Luminescent Photoelectrochemical Cells. 6. Spatial Aspects of the Photoluminescence and Electroluminescence of Cadmium Selenide Electrodes[1]

Holger H. Streckert, Jiu-ru Tong, and Arthur B. Ellis*

Contribution from the Department of Chemistry,
University of Wisconsin—Madison, Madison, Wisconsin 53706. *Received June 18, 1981*

Abstract: Samples of single-crystal, n-type CdSe emit when excited with ultraband gap excitation. The emission band ($\lambda_{max} \approx 720$ nm) is near the band gap of CdSe (~1.7 eV); its energy, decay time, and temperature dependence are consistent with its description as edge emission. Photoluminescence (PL) spectra can be dependent on excitation wavelength and show evidence of self-absorption effects: PL spectra obtained with 457.9-nm excitation are broadened in the high-energy portion of the band relative to spectra obtained with more deeply penetrating 632.8-nm excitation. Measured PL efficiencies, ϕ_r, are $\sim 10^{-4}$ in air at 295 K. When CdSe is used as the photoanode of photoelectrochemical cells employing aqueous polychalcogenide electrolytes, emission is quenched by the passage of photocurrent resulting from ultraband gap excitation. Electroluminescence (EL) can be observed from CdSe when the semiconductor is used as a dark cathode in aqueous, alkaline peroxydisulfate electrolyte. The EL spectrum is similar to the PL spectrum, suggesting the involvement of a common emissive excited state. Differences in the breadths of the spectra, however, indicate that, on average, EL is produced nearer to the semiconductor–electrolyte interface than PL under comparable experimental conditions. Measured EL efficiencies, $\bar{\phi}_{EL}$, approaching 10^{-3} at −1.50 V vs. SCE are comparable to PL efficiencies measured at this potential in hydroxide solution and provide evidence that the emissive excited state can be efficiently populated in an EL experiment; these lower-limit estimates of $\bar{\phi}_{EL}$ and ϕ_r decline in passing to potentials near the onset of EL, ~−0.9 V vs. SCE. Spatial features of these comparisons are discussed. Evidence that (near-) surface contributions to PL spectra can be enhanced by chemical or photoelectrochemical treatment of the CdSe surface is also presented.

The study of interfacial charge-transfer processes at semiconductor electrodes is under active investigation, as befits the semiconductor's role as the key element of photoelectrochemical cells (PECs).[2-4] We have recently reported the use of luminescence as a tool for examining charge-transfer events occurring at n-type CdS and CdS:Te (Te-doped CdS) electrodes.[1,5,6] Photoluminescence was studied while these electrodes served as photoanodes in PECs employing polychalcogenide electrolytes; under certain conditions photoluminescence could be quenched by the passage of photocurrent.[5] Electroluminescence could be initiated by using the semiconductors as dark cathodes in alkaline, peroxydisulfate media.[6]

Among the most widely studied semiconductor electrodes is n-type CdSe. The popularity of CdSe derives in part from its relatively small band gap of ~1.7 eV[7] and the ease with which single-crystal, polycrystalline, and thin film samples can be fashioned into electrodes for PEC usage.[8] In this paper we examine luminescence from single-crystal, n-type CdSe electrodes for which we demonstrate that photoluminescence can be perturbed and electroluminescence initiated by interfacial charge-transfer processes. Besides serving to extend the range of materials to which the emissive probe is applicable, CdSe affords insight into spatial and mechanistic aspects of photoluminescence and electroluminescence: comparison of spectral distributions can be exploited to infer that photoluminescence and electroluminescence occur from a common excited state but differ in their spatial origins under our experimental conditions. Comparison of measured efficiencies for the two kinds of emission at several potentials suggests that the emissive excited state can be efficiently populated in EL experiments, although spatial factors must be considered in making this comparison. Additionally, we find evidence that (near-) surface contributions to photoluminescence from CdSe can be enhanced by chemical or photoelectrochemical treatment of the semiconductor surface.

Results and Discussion

Photoluminescence (PL) and electroluminescence (EL) represent two methods for populating the excited-state manifold of CdSe. PL studies, to be described first, were conducted in air and in a PEC. These experiments aid in the assignment of the emissive transition and detail its spectral distribution, efficiency, and perturbation by the passage of current in a PEC. Subsequently, we discuss the analogous EL characteristics of spectral distribution, efficiency, and potential dependence. Implications of comparisons of PL and EL properties are also discussed in this section. In the final section we describe the effects of various surface treatments on the PL properties of CdSe.

A. Photoluminescence. 1. Origin of Emission and Spectral Distribution. Excitation of single-crystal, n-type CdSe in air with lines from an Ar ion laser produces cherry red luminescence at the site of irradiation. A front-surface emission spectrum, obtained with 457.9-nm excitation, is displayed as the dashed curve of Figure 1; the sample had been etched with Br_2/MeOH, placed in an emission spectrometer and inclined at ~45° to both the excitation beam and the emission detection optics. Corresponding to the red emission is a sharp band whose maximum occurs at ~720 nm, approximately the band gap energy of CdSe. This band has been reported previously[9a] and its energy is consistent with a description as edge emission.[9b] Although we are uncertain as to the exact origin of this radiative transition in our samples, additional support for such a description comes from the tem-

---

[1] Part 5 of this series: Karas, B. R.; Streckert, H. H.; Schreiner, R.; Ellis, A. B. *J. Am. Chem. Soc.* **1981**, *103*, 1648.

[2] Bard, A. J. *Science (Washington, D.C.)* **1980**, *207*, 139.

[3] Wrighton, M. S. *Acc. Chem. Res.* **1979**, *12*, 303.

[4] Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189.

[5] (a) Karas, B. R.; Ellis, A. B. *J. Am. Chem. Soc.* **1980**, *102*, 968. (b) Ellis, A. B.; Karas, B. R. *Adv. Chem. Ser.* **1980**, *No. 184*, 185.

[6] Streckert, H. H.; Karas, B. R.; Morano, D. J.; Ellis, A. B. *J. Phys. Chem.* **1980**, *84*, 3232.

[7] Wheeler, R. G.; Dimmock, J. *Phys. Rev.* **1962**, *125*, 1805.

[8] (a) Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 6855. (b) Skyllas Kazacos, M.; Miller, B. *J. Electrochem. Soc.* **1980**, *127*, 2378. (c) Colbow, K.; Harrison, D. J.; Funt, B. L. *Ibid.* **1981**, *128*, 547. (d) Russak, M. A.; Reichman, J.; Witzke, H.; Deb, S. K.; Chen, S. N. *Ibid.* **1980**, *127*, 725. (e) Noufi, R. N.; Kohl, P. A.; Bard, A. J. *Ibid.* **1978**, *125*, 375. (f) Manassen, J.; Hodes, G.; Cahen, D. *Ibid.* **1977**, *124*, 532.

[9] (a) Oelgart, G.; Stegmann, R.; John, L. *Phys. Status Solidi A* **1980**, *59*, 27. (b) Halsted, R. E. In "Physics and Chemistry of II-VI Compounds"; Aven, M., Prener, J. S., Eds.; North-Holland Publishing Co.: Amsterdam, 1967; Chapter 8.

0002-7863/82/1504-0581$01.25/0

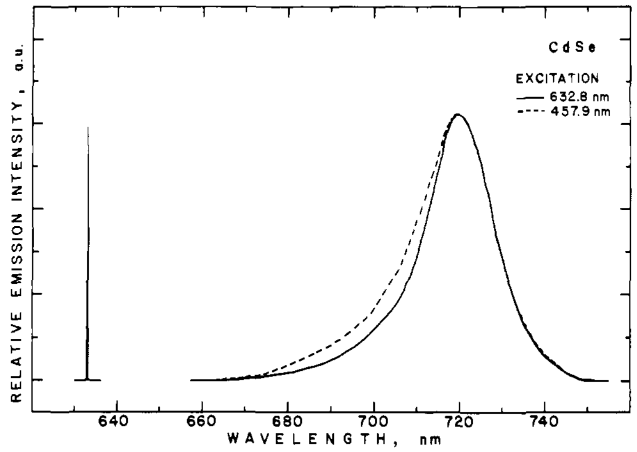

Figure 1. Uncorrected, front-surface PL spectra of n-CdSe obtained in air with 632.8-nm (solid line) and 457.9-nm (dashed line) excitation. Both spectra were taken in identical samples and excitation beam geometries; the ~0.20-cm^2 surface area was excited with 5.0 and 15 mW of 632.8- and 457.9-nm light, respectively, delivered in laser beams of ~ 0.03-cm^2 area. The emission intensity from 457.9-nm excitation was ~2 times larger but has been scaled down to match the intensity from 632.8-nm light at $\lambda_{max} \approx 720$ nm. A spectral resolution of 0.3 nm was employed, as illustrated by the 632.8-nm excitation spike which is shown at 1/200 of the sensitivity used for the corresponding emission band.

