The time dependence of rate coefficients and fluorescence anisotropy for non-delta production

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The time dependence of rate coefficients and fluorescence anisotropy for a general production rate is obtained in a common equation. Steady-state and phase-modulation results are recovered as special cases. Some implications of the results obtained are discussed.

1. Introduction

Quantities arising in luminescence spectroscopy such as fluorescence anisotropy r and rate coefficients k are generally time-dependent functions for the case of delta-function production of the respective excited species.

The time dependence of the anisotropy is usually due to rotational motion of the emitter [1] or to electronic energy transport [2] while the rate coefficient dependence on time may result, for instance, from diffusion influenced collisional quenching [3] or electronic energy transfer [4]. The anisotropy and rate coefficients pertaining to delta-impulse excitation conditions will be denoted by $r_\delta(t)$ and $k_\delta(t)$.

For a general production rate $P(t)$, the respective anisotropy r and rate coefficient k differ from r_δ and k_δ. An obvious case is the steady state achieved for continuous production, where the quantities $\bar{r}$ and $\bar{k}$ are even time independent. While particular relations for $\bar{r}$ and $\bar{k}$ have long been known [5,6], the general equation for the production rate dependence of rate coefficients was only recently obtained [7]. On the other hand, the explicit connection between anisotropy and production rate appears not to exist in the literature in a general fashion, although the necessary relations are well known.

In this work, it is shown that the equation obtained for rate coefficients [7] is also valid for fluorescence anisotropy. Some implications are discussed.

2. The production rate dependence equation

The production rate dependence of rate coefficients was obtained in [7] as

$$k = \frac{P \otimes (k_\delta f)}{P \otimes f}, \tag{1}$$

where $\otimes$ stands for convolution and f is the survival probability of the excited species following delta-function production.

We now give for eq. (1) a simple interpretation, by merely rewriting it as

$$k = \int_0^t w(t, t_0) k_\delta(t - t_0) \, dt_0, \tag{2}$$

where

$$w(t, t_0) = \frac{P(t_0) f(t - t_0)}{\int_0^t P(t_0) f(t - t_0) \, dt_0}. \tag{3}$$

The function $w(t, t_0)$ is recognized as the fraction of emitters present at time t that was produced at time t_0. Therefore, the rate coefficient k is but the weighted average of time-shifted rate coefficients k_δ.

This additivity of rate coefficients, expressed in eq. (2), is not totally surprising, as it is already embodied in the starting convolution relation [7] $A = P \otimes f$, A being the excited species population.

Given the additive nature of anisotropy [8] and the above discussion, it is apparent that eq. (2) also applies to this function; hence

$$r = \frac{P \otimes (r_\delta f)}{P \otimes f}, \tag{4}$$

and for a mixture of n excited species, eq. (4) generalizes to

$$r = \frac{P \otimes \left(\sum_{i=1}^n \kappa_{ri} N_{0i} r_{i\delta} f_i \right)}{P \otimes \left(\sum_{i=1}^n \kappa_{ri} N_{0i} f_i \right)} = \frac{P \otimes \left(\sum_{i=1}^n \alpha_i r_{i\delta} f_i \right)}{P \otimes \left(\sum_{i=1}^n \alpha_i f_i \right)}, \tag{5}$$

where κ_{ri} and N_{0i} are the radiative rate constant and the initial number of the ith species, respectively, and α_i are the respective pre-exponential factors in the global decay law.

For excitation with vertical polarization, the anisotropy is defined as [8,9]

$$r(t) = \frac{I_\parallel(t) - I_\perp(t)}{I_\parallel(t) + 2I_\perp(t)}, \tag{6}$$

where $I_\parallel$ is the emission intensity component that is vertically polarized and $I_\perp$ is the horizontally polarized remainder. The denominator in eq. (6) is proportional to the excited state population [8,9]

$$I_\parallel + 2I_\perp = \alpha P \otimes f, \tag{7}$$

where α is a constant. It follows from eqs. (4)–(7) that

$$I_\parallel = \alpha/3 P \otimes \left[f(1 + 2r_\delta) \right], \tag{8}$$

$$I_\perp = \alpha/3 P \otimes \left[f(1 - r_\delta) \right]. \tag{9}$$

3. Special cases

Specific forms for the production rate $P(t)$ are now considered.

