1504 *J. Phys. Chem. A* **1999,** *103,* 1504−1508

Resonant Fluorescence Quenching of Aromatic Hydrocarbons by Carbon Disulfide

Henning Groenzin and Oliver C. Mullins*
Schlumberger-Doll Research, Ridgefield, Connecticut 06877

William W. Mullins
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Received: August 4, 1998; In Final Form: November 16, 1998

The reduction of fluorescence intensities and of fluorescence lifetimes is determined as a function of carbon disulfide (CS_2) concentration for four fluorophores. The quenching efficiency of CS_2 depends strongly on the energy of the electronic absorption edge of the dye; quenching increases as the dye electronic edge approaches that of CS_2. These results are described by the quantum two-level system. Comparison of Stern−Volmer plots of intensity and lifetime data shows that quenching is predominantly diffusion-mediated and furthermore demonstrates that the interaction range is about 6 Å. The impact of CS_2 on the fluorescence spectra of important natural materials is discussed.

I. Introduction

Fluorescence is a powerful analytic technique that can be used to probe molecular structure and dynamics in a wide variety of ways. The interaction of chromophores either in collision (via long- or short-range interactions) or in complexes can result in reduction of fluorescence intensity or in the appearance of dramatically altered spectra.[1,2] This body of rich dynamics makes fluorescence an ever useful and productive method. Intermolecular interactions often result in significantly altered electronic-state relaxation and thus can be investigated via fluorescence. For instance, recent investigations of interfacial phenomena[3,4] and intermolecular interactions in films[5−7] and lipid bilayers[8] have successfully employed fluorescence methods.

Quenching or radiationless relaxation is a common result of the interaction of electronically excited molecules with certain classes of molecules. For example, molecular oxygen can quench excited fluorophores via several pathways.[9] If allowed by energetics, the electronic excitation energy can be transferred from the excited fluorophore to molecular oxygen exciting the $^1\Delta_g$ state of oxygen. Oxygen, with its large magnetic moment, can also induce intersystem crossing of the excited fluorophore. Consequently, detailed knowledge of molecular interactions is required for understanding the interactions of oxygen with excited fluorophores.

CS_2 is another small molecule with interesting fluorescence properties. Gaseous CS_2 exhibits fast and slow fluorescence components;[10] by investigation of collisional relaxation effects, different lifetimes were associated with different vibronic transitions.[11] CS_2 is widely used as a solvent for various hydrocarbon systems. As an example, an investigation of carotenoids using fluorescence methods has been performed with CS_2 as the solvent.[12] CS_2 is also an excellent solvent for aromatic hydrocarbons in naturally occurring carbonaceous systems such as petroleum and as such is a candidate for use in practical applications. Fluorescence is an excellent probe of molecular structure and dynamics in petroleum[13] as well as a powerful tool for related environmental applications.[14,15] The issue arises as to the possibility of significant solvent effects between CS_2 and the solutes to be probed via fluorescence. Of course, solutes with a larger HO−LU (highest occupied to lowest unoccupied molecular orbital) energy gap than CS_2 cannot be probed in a CS_2 solution because of nonresonant quenching by CS_2. However, one might incorrectly assume that CS_2 can be used without spectral distortion for solutes with an HO−LU gap lower than that of CS_2.

In this paper, we investigate the effect of CS_2 on the fluorescence emission properties of four aromatic hydrocarbon fluorophores. Both fluorescence spectral intensities and fluorescence lifetimes are measured as a function of CS_2 concentration for deaerated solutions. The quenching efficiency strongly depends on the HO−LU energy gap of the dye. The quantum two-level system treatment accounts for this energy dependence, yielding a perturbation energy of 419 cm^{-1}. The Stern−Volmer plots that are generated from the fluorescence intensity and lifetime data indicate the applicability of simple models that account for the quenching. Furthermore, comparison of the intensity and lifetime quenching rates indicates that effective interaction range is about 6 Å. Strong spectral distortions preclude the use of CS_2 for routine spectral analysis of naturally occurring systems such as crude oil.