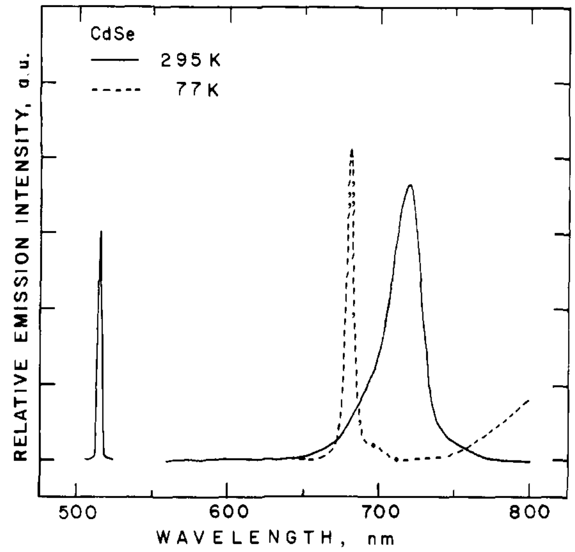

Figure 2. Uncorrected PL spectra of n-CdSe at 77 K (dashed line) and 295 K (solid line), the latter taken at 60 times the sensitivity of the former. The sample was excited with identical intensities of 514.5-nm light without disturbing the experimental geometry. A spectral resolution of 3.0 nm was employed throughout this experiment.

perature dependence and decay time of the emission.

Figure 2 reveals that cooling the sample to 77 K causes a pronounced blue shift of λ_{max} to ~680 nm with ultraband gap 514.5-nm excitation. This shift of ~0.10 eV is in accord with the reported optical band gap temperature coefficient for CdSe of -4.6×10^{-4} eV/K over the range of 90–400 K.[10] The 77 K spectrum of Figure 2 also displays a weak shoulder at ~700 nm and the onset of another emission band whose uncorrected λ_{max} is at ~830 nm. We do not see these features at room temperature in PL experiments and are uncertain as to their origin. Decay-time experiments for the 720-nm band were conducted at 295 K in air, exciting with either the 337-nm line of a N_2 laser or the 455-nm output of a N_2-pumped dye laser. Decay times of ~20 ns ($\tau_{1/e}$) are in accord with a value previously reported for similar CdSe samples.[11] Such short decay times are typical for edge emission.[12,13b] Taken together, the energy, temperature dependence, and decay time of the 720-nm band support its classification as edge emission.

The spectral distribution of the 720-nm band merits additional comment. We find that for a given sample geometry the emission spectrum can be dependent on the ultraband gap excitation wavelength. Figure 1 demonstrates that excitation with the 632.8-nm line of a He–Ne laser produces a slightly different spectrum than that obtained with 457.9-nm irradiation. The latter is somewhat broader (fwhm of 22 vs. 19 nm with ~0.3-nm resolution) with the discrepancy occurring almost exclusively in the high-energy tails of the two curves. We ascribe this difference to self-absorption, an effect which has previously been noted in semiconductors exhibiting edge emission.[13] The absorptivities of CdSe for 460- and 630-nm light have been measured to be ~1.85 $\times 10^5$ and 0.65×10^5 cm^{-1}, respectively, and are essentially independent of polarization at these wavelengths.[14] The almost threefold difference in absorptivities implies that the luminescence produced from the longer excitation wavelength will have a longer average path length to traverse through the semiconductor in order to be detected. Since the absorptivity, α, of CdSe increases with decreasing wavelength ($\alpha \lesssim 10^3$ cm^{-1} for $\lambda \gtrsim 720$ nm; $\alpha \gtrsim 10^4$ cm^{-1} for $\lambda \lesssim 710$ nm),[14] we expect and observe the high-energy portion of the emission band to be more strongly absorbed for more deeply penetrating excitation wavelengths.

Because the effect displayed in Figure 1 is small, we sought other means to establish its validity. Besides observing the effect for CdSe on two different emission spectrometers, we also examined $CdS_{0.74}Se_{0.26}$ and $CdS_{0.49}Se_{0.51}$. These two materials possess sharp emission bands near their band gaps with λ_{max} values of ~560 and 615 nm, respectively.[9a] They, too, exhibit slightly truncated high-energy tails when excited with 514.5- as opposed to 457.9-nm light;[15] this spectral mismatch is consistent with a higher absorptivity at the latter excitation wavelength inferred from absorption spectra of other CdS_XSe_{1-X} ($0 \leq X \leq 1$) samples.[14,16]

2. Efficiency. The quantum efficiency of PL, defined as photons emitted per photons absorbed and symbolized by ϕ_r, was estimated by two techniques. The first provides an upper limit on ϕ_r by establishing experimental conditions which lead to larger values of ϕ_r. Decreasing the temperature often has this effect. We chose an excitation wavelength, 514.5 nm, where the CdSe absorptivity at 77 K is virtually unchanged from its 295 K value.[14] Figure 2 demonstrates that by lowering the temperature to 77 K an ~20-fold enhancement in ϕ_r obtains when the areas under the edge emission bands are corrected for relative detection sensitivity. The value of 0.05 is, therefore, an upper limit on the 295 K radiative efficiency.

A second estimate was made on the basis of a technique developed by Wrighton et al.[17] The intensity of laser light reflected from CdSe is subtracted from the intensity reflected from a nonabsorbing standard, a MgO pellet, in the same geometry. This difference represents the number of photons absorbed by CdSe and is divided into the number of photons emitted by CdSe; the intensities are obtained by determining the areas under the appropriate bands (see Experimental Section). This ϕ_r measurement, obtained by using several ultraband gap excitation wavelengths and samples, gave values of $(\sim 0.9\text{–}4) \times 10^{-4}$. This range is consistent with the upper limit obtained by the preceding method. The error in the reflectance-based technique has been estimated

---

(10) Bube, R. H. *Phys. Rev.* **1954**, *98*, 431.

(11) Harzion, Z.; Croitoru, N.; Gottesfeld, S. *J. Electrochem. Soc.* **1981**, *128*, 551.

(12) Pankove, J. I. "Optical Processes in Semiconductors"; Prentice-Hall: Englewood Cliffs, NJ, 1971; Chapter 6.

(13) (a) Schairer, W.; Gramann, W.; Bludau, W. *Inst. Phys. Conf. Ser.* **1977**, *No. 33a*, 344. (b) Lehmann, W. *Solid-State Electron.* **1966**, *9*, 1107.

(14) Parsons, R. B.; Wardzynski, W.; Yoffe, A. D. *Proc. R. Soc. London, A* **1961**, *262*, 120.

(15) Streckert, H. H.; Tong, J.; Carpenter, M. K.; Ellis, A. B. *J. Electrochem. Soc.*, in press.

(16) Dutton, D. *Phys. Rev.* **1958**, *112*, 785.

(17) Wrighton, M. S.; Ginley, D. S.; Morse, D. L. *J. Phys. Chem.* **1974**, *78*, 2229.

