

Distinctive characteristics of the decay function for phosphorescence in the presence of reabsorption

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Received: 24 April 2014 / Accepted: 14 June 2014 / Published online: 11 July 2014
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Abstract The phosphorescence decay under the effect of significant excited-state absorption has a distinctive signature: it is initially concave, switching to convex (pure exponential decay) after a certain time. A simple one-parameter decay function satisfactorily reproducing the experimental decays is discussed, and some of its peculiar mathematical properties analyzed.

Keywords Luminescence decay · Relaxation function · Inverse Laplace transform · Kinetics

Mathematics Subject Classification 44A10 Laplace transform · 78A10 physical optics

1 Introduction

The time evolution of the intensity of light spontaneously emitted by a sample after excitation (usually optical) is called luminescence decay. This emission is recorded for a narrow wavelength range, and results, in general, from a sum of weighted contributions of several emitting species. The mathematical function describing the decay, $I(t)$, is called the decay law or *decay function*. For convenience, this function is usually normalized at $t = 0$. In favorable situations, the decay function follows from a detailed model, but such a model is not always available and it may happen that an empirical decay function embodies all that is known (at a certain stage) about the luminescence kinetics of a particular system.

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The luminescence decay can always be written in the following form [1]:

$$I(t) = \int_0^{\infty} g(k)e^{-kt} dk, \quad (1)$$

with $I(0) = 1$. This relation is valid as $I(t)$, understood here as a monotonic function with a finite “light sum” ($\int_0^{\infty} I(t)dt$, proportional to the total number of light quanta emitted) always has an inverse Laplace transform, $g(k)$. The function $g(k)$, also called the *eigenvalue spectrum*, is normalized, as $I(0) = 1$ implies $\int_0^{\infty} g(k)dk = 1$. In many situations the function $g(k)$ is nonnegative for all $k > 0$, and $g(k)$ can be regarded as a distribution of rate constants (strictly, a probability density function) [1–3]. It was previously shown [2] that this is always the case for *completely monotonic functions*, i.e., functions for which

$$(-1)^n I^{(n)}(t) > 0 \quad (n = 0, 1, 2, \dots). \quad (2)$$

However, in a few cases the decay function does not comply with this definition and the respective $g(k)$ also takes negative values [2,3]. An even more extreme case is disclosed here: A physically relevant and *stricto sensu* (i.e. monotonic) decay function that nevertheless does not always have a computable inverse Laplace transform.

2 A decay function for phosphorescence reabsorption

Phosphorescence photons are usually emitted by molecules in the triplet state. If the phosphorescence spectrum overlaps the triplet–triplet absorption spectrum of the same substance, part of these photons are reabsorbed [4–6]. The effect can be significant for high triplet concentrations. However, and following pulsed excitation, the triplet concentration continuously decreases with time. In this way, the reabsorption probability decreases continuously and approaches zero for sufficiently long times. As a consequence, the phosphorescence decay asymptotically approaches an exponential function governed by the intrinsic phosphorescence lifetime, τ_P . This characteristic trait of phosphorescence reabsorption leads to a unique type of decay with an initial concave part [4,6] see Fig. 1.

A simple decay function that describes with very good accuracy experimental phosphorescence decays in the presence of excited-state absorption is

$$P(t) = \frac{1}{a + (1 - a) \exp\left(\frac{t}{\tau_P}\right)}, \quad (3)$$

where $P(t)$ is the phosphorescence intensity and a is a dimensionless parameter accounting for reabsorption, $1 > a \geq 0$, see Fig. 2. For very small a , i.e. negligible reabsorption, Eq. 3 reduces to an exponential decay. The same occurs for sufficiently long times irrespective of the value of a .

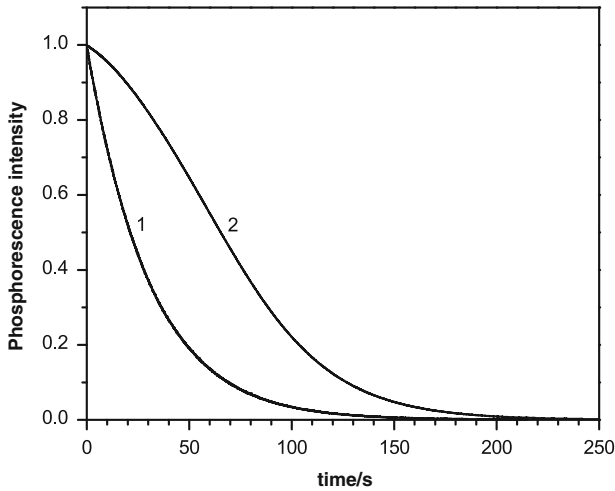


Fig. 1 Experimental phosphorescence decays of perdeuterated coronene in a polymer film at 77 K, in the absence (1) and presence (2) of excited-state reabsorption. In the absence of reabsorption the decay is exponential, with a lifetime of 29 s. In the presence of reabsorption, the decay displays a characteristic initial concave part, but remains asymptotically exponential, with the intrinsic decay time (29 s)

