model when θ is defined in terms of the fractional change in ΔD (vide supra), we take this as evidence that D, like W, is linked to a corresponding fractional change in N_s. Alternatively, the good Langmuir fits could be the result of a fractional change in S,[24] if it exists and is coupled to the change in dead-layer thickness. However, changes in S alone are inconsistent with the excitation wavelength dependence of the adduct-induced PL changes.[13]

The interaction of the dipolar aniline species with the surface Cd sites can be likened to the formation of a weak donor–acceptor complex (Figure 7). As shown in part A of the figure, the donor HOMO and acceptor LUMO are slightly stabilized and destabilized, respectively, by the formation of the complex, but there is little transfer of charge density between them; accordingly, the complex is readily dissociated. Part B of Figure 7 presents the analogous picture for aniline adsorption onto CdS(e). The surface states are drawn as having a distribution of energies to reflect the variety of recombination sites inferred from the temporal PL data. These surface states may interact with the aniline HOMO (which has both π and nitrogen lone pair character[25]) to produce a new distribution that can lead to a reduction in depletion width by shifting the energies of the surface states closer to the conduction band edge and reducing their overall electronic occupancy.[26] As in the case of the donor–acceptor complex, there is little charge density transferred between the adsorbed molecule and the solid, permitting ready dissociation of the adsorbate.

Although Figure 7 focuses on interactions of aniline as a donor, strong electron-withdrawing substituents like *p*-CN may cause the molecule to interact with the surface states as an acceptor (through its LUMO), leading to surface state energies that have been shifted closer to the valence band edge, resulting in increased electronic occupancy, and a larger depletion width. In the cases of the *m*-CN and *m*-CF_3 derivatives, which gave essentially no PL changes for the etched CdSe sample of Figures 2 and 3, the molecules' donor and acceptor roles appear to offset one another. The extent of the orbital interactions depends, of course, on the relative energies of the orbitals of the two phases and their overlap.

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[23] Smith, R. A. *Semiconductors*, 2nd ed.; Cambridge University Press: Cambridge, UK, 1978; pp 220–225.

[24] Benjamin, D.; Huppert, D. *J. Phys. Chem.* **1988**, *92*, 4676.

[25] Streets, D. G.; Hall, W. E.; Ceasar, G. P. *Chem. Phys. Lett.* **1972**, *17*, 90.

[26] The surface states discussed may be considered to be Shockley chemisorption states: Tomasek, M.; Koutecky, J. *Int. J. Quantum Chem.* **1969**, *3*, 249.