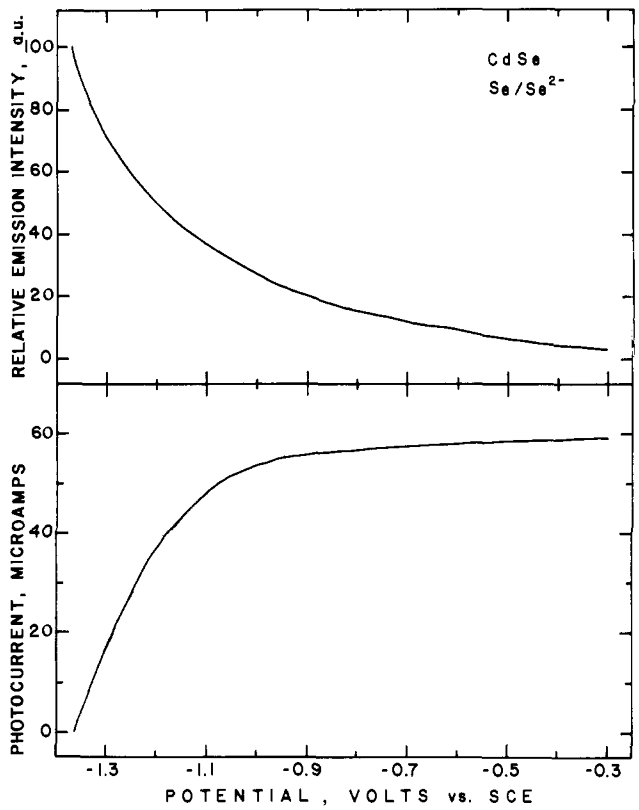

Figure 3. Photocurrent (bottom frame) and emission intensity (top frame) monitored at $\lambda_{max} \approx 720$ nm vs. potential for a CdSe single-crystal electrode excited at 514.5 nm in 5 M KOH/0.11 M Se^{2-}/0.004 M Se_2^{2-} electrolyte. The Ar ion laser was beam expanded and irradiated the ~0.30-cm^2 exposed area of the electrode with ~0.15 mW of power. The *iLV* curves were swept at 10 mV/s. The electrolyte redox potential was −0.96 V vs. SCE.

as ±25%; however, our absolute values will be low, owing to self-absorption.[17]

3. **PEC Studies.** The PL observed from CdSe in air can also be seen when the semiconductor is used as the photoanode in a PEC employing aqueous alkaline diselenide electrolyte. We used a one-compartment cell with a Pt foil counterelectrode and SCE reference electrode to examine the potential dependence of luminescence. The PEC was assembled in the sample compartment of an emission spectrometer to permit quantitative characterization of luminescence. Since we found that only the emission intensity and not its spectral distribution was significantly affected by the potentials utilized (2.0-nm resolution), we monitored emission by simply sitting at λ_{max}, ~720 nm.

The interrelationship of photocurrent, luminescence, and voltage (*iLV* curves) is presented in Figure 3. The data were obtained in 5 M OH^-/0.11 M Se^{2-}/0.004 M Se_2^{2-} diselenide electrolyte with 514.5-nm excitation. As was observed for CdS:Te electrodes with ultraband gap excitation, increasingly negative bias diminishes photocurrent and augments emission intensity.[1,5] For these excitation wavelengths the electron-hole (e^-–h^+) pairs created by light are formed almost entirely within the depletion region where maximum band bending occurs; increasingly negative bias reduces band bending for an n-type semiconductor.[18] Luminescence, a measure of e^-–h^+ pair recombination, competes with photocurrent which derives from e^-–h^+ pair separation; emission is thus progressively favored as band bending decreases. Figure 3 indicates that the emission intensity increases by a factor of ~35 in passing from −0.30 V vs. SCE to open circuit. A relationship observed in CdS:Te emissive studies relating photocurrent quantum efficiency, ϕ_x, to open-circuit and in-circuit radiative quantum efficiencies (ϕ_{r_0} and ϕ_{r_i}, respectively) is given in eq 1.[19] The ratio

$$\phi_{r_0}/\phi_{r_i} = 1/(1 - \phi_x) \qquad (1)$$

of 35, corresponding to a ϕ_x value at −0.30 V vs. SCE of 0.97, is in good agreement with a direct measurement of 0.95; the measured value is uncorrected for reflection and electrolyte absorption. In general, we obtained very good agreement between *iLV* curves and eq 1 for CdSe-based PECs employing diselenide electrolyte with CdSe samples etched in Br_2/MeOH. The maximum monochromatic optical-to-electrical energy conversion efficiency represented by Figure 3 is ~6%. At the maximum efficiency point the output voltage and photocurrent density are 0.24 V and 0.12 mA/cm^2, respectively.

We also found that *iLV* curves generated in polysulfide electrolyte were in accord with eq 1. Since an exchange reaction, simplified in eq 2, has been reported in this medium, we sought

$$CdSe(s) + S^{2-}(aq) \rightarrow CdS(s) + Se^{2-}(aq) \qquad (2)$$

evidence for it from emissive features.[20] Prolonged photolysis at *514.5 nm* (average photocurrent of *~10* mA/cm^2 for a total of 33 C/cm^2) produced no significant changes in the emission spectral distribution (457.9-nm excitation) between 500 and 800 nm. If appreciable exchange had occurred, the absence of emission from a CdS- or CdS_XSe_{1-X}-like surface may be due to a nonemissive morphology or to extensive quenching by, e.g., traps, electrolyte species, or CdSe. The emissive probe under these conditions may also not be sufficiently surface sensitive to detect an altered surface.

B. Electroluminescence. 1. Current–Voltage Properties. Studies of EL from n-CdSe were conducted in N_2-purged, alkaline, peroxydisulfate electrolyte (5 M OH^-/0.1 M $S_2O_8^{2-}$); the one-compartment cell also contained a Pt foil counterelectrode and SCE reference electrode. The mechanism proposed for EL in this medium is shown in Scheme I.[21] Essentially, an electron in or

Scheme I

$$S_2O_8^{2-} + e^-_{CB} \rightarrow SO_4^{2-} + SO_4^{-}\cdot \qquad (3)$$

$$SO_4^{-}\cdot \rightarrow SO_4^{2-} + h^+_{VB} \qquad (4)$$

$$e^- + h^+ \rightarrow \text{light} \qquad (5)$$

near the conduction band (e^-_{CB}) reduces $S_2O_8^{2-}$ to produce a sulfate radical which is sufficiently oxidizing to inject a hole into the valence band (h^+_{VB}). The radiative recombination of the injected hole with an electron leads to the observed luminescence. If the recombining electron and hole are near the band edges, then edge emission is expected. On the other hand, if either or both of these species are located in intraband gap states, subband gap emission is anticipated. Such emission has been reported as evidence for surface states.[21a,b] Systems with deliberately introduced intraband gap dopant states such as CdS:Te also exhibit subband gap emission.[6]

The redox potentials of eq 3 and 4 have been estimated to be ≤+0.6 and ≥+3.4 V vs. NHE, respectively.[21c] The reaction sequence of eq 3–5 should be initiated at potentials cathodic of the flat-band potential, E_{FB}, where CdSe is expected to function as a dark cathode. In aqueous, alkaline media E_{FB} has been

---

(18) Gerischer, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *58*, 263.

(19) (a) Karas, B. R.; Morano, D. J.; Bilich, D. K.; Ellis, A. B. *J. Electrochem. Soc.* **1980**, *127*, 1144. (b) Ellis, A. B.; Karas, B. R. *ACS Symp. Ser.* **1981**, *No. 146*, 295. (c) Ellis, A. B.; Karas, B. R.; Streckert, H. H. *Faraday Discuss. Chem. Soc.* **1980**, *No. 70*, 165.

(20) (a) Heller, A.; Schwartz, G. P.; Vadimsky, R. G.; Menezes, S.; Miller, B. *J. Electrochem. Soc.* **1978**, *125*, 1156. (b) Cahen, D.; Hodes, G.; Manassen, J. *Ibid.* **1978**, *125*, 1623. (c) Gerischer, H.; Gobrecht, J. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 520. (d) Noufi, R. N.; Kohl, P. A.; Rodgers, J. W., Jr.; White, J. M.; Bard, A. J. *J. Electrochem. Soc.* **1979**, *126*, 949. (e) DeSilva, K. T. L.; Haneman, D. *Ibid.* **1980**, *127*, 1554. (f) Cahen, D.; Vainas, B.; Vandenberg, J. M. *Ibid.* **1981**, *128*, 1484.

(21) (a) Pettinger, B.; Schöppel, H.-R.; Gerischer, H. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 849. (b) Beckmann, K. H.; Memming, R. *J. Electrochem. Soc.* **1969**, *116*, 368. (c) Memming, R. *Ibid.* **1969**, *116*, 785.

