



Monomer-excimer mixed fluorescence decays in the phasor space



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ABSTRACT

Phasor plots (plots of the Fourier sine transform vs. the Fourier cosine transform, for one or several angular frequencies) of the fluorescence intensity decay are being increasingly used in studies of homogeneous and heterogeneous systems. In this work, the phasor approach is applied to monomer-excimer systems with a focus on mixed decays, i.e. decays with both monomer and excimer contributions. The phasors of mixed decays fall on a straight line delimited by the excimer and monomer phasors. With a fixed concentration, and by continuously increasing the emission wavelength, the phasor moves from pure monomer to pure excimer. At a certain intermediate wavelength, which is concentration-dependent, the phasor crosses the universal semicircle and the decay becomes single exponential. This is an interesting case of an exponential decay not corresponding to a single fluorescent species. All results are demonstrated experimentally with pyrene in methylcyclohexane at room temperature, for which a full phasor picture emerges, combining in a single diagram monomer, excimer and mixed decays measured at several concentrations, showing the graphical power of the phasor approach.

1. Introduction

Intermolecular excimer formation and decay is a well-known photochemical process, whose time-evolution following a flash (exciting the monomer) implies the existence of a rise-time in the respective fluorescence “decay”.

A *luminescence decay function*, $I(t)$, is the function describing the time dependence of the intensity of radiation spontaneously emitted at a given wavelength, by a previously excited sample. For convenience, and without loss of generality, the decay function can be area normalized,

$$E(t) = \frac{I(t)}{\int_0^\infty I(t) dt} \quad (1)$$

This definition has the advantage of including “decay” functions that start from zero, as occurs with excimers and other electronically excited products of photochemical processes. The function $E(t)$ has the meaning of the emission probability of a photon between t and $t + dt$, given that the photon was emitted.

The cosine and sine Fourier transforms of $E(t)$, $G(\omega)$ and $S(\omega)$, respectively, are defined by [1–4]

$$G[E] = G(\omega) = \int_0^\infty \cos(\omega u) E(u) du \quad (2)$$

$$S[E] = S(\omega) = \int_0^\infty \sin(\omega u) E(u) du \quad (3)$$

where ω is the angular frequency.

Each decay function, for a given frequency, is mapped onto a point inside the unit circle defined by $G^2 + S^2 = 1$, called the *phasor space*, see Fig. 1. It also follows from Eqs. (2) and (3) that $G(0) = 1$ and $S(0) = 0$, whereas $S(\infty) = G(\infty) = 0$, see Fig. 1. The universal semicircle [2–4], located in the first quadrant, and given by

$$S = \sqrt{G(1 - G)} \quad (4)$$

defines the loci of all exponential decays. Other decay functions follow different paths between the two extreme points ($\omega = 0$ and $\omega = \infty$), when going from zero to infinite frequency. The outer boundary for two-exponential decays, located in the first and second quadrants, is given by Eqs. (5) and (6) [5,6],

$$S^+(G) = \frac{1}{8} (3 - \sqrt{1 + 8G})^{1/2} (1 + \sqrt{1 + 8G})^{3/2} (-1/8 < G < 1) \quad (5)$$

$$S^-(G) = \frac{1}{8} (3 + \sqrt{1 + 8G})^{1/2} (1 - \sqrt{1 + 8G})^{3/2} (-1/8 < G < 0) \quad (6)$$

which are the upper (S^+) and lower (S^-) branches of the curve.

For a given frequency, the (G, S) pair defines a point or, equivalently, a vector $\mathbf{P}(\omega) = G(\omega) \mathbf{e}_1 + S(\omega) \mathbf{e}_2$, called the *phase vector* or *phasor*. This vector is the basis of the *phasor approach* to time-resolved

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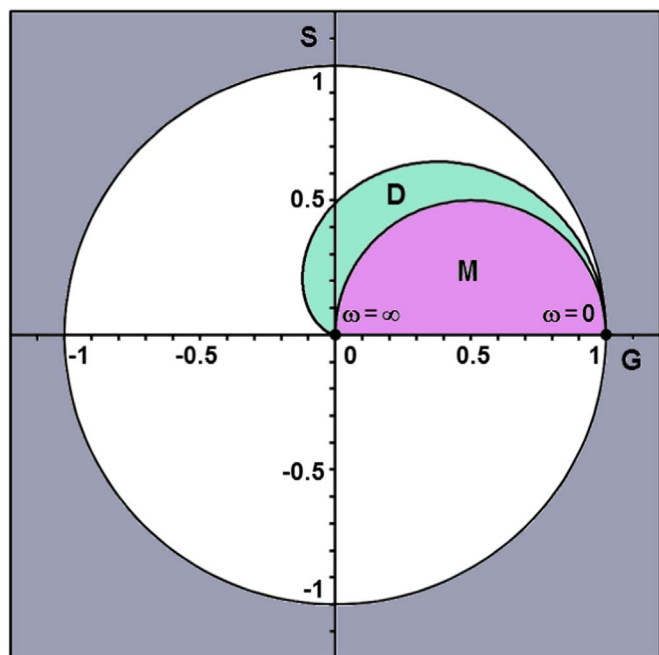


Fig. 1. The phasor space (unit circle), the universal semicircle and the outer boundary curve for two-exponential decays. Also shown are the (truly) universal points corresponding to all decay functions for zero and infinite frequencies. Monomer (M) phasors fall in the violet area whereas excimer (D) phasors fall in greenish blue one [6]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

luminescence (mainly fluorescence) [2–28], which provides a simple graphical and model-independent (when using experimental data) portrait of the kinetic properties of a system. Processes such as quenching, solvent relaxation, energy transfer and excimer formation are defined by characteristic trajectories in the plane (at a fixed frequency or using several frequencies).

