Anthracene as the Origin of the Red-Shifted Emission from Commercial Zone-Refined Phenanthrene Sorbed on Mineral Surfaces

Z. Wang,* S. L. Hemmer, D. M. Friedrich,† and A. G. Joly

Pacific Northwest National Laboratory, Richland, Washington 99352

Received: October 27, 2000; In Final Form: February 28, 2001

The origin of the red-shifted fluorescence emission spectra observed for commercial zone-refined phenanthrene (purity 99.5+%) in concentrated cyclohexane solution and as sorbates on porous silica at high loading levels was studied by absorption and fluorescence spectroscopy as well as fluorescence quenching measurements. The absorption and fluorescence spectra indicate that a small amount of anthracene is present in the zone-refined phenanthrene. In concentrated phenanthrene solution and highly phenanthrene-loaded porous silica, excitation energy transfer from phenanthrene to the anthracene impurity results in the reduction of the phenanthrene fluorescence intensity and the appearance of the anthracene fluorescence emission at longer wavelength. A Stern−Volmer plot for quenching of phenanthrene fluorescence by anthracene in cyclohexane indicates both dynamic and static energy transfer mechanisms. For phenanthrene sorbed on mineral surfaces, the dynamic pathway is limited. Therefore, the appearance of anthracene fluorescence due to energy transfer from excited phenanthrene can serve as a spectral probe for polyaromatic hydrocarbon (PAH) aggregation and association on mineral surfaces.

Introduction

The sorption and desorption of polynuclear aromatic hydrocarbons (PAH) at mineral interfaces has been the focus of much recent research because of environmental concerns.[1−8] In a large portion of the published literature on this subject, phenanthrene has been the most commonly used model sorbate.[6−12] The wide use of phenanthrene is often attributed to its low Henry constant, low polarity, relative photophysical stability, and low yet manageable solubility in water, as well as a large literature base which facilitates comparison among the published work.

Several spectroscopic features make phenanthrene a useful probe of PAH sorption.[13−19] The first and second excited states, S_1 and S_2, are readily accessible in the near-UV region. The absorption band origins are located at 351 and 292 nm with molar absorptivities of ∼200 and 14 000, respectively.[13] In solution phase, excitation into either band leads to a bright, spectrally structured fluorescence (quantum yield 0.13) extending from 350 to 450 nm with a maximum located at 368.5 nm.[13] In both batch and column sorption experiments, detection of phenanthrene has been achieved mainly by recording the fluorescence spectra or the fluorescence intensity after UV excitation.[6−12]

Currently available commercial phenanthrene has purity levels between 96% and 99.5% (Aldrich, zone-refined). For an overwhelming majority of research work involving phenanthrene, it is used as purchased without further purification. Our recent fluorescence spectroscopic measurements, as well as those reported by others[15] for phenanthrene (Aldrich, zone refined, 99.5%) sorbed to porous silica at different phenanthrene loading levels, indicate that at low phenanthrene loading levels, the fluorescence spectrum of phenanthrene is similar to that of phenanthrene at low solution concentration. However, at high phenanthrene loading levels or in concentrated phenanthrene solutions, the typical fluorescence emission is either greatly reduced or completely diminished, and a new set of bands between 380 and 500 nm appears with a spectral maximum located at ca. 412 nm. For sorbed phenanthrene the appearance of these bands has not been explained. The objective of this article is to address the origin of these new fluorescence bands.

Studies of phenanthrene sorption/desorption with fluorescence detection reported in the literature involve a wide range of phenanthrene concentrations. Extremely high localized concentrations may be encountered, particularly in samples generated by spiking solid phenanthrene into solid sorbent in which the dissolution of phenanthrene is less well defined or characterized.[20,21] Without detailed knowledge of the spectral characteristics and the molecular state of sorbed phenanthrene, research results may become difficult to interpret and the conclusions reached thereafter could be erroneous. In the present work, spectral comparison among solutions of single crystalline phenanthrene, anthracene, and phenanthrene with added anthracene indicates that longer wavelength emission in commercial phenanthrene is due to anthracene present as an impurity. In solid and concentrated solutions of commercial phenanthrene, energy transfer occurs between excited phenanthrene and ground-state anthracene upon excitation in the phenanthrene absorption band, resulting in the reduction of the phenanthrene emission intensity and the appearance of anthracene fluorescence emission. In solution, the energy transfer occurs via both dynamic and static mechanisms. However, in the solids energy transfer requires molecular contact between phenanthrene and anthracene molecules.[22] Therefore, the presence of anthracene in phenanthrene and its characteristic fluorescence emission upon excitation of phenanthrene provide a unique spectroscopic probe to distinguish between associated or aggregated PAH and isolated PAH molecules.