Steady-state

The steady state is conveniently obtained by making $P(t) = U(t)$, $U(t)$ being the step function, and taking the limit $t \to \infty$ in eq. (1). One obtains

$$\bar{k} = \frac{\int_0^\infty k_\delta(u) f(u) \, du}{\int_0^\infty f(u) \, du}, \tag{10}$$

with a similar equation being valid for the steady state anisotropy,

$$\bar{r} = \frac{\int_0^\infty r_\delta(u) f(u) \, du}{\int_0^\infty f(u) \, du}. \tag{11}$$

The survival probability $f(t)$ can often be written as

$$f(t) = \exp(-\Gamma t) \exp\left(-\int_0^t k_\delta(u) \, du\right), \tag{12}$$

where Γ is the decay constant, e.g. the inverse lifetime, $1/\tau$, if k_δ refers to external processes of quenching or the radiative rate constant, k_r, if k_δ refers to the nonradiative rate coefficient. In some cases the intrinsic decay is strongly nonexponential owing to the time dependence of the nonradiative rate decay coefficient, as with small molecules in the gas phase (quantum beats) [10] or some dyes in fluid media (torsional relaxation) [11]. In these situations, the steady-state nonradiative rate constant is obtained by substituting eq. (12) for $f(t)$ in eq. (10), yielding

$$\bar{k}_{nr} = \frac{1}{\int_0^\infty f(u) \, du} - k_r. \tag{13}$$

The fluorescence quantum yield, as obtained in steady-state measurements, is therefore given by [12]

$$\Phi_f = \frac{k_r}{k_r + \bar{k}_{nr}} = k_r \int_0^\infty f(u) \, du. \tag{14}$$

The information obtainable from steady-state measurements on nonradiative processes is therefore limited to its average rate coefficient $\bar{k}_{nr}$. On the other hand, simultaneous determination of the fluorescence quantum yield and of the decay function $f(t)$ enables one to calculate the radiative rate constant, regardless of the form of $f(t)$, cf. eq. (14).

The previous relations also apply in the case of external quenching processes. Assuming for simplicity that the intrinsic decay is single exponential, i.e. characterized by a lifetime τ, one obtains the analogue of eq. (13)

$$\bar{k} = \frac{1}{\int_0^\infty f(u) \, du} - \frac{1}{\tau}, \tag{15}$$

and a generalized Stern–Volmer relation

$$\frac{\Phi_f^0}{\Phi_f} = 1 + \bar{k}\tau, \tag{16}$$

where Φ_f^0 is the fluorescence quantum yield in the absence of quenching, $\Phi_f^0 = k_r \tau$. This generalized Stern–Volmer relation applies to quenching processes where transient effects are important and implies nonlinear plots of Φ_f^0/Φ_f versus quencher concentration.

Harmonic production

The production rate used in phase-modulation fluorometry is composed of a sinusoidal term added to a constant background,

$$P(t) = 1 + m \cos \omega t, \tag{17}$$

m being the modulation and ω the circular frequency.

Using eqs. (8) and (9) one obtains, for all times of interest,

$$I_{\parallel} = \int_0^{\infty} I_{\parallel\delta}(u)\,\mathrm{d}u + m\left(F_{\mathrm{c}}\left[I_{\parallel\delta}\right]\cos\omega t + F_{\mathrm{s}}\left[I_{\parallel\delta}\right]\sin\omega t\right), \tag{18}$$

$$I_{\perp} = \int_0^{\infty} I_{\perp\delta}(u)\,\mathrm{d}u + m\left(F_{\mathrm{c}}[I_{\perp\delta}]\cos\omega t + F_{\mathrm{s}}[I_{\perp\delta}]\sin\omega t\right), \tag{19}$$

where F_{c} and F_{s} stand for the Fourier cosine and sine transforms, respectively. From eq. (5) the frequency-dependent anisotropy becomes

$$r_{\omega} = \frac{\displaystyle\int_0^{\infty} r_{\delta}f\,\mathrm{d}u + m\left(F_{\mathrm{c}}[r_{\delta}f]\cos\omega t + F_{\mathrm{s}}[r_{\delta}f]\sin\omega t\right)}{\displaystyle\int_0^{\infty} f\,\mathrm{d}u + m\left(F_{\mathrm{c}}[f]\cos\omega t + F_{\mathrm{s}}[f]\sin\omega t\right)}. \tag{20}$$