II. Experimental Section

Exalite 404, Exalite 411, and Exalite 428 were obtained from Exciton, and perylene was obtained from Aldrich Chemical Co.; all were used without further purification. These four fluorophores consist of hydrogen and carbon only with various configurations of aromatic rings, precluding potential complications from heteroatoms. The crude oil sample used here was obtained from the Delaware Sands in the vicinity of Roswell, New Mexico. (No effect from the Roswell incident was detected.) Toluene was used as the solvent for all samples.

Fluorescence spectra were collected with the PTI A-720 steady-state subsystem coupled to the PTI C-72 lifetime fluorescence spectrometer. The steady-state light source uses a CW 75 W Xe lamp ensuring a strong signal. For the three

10.1021/jp983261s CCC: $18.00

exciton dyes, the intensity data used for the Stern−Volmer plots correspond to excitation at 390 nm and emission at 410 nm. For perylene, the wavelengths of 390 nm excitation and 450 nm emission were used. For a given dye, the Stern−Volmer slopes were independent of emission wavelength as expected.

The lifetime decay curves were collected using a PTI GL3300 nitrogen laser source pumping a GL-302 dye laser. For the Exalite dyes, excitation was at 337 nm with emission at 380 nm. For perylene lifetime measurements, the dye laser was used with DPS dye, excitation was at 400 nm, and emission was at 450 nm. The intrinsic time width of the system is obtained from the "decay" curve of intensity vs time for a scattering solution and with the emission wavelength set equal to the excitation wavelength. The decay curve of the sample is measured, and deconvolution software allows determination of the lifetime. The time resolution of the system is less than 300 ps. For all dye samples a single-exponential decay was used for fitting. Optical absorption spectra were obtained with a Cary 500 UV−visible−NIR spectrometer.

For fluorescence analysis, individual toluene solutions of the fluorophores were prepared with a concentration in the 10^{-6} M range. Individual stoppered cuvettes of these solutions were deaerated with nitrogen using input and vent needles. Small quantities of CS_2 of known mass were added to the deaerated cuvettes. Deaeration was again performed; determinations were made that deaeration could be achieved without driving off the added CS_2 by keeping track of the mass of solution and by observing the effect of very long deaeration times.

III. Theory

Resonant Interaction. The dependence of efficient quenching on the requirement of proximate energy states implies a resonant interaction. We assume the standard two-level mixing scheme where an excited state of the dye resonantly mixes with that of CS_2.

$$\psi = c_d\phi_d + c_{CS_2}\phi_{CS_2} \quad (1)$$

where c_i is the coefficient of the pure basis vector ϕ_i for eigenstate ψ. The square of c_{CS_2} gives the efficiency of quenching by CS_2 for the dyes. c_{CS_2} is given by eq 2 (assuming no diagonal element perturbations),[16]

$$c_{CS_2} = \sin(^1/_2 \arctan(2W_{12}/\Delta E)) \quad (2)$$

where W_{12} is the coupling interaction energy causing wave function mixing and ΔE is the energy difference between the two states of interest. For the case treated here, ΔE is the energy difference between the lowest electronic excited states of CS_2 and the dye.

Fluorescence Quenching. Dye molecules are assumed to be quenched by CS_2 molecules in two ways. (1) One way is instantaneous quenching (with fixed efficiency ϵ) when one CS_2 molecule lies within a critical radius R_c containing n molecules around the dye molecule. We call this "sphere-of-action" quenching.[2] (2) A second way is diffusive quenching caused by the encounter of diffusing excited dye and CS_2 molecules. Diffusive quenching also depends on efficiency ϵ, but this dependence is implicitly accounted for in the rate constant. Thus, a fraction of the dye molecules excited at any given moment are quenched instantaneously and the remaining ones either undergo diffusional quenching or spontaneous decay. The sphere-of-action assumption approximates a radially dependent quenching efficiency by a step function with a discontinuity at R_c. We do not distinguish between quenching mechanisms induced via electron exchange vs Coulomb (or Forster) interactions.