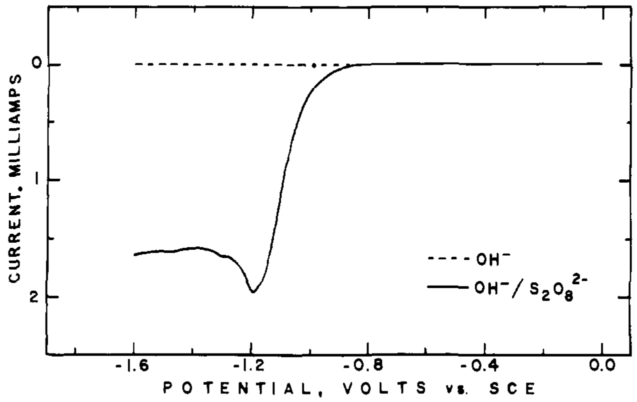

Figure 4. Current–voltage curves for a CdSe electrode. The dashed line represents data obtained in 5 M NaOH electrolyte; the solid line was obtained after this electrolyte was made 0.1 M in $K_2S_2O_8$. Both curves were swept at 20 mV/s. The CdSe electrode surface area was ~0.30 cm^2.

estimated to lie at ~−0.7 V vs. SCE.[22] Consistent with this observation, Figure 4 demonstrates that addition of $S_2O_8^{2-}$ to a solution of OH^- dramatically increases the cathodic current at a CdSe electrode for potentials cathodic of ~−0.8 V vs. SCE.

Although the current for potentials $\gtrsim$−1.6 V is predominantly due to reduction of $S_2O_8^{2-}$, another electrochemical process which could contribute to the observed current is reduction of the electrode to yield surface Cd, eq 6. An analogous reaction has

$$CdSe(s) + 2e^- \rightarrow Cd(s) + Se^{2-}(aq) \qquad (6)$$

been reported for CdS in neutral media and can be photoassisted;[23a] evidence for the reaction was the appearance, after reduction, of a sharp anodic stripping peak accompanied by changes in electrode reflectivity[23a] and photoacoustic signal.[23b] In OH^- or $OH^-/S_2O_8^{2-}$ electrolytes, we generally did not observe an anodic stripping peak in i–V curves (0.0 to −1.5 V) of CdSe obtained in the dark. That a surface layer might be present, however, was suggested by decays in current which were observed when the CdSe electrode was brought into circuit in OH^- or $OH^-/S_2O_8^{2-}$ electrolyte at potentials cathodic of ~−1.2 V. If electrode reduction were occurring, earlier studies on CdS suggested that anodic cycling might reverse such surface changes.[6,21a,23] Evidence that reproducible i–V properties could be obtained in $OH^-/S_2O_8^{2-}$ electrolyte with anodic cycling was indicated by pulse experiments: repetitively pulsing the electrode between 0.0 V (11 s) and potentials cathodic of ~−0.9 V (1 s) gave reproducible coulombs during the cathodic cycle over hundreds of pulses. Additionally, as with CdS,[6] little weight loss was found in long-term pulse experiments with CdSe.[24] Although these results could be ascribed to reversal of electrode reduction during the anodic cycles, any such conclusions await a detailed characterization of the electrochemistry of CdSe in $OH^-/S_2O_8^{2-}$ electrolyte. We call attention to the possible presence of a surface layer primarily because it could influence any or all of the EL characteristics to be described.

2. Spectral Distribution. An EL spectrum could be obtained by assembling the cell in the emission spectrometer. We found that EL signals generally mimicked the cathodic current in decaying from their initial values to much lower steady-state values. Reproducible transient maximum EL intensities (recorder response time of ~0.3 s) could be obtained by repetitively pulsing the electrode between 0.0 V (11 s) and a potential cathodic of ~−1.0 V vs. SCE (1 s), the potential at which EL first becomes visible to the dark-adapted eye. Slowly scanning the emission monochromator then produced a series of lines constituting the EL spectrum, Figure 5. For certain sample geometries in the emission spectrometer, the use of potentials cathodic of −1.3 V gave sufficiently intense steady-state EL signals so as to render the pulse technique unnecessary. In these cases no difference in the spectral distribution obtained by the two techniques was observed.

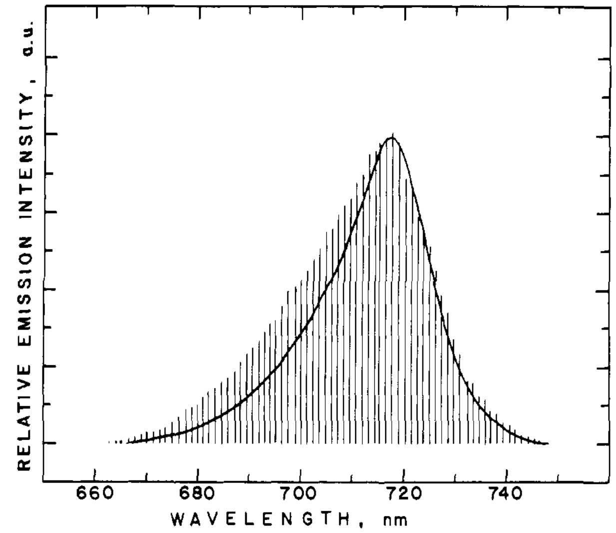

Figure 5. Uncorrected PL (solid curve) and EL (vertical lines) spectra of CdSe obtained in the same sample geometry. The PL spectrum was taken with the CdSe electrode immersed in 5 M NaOH electrolyte at −1.50 V vs. SCE. An Ar ion laser whose beam was expanded and masked to fill the ~0.30-cm^2 electrode surface was used for excitation; 0.4 mW of 514.5-nm light was delivered to the electrode. The EL spectrum was taken in 5 M NaOH/0.1 M $K_2S_2O_8$ electrolyte. The electrode was continuously pulsed between 0.0 V (11 s) and −1.50 V vs. SCE (1 s) while the emission spectrum was scanned at 6 nm/min. For both EL and PL a spectral resolution of 0.3 nm was employed. The EL spectrum has been scaled down to match the PL intensity at $\lambda_{max} \approx 720$ nm.

Figure 5 shows that the EL spectrum, like the PL spectrum, is characterized by a single sharp band with λ_{max} at ~720 nm. No other bands were observed out to 1000 nm at the sensitivity employed to obtain Figure 5. We made a direct comparison of EL and PL spectra by using the same sample in an identical geometry for both spectra. First, the CdSe sample was irradiated in air with 514.5-nm excitation to generate a PL spectrum. Subsequently, the EL spectrum was obtained in 5 M OH^-/0.1 M $S_2O_8^{2-}$ solution by pulsing between 0.0 and −1.50 V. Finally, the PL spectrum was obtained in 5 M OH^- electrolyte at −1.50 V vs. SCE and gave essentially the same spectral distribution (perhaps very slightly broadened) as the initial PL spectrum taken in air. Figure 5 reveals that the PL spectrum is narrower: fwhm values for the PL and EL spectra are 21 and 27 nm, respectively, using a spectral bandwidth of 0.3 nm. We observed EL and PL spectral discrepancies of this nature with several CdSe samples at potentials from −1.2 to −1.5 V vs. SCE, on two spectrometers, and with the sulfoselenide samples described above.

That the spectral mismatch of Figure 5 is almost entirely in the high-energy tail can again be interpreted in terms of self-absorption effects. Our results provide evidence that, on average, EL is produced nearer to the CdSe-electrolyte interface than PL. Estimating the magnitude of this difference is difficult. We can say that the EL spectrum of Figure 5 is significantly broader than any PL spectrum we have measured. However, a rigorous analysis for the case at hand would require knowing, e.g., the role of a surface layer (vide supra) and the diffusion length and spatial distribution of injected holes.

3. Efficiency. The EL efficiency was determined in both pulse and steady-state experiments at several different electrode potentials using measures adapted from studies of electrogenerated chemiluminescence (ecl).[25] The steady-state, instantaneous EL efficiency, ϕ_{EL}, is given by eq 7 and determined by simply sitting

---

[22] Ellis, A. B.; Kaiser, S. W.; Bolts, J. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 2839.

[23] (a) Kolb, D. M.; Gerischer, H. *Electrochim. Acta* **1973**, *18*, 987. (b) Masuda, H.; Fujishima, A.; Honda, K. *Chem. Lett.* **1980**, 1153.