Experimental Section

Commercial phenanthrene (99.5+%, zone-refined) and Davisil silica particles (150 Å average pore size, 314 m^2/g surface

---

* To whom correspondence should be addressed (zheming.wang@pnl.gov).

† Current address: Optical Coating Laboratory, Inc., 2789 Northpoint Parkway, Santa Rosa, CA 95407-7397. E-mail: Don_Friedrich@ocli.com.

10.1021/jp003983v CCC: $20.00

area), anthracene, (99.9+% Gold label), cyclohexane (spectrophotometric grade), and ethanol (spectrophotometric grade) were purchased from Aldrich. A portion of a phenanthrene single crystal (100%, pure) was received as a gift from Dr. A. R. McGhie at the Laboratory for Research on the Structure of Matter, University of Pennsylvania. Phenanthrene and anthracene solutions of cyclohexane and ethanol were prepared by weighing an accurate amount of the chemical and dissolving in a measured amount of solvent. Solutions of lower concentrations were made from accurate dilutions of the concentrated solutions in the corresponding solvent.

For phenanthrene fluorescence quenching by anthracene, a series of phenanthrene/anthracene mixtures was prepared. In these solutions the concentration of phenanthrene remained constant while the concentration of anthracene varied, resulting in solutions with phenanthrene:anthracene ratios between 1:0 to 1:10. All solutions were purged with dry nitrogen for at least 5 min prior to spectroscopic measurement, and the solute concentration change caused by solvent evaporation during N_2 purging was corrected gravimetrically.

Loading of phenanthrene in Davisil silica was performed by a method similar to that of Nam and Alexander.[20] Briefly, 0.5 g of Davisil silica particles were added to 20 mL of the phenanthrene solutions in cyclohexane at concentrations of 3×10^{-5} M and 1×10^{-2} M, respectively. The mixture was gently shaken in a sealed vial with Teflon cap for about 4 h, and then the vials were opened and placed in a desiccator attached to a vacuum line to remove the solvent by evaporation. During the evaporation the vials were periodically rotated manually to ensure uniform coverage of solvent. The process was continued until the vials reached a constant weight. For the calculation of loading level, a complete sorption was assumed.

UV−visible absorption spectra were measured on a Cary III spectrometer with 0.1, 1, and 5 cm path length quartz spectrophotometric cells, depending on the concentration of the solutions. For absorption spectra of phenanthrene sorbed to silica particles, absorption spectra of the blank silica particles were recorded, and these spectra were subtracted from the corresponding absorption spectra of phenanthrene-loaded silica particles to correct for the light scattering in porous medium. Fluorescence excitation and emission spectra were taken on a SPEX Fluorolog II fluorimeter equipped with two double monochromators (SPEX1681), a 450 W xenon lamp, and a cooled photomultiplier tube detector. The monochromators of the fluorimeter were calibrated using mercury lines.

Fluorescence lifetime measurements were carried out on a conventional time-correlated-single-photon-counting apparatus.[23] Each decay curve has a minimum peak intensity of 10^4 counts. Fluorescence lifetimes were calculated by fitting the experimental decay curves with either the WaveMetrics' IGOR or the Globals Unlimited program.[24]

Results and Discussion

The absorption (Figure 1 panel A) and emission spectra (Figure 1 panel B) of pure phenanthrene (a), commercial zone-refined phenanthrene in dilute (b) and concentrated (c) cyclohexane solutions, as sorbates in Davisil 150 porous silica at low (d) and high (e) loading levels and as a thin polycrystalline film (f) are shown in Figure 1. For convenience of discussion we label commercial zone-refined phenanthrene in dilute cyclohexane solution and sorbed in silica at low loading level as type L samples and those in concentrated cyclohexane solution, sorbed in silica at high loading level, and polycrystalline film as type H samples. As seen in Figure 1A, for all samples (traces a−f) the absorption spectra are similar. Each absorption spectrum consists of a strong absorption band in the region between 250 and 300 nm ($\lambda_{\max}$ =292 nm) and a set of weaker absorption bands in the region between 300 and 355 nm. For absorption spectra involving commercial phenanthrene, a few very weak bands can be distinguished from the spectral baseline (traces b and c). Such weak bands are clearly absent from the absorption spectrum of pure phenanthrene (trace a).