We first calculate the fraction of excited dye molecules that remain unquenched from the sphere-of-action quenching. If the concentration q of quencher molecules is small, f_F is the sum of fraction of dye molecules that have no CS_2 within the critical radius R_c plus the fraction of dye molecules that have one CS_2 molecule but that remain unquenched because of the smaller than unit efficiency ϵ. Using Poisson statistics, we obtain

$$f_F = e^{-nq/S}(1 + (1 - \epsilon)nq/S) \quad (3)$$

where S is the solvent molarity. For small q, eq 3 becomes

$$f_F = 1 - \epsilon nq/S \quad (4)$$

which also follows from binomial statistics.

The rate equation for excited-state population E of dye molecules may now be written as

$$dE/dt = AJc(1 - \epsilon nq/S) - k_{F_o}E - k_q qE \quad (5)$$

where A is the absorption coefficient of the dye of concentration c, J is the photon flux, k_{F_o} is the intrinsic (fluorescence) decay rate of the excited dye molecules, and k_q is the diffusion quenching constant associated with diffusive encounters of dye with CS_2. The first term represents the production of E molecules due to the excitation of the available (unexcited) dye molecules, and the last two terms give the loss of E molecules due to the two process discussed above.

Setting $dE/dt = 0$ in eq 5 to obtain the steady-state value of E, letting $E_o = AJc/k_{F_o}$ represent the steady-state value of E for $q = 0$, and noting that $E/E_o = I/I_o$, where I is the emitted fluorescence intensity, we obtain

$$I_o/I - 1 = (k_q/k_{F_o} + \epsilon n/S)q \quad (6)$$

Thus, the slope of the (linear) Stern−Volmer plot gives the sum of the quenching caused by diffusion and by sphere-of-action quenching. These effects may be separated by measuring the fluorescence lifetime τ_F, which is given from eq 5 by setting $J = 0$. The result may be expressed in the familiar form

$$\tau_{F_o}/\tau_F - 1 = (k_q/k_{F_o})q \quad (7)$$

where τ_{F_o} is the lifetime when $q = 0$.

IV. Results and Discussion

Fluorescence Intensity. Figure 1 shows a series of spectra of Exalite 404 as a function CS_2 concentration. Here, the (0,0) band was excited, so the measured emission corresponds to higher vibrational states. With higher CS_2 concentration, the intensity is uniformly lowered, independent of emission wavelength. Similar plots were obtained for Exalite 411, Exalite 428, and perylene. Figure 2 shows the Stern−Volmer plot for the fluorescence intensity data obtained from the data in Figure 1 for Exalite 404 and for comparable data for the other dyes. The slopes are shown in the figure obtained from a $y = mx$ fit. The Stern−Volmer plots are found to be quite linear, indicating the applicability of eq 6. Furthermore, it is evident that the slopes of the Stern−Volmer plots are dramatically different for the dyes, showing that the quenching efficiency of CS_2 varies considerably.

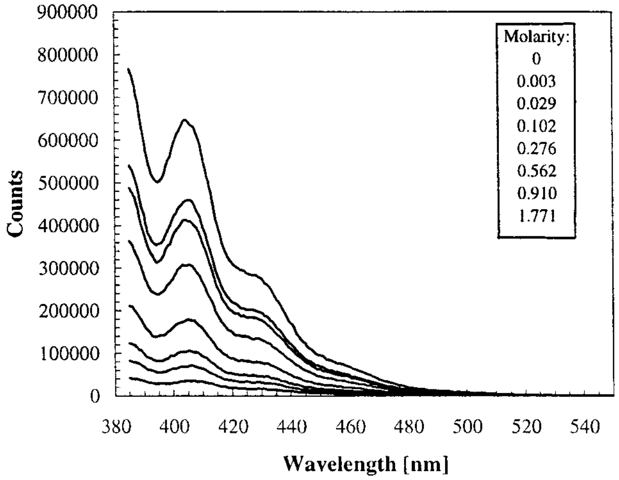

Figure 1. Fluorescence emission spectra of Exalite 404 with different molarities of CS_2. A monotonic and large reduction of fluorescence intensity is observed with CS_2 addition.