When the measurement technique used is frequency domain fluorimetry, based on sinusoidally modulated excitation, G and S are directly related to the two parameters obtained for each frequency, which are the modulation ratio, M , and the phase shift, Φ , by $G = M \cos \Phi$ and $S = M \sin \Phi$, hence $\tan \Phi = S/G$ and $M = |P| = \sqrt{G^2 + S^2}$ [1–4].

When the measurement technique used is time domain fluorimetry, the phasor must be computed (numerically or analytically) from the measured decay according to Eqs. (2) and (3), at a conveniently chosen frequency (or set of frequencies). This decay is often distorted by the instrument response function (IRF), and the effect can be significant in phasor plots [28]. In order to remove its effect, the experimental decay can be fitted with an empirical decay law, e.g. a sum of exponentials, from which the sine and cosine transforms are then computed. An alternative correction procedure was described recently [28].

The precise location of the decay in the plane, defined by its phasor, is a function of frequency and decay characteristics. Single exponential decays lie on the universal (semi)circle, as mentioned. Complex decays usually, but not always, fall inside it [5]. In the common case of a two-exponential decay with positive amplitudes, the corresponding point falls on a straight line (“tie line”) connecting the phasors of the two components [2–5]. Analogously to the lever rule of thermodynamic phase diagrams, the fractional contribution of each of the two components to the total intensity is given by the length of the segment connecting the decay point (“average lifetime”) to the opposite component, divided by the length of the full segment uniting the two extreme points (components) [2–5,10–12,16].

Monomer-excimer kinetics was recently studied within the phasor framework [6]. The monomer phasor falls inside the universal circle,

whereas the excimer phasor lies outside it, but within the double exponential outer boundary curve, Fig. 1. The monomer and excimer phasors, along with those corresponding to the two exponential components of the decays, fall on a common straight line and obey the generalized lever rule [6].

The purpose of the present work is to study decays containing both monomer and excimer contributions (mixed decays) according to the phasor approach, both theoretically and experimentally.

2. Experimental section

2.1. Materials

Pyrene was from Koch-Light Laboratories (pure) and methylcyclohexane (MCH) (99%, spectrophotometric grade) was from Sigma-Aldrich.

2.2. Methods

Absorption spectra were recorded on a UV-3101PC UV–vis–NIR spectrophotometer. Fluorescence spectra were obtained with a Fluorolog F112A fluorimeter in right-angle (dilute solutions) or front-face (remaining solutions) configurations. Emission spectra were corrected for the spectral response of the optics and photomultiplier. The excitation wavelength was always 335 nm, and the excitation and emission slits were 9 nm and 4.5 nm, respectively. Time-resolved fluorescence intensity decays were obtained by the single-photon timing method with laser excitation and microchannel plate detection, with the set-up already described [23]. Briefly, the set-up consisted of a mode locked DPSS Nd:YVO₄ green laser (Vanguard 2000-HM532, Spectra Physics) synchronously pumping a cavity dumped dye laser (701, Coherent, delivering frequency-doubled 3–4 ps pulses of about 40 nJ/pulse at 3.4 MHz) working with DCM. Intensity decay measurements were made by an alternating collection of impulses and decays with the emission polarizer set at the magic angle position. Impulses were recorded slightly away from the excitation wavelength with a scattering suspension, thus defining the instrument response function (IRF). For the decays, a cut-off filter was used to effectively remove excitation light. Emission light was passed through a depolarizer before reaching the monochromator (Jobin-Yvon HR320 with a 100 lines mm⁻¹ grating) and detected using a Hamamatsu 2809U-01 microchannel plate photomultiplier. Excitation wavelength was 335 nm and the emission wavelengths (2 nm bandwidth) were between 380 nm (pure monomer) and 540 nm (pure excimer). A front-face geometry was used except for the dilute solutions. Accumulation conditions were typical of fluorescence lifetime measurements, with no fewer than 10,000 counts in the maximum channel, using 1024 channels. The timescale varied between 425 ps/channel for the fastest decays (2.2 mM solution) and 2 ns/channel for the slowest ones. Degassing, immediately prior to measurement, was achieved by bubbling argon previously saturated in MCH vapor.

3. Results and discussion

3.1. Monomer-excimer kinetics: general results

Intermolecular excimer formation kinetics is described by the kinetic scheme [3,29,30]:

In nonviscous solvents, where diffusional transient effects are negligible, the solution of the rate equations corresponding to Scheme 1 (“Birks’ kinetics”) is well-known [3,29]:

$$[M^*](t) = \frac{[M^*]_0}{\lambda_2 - \lambda_1} [(\lambda_2 - X) e^{-\lambda_1 t} + (X - \lambda_1) e^{-\lambda_2 t}] \quad (7)$$

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