[24] A 0.1683-g crystal of CdSe (~0.6-cm^2 surface area) showed undetectable weight loss after 14 h of continuous pulsing (1 s at 0.00 V and 1 s at −1.50 V vs. SCE) in ~20 mL of $OH^-/S_2O_8^{2-}$ electrolyte. Approximately 120 C of charge were passed during the experiment.

$$\phi_{EL} = \frac{\text{emitted light (einsteins/s)} \times F}{\text{current due to hole injection}} \tag{7}$$

$$\bar{\phi}_{EL} = \frac{\text{total emitted light (einsteins)} \times F}{\text{total coulombs due to hole injection}} \tag{8}$$

at a given potential; integrated EL efficiency, $\bar{\phi}_{EL}$, is given by eq 8 and determined in the pulse experiments described earlier. In both expressions F is Faraday's constant. The numerators of these equations were obtained by placing a radiometer next to the sole exposed face of the emitting electrode. Either the power in μW was read for the constant-potential experiment of eq 7 or the integrated energy over a single-pulse experiment was determined in μJ for eq 8. The values obtained were converted to einsteins/s or einsteins, respectively, at 720 nm; the narrowness of the spectral distribution makes this a reasonable approximation. Because not all of the emitted photons are collected, we are underestimating the numerators of eq 7 and 8. The denominators for these equations are obtained by using the *total* current or coulombs accompanying the radiometric measurement rather than just that fraction due to hole injection; current and coulombs are not corrected for background values obtained in the absence of $S_2O_8^{2-}$, although these are <5% at all the potentials employed. Our procedure overestimates the denominator by a factor of 2, if eq 3-5 are accurate representations of the EL mechanism, but is, we feel, a more justified procedure in the absence of detailed mechanistic knowledge. A consequence of our data treatment is that the EL efficiencies are lower limits.

Table I is a compilation of ϕ_{EL} and $\bar{\phi}_{EL}$ values at different potentials. We find that the two efficiency measurements are usually very similar and reasonably reproducible at repeated potentials. Since we found $\bar{\phi}_{EL}$ to be easier to measure at the more positive potentials employed, we conducted most of the efficiency measurements using the pulse technique. In terms of magnitude, $\bar{\phi}_{EL}$ is $\sim 10^{-5}$ at the threshold potential of ~−0.9 V and increases with cathodic potential up to ~−1.5 V vs. SCE where it approaches 10^{-3}.

The energetically similar spectral bands observed in PL and EL experiments suggest the involvement of a common emissive excited state and prompt a direct comparison of efficiencies. By analogy with ecl studies, ϕ_{EL} or $\bar{\phi}_{EL}$ can be factored into an efficiency for excited-state population, ϕ_{ES} (excited states populated per holes injected), and the radiative efficiency, ϕ_r, which can be defined in this context as photons emitted per excited states populated. Although the ϕ_r values obtained by the reflectance technique are similar to our best $\bar{\phi}_{EL}$ values, we sought to compare the two under as similar conditions as possible. To do this, we measured $\bar{\phi}_{EL}$ at −1.50 V vs. SCE with the radiometer placed a few centimeters away from the electrode surface and covered with filters ($\lambda \lesssim 570$ nm absorbed). This procedure prepares the radiometer for rejection of the excitation wavelength in the following PL experiment: without disturbing the geometry, the electrolyte was changed to 5 M OH^- and the PL efficiency, ϕ_r, was determined at −1.50 V and several other potentials, exciting at 514.5 nm. This solution was then made 0.1 M in $S_2O_8^{2-}$ and $\bar{\phi}_{EL}$ was determined at several potentials. A final $\bar{\phi}_{EL}$ measurement was made by removing the filters and repositioning the radiometer as near to the electrode as possible. This procedure provides a factor by which the measured ϕ_r and $\bar{\phi}_{EL}$ values are scaled up to correct for the artificially low emission intensities recorded under the initial conditions. In calculating ϕ_r, we have assumed that the same scaling factor used in determining $\bar{\phi}_{EL}$ can also be applied to the ϕ_r determination; our observation that $\bar{\phi}_{EL}$ and ϕ_r scale by similar factors for different positions of the filter-covered radiometer suggests this to be the case. With this assumption, ϕ_r, like $\bar{\phi}_{EL}$, is a lower limit, since not all of the emitted light is collected and the incident power is uncorrected for reflective losses.

Table I. Estimates of Electroluminescence Efficiency[a]

A. Pulse Experiments[b]

potential, V vs. SCE	total emitted light, μJ (10^{12} einsteins)[c]	$10^3 \times$ total couloumbs (10^8 mol e^-)[d]	$10^4\bar{\phi}_{EL}$[e]
−0.95	0.010 (0.060)	0.084 (0.087)	0.69
−1.10	1.2 (7.2)	2.2 (2.3)	3.1
−1.30	7.7 (46)	6.6 (6.8)	6.8
−1.50	8.2 (49)	6.8 (7.0)	7.0
−1.10	1.3 (7.8)	2.3 (2.4)	3.3
−1.30	7.4 (45)	6.5 (6.7)	6.7
−1.50	8.3 (50)	6.8 (7.0)	7.1
−1.10	1.2 (7.2)	2.3 (2.4)	3.0
−1.00	0.12 (0.72)	0.67 (0.69)	1.0
−0.95	0.012 (0.072)	0.10 (0.10)	0.72
−0.90	0.00080 (0.0048)	0.041 (0.042)	0.11

B. Steady-State Experiments[f]

potential, V vs. SCE	emitted light, μW (10^{12} einsteins/s)[g]	total i, mA (10^8 mol e^-/s)[h]	$10^4\phi_{EL}$[i]
−1.10	0.65 (3.9)	1.02 (1.06)	3.7
−1.30	1.0 (6.0)	1.14 (1.18)	5.1
−1.50	1.4 (8.4)	1.16 (1.20)	7.0
−1.10	0.47 (2.8)	0.85 (0.88)	3.2
−1.30	1.1 (6.6)	1.22 (1.26)	5.2
−1.50	1.5 (9.0)	1.25 (1.30)	6.9

[a] An n-type CdSe single crystal was used as the working electrode in a one-compartment EL experiment conducted in a N_2-purged 5 M NaOH/0.1 M $K_2S_2O_8$ electrolyte; the Pt foil counterelectrode was 1 × 3 cm. The geometry of the CdSe electrode relative to the radiometer used for detection of emission was invariant throughout all of the experiments given in the table. Table entries for emitted light, coulombs, and current are given for the 0.30-cm^2 surface area of the CdSe electrode. [b] These experiments were conducted by pulsing the CdSe electrode between 0.0 V (11 s) and the indicated potential (1 s). Table entries for each potential are representative values. At least five pulse sequences were used at each potential, yielding $\bar{\phi}_{EL}$ values within 10% of one another. Experiments were carried out in the sequence given in the table. [c] Total emitted light collected per pulse with a radiometer operated in its integrating mode. The radiometer was placed ~1 cm away from the emitting electrode. If all of the indicated energy were converted to 720-nm photons, the quantity of einsteins given in parentheses would be obtained. [d] Total coulombs collected per pulse with a digital coulometer. The value in parentheses is the corresponding quantity of electrons in the external circuit, obtained by dividing the coulombs by Faraday's constant. [e] Integrated EL efficiency. This value is derived by dividing the einsteins by the moles of electrons from the preceding columns. These efficiencies are lower limits, as described in the text. [f] These experiments were conducted by potentiostating the CdSe electrode at the indicated potentials. Experiments were carried out in the sequence given in the table. [g] Emitted light collected with the radiometer in the geometry of footnote *c*. Conversion of the measured power as described in footnote *c* yields the quantity of einsteins/s given in parentheses. [h] Total current measured at the indicated potential. The value in parentheses is the corresponding quantity of electrons/s in the external circuit, obtained by dividing the current by Faraday's constant. [i] Steady-state, instantaneous EL efficiency. This value is derived by dividing the einsteins/s by the moles of electrons/s from the preceding columns. These efficiencies are lower limits, as described in the text.