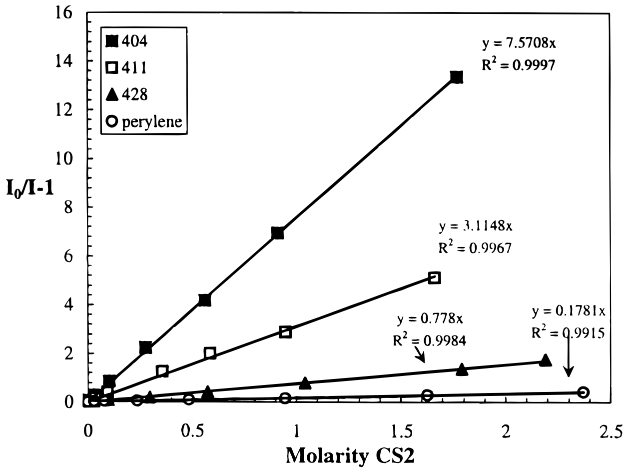

Figure 2. Stern−Volmer plots for Exalite 404, Exalite 411, Exalite 428, and perylene. The Stern−Volmer plots are linear, showing the applicability of eq 6. The slopes that are proportional to the CS_2 quenching rate show a dramatic dependence on the particular dye.

TABLE 1: HO−LU Gap, Intrinsic Lifetime, and Quenching Rate Constant by CS_2 for Four Dyes

dye	HO−LU energy cm^{-1}	lifetime ns	k_q $/M_{CS_2}/s^a$
Exalite 404	30 030	0.61	1.25×10^{10}
Exalite 411	28 902	0.62	5.00×10^{9}
Exalite 428	27 701	0.53	1.46×10^{9}
perylene	22 779	5.84	3.08×10^{7}
CS_2	31 447		

[a] Where M_{CS_2} means moles CS_2 per liter.

Table 1 lists for the dyes, the HO−LU energy gap for the 0−0 band obtained from the absorption spectrum (also for CS_2), the lifetimes, and the Stern−Volmer slopes multiplied by k_{F_0}. This last column gives k_q in the absence of sphere-of-action quenching and is a measure of the effectiveness of CS_2 quenching for the dyes. That is, eq 6 is used to fit the data where $n = 0$. This gives a zeroth-order approximation of k_q. As the HO−LU transition of the dye approaches that of CS_2, the rate of quenching (k_q) rises rapidly.

Figure 3 shows the fit of the quenching rates vs energy difference to eq 2 with a mulplicative prefactor that accounts for diffusion. The fit is quite good, indicating that this resonant interaction model accounts for the fundamentals of the observed energy dependence of k_q. The value of the interaction energy coupling is 419 cm^{-1}.

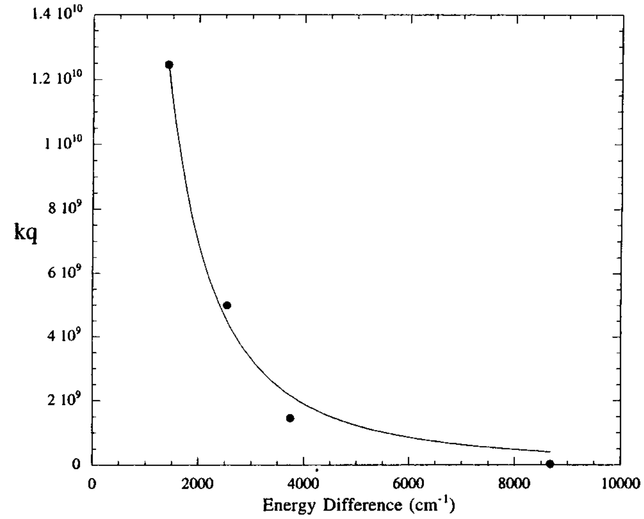

Figure 3. Dependence of the CS_2 quenching effectiveness is traced to the wave function mixing. The variation in the quenching rate constant by CS_2 for different dyes derives from the energy mismatch (ΔE) between the CS_2 and dye first excited states. The off-diagonal matrix element has a value of 419 cm^{-1}.