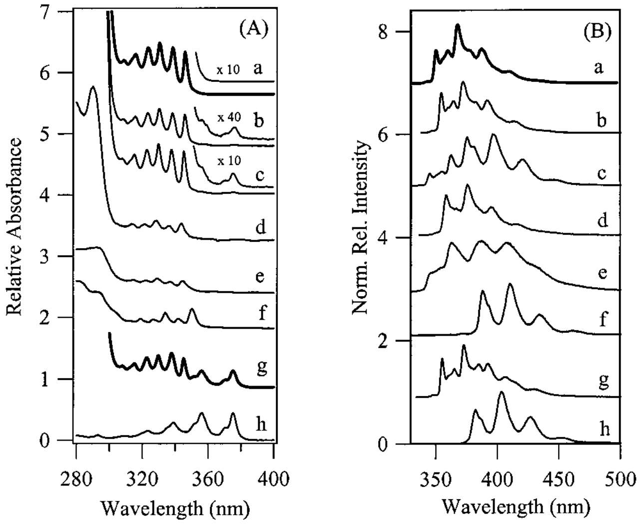

Figure 1. Absorption (A) and emission spectra (B) of (a) pure phenanthrene in cyclohexane solution (0.1 M); (b) zone-refined phenanthrene in cyclohexane solution (5.8×10^{-4} M); (c) zone-refined phenanthrene in cyclohexane solution (0.03 M); (d) phenanthrene sorbates in porous Davisil silica at 0.21 mg/g loading; (e) phenanthrene sorbates in porous Davisil silica at 0.071 g/g loading; (f) phenanthrene crystalline film; (g) a mixture of 5.8×10^{-4} M phenanthrene and 2.4 $\times$ 10^{-5} M anthracene in cyclohexane solution; (h) anthracene in cyclohexane solution (1×10^{-5} M). All traces were rescaled in absorbance/intensity and offset in relative position for clarity. Traces a−c in panel (A) were further magnified to show the weak bands in the wavelength range of 350−400 nm. For the emission spectra in panel (B), λ_{ex} = 292 nm.

Significant differences in the fluorescence emission spectra are observed when the samples are excited at the absorption maximum (292 nm), (Figure 1B). For the L type and pure phenanthrene samples (traces a, b, and d), emission spectra are composed of a set of bands in the spectral region from 350 to 450 nm with a spectral maximum of 368.5 nm. For type H samples (traces c, e, and f), in addition to the emission bands observed for type L and pure phenanthrene samples, several emission bands are observed at longer wavelength with a spectral maximum typically located at 412.0 nm. For microcrystalline films of commercial zone-refined phenanthrene, the latter dominates the emission spectrum (trace f).

The emission spectra of type L and pure phenanthrene samples are the same as those obtained by Barbas et al. for commercial zone-refined phenanthrene sorbed in 6 nm pore size porous silica particles at low loading levels (0.018 g/g) while the emission spectra of type H samples are close to their results for either phenanthrene microcrystals or as sorbates on porous silica at high loading levels (0.18 g/g).[15] For solution samples, the relative fluorescence intensity, i.e., the fluorescence quantum yield, of phenanthrene dropped as phenanthrene concentration increased, indicating the presence of concentration quenching. A similar effect has also been reported by Kiserow et al. in a polymer matrix.[25]

The energetics responsible for the electronic transitions involved in the absorption spectra and fluorescence emission spectra have been studied previously in dilute cyclohexane solutions[13] and for single crystals at 20 K.[14] The first excited state, S_1, of phenanthrene is located ~28 500 cm^{-1} above the ground state, S_0. In the absorption spectra these are the bands located from 300 to 355 nm. The second electronic excited state, S_2, is ~34 000 cm^{-1} above the ground state and appears in the spectral region between 260 nm to 300 nm. The multiple bands of the spectra in each region correspond to electronic transitions to different vibronic levels. From symmetry considerations, electronic transition to S_1 is "forbidden" and transition to S_2 is "allowed" and, therefore, the latter is almost seventy times stronger. According to Kasha's rule,[26] higher excited electronic states relax to S_1 via fast nonradiative internal conversion processes, and thus fluorescence emission originates solely from S_1. It is known that for some molecules, such as anthracene and pyrene, excimers may form in both solid and solution states.[22] Such excimers are often characterized by their broad, structureless emission spectra at longer wavelengths. The absence of excimer-like spectra from single-crystal phenanthrene at 20 K as well as phenanthrene solutions[13,15,19] suggests that phenanthrene either does not form excimers, or if formed, its excimer emission intensity is negligible.