Table II summarizes the results of these parallel EL and PL efficiency measurements. We find that ϕ_r increases with cathodic potential from $\sim 4 \times 10^{-4}$ at −0.83 V (open circuit) to $\sim 1 \times 10^{-3}$ at −1.50 V vs. SCE. Between −1.00 and −1.50 V, $\bar{\phi}_{EL}$ increases from $\sim 1 \times 10^{-4}$ to 6×10^{-4}. Although the aforementioned uncertainties in $\bar{\phi}_{EL}$ and ϕ_r preclude a more precise comparison, our data suggest that the two efficiencies are very comparable at −1.50 V vs. SCE. If $\bar{\phi}_{EL}$ were limited to ϕ_r by ϕ_{ES} as defined above, our measurements would indicate that ϕ_{ES} is substantial and perhaps as large as unity at −1.50 V vs. SCE.

---

(25) (a) Bard, A. J.; Keszthelyi, C. P.; Tachikawa, H.; Tokel, N. E. In "Chemiluminescence and Bioluminescence"; Cormier, M. J., Hercules, D. M., Lee, J., Eds.; Plenum Press: New York, 1973; pp 193-208. (b) Faulkner, L. R.; Bard, A. J. *Electroanal. Chem.* **1977**, *10*, 1-95. (c) Keszthelyi, C. P.; Tokel-Takvoryan, N. E.; Bard, A. J. *Anal. Chem.* **1975**, *47*, 249.

Table II. Comparisons of Photoluminescence and Electroluminescence Efficiencies[a]

potential, V vs. SCE	$10^4 \overline{\phi}_{EL}$[b]	$10^4 \phi_r$[c]
−1.50	5.1	
−0.83		3.5
−0.95		7.4
−1.00		9.2
−1.50		13
−0.83		3.8
−0.95		6.8
−1.00		9.6
−1.50		13
−1.50	5.7	
−1.00	0.89	

[a] A CdSe electrode (that used to obtain the Table I data) was used in an identical geometry throughout these experiments. EL experiments for determining $\overline{\phi}_{EL}$ were conducted in 5 M NaOH/0.1 M $K_2S_2O_8$ electrolyte; PL experiments for determining ϕ_r were carried out in 5 M NaOH electrolyte. Experiments were run at the indicated potential in the order given in the table. [b] Integrated EL efficiency determined on the basis of the procedure described in footnotes *b–e* of Table I. All measurements of $\overline{\phi}_{EL}$ and ϕ_r were made with the radiometer placed some distance away from the electrode and covered with filters, as described in the Experimental Section. A final $\overline{\phi}_{EL}$ measurement was made by removing the filters and repositioning the radiometer as near to the electrode as possible. This procedure provides a factor (30) by which the table entries have been scaled up to correct for the artificially low emission intensities recorded under the initial conditions. Values of $\overline{\phi}_{EL}$ are lower limits, as discussed in the text. [c] PL efficiency for "head-on" irradiation of CdSe with 514.5-nm excitation. The emitted intensity was measured and scaled up as described in footnote *b*. The incident beam was 10× expanded and masked to fill the electrode surface; its power was ~5 mW. With the assumption that the scaling factor is the same for PL and EL (same spatial distribution of light in front of the electrode), the values of ϕ_r are lower limits, since not all of the emitted light is collected and the incident power is uncorrected for reflective losses.

A proviso to this analysis concerns the spatial discrepancy in EL and PL. Strictly speaking, the two emissive efficiencies can only be compared when they originate from the same region of space; the mismatch in spectral distribution indicates that they emanate from different regions of the electrode. Although we have shown that the lower-limit estimates of EL and PL efficiency can be similar and that they exhibit the same trend with potential, there are potentials (−1.00 V in Table II, e.g.) where the discrepancy in efficiencies is more substantial than at −1.50 V. Such a disparity, if significant, could reflect differences not only in ϕ_{ES} but also in the ϕ_r values appropriate to the two experiments. That is, the dissimilar spatial regions inferred for the PL and EL experiments could have different ϕ_r values associated with them because of local variations in environment, and these values could be potential dependent. Among the factors which might affect any of the efficiencies (ϕ_r, ϕ_{EL}, or ϕ_{ES}) through a potential dependence are nonradiative recombination through surface states, the spatial distribution of injected holes, the presence of an accumulation region which would affect the concentration of near-surface electrons available for radiative recombination, and electrochemistry (presence of a surface layer from electrode reduction, e.g.). In summary, until the spatial origins of PL and EL can be determined more accurately, conclusions regarding ϕ_{ES} based on direct comparisons of EL and PL efficiencies must be made with caution.

C. Effects of Surface Treatment on PL Properties. Although our data indicate that PL is not produced, on average, as near the semiconductor surface as EL, we found evidence that the spatial distribution of PL could be influenced by surface treatments. The studies described thus far were conducted with samples etched with Br_2/MeOH. If the PL spectrum of such a sample were taken in air or with the sample immersed in water, little difference was observed. Addition of OH^- to the water, however, often resulted in up to threefold enhancements of emission intensity for CdSe from the same incident intensity. A slight broadening of the high-energy portion of the emission band occasionally accompanies the increase in emission intensity and suggests a greater contribution to the luminescence from regions nearer the surface.

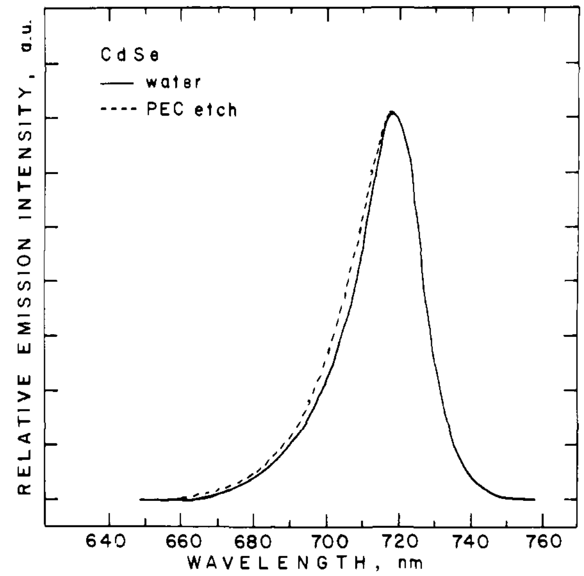

Figure 6. Uncorrected PL spectra of CdSe obtained in a common sample geometry in water (solid curve) and after a photoelectrochemical (PEC) etching treatment (dashed curve). The sample had its entire ~0.30-cm² surface area excited with ~2 mW of 514.5-nm light. Etching was carried out by bringing the electrode into circuit at 0.00 V vs. SCE in 3 M NaOH solution and passing ~7 mC of charge. The PL spectrum (dashed curve) was obtained after the electrode had been taken out of circuit and a stable PL signal observed. Its actual intensity is about 10 times that of the solid curve but has been scaled down to match the latter at $\lambda_{max} \approx 720$ nm. For both PL spectra a resolution of 1.0 nm was employed.

More dramatic changes were often found by using a literature treatment described as PEC etching.[26,27] With this technique the photoanodic decomposition of CdSe was permitted to occur; chemical removal of the damaged layer was reported to yield better current–voltage properties. Our studies differ in the use of a strongly alkaline medium for PEC etching of the sample. We display in Figure 6 the effects of a PEC etch on PL properties. The solid curve is the PL spectrum of CdSe in water. With the sample in the same geometry, NaOH was added (3 M final concentration) and the emission intensity at ~720 nm was found to almost triple.[28] The electrode was then brought into circuit at 0.0 V vs. SCE and irradiated without disturbing the geometry. After ~7 mC of charge had been passed, the electrode was taken out of circuit. The emission intensity increased over a period of a few seconds, presumably due to removal of surface species by the stirring action. The dashed curve of Figure 6 shows the PL spectrum after the PEC etch. Besides yielding a 10-fold intensity enhancement relative to the spectrum obtained in water, the PEC etch resulted in a broader spectrum (fwhm of 24 vs. 21 nm) with the difference again manifested in the high-energy tail. The magnitude of the intensity enhancement was dependent on the duration of the etch treatment. We have seen up to 50-fold increases in emission intensity; prolonged etching reduced the effect. In general, the enhancement was sufficiently large to be easily visible to the eye.

Because we do not have a good measure of photons absorbed

---

(26) (a) Tenne, R.; Hodes, G. *Appl. Phys. Lett.* **1980**, *37*, 428. (b) Tenne, R. *Ber. Bunsenges Phys. Chem.* **1981**, *85*, 413.

(27) Liu, C. J.; Olsen, J.; Saunders, D. R.; Wang, J. H. *J. Electrochem. Soc.* **1981**, *128*, 1224.