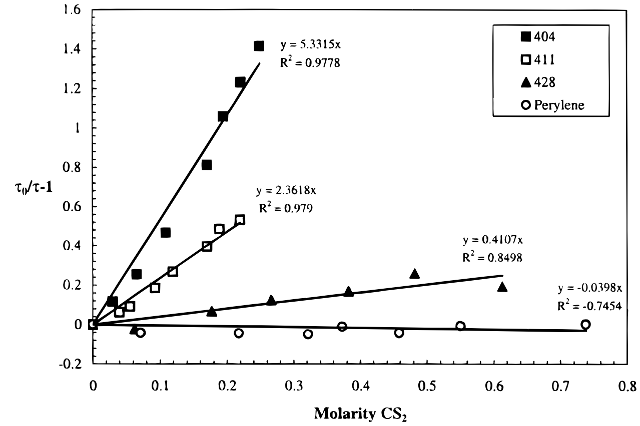

Figure 4. Stern−Volmer plots obtained for fluorescence lifetimes vs CS_2 concentration for Exalite 404, Exalite 411, Exalite 428, and perylene. The same features are evident for the lifetime and intensity data (Figure 2). CS_2 shows dramatically different efficiencies for quenching the different dyes. The slopes of the lifetime curves are somewhat smaller than those of the intensity plots, illustrating that some sphere-of-action quenching is occurring in addition to diffusion quenching. The one negative slope is considered to be zero within error.

From eq 2 and the fitted parameters in Figure 2, one can obtain the extrapolation of k_q to the value that would be obtained if the dye has the same HO−LU gap as CS_2. The extrapolated value of k_q is $\sim 10^{11}$ $M_{CS_2}^{-1}$ s^{-1}. This value is approximately equivalent to the diffusion limit rate constants for small molecules (but depends on the value of R_c). Thus, the quenching of dyes by CS_2 is about unit efficiency provided the electronic states are degenerate. This large value also implies a large value of R_c and thus some degree of sphere-of-action quenching in addition to diffusion quenching.

Fluorescence Lifetime. Equation 7 describes the diffusion-mediated quenching of the dyes by CS_2. The fluorescence lifetimes for the different dyes were measured for various CS_2 concentrations, and the corresponding the Stern−Volmer plots are shown in Figure 4. The lifetime plots exhibit somewhat more scatter than the intensity plots because the lifetime is determined from a two-parameter deconvolution fit while the intensity is

TABLE 2: Stern−Volmer Slopes (in Units of M_{CS_2}) from Fluorescence Intensities and Lifetimes

dye	slope (M_{CS_2}) from intensity	slope (M_{CS_2}) from lifetime
Exalite 404	7.57	5.32
Exalite 411	3.11	2.42
Exalite 428	0.78	0.55
perylene	0.18	−0.04

obtained directly from the data. Nevertheless, the same trends are exhibited by the intensity and lifetime data. Table 2 compares the Stern−Volmer slopes obtained with the fluorescence intensity and fluorescence lifetime data.

The last entry is negative but presumably zero within error. The salient features of the intensity and lifetime data are quite similar. A large, systematic variation of quenching efficiency is indicated by both data sets. Moreover, the absolute magnitudes of entries in the two data sets are close; thus, the simple diffusional quenching model represented by eq 7 is the predominant factor governing the quenching. Nevertheless, the difference between the dependence of quenching on CS_2 concentration calculated from intensities vs lifetimes can be used to estimate the significance of the sphere-of-action quenching and thus the critical interaction distance.

Critical Interaction Distance

The sphere-of-action quenching mechanism depends on R_c^3, while the diffusional quenching mechanism depends linearly on R_c. Fluorescence intensity depends on both sphere-of-action quenching and diffusional quenching, while fluorescence lifetime quenching depends only on diffusional quenching. By coupling the different scaling of quenching on R_c to the ratios of Stern−Volmer slopes from lifetime and intensity data, one can estimate the magnitude of R_c. The ratio R_{sv} of the Stern−Volmer slopes (see Table 2) for intensity vs lifetime data is obtained from eqs 6 and 7 to give eq 8:

$$R_{sv} = 1 + \epsilon n k_{F_o}/(S k_q) \tag{8}$$

The diffusion quenching constant k_q can be related to the diffusion-controlled limit,[17] where $k_q = \epsilon k_D$.