The fact that the longer wavelength emission bands are absent in pure single crystal and type L samples but appear in type H samples points to the possibility of the presence of an impurity in the commercial phenanthrene. For phenanthrene the most likely impurity is anthracene. It is known that anthracene forms a continuous series of solid solutions with phenanthrene and, therefore, its removal from phenanthrene is rather difficult.[14] To test such a hypothesis, known concentrations of anthracene were added to dilute phenanthrene solutions and the absorption spectra of the resulting solutions were recorded. In addition, fluorescence lifetimes of the longer wavelength emission bands were measured.

As shown in Figure 1 (panel A, trace g) addition of anthracene to phenanthrene solution causes the appearance of absorption bands at longer wavelengths (357 and 376 nm) in the absorption spectrum, consistent with those of anthracene in the same solvent (trace h). Comparison of the shape and position of the bands at 357 and 376 nm in a phenanthrene−anthracene mixture (trace g) with those that appear in the commercial phenanthrene solutions (traces b and c) clearly indicates that the longer wavelength absorption bands in commercial phenanthrene originate from anthracene. It is known that anthracene also has absorption bands located at 340, 325, and 308 nm.[13] However, due to the low relative concentration of anthracene in the phenanthrene solution, these bands are overwhelmed by the absorption bands of phenanthrene in the same region. The fluorescence lifetime obtained by excitation at 376 nm while observing fluorescence at 430 nm for the phenanthrene−anthracene mixture solution in cyclohexane was found to be 4.8 ns. This is the same as that of anthracene isolated in the same solvent, and much shorter than the fluorescence lifetime of phenanthrene (45.8 ns) obtained by exciting at 292 nm and observing at 368.5 nm.

From quantitative analysis of the absorption spectra of commercial zone-refined phenanthrene, it was found that the relative concentration of the anthracene impurity is constant at all phenanthrene concentrations. Using Beer's law the relative molar concentration of anthracene, which is the same as weight concentration in this case, in commercial phenanthrene was calculated from the molar absorptivities and absorbencies of anthracene and phenanthrene. Using this analysis, the value obtained was 0.4%, which agrees well with the manufacturer's specification of phenanthrene purity 99.5+%. This also suggests that other impurities, if any, will be at negligible concentration levels.

The occurrence of anthracene emission when exciting at the phenanthrene absorption band indicates that energy transfer from phenanthrene to anthracene occurs. The fact that such an energy transfer occurs only in type H samples suggests that it is dependent on phenanthrene concentration or the intermolecular distance. Energy transfer between a singlet excited molecule P*, and the ground-state molecule A, requires that (a) the energy of the first singlet excited state of A lies below that of P* and (b) the molecule A be in the vicinity of P*.[22] The first excited state of anthracene is located at 26 700 cm^{-1}, 2200 cm^{-1} lower that that of phenanthrene (28 900 cm^{-1}),[22] satisfying requirement (a). Therefore, it is because of the requirement (b) that such energy transfer occurs only for Type H phenanthrene samples. For phenanthrene thin films, the crystal packing requires that molecules of phenanthrene and anthracene be at the contact distance. For phenanthrene sorbed in Davisil silica, association between adjacent phenanthrene and anthracene molecules may occur once the concentration of phenanthrene is sufficient to satisfy requirement (b). Therefore, for solids, fluorescence quenching and energy transfer from phenanthrene to anthracene occurs by a static mechanism. However, molecular interaction in solution is more complicated. For solutions with a low viscosity solvent there are two mechanisms by which energy transfer and fluorescence quenching can occur. One is through molecular collision (dynamic) and the other is through the formation of dimers (static). Under steady-state conditions, the collisional process follows the Stern and Volmer relationship:[22,27]