(28) Titrating with acid back to pH 7 reverses the effect; subsequent addition of OH^- usually does not give as large an emission enhancement as originally observed, suggesting that a permanent surface change may have occurred.

in the PEC-etch experiment, it is difficult to measure the change in ϕ_r caused by this treatment. However, the increase in emitted intensity is of such a magnitude as to suggest that ϕ_r has increased substantially. The concomitant spectral mismatch of Figure 6 indicates a PL spatial distribution which is also nearer, on average, to the semiconductor–electrolyte interface after the etch treatment.

The observation that surface treatments can enhance (near-) surface contributions to PL spectra is intriguing and could have important implications for using PL to study interfacial interactions. At present we are uncertain as to the origin of the observed effects. One contributing factor may be that etching produces a more emissive surface morphology; the morphology has been reported to change as a result of PEC etching in acidic media.[26] Another possibility is based on efficient quenching of emission from the surface and near-surface regions of CdSe by electrolyte species or surface states. The PEC etch may result in a surface layer which insulates the near-surface region from this quenching to some extent and thus enhances its contribution to the PL spectrum. In principle, these effects might be investigated by controlling the spatial distribution of emissive sites. Such studies are presently in progress in our laboratory.

Experimental Section

Materials. Single-crystal, vapor-grown *c* plates (10 × 10 × 1 mm) of n-type CdSe, $CdS_{0.74}Se_{0.26}$, and $CdS_{0.49}Se_{0.51}$ were obtained from Cleveland Crystals, Inc., Cleveland, OH. These materials had resistivities of $\sim$2 Ω cm (4-point probe method) and were cut into rectangularly shaped pieces $\sim$0.3 cm^2 × 1 mm; the samples were etched in Br_2/MeOH and mounted as electrodes as described previously.[5a] Chemicals which were used as received were NaOH and $Na_2S\cdot 9H_2O$ (Mallinckrodt), sublimed sulfur, $K_2S_2O_8$, KOH, and MgO (all from Baker), Se (99%; source unknown), $MnBr_2\cdot 4H_2O$ (Aldrich), and Et_4NBr (Eastman). The preparation of diselenide, polysulfide, and peroxydisulfate electrolytes has been described.[5a,6]

Optical Measurements. Uncorrected emission spectra were obtained with two spectrometers. The first is an Aminco-Bowman model which has been described previously;[5a] spectra of $\gtrsim$1.0-nm bandwidth could be obtained out to 800 nm with the Hamamatsu R446S PMT employed for red response. A second spectrometer was constructed around a McPherson Model 270, 0.35-m monochromator equipped with gratings blazed at either 500 or 1000 nm. The monochromator was interfaced to either the R446S PMT or to an EMI Model 9684B PMT (S-1 response) cooled with dry ice/methanol. Signals from either PMT were amplified by a Keithley Model 414S picoammeter and displayed on a Houston Model 2000 x–y recorder. Samples used in PL experiments were generally oriented at $\sim$45° to both the excitation beam and the emission detection optics. Irradiation sources included a Coherent Radiation CR-12 Ar ion laser and a Model 80 He–Ne laser; plasma lines from the Ar ion laser were eliminated by passing the 2–3-mm diameter beam through either an Oriel Model 7240 grating monochromator or through Oriel interference filters (488.0 and 514.5 nm; fwhm of 10 nm). The beams from both lasers were often passed through a 10X beam expander and masked to fill the electrode surface. Excitation from the Ar ion laser was plane polarized; the 632.8-nm output from the He–Ne laser was unpolarized, but in some experiments was made to match the polarization of the Ar ion laser by using a Melles Griot laser-polarizing beam splitter. Laser intensity was adjusted by changing the power or by neutral density filters. The intensity was measured with a Scientech 362 power energy meter (flat response, 250–35 000 nm) or a Tektronix J16 radiometer equipped with a J6502 probe head (flat response, 450–950 nm). An E G & G Model 550-1 radiometer (flat response, 460–975 nm) equipped with a Model 550-3 pulse integration module was used for integrated energy measurements of the light produced in pulse EL experiments. A quartz disk was used as a beam splitter during experiments requiring continuous monitoring of laser intensity. Laser excitation was filtered in emission spectral measurements by placing a Corning 3-66 filter, ferricyanide (0.03 M $K_3Fe(CN)_6$/0.6 M HCl; 1.0-cm path length cell) or polychalcogenide (1 M OH^-/1 M S^{2-}/1 M S/0.2 M Se; 1.0-cm path length cell) filter solutions in front of the PMT.

PL Spectra and Decay Times. PL spectra were obtained as a function of excitation wavelength with both emission spectrometers. Unexpanded 457.9- and 632.8-nm excitation beams from the Ar ion and He–Ne lasers, respectively, were focused on the same region of a CdSe sample and the emission spectra recorded at 0.3- and 1.0-nm resolution on the McPherson and Aminco-Bowman spectrometers, respectively; the experiments were repeated with the sulfoselenide samples, exciting with the beam-expanded 457.9- and 514.5-nm lines of the Ar ion laser. For CdSe, the spectral mismatch described in the text was observed for several sample geometries including "head-on" excitation along the *c* axis (vide infra, "PL Efficiency"). In several geometries both unpolarized and plane-polarized (same plane as the 457.9-nm excitation) He–Ne laser excitation was employed and was found not to appreciably affect the spectral mismatch. PL spectra (600–800 nm) of CdSe at 77 K were recorded at 3.0-nm resolution on the Aminco-Bowman spectrometer with 514.5-nm excitation as has been described previously;[1] the experiment was repeated on the McPherson spectrometer from 600 to 1100 nm. Decay times for CdSe were obtained in air with both 337- and 455-nm excitation using instrumentation and techniques previously reported.[1] Peak intensities of $\sim$30 and 100 kW/cm^2 were used at 337 and 455 nm, respectively.

PL Efficiency. Estimates of ϕ_r based on either the temperature dependence of PL spectra or on a reflectance technique[17] required corrected emission spectra. We determined crude correction factors for the Aminco-Bowman spectrometer equipped with the R446S PMT as follows: We first measured the output of the high-pressure Xe lamp which is part of the spectrometer with the Model 550-1 radiometer; the output was measured from 400 to 800 nm (2.0-nm bandwidth) by using the spectrometer's excitation monochromator and expressed in relative einsteins. Subsequently, the monochromatized output of the Xe lamp was reflected off a mirror into the emission detection optics and the detected intensity recorded at 10-nm intervals. The correction factors thus acquired were applied to areas under the edge emission bands at 77 and 295 K to yield an upper limit to ϕ_r at 295 K. A second estimate of ϕ_r was made by placing the CdSe sample in a quartz cuvette positioned in the Aminco-Bowman spectrometer's sample compartment as previously described.[17] The central portion of the sample was irradiated "head-on" with masked, expanded laser beams. Some of the emitted and reflected incident light was deflected into the detection optics by a mirror. The emission spectrum was then recorded with a calibrated neutral density filter present while the excitation region was scanned; the filter was removed while the emission band was scanned. At this point the sample was replaced by a highly reflective MgO pellet (pressed at 12 000 lbs) and the excitation line recorded by using a more absorbing neutral density filter. The difference in areas of the reflected light between MgO and CdSe represents photons absorbed by the semiconductor and is divided into the area under the emission band, representing photons emitted. Both the absorbed and emitted intensities are corrected for relative detector response. The salt $[Et_4N]_2[MnBr_4]$, prepared as described in the literature,[29] served as a standard and gave a ϕ_r value similar to that previously reported.[17]

PEC Experiments. Cells suitable for conducting PEC studies in polysulfide and diselenide electrolytes have been described.[5a] Potentiostatic *iLV* curves were obtained by using a PAR Model 173 potentiostat/galvanostat, a Model 175 programmer, and a Model 179 digital coulometer/I to E converter; the techniques used to generate these curves and to measure photocurrent quantum efficiency have been reported.[5a] The Aminco-Bowman spectrometer (2.0-nm resolution) was used exclusively for obtaining *iLV* data with the emission intensity monitored at $\lambda_{max} \approx$ 720 nm.[5a] Evidence for an exchange reaction involving CdSe and polysulfide electrolyte was probed by obtaining *iLV* curves and complete emission spectra (457.9-nm excitation) before and after prolonged irradiation with 514.5-nm excitation at −0.30 V vs. SCE. Although these data were obtained with the Aminco-Bowman spectrometer, the long-term photolysis was conducted outside of the spectrometer to more easily obtain higher light intensities. As a consequence, the emission data obtained before and after the irradiation period were not taken in identical geometries.