$$k_D = 4\pi N_{av}(D_1 + D_2)R_c \tag{9}$$

where N_{av} is Avogadro's number and D_i are the diffusion constants of the dye and quencher. Substituting eq 9 into eq 8, one obtains

$$R_{sv} = 1 + \frac{n k_{F_o}}{S 4\pi N_{av}(D_1 + D_2)R_c} \tag{10}$$

One can estimate the constants in eq 10. Using $D_{dye} \ll D_{CS_2} \approx 2 \times 10^{-5}$ cm^2/s (from ref 18) and using one molecular diameter (3×10^{-8} cm) as the unit for R_c (so R_c becomes dimensionless), 10^9/s for k_{F_o}, and 10 mol/L for S, one obtains

$$R_{sv} = 1 + \frac{1}{14\pi}\frac{n}{R_c} \tag{11}$$

We can approximate the value of n to be $n = {}^4/_3\pi R_c^3$ where R_c is in units of molecular diameter. For example, for $R_c = 1$, one would obtain four nearest-neighbor molecules in the immediate coordination sphere. Alternatively, one could use a lookup table for values of n given a value of R_c, but the conclusion would be about the same.

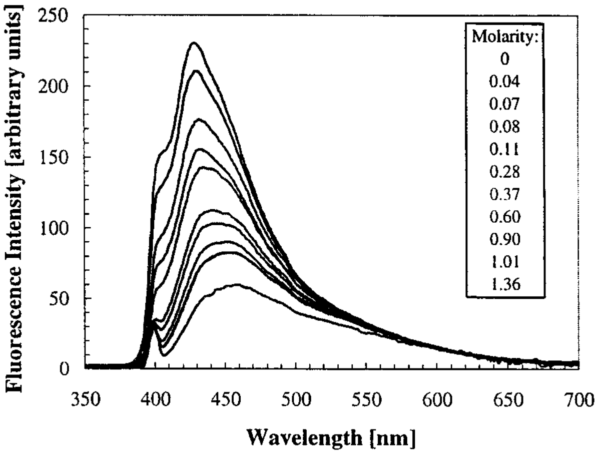

Figure 5. Fluorescence spectra of a crude oil vs CS_2 concentration. Crude oils contain a complex mixture of aromatic hydrocarbons. As more CS_2 is added, the blue emitting fluorophores are quenched while the red emitting fluorophores are essentially unperturbed. CS_2 is not a desirable solvent for spectral analysis of complex samples such as crude oils.

$$R_{sv} = 1 + 0.1R_c^2 \tag{12}$$

If R_c is 3 molecular diameters, then the ratio of the slopes is 2. Table 2 shows that for the Exalite dyes the ratio of Stern−Volmer slopes for intensity to lifetime data are about the same; the average of the ratio is 1.4. With sphere-of-action quenching included, the values in Table 1 for k_q are divided by 1.4. We do not use the perylene data because the error in the lifetime slope is larger than the size of the effect. From eq 12 the quenching interaction range of CS_2 is calculated to be 2 molecular diameters, about 6 Å.

Application of Results

Fluorescence spectroscopy is used in a variety of environmental and industrial applications, especially on systems that contain complex mixtures of fluorophores. For instance, fluorescence methods are used ubiquitiously in the detection and analysis of crude oils and asphaltenes.[13] CS_2 is one of a few good candidate solvents for heavy-end aromatic hydrocarbons. However, energy-dependent quenching induced by CS_2 gives rise to strong spectral distortions, making CS_2 less than desirable as the chosen solvent. Figure 5 shows the fluorescence emission spectra of a light crude oil in toluene with various amounts of CS_2 added. As the CS_2 concentration increases, the blue emission is rapidly reduced while the reddest emission is unaffected. The Stern−Volmer plots of these data yield slopes comparable with those obtained from the pure dyes, illustrating the general nature of our findings.