However, in phase-modulation fluorometry the only observables are the phase ϕ and the modulation m for each polarized component [13]

$$I_{\parallel} = C_{\parallel}\left[1 + m_{\parallel}\cos(\omega t - \phi_{\parallel})\right], \tag{21}$$

$$I_{\perp} = C_{\perp}\left[1 + m_{\perp}\cos(\omega t - \phi_{\perp})\right], \tag{22}$$

$C_{\parallel}$ and $C_{\perp}$ being constants. Comparison of eq. (18) with eq. (21) yields

$$\tan\phi_{\parallel} = \frac{F_{\mathrm{s}}\left[I_{\parallel\delta}\right]}{F_{\mathrm{c}}\left[I_{\parallel\delta}\right]}, \tag{23}$$

$$\frac{m_{\parallel}}{m} = \left(F_{\mathrm{c}}\left[I_{\parallel\delta}\right]^2 + F_{\mathrm{s}}\left[I_{\parallel\delta}\right]^2\right)^{1/2} \Big/ \int_0^{\infty} I_{\parallel\delta}(u)\,\mathrm{d}u. \tag{24}$$

Analogous relations are obtained for the perpendicular component. From eq. (23) and the corresponding one for $\phi_{\perp}$ it is found that

$$F_{\mathrm{s}}[r_{\delta}f] = \frac{1}{2(\tan\phi_{\parallel} - \tan\phi_{\perp})}\left[(2\tan\phi_{\parallel} + \tan\phi_{\perp})F_{\mathrm{s}}[f] - 3\tan\phi_{\parallel}\tan\phi_{\perp}F_{\mathrm{c}}[f]\right], \tag{25}$$

$$F_{\mathrm{c}}[r_{\delta}f] = \frac{1}{2(\tan\phi_{\parallel} - \tan\phi_{\perp})}\left[3F_{\mathrm{s}}[f] - (\tan\phi_{\parallel} + 2\tan\phi_{\perp})F_{\mathrm{c}}[f]\right]. \tag{26}$$

A plot of the Fourier transform pairs, one for each frequency, would be the analogue of the well known Cole–Cole plot in electric polarization [14], thus providing model independent information on depolarization (e.g., rotational dynamics). Plots of the Fourier sine transform multiplied or divided by the frequency as a function of the cosine Fourier transform, as used in electric polarization studies [15] are also possible. For instance, if f and r_{δ} are exponential functions of time

$$f(t) = \mathrm{e}^{-t/\tau}, \tag{27}$$

$$r_{\delta}(t) = r_0\,\mathrm{e}^{-t/\tau_{\mathrm{r}}}, \tag{28}$$

one obtains the following linear relationships

$$\frac{F_{\mathrm{s}}[r_{\delta}f]}{\omega} = \frac{1}{a}F_{\mathrm{c}}[r_{\delta}f], \tag{29}$$

$$\omega F_{\mathrm{s}}[r_{\delta}f] = r_0 - aF_{\mathrm{c}}[r_{\delta}f], \tag{30}$$

where

$$a = \frac{1}{\tau} + \frac{1}{\tau_r}. \tag{31}$$

These plots allow a straightforward evaluation of the fundamental anisotropy r_0 and rotational correlation time τ_r, whereas deviations to straight lines indicate more complex decays arising, for example, from anisotropic rotational motion [1].

4. Conclusions

The production rate dependence of rate coefficients was shown to be applicable also to fluorescence anisotropy. Some relations derived from it suggest alternative or complementary data analysis procedures for the phase-modulation technique.

Acknowledgement

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[12] Bagchi and Fleming [11] obtained recently an equation similar to eq. (14), which they claim to be approximate. In fact their equation is not correct only because the radiative rate constant is added twice in the denominator.

[13] Often, the phase difference $\phi_\perp - \phi_\parallel$ and the amplitude ratio $m_\parallel / m_\perp$ are the only quantities determined, see, e.g., J.R. Lakowicz, G. Laczko, I. Gryczynski, H. Szmacinski and W. Wiczk, Ber. Bunsenges. Phys. Chem. 93 (1989) 316.

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