EL Current–Voltage Properties. Current–voltage curves relevant to EL studies were taken in both 5 M NaOH and 5 M NaOH/0.1 M $K_2S_2O_8$. The curves were swept in a cathodic direction at 20 mV/s, beginning at 0.0 V vs. SCE; scans were reversed at various potentials. Electrolytes were stirred by a N_2 purge.

EL Spectra. Pulse and steady-state EL spectra were obtained in both the Aminco-Bowman and McPherson-based spectrometers; experiments in the Aminco-Bowman instrument have been described previously.[6] Steady-state EL spectra generally required potentials cathodic of ~ -1.3 V vs. SCE in 5 M OH^-/0.1 M $S_2O_8{}^{2-}$ electrolyte with the electrode placed very near the emission detection optics. Pulsing the electrode between 0.0 V (11 s) and potentials cathodic of ~ -1.0 V (1 s) gave sufficiently intense and reproducible transient signals (recorder response time of 0.3 s) to permit the EL spectrum to be obtained as a series of vertical lines as the emission monochromator was swept. Direct comparisons of EL and PL spectra were made on both spectrometers with the CdSe and sulfoselenide samples; the bandwidths of the Aminco-

---

(29) Gill, N. S.; Taylor, F. B. *Inorg. Synth.* **1967**, *9*, 136.

Bowman and McPherson-based spectrometers were 1.0 and 0.3 nm, respectively. First, the PL spectrum was obtained in air by using beam-expanded laser lines. Without disturbing the sample geometry, 5 M OH^-/0.1 M $S_2O_8^{2-}$ electrolyte was added and the EL spectrum was obtained at the potential of interest by the pulse sequence given above. The electrolyte was then changed to 5 M OH^- and the PL spectrum taken at the same potential used in the EL experiment, again without altering the sample geometry.

EL Efficiency. The integrated EL efficiency, $\bar{\phi}_{EL}$, was estimated by placing the probe head of the EG & G radiometer as close as possible (within ~1 cm) to the sole exposed CdSe crystal face. The electrode was pulsed to a given potential for 1 s as described above and the total emitted energy (in μJ) per pulse measured with the EG & G Model 550-3 accessory. Total coulombs passed during this pulse were measured with the digital coulometer. These measurements were repeated as a function of potential. The instantaneous, steady-state EL efficiency, ϕ_{EL}, was determined in the same geometry and has been described previously, differing only in the use of the EG & G radiometer.[6] A measurement of ϕ_r and $\bar{\phi}_{EL}$ in the same geometry was made by first placing the EG & G radiometer about 3 cm from the electrode and angled so that it would not obstruct a laser beam incident "head on" on the electrode. The radiometer probe head was then covered with a Laser-Gard Ar ion laser goggle window (optical density of 11 at 514.5 nm) on top of a Corning 2-64 filter and $\bar{\phi}_{EL}$ measured. The electrolyte was then changed to 5 M OH^- and the CdSe electrode irradiated with 514.5-nm light at the potential used in the $\bar{\phi}_{EL}$ determination. Emitted light was detected with the radiometer and sample in the same geometry employed for the $\bar{\phi}_{EL}$ measurement; the incident light was detected with the Scientech power energy meter. This experiment was repeated at several potentials. The electrolyte was then made 0.1 M in $S_2O_8^{2-}$ and $\bar{\phi}_{EL}$ measured at several potentials. Finally, $\bar{\phi}_{EL}$ was determined with the filters removed and the radiometer repositioned to minimize the distance to the electrode. The filter-covered radiometer was also placed in several other geometries to determine to what extent ϕ_r and $\bar{\phi}_{EL}$ scaled together. It should be mentioned that for all of the efficiency measurements described in this section the flat-response window of the radiometer was removed, thereby minimizing the electrode–radiometer distance. Consequently, measured values were corrected by a factor determined at larger distances where the window could be added and removed without disturbing the relative electrode–radiometer geometry; the correction factor used for the CdSe sample was in good agreement with the manufacturer's value for the wavelength region involved. For the experiments in this section, electrolytes were stirred magnetically while being N_2 purged.

Effects of Surface Treatment on PL Properties. A cell suitable for PEC studies was assembled in the Aminco-Bowman spectrometer. PL spectra of CdSe were obtained sequentially in air, water, and 3 M NaOH by using a single geometry and a resolution of 1.0 nm. The beam-expanded 514.5-nm line of the Ar ion laser was masked to fill the CdSe surface and delivered ~2 mW of power in all experiments. The Corning 3-66 filter and neutral density filters were used while the emission band and reflected excitation spike, respectively, were scanned. Without disturbing the geometry, the electrode was brought into circuit in the 3 M NaOH electrolyte at 0.0 V vs. SCE and irradiated until ~7 mC of charge had been passed (PEC etching). At this point the electrode was taken out of circuit. A stable emission intensity was observed after several seconds at which time the emission spectrum was recorded under conditions identical with those previously used in this experiment. The PEC etch was repeated for various irradiation periods, and spectra were recorded after each treatment. Solutions were stirred by a N_2 purge.

Acknowledgment. This work was generously supported by the Office of Naval Research. Financial support for J.-r.T. as a visiting scholar at the UW—Madison by the People's Republic of China is greatly appreciated. A.B.E. gratefully acknowledges support as an Alfred P. Sloan Fellow (1981–1983).

A Theory of Nuclear Substitution and the Hemistructural Relationship. The Origin of Bond Length and Bond Energy Additivity

Joseph R. Murdoch

Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received April 10, 1980*

Abstract: A general problem that arises in the treatment of substituent effects on rates and equilibria of chemical reactions is evaluating the changes in energy and geometric structure that occur when a fragment is removed from a molecule and replaced by a new one. This question is approached from an ab initio viewpoint using analytical SCF Hartree–Fock theory. For different series of compounds, relative substituent effects on reaction rates, equilibria, or molecular properties are often very similar and can be described in terms of group contributions plus interactions between groups. The origin of this phenomenon is examined by considering a common geometry constraint, which has been generalized to define a hemistructural relationship. For diatomics (A–A, A–C, C–C), it is equivalent to bond-length additivity. An important consequence of the hemistructural relationship is that all of the information necessary for determining the properties of the hemistructural molecule (A–C) can be obtained from the two parent structures (A–A and C–C). *No new information is needed.* Ultimately, all empirical observations of transferable substituent effects and molecular properties can be traced to this fact. The hemistructural relationship serves as a fundamental basis for transferability within the Born–Oppenheimer, nonrelativistic limit. Some of the consequences of this transferability are examined, and it is shown that the response of the total energy (E), the kinetic energy (T), and the total potential energy (V) to multiple substituent effects is fundamentally simpler than the corresponding response of the orbital energy (E_o) and the individual potential energy components (V_{nn}, V_{ne}, V_{ee}). The Hellmann–Feynman theorem is used to show that when fragment transfer (A–A + C–C $\rightarrow$ 2A–C) is described by first-order corrections to the wave function, an equilibrium A–C bond length will occur at the mean of corresponding A–A and C–C equilibrium bond lengths for arbitrary A,C fragments. An important result is that bond length and bond energy additivity can be observed even when large interactions (compared to deviations from additivity) occur between the A,C fragments. Additivity is observed because compensating changes in electronic structure take place in the two molecular fragments. Such a result is a fundamental departure from existing ideas on substituent effects and suggests that models of molecular structure based on interactions between transferable groups will require significant revision.

I. Introduction

It is well known that the energy of a molecule can often be expressed as the sum of the energies of its individual bonds and that these bond energies can frequently be "transferred" from one molecule to another.[1-3] The degree to which bond energies are invariant from one molecule to another has been thought to depend on the extent to which each molecular fragment experiences similar attractions and repulsions in different environments.[3] This concept of bond or fragment transferability has played a fundamental role in shaping our concepts of chemical bonding and structure.

A simple example illustrating these points is a comparison of

0002-7863/82/1504-0588$01.25/0 © 1982 American Chemical Society