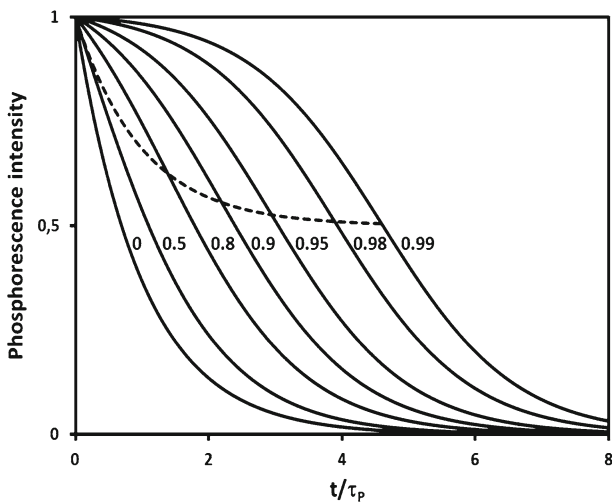


Fig. 2 Phosphorescence decay function, Eq. 3. The value next to each curve is the respective a parameter. The dashed line is formed by the loci of the inflection points t_i , dividing the concave ($t < t_i$) and convex ($t > t_i$) parts of the decay function

The fitting of Eq. 3 to an experimental phosphorescence decay with strong reabsorption ($a = 0.88$) is shown in Fig. 3. It is seen that the fit, although not perfect (residuals plot deviates from white noise), is quite satisfactory, as the residuals are very small. The general adequacy of the function was confirmed by fitting several phosphorescence decays with various degrees of reabsorption (not shown).

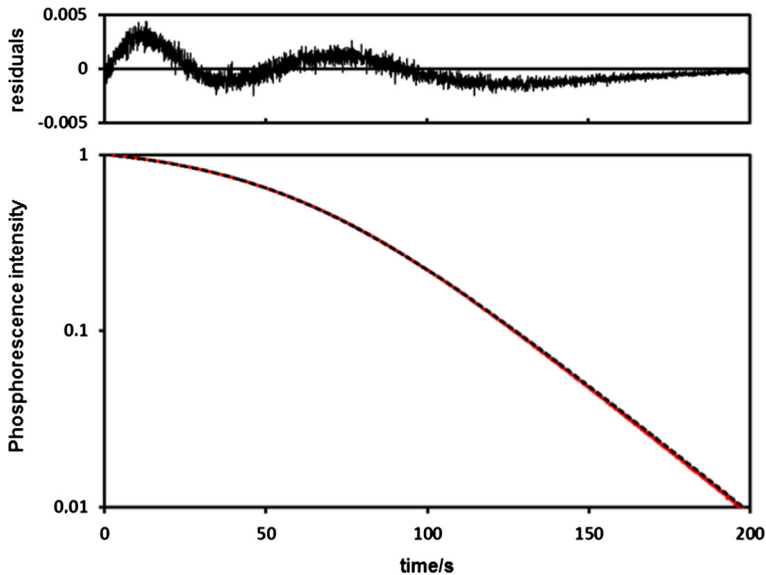


Fig. 3 Fitting of the phosphorescence decay function, Eq. 3 (black dash), to the phosphorescence decay (red line) corresponding to curve 2 of Fig. 1, where strong reabsorption occurs. Fitted reabsorption parameter by nonlinear least-squares was $a = 0.88$ (phosphorescence lifetime was fixed at the intrinsic value, 29 s) (Color figure online)

3 Further mathematical properties of the phosphorescence decay function

The phosphorescence decay function Eq. 3 has an inflexion point at $\frac{t}{\tau_P} = \ln\left(\frac{a}{1-a}\right)$ for $1 > a > 1/2$, where it takes the value $P = 1/(2a)$ and switches from concave to convex shape, see Fig. 2.

The decay function is well-behaved, in the sense that its integration over time is finite [2, 3],

$$\int_0^{\infty} \frac{dt}{a + (1-a) \exp\left(\frac{t}{\tau_P}\right)} = \frac{\tau_P}{a} \ln\left(\frac{1}{1-a}\right). \quad (4)$$

This result is useful in cases where the phosphorescence decay is described by a sum of terms of the type of Eq. 3, as it is necessary for the calculation of the respective fractional contributions.