$$\frac{Q_P}{Q_{AP}} = 1 + K_{AP}\cdot[A] \tag{1}$$

where Q_P refers to the quantum yield of phenanthrene in the absence of energy transfer, Q_{AP} refers to that in the presence of anthracene, K_{AP} (= $k_{AP}\cdot\tau_P$) is the Stern−Volmer coefficient of energy transfer, k_{AP} is the quenching rate parameter, and τ_P is the fluorescence lifetime of phenanthrene in the absence of anthracene. When only dynamic quenching is present, a plot of Q_P/Q_{AP} as a function of the acceptor (quencher) concentration results in a straight line with a slope of K_{AP}. However, when static quenching is present, such a plot is curved upward. The simultaneous presence of both dynamic and static quenching has been observed in many systems.[28−30] The upward deviation in the Stern−Volmer plot occurs because only a certain fraction of the excited molecules are quenched by the collisional process. Other excited molecules are quenched almost instantaneously because a quencher molecule happens to be present in nearby proximity at the time of excitation, i.e., those excited molecules are quenched through a static process. Several models involving a ground-state complex, a sphere of interaction, and transient effects have been proposed to describe the static quenching processes.[31−33] A detailed description of these models is beyond the scope of this work. In this work "static quenching" represents a sufficient association between two or more molecules that increases the rate of nonradiative de-excitation. Such an association can be ground-state dimers, excimers, or exciplexes between two molecules, or higher molecular aggregates.

Fluorescence emission spectra of a series of phenanthrene solutions with constant phenanthrene concentrations of 2×10^{-4} M and variable anthracene concentration from 2×10^{-4} M to 2×10^{-3} M were recorded, and a Stern−Volmer plot was

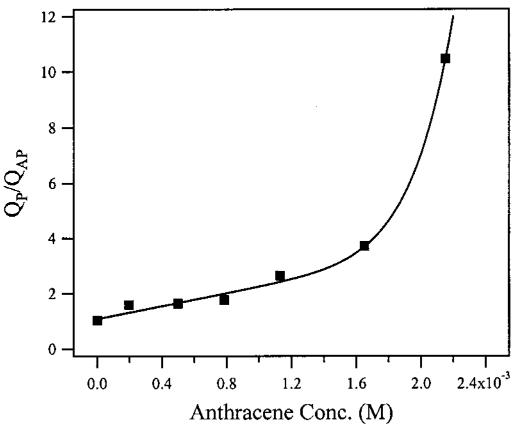

Figure 2. Phenanthrene fluorescence quenching by anthracene in cyclohexane solution at different anthracene concentrations. $\lambda_{ex} = 292$ nm. $\lambda_{em} = 368.5$ nm.

obtained using eq 1 (Figure 2). As seen from Figure 2, the plot of Q_P/Q_{AP} vs [A] curves upward as anthracene concentration increases, clearly indicating that, in solution, static quenching plays a role in the energy transfer from phenanthrene to anthracene. Using the data points at lower concentrations, a Stern−Volmer constant of 1200 L/mol was obtained for the dynamic quenching. Considering the long fluorescence lifetime of phenanthrene (45.8 ns) such a value is reasonable as compared with those reported by others.[22]

The molecular state of phenanthrene sorbed at a mineral surface offers direct information about the extent of surface coverage and sorption sites that cannot be obtained from other conventional methods. Such information is critical for the understanding of the relative sorption strength and the dynamic sorption process. In traditional sorption studies, surface areas are determined either by N_2 BET or Hg intrusion methods, whereas sorption capacity and site density are extrapolated from the macroscopic sorption isotherm. Obviously the effective surface area for sorption of large molecules such as phenanthrene will be smaller since part of the surface area will not be accessible due to spatial restrictions. The macroscopic isotherm data do not offer any direct information about adsorption site identity or structures. In addition, sorption on heterogeneous mineral surfaces is likely a dynamic process. During the sorption process, molecules initially sorbed to the surface continually modify the sorption sites on the entire surface. For example, molecules that encounter the surface after significant sorption has already occurred have the choice of either being sorbed at an unoccupied surface site or being associated with an already sorbed phenanthrene molecule. If aggregation occurs on the surface, sorption capacity will be an ill-defined parameter because there is no way to ascertain when a monolayer coverage has been reached. Therefore, fluorescence from anthracene following energy transfer from excited phenanthrene provides a convenient experimental model to probe PAH molecular association/aggregation on mineral surfaces.

Quantitative fluorescence analysis of phenanthrene samples may involve commercial phenanthrene at a variety of concentration levels as well as different phenanthrene purity grades. The present results indicate that the molecular state of phenanthrene determines its fluorescence behavior (e.g., quantum yield and lifetime). Any quantitative measurement of phenanthrene is valid only when the phenanthrene molecules are in the same molecular state−the monomeric state.

