Analysis of factors affecting luminescence decays: Concentration distribution of excited molecules in the reaction cell

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A B S T R A C T

An explicit method for calculating the spatial distribution of excited species in the reaction cell is presented. This method is used to analyze the relation between experimental conditions (excitation wavelength, ground state concentration, and laser intensity) and the observed luminescence decays (and the corresponding reaction kinetics) in both transient emission and transient absorption pulse laser photolysis experiments. Subsequently, the analysis was applied to the experimental conditions of previously extensively studied pyrene excimer formation in cyclohexane (J.B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970) and significantly different data were obtained in the redesigned experiment; the excimer formation and decay rate constants at 23.5 °C were found to be $(4.77 \pm 0.04) \times 10^9 \, M^{-1} \, s^{-1}$ and $(2.07 \pm 0.01) \times 10^7 \, s^{-1}$, respectively. Most importantly, the excimer dissociation into a singlet excited pyrene and ground state pyrene was found to be negligible, which is an important result that crucially affects the data processing in many previous and current applications of excimer formation.

1. Introduction

The excited molecules that participate in photochemical reactions are generally produced by excitation using a laser or high intensity flash lamp. We recently showed that an inappropriate choice of excitation wavelength has created an artifact in many studies of the pyrene excimer kinetics [1]. The pyrene excimer kinetics was originally studied by Birks et al. [2]. A hydrogen lamp was used as the excitation source even though the absorbance of pyrene was high in the range of wavelengths produced. Although the authors were not aware, this high absorbance resulted in nonhomogeneous kinetics, a lack of pseudo-first order conditions, and singlet–singlet annihilation. Consequently, mixed order luminescence decays of the pyrene monomer were observed, and the reverse reaction of excimer formation was erroneously included in the reaction scheme to account for the non-exponential decays observed. Birks included these results in his well-known textbook *Photophysics of Aromatic Molecules* [3]. Many other researchers did not consider the effects of the excitation wavelength (commonly choosing lasers with wavelengths that correspond to high extinction coefficients of pyrene) and followed the Birks scheme or slightly adapted it as the pyrene excimer found many biological applications [4–7]. The absence of a discussion of effects of the

distribution of the excited molecules in the reaction cell has propagated all the way to teaching at the undergraduate level. In fact, two educational articles noted the high absorbance of pyrene at 337 nm, but both failed to relate the nonhomogeneous distribution of the excited state to the kinetics [8,9]. Thus, this work provides the theoretical background used to reinvestigate the pyrene excimer kinetics and gives the first comprehensive discussion of the effects of the distribution of the excited state in the reaction cell on observed luminescence decays.

The excitation wavelength is not the only factor that determines the observed luminescence decay. The choice of excitation intensity and ground state concentration also can lead to unwanted artifacts and can determine the applicability of pseudo-first order kinetics. For instance, very high intensities can lead to unwanted reactions such as photo-ionization or singlet–singlet annihilation. The difference between choosing excitation wavelength and choosing intensity/concentration to obtain homogeneous and pseudo-first order kinetics is subtle and is discussed in detail throughout Section 3.

An appropriate selection of experimental factors is critical for studying any photochemical reaction, and the effects of this selection on the observed luminescence decays are not covered in the literature. No textbook on photochemistry includes a detailed discussion of these effects. To fill this void, we elaborate on the application of Beer's law to determine the distribution of the excited states in the reaction cell and its effect on the kinetics observed. In particular, we show how this calculation can be

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applied to transient emission and transient absorption laser photolysis experiments. The analysis discussed is also useful in more complex kinetic models that depend on the statistical distribution of the excited state by allowing for the inclusion of the concentration gradient [4].

2. Experimental section

Pyrene was obtained from Aldrich Chemical Company and was purified by recrystallization from methanol and column chromatography. Cyclohexane (OmniSolv®) was obtained from EMD Millipore and was used as received because it passed spectrophotometric tests. The excitation source used to obtain excited state distribution photographs and perform laser photolysis experiments was an Optical Building Blocks tunable dye laser (model 1012, pulse half-width=0.8 ns, single-shot mode, pumped by a OL-4300 nitrogen laser, 1 mJ/pulse). A 400 nm interference filter and a 500 nm cutoff filter were used in conjunction with a 2 GHz Electro-Optics Technology Inc photodiode (model 23-2618A) and a Tektronix 500 MHz oscilloscope (model TDS 3022B) to observe monomer and excimer emission, respectively. Absorption spectra were obtained using a Cary 4000 Varian UV–vis spectrometer.