The decay function given by Eq. 3 cannot be represented by a distribution of rate constants. Indeed, it is not a completely monotonic function of time, which is a necessary condition, as mentioned in the Introduction. This can be shown explicitly by rewriting Eq. 3 and performing a series expansion in powers of $\exp\left(-\frac{t}{\tau_P}\right)$:

$$P(t) = \frac{1}{1-a} \frac{\exp\left(-\frac{t}{\tau_P}\right)}{1 + \alpha \exp\left(-\frac{t}{\tau_P}\right)} = \frac{1}{1-a} \sum_{n=1}^{\infty} (-\alpha)^{n-1} \exp\left(-\frac{nt}{\tau_P}\right), \quad (5)$$

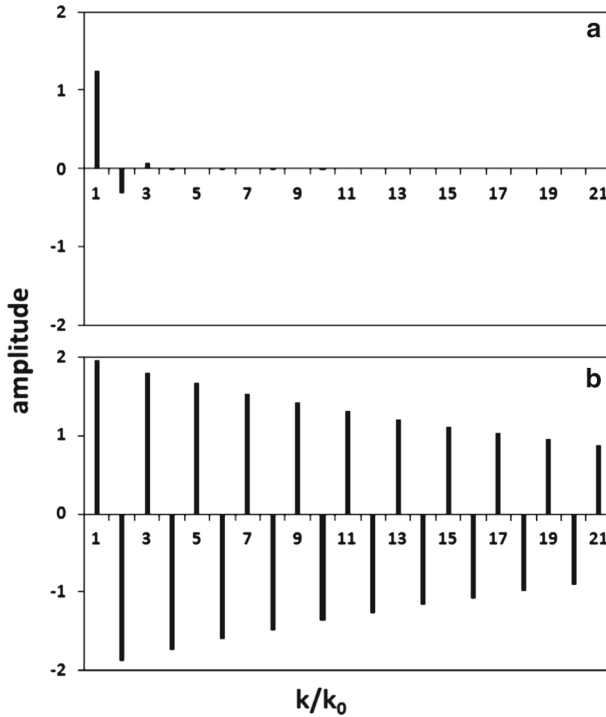


Fig. 4 The amplitude spectrum for: **a** $a = 0.2$ and **b** $a = 0.49$

where $\alpha = a/(1 - a)$. For $a \leq 0.1$ the decay is well represented by the sum of the first three exponentials, but no less than fifteen terms (exponentials) are already needed when $a = 0.4$.

Termwise Laplace transform inversion of Eq. 5 yields, with $k_0 = 1/\tau_p$,

$$g(k) = \frac{1}{1 - a} \sum_{n=1}^{\infty} (-\alpha)^{n-1} \delta(k - nk_0), \tag{6}$$

where $g(k)$ is the inverse Laplace transform of $P(t)$, cf. Eq. 1.

It follows from Eq. 6 that $g(k)$ is given by an alternating series of delta functions, i.e., the rate constant spectrum is infinite and discrete, with monotonically decreasing amplitudes, but alternating between positive and negative values, Fig. 4.

Nevertheless, this result holds only for $a \leq 0.5$. For $a > 0.5$ the decay function no longer has a computable inverse Laplace transform, as the series expansion, Eq. 5, is convergent only after the inflection point, $t_i = \tau_p \ln\left(\frac{a}{1-a}\right)$ (the decay function is concave for $t < t_i$ and convex afterwards).

For shorter times the decay is represented instead by a series in powers of $\exp\left(\frac{t}{\tau_p}\right)$,

$$P(t) = \frac{1}{1 + (1 - a)\left(e^{\frac{t}{\tau_p}} - 1\right)} = \sum_{n=0}^{\infty} \left[-(1 - a)\left(e^{\frac{t}{\tau_p}} - 1\right)\right]^n, \tag{7}$$

which, in turn, is convergent for $\frac{t}{\tau_P} < \ln\left(\frac{2-a}{1-a}\right)$. In this way, the two series are valid in a common narrow interval, $\ln\left(\frac{a}{1-a}\right) < \frac{t}{\tau_P} < \ln\left(\frac{2-a}{1-a}\right)$.

Using an analytical inversion formula [7], it is possible to obtain a formal inverse Laplace transform for the decay function, valid for any value of the a parameter,

$$g(k) = \frac{2(1-a)\tau_P}{\pi} \int_0^{\infty} \frac{\sin \omega \sin(k\tau_P\omega) d\omega}{a^2 + 2a(1-a)\cos \omega + (1-a)^2} \quad a \in [0, 1[, \quad (8)$$

however this representation does not appear to be amenable to numerical computation.

4 Conclusions

A simple one-parameter decay function satisfactorily reproducing phosphorescence decays under the effect of excited-state absorption (triplet–triplet absorption) was discussed, and some of its peculiar mathematical properties analyzed, including the initial concavity and the inverse Laplace transform.

Acknowledgments This work was carried out within projects PTDC/QUI–QUI/123162/2010 and RECI/CTM-POL/0342/2012 (FCT, Portugal). TP was supported by a research grant from project PTDC/QUI–QUI/123162/2010 (FCT, Portugal).

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