Acknowledgment. The authors thank Dr. A. R. McGhie at the Laboratory for Research on the Structure of Matter, University of Pennsylvania for providing single crystalline phenanthrene. This research was supported by the Environmental Technology Partnerships (ETP) Program, Office of Biological and Environmental Research (BER), Office of Energy Research, U.S. Department of Energy. Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

References and Notes

(1) Wu, S. C., and Gschwend, P. M. *Environ. Sci. Technol.* **1986**, *20*, 717.

(2) Pignatello, J. J., and Xing, B. *Environ. Sci. Technol.* **1996**, *30*, 1.

(3) Ball, W. P.; Roberts, P. V. *Environ. Sci. Technol.* **1991**, *25*, 1237.

(4) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: New York, 1993.

(5) Mader, B. T.; Uwe-Goss, K.; Eisenreich, S. J. *Environ. Sci. Technol.* **1997**, *31*, 1079.

(6) Luthy, R. G.; Aiken, G. R.; Brusseau, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Reinhard, M.; Traina, S. J.; Weber, W. J., Jr.; Westall, J. C. *Environ. Sci. Technol.* **1997**, *31*, 3341.

(7) Huang, W.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 3238.

(8) Cornelissen, G.; Van Noort, P. C. M; Govers, H. A. J. *Environ. Sci. Technol.* **1998**, *31*, 3124.

(9) Young, T. M.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1997**, *31*, 1692.

(10) Huang, W.; Schlautman, M. A.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1996**, *30*, 2993.

(11) Piatt, J. J.; Backhus, D. A.; Capel, P. D.; Eisenreich, S. J. *Environ. Sci. Technol.* **1996**, *30*, 751.

(12) Jones, K. D.; Tiller, C. L. *Environ. Sci. Technol.* **1999**, *33*, 580.

(13) Berlman, Isadore B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed; Academic Press: New York, 1971.

(14) McClure, D. S. *J. Chem. Phys.* **1952**, *20*, 682.

(15) Barbas, J. T.; Sigman, M. E.; Dabestani, R. *Environ. Sci. Technol.* **1996**, *30*, 1776.

(16) Liu, Y. S.; de Mayo, P.; Ware, W. R. *J. Phys. Chem.* **1993**, *97*, 5995.

(17) Liu, Y. S.; Ware, W. R. *J. Phys. Chem.* **1993**, *97*, 5980.

(18) Tro, N. J.; Nishimura, A. M.; George, S. M *J. Phys. Chem.* **1989**, *93*, 3276.

(19) Rhodes, T. A.; Fox, M. A. *J. Phys. Chem.* **1996**, *100*, 17931.

(20) Nam, K.; Alexander, M. *Environ. Sci. Technol.* **1998**, *32*, 71.

(21) Reid, B. J.; Northcott, G. L.; Jones, K. C.; Semple, K. T. *Environ. Sci. Technol.* **1998**, *32*, 3224.

(22) Birks, J. B. *Organic Molecular Photophysics*; John Wiley & Sons: New York, 1973.

(23) Holtom, G. R. *SPIE* **1990**, *1204*.

(24) Beechem, J. M.; Gratton, E.; Mantulin, W. W. G*lobals Unlimited*. University of Illinois at Urbana-Champaign, 1988.

(25) Kiserow, D. J.; Itoh, Y.; Webber, S. E. *Macromolecules* **1997**, *30*, 2934.

(26) Kasha, M. *Disc. Faraday Soc.* **1950**, *9*, 14.

(27) Stern, O.; Volmer, M. *Phys. Z.* **1919**, *20*, 183.

(28) Eftink, M. R.; Ghiron, C. A. *Anal. Biochem.* **1981**, *114*, 199.

(29) Zeng, H.; Durocher, G. *J. Lumin.* **1995**, *63*, 75.

(30) Eftink, M. R.; Ghiron, C. A. *J. Phys. Chem.* **1976**, *80*, 486.

(31) Boaz, H.; Rollefson, G. K. *J. Am. Chem. Soc.* **1950**, *72*, 3435.

(32) Frank, I. M.; Vavilov, S. I. *Phys. Z.* **1931**, *69*, 100.

(33) Smoluchowski, M. V. *Z. Phys. Chem.* **1917**, *92*, 129.