3. Results and discussion

3.1. Concentration and distribution of the excited state

In order to study a photochemical reaction, the absorption spectrum of the molecule that will be excited should first be examined. As will be shown, this step is necessary to achieve the appropriate reaction conditions by choice of the excitation wavelength. Using the molar extinction coefficient, ε, obtained from the absorption spectrum and selecting a laser with sufficiently short pulse width (assumed to a be δ-function), the distribution of excited state molecules throughout the reaction cell (assumed 1 cm for all examples) can be calculated using one of the most well-known equations in chemistry, Beer's law. Combining Beer's law with the definition of absorbance gives

$$A = \varepsilon c_g l = -\log_{10}\frac{I}{I_0} \tag{1}$$

where A is the absorbance, l is the penetration depth, c_g is the ground state concentration, I is the intensity at penetration depth l, and I_0 is the intensity at $l=0$. Eq. (1) can be rewritten as

$$I(l) = I_0 10^{-\varepsilon c_g l} \tag{2}$$

The intensity at the distance l from the front cell wall, $I(l)$, is proportional to the total number of photons absorbed by the sample. Further, the number of excited molecules is equal to the number of photons absorbed. Therefore, we can write

$$C(l) = C_0 10^{-\varepsilon c_g l} = C_0 10^{-A} \tag{3}$$

where $C(l)$ is the concentration of the excited state at penetration depth l and C_0 is the initial concentration of the excited state ($l=0$). Fig. 1 shows calculated concentration gradients in a 1 cm cell obtained using Eq. (3) for different absorbance values. As the absorbance increases, the concentration gradient increases with almost all of the excited state molecules at the very front of the cell at high absorbances (the concentration gradient is defined as dC/dl where C is the concentration of the excited molecules and l is the laser beam penetration depth).

The distributions in Fig. 1 can be visualized by observing emission intensity in a sample cell after excitation by a laser pulse. To demonstrate this, solutions of pyrene in decane were
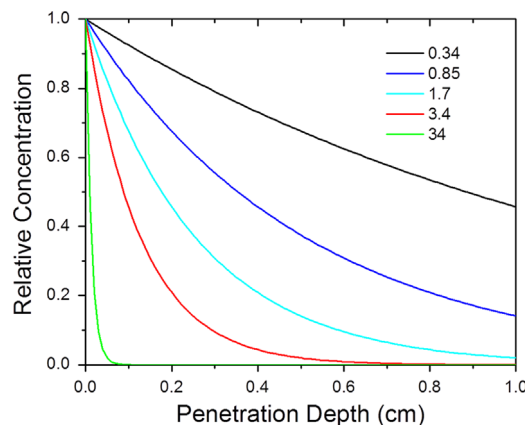

Fig. 1. Distribution of excited molecules within a 1 cm cell as a function of penetration depth corresponding to different absorbance values.

prepared such that the absorbance values at 337 nm are equal to those shown in Fig. 1. The solutions were purged with nitrogen to prevent the decrease of emission intensity due to quenching by oxygen. Fig. 2 shows photographs taken from the side of the cell at a 90° angle from the nitrogen laser beam immediately after excitation (the monomer emission is violet blue while the excimer emission is cyan blue).

In order to apply Eq. (3) to calculate the absolute concentration of the excited state throughout the reaction cell, the initial concentration, C_0, must be determined. Then, Eq. (3) can be used to calculate the absolute concentrations throughout the cell. The total number of photons, n, emitted in a laser pulse is given by

$$n = \frac{E_p\lambda}{hc} \tag{4}$$

where E_p is the pulse energy, λ is the excitation wavelength, h is Planck's constant, and c is the speed of light. Using the fact that all photons must be absorbed in an infinite length, we can obtain

$$\frac{n}{\sigma} = C_0 \int_0^\infty 10^{-\varepsilon c_g l} dl \tag{5}$$

where σ is the cross-sectional area of the pulse, which can be measured in the UV using radiochromic film. It is important, however, to only use the cross-sectional area of the pulse incident with the reaction cell, if the whole pulse is not within the cell. If the distribution of photons in the pulse is not uniform, it may be necessary to perform this calculation over smaller regions that are approximately uniform. Integrating and rearranging Eq. (5) gives

$$C_0 = \frac{n\varepsilon c_g \ln 10}{\sigma} = \frac{E_p\lambda\varepsilon c_g \ln 10}{hc\sigma}. \tag{6}$$

The value of C_0 can then be calculated using only the absorption spectrum and easily measured characteristics of the pulse (E_p, λ, and σ). This value is critical in determining the appropriate excitation wavelength. As will be discussed, the value of C_0 must be known to ensure the applicability of the pseudo-first order kinetics formalism. Fig. 3 shows the absolute concentration gradient corresponding to two different concentrations of pyrene in decane calculated using Eqs. (3) and (6).

3.2. Kinetic consequences

3.2.1. First order reactions

The first order reactions that can be observed after excitation by a laser pulse involve the radiative and nonradiative deactivation of the excited state. We will consider the decay of the singlet