Conclusions

Strong, energy-dependent quenching of fluorophores by CS_2 is measured. A treatment using a quantum two-level system accounts for the dramatic energy dependence. The off-diagonal coupling interaction energy is found to be 419 cm^{-1}. Comparison of fluorescence lifetime and intensity data shows that the quenching by CS_2 is predominantly diffusion-mediated. Furthermore, these comparisons indicate that the quenching range is ~6 Å. Spectral distortions induced by CS_2 of environmentally important samples are shown, precluding its use for spectral analytical applications.

Glossary

A	absorption coefficient.
c	dye (fluorophore) concentration.
c_{CS_2}, c_d	wave function mixing coefficients corresponding to CS_2 and the dye, respectively.
D_i	diffusion constant of component i.
ΔE	zeroth-order energy difference between two states that undergo quantum mechanical mixing
E_o	excited-state population of the dye in the absence of quenching
E	excited-state population of the dye
ϵ	efficiency of quenching of dyes by CS_2, dependent on the dye HO−LU gap
f_F	fraction of originally excited dye molecules that remain excited after “sphere-of-action” quenching deexcitation. This fraction is subsequently subjected to diffusional quenching.
I_o	intrinsic fluorescence intensity
I	measured fluorescence intensity
J	photon flux
k_{F_o}	intrinsic fluorescence decay rate
k_F	measured fluorescence decay rate
k_D	diffusion rate.
k_q	diffusional quenching rate
M_{CS_2}	concentration of CS_2 in mol/L
n	number of molecules inside sphere with radius R_c.
N_{av}	Avogadro’s number
q	quencher molarity
R_c	sphere-of-action radius
R_{sv}	ratio of Stern−Volmer slopes obtain for intensity data (numerator) vs lifetime (denominator)
S	solvent molarity
τ_{F_o}	intrinsic fluorescence lifetime
τ_F	measured fluorescence lifetime
W_{12}	coupling interaction energy causing wave function mixing

References and Notes

(1) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978.

(2) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983.

(3) Hartings, J. M.; Poon, A.; Xiaoyun, P.; Chang, R. K.; Leslie, T. M. *Chem. Phys. Lett*. **1997**, *281*, 389.

(4) Lalo, C.; Deson, J.; Gédéon, A.; Fraissard, J. *Chem. Phys. Lett*. **1997**, *279*, 230.

(5) Sluch, M. I.; Samuel, I. D. W.; Petty, M. C. *Chem. Phys. Lett*. **1997**, *280*, 315.

(6) Bojarski, P. *Chem. Phys. Lett*. **1997**, *278*, 225.

(7) Vitukhnovsky, A. G.; Sluch, M. I.; Warren, J. G.; Petty, M. C. *Chem. Phys. Lett*. **1991**, *184*, 235.

(8) Holmes, A. S.; Birch, D. J. S.; Suhling, K.; Imhof, R. E.; Salthammer, T.; Dreeskamp, H. *Chem. Phys. Lett*. **1991**, *186*, 189.

(9) Kikuchi, K. *Chem. Phys. Lett*. **1991**, *183*, 103.

(10) Silvers, S. J.; McKeevers, M. R. *Chem. Phys*. **1976**, *18*, 333.

(11) Orita, H.; Morita, H.; Nagakura, S. *Chem. Phys. Lett*. **1981**, *81*, 33.

(12) Gillbro, T.; Cogdell, R. J. *Chem. Phys. Lett*. **1989**, *158*, 312.

(13) Mullins, O. C., Sheu, E. Y., Eds. *The Structures and Dynamics of Asphaltenes*; Plenum Press: New York, 1998.

(14) Lin, J.; Hart, S. J.; Taylor, T. A.; Kenny, J. E. *Proc. SPIE*−*Int. Soc. Opt. Eng*. **1994**, *2367*, 70.

(15) Lohmannsroben, H.-G.; Kauffmann, C.; Roch, Th. *Proc. Europto Ser*., *SPIE* **1997**, *3107*, 305.

(16) Cohen-Tannoudji, C.; Diu, B.; Laloe, F. *Quantum Mechanics*; John Wiley & Sons: New York, 1977.

(17) Berry, R. S.; Rice, S. A.; Ross, J. *Physical Chemistry*; John Wiley & Sons: New York, 1980.

(18) Lide, D. R., Frederikse, H. P. R., Eds. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1996.