Journal of Fluorescence, Vol. 16, No. 2, March 2006 (© 2006)
DOI: 10.1007/s10895-005-0052-x

Fluorescence Decays and Photon Propagation Times

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Received October 31, 2005; accepted December 16, 2005

The effect of the time of flight of the exciting and emitted photons on fluorescence decays is studied. Experimental results for a long lifetime molecule (coronene) are analysed according to the fluorescence decay law previously obtained by the authors. The developed model accounts well for the main features of the observations. The inclusion of photon propagation times is essential for a correct description of the fluorescence decays under the described circumstances.

KEY WORDS: Fluorescence decays; photon propagation times; single photon timing; coronene.

INTRODUCTION

The space and time scales of most laboratory fluorescence measurements are such that it is appropriate to neglect the finiteness of the speed of light, which is approximately 0.3 mm/ps in a vacuum, and a little less in common solvents, e.g. 0.23 mm/ps in water for visible radiation. The propagation time of radiation is on the other hand at the heart of both Rayleigh and fluorescence LIDAR (Light Detection And Ranging) techniques [1] employed in environmental and atmospheric studies. In these techniques it is the fluorescence lifetime role that is negligible.

However, when dealing with very short time scales (femtoseconds) and/or extended laboratory systems (more than a few centimetres in linear dimension) in the nanosecond or picosecond range, both the fluorescence lifetimes and the propagation time of radiation are important.

We have previously considered the effect of the time of flight of the photons in a mainly qualitative way in the context of atomic and molecular radiative transfer [2, 3], and quantitatively for two specific excitation-detection geometries [4]. The model developed was successfully applied to a system with an intermediate fluorescence lifetime (Rhodamine 101 solution) and to a purely scattering system (suspension of silica nanoparticles) [4]. We also showed that from the time dependence of the recorded signal (fluorescence or back-scattered light) the absorption or scattering coefficient of the sensed medium can be determined [4].

In this work we summarize the effect of the time of flight of the photons on fluorescence decays. Fluorescence decay laws are given for two model geometries, one spherical, and another linear. Experimental results (coronene) are obtained for the linear case, and analysed according to the developed model. It is shown that the model accounts well for the main features of the recorded decays, and that the inclusion of photon propagation times is essential for a correct description of fluorescence decays under the described circumstances. Radiation propagation times cannot also be neglected in millimetre-sized systems when times shorter than a few picoseconds are concerned.

EXPERIMENTAL

Systems Studied

The system studied was a solution of coronene, Scheme 1, in ethanol, with a concentration of 1.3×10^{-7} M. Coronene (hexabenzobenzene, Koch-Light Laboratories Ltd) and ethanol (Merck, spectroscopic grade) were used as supplied.

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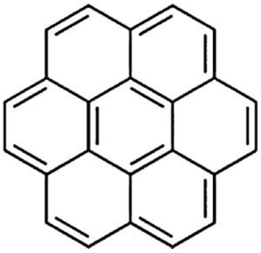

Scheme 1.

Fluorescence Measurements

A glass cylindrical tube with a quartz wall, with an inner radius of 1.8 and 120 cm length was filled with the solution. The excitation and detection geometry is shown in Fig. 1. The excitation beam, initially at a right angle with the tube, is redirected into the tube, along its axis, by means of a small mirror, located 3 cm away from the tube wall. The fluorescence emission is collected with a large lens, placed along the cylinder axis and 10 cm away from the tube end.

Time resolved picosecond fluorescence measurements were performed using the single–photon timing method with laser excitation. The set-up consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye (Rhodamine 6G) laser, delivering frequency-doubled 5 ps pulses at a repetition rate of 3.4 MHz. Intensity decay measurements were made by alternate collection of impulse and decay, with the emission polarizer set at the magic angle position. Impulse was recorded slightly away from excitation wavelength with a scattering suspension (1 cm cell). For the decays, a WG360 Corion cut-off filter was used, effectively removing all excitation light. The coronene solution was excited at 300 nm, and the fluorescence emission recorded at 446 nm. The emission signal passed through a depolarizer, a Jobin-Yvon HR320 monochromator with a grating of 100 lines/nm, and was recorded on a Hamamatsu 2809U-01 microchannel plate photomultiplier as a detector. A time scale of 104.4 ps/channel was used. The instrument response function had an effective FWHM of 35 ps.

MODEL GEOMETRIES

We have previously shown that the fluorescence decay for a spherical medium, with an isotropic delta excitation source (with radius r_0) and the detector located in the centre, is given by [4]

$$I(t) = \exp(-t/\tau) \int_{r_0}^{R(t)} \frac{\exp[(2/(v\tau) - \beta)r]}{4\pi r^2}\, dr \qquad (1)$$

where $R(t)$ is given by

$$R(t) = \begin{cases} r_0 + \frac{vt}{2} & \text{if } t < 2R_s/v \\ R_s & \text{if } t \geq 2R_s/v \end{cases} \qquad (2)$$

R_s being the radius of the sphere. In Eq. (1), τ is the fluorescence lifetime, v is the speed of light in the medium, β is the absorption coefficient at the excitation wavelength and r the distance from the centre. The maximum round-trip time $t_r = 2R_s/v$ is a characteristic photon propagation time for the system.

The spherical model geometry is the simplest situation possible, but is not a common one. A more realistic case occurs when the detector is located outside the medium, usually at a considerable distance from the boundary. We then addressed the quasi-one-dimensional case depicted in Fig. 1, where excitation is linear (light beam originating from the boundary) and occurs along the symmetry axis. For this case, the total fluorescence reaching the detector is [4]

$$I(t) = \begin{cases} N(e^{-(\beta vt/2)} - e^{-(t/\tau)}) & \text{if } t < t_r \\ N[e^{((2/v\tau)-\beta)L} - 1]e^{-(t/\tau)} & \text{if } t \geq t_r \end{cases} \qquad (3)$$

with $t_r = 2L/v$, which is again the maximum round-trip time, and with a normalization coefficient

$$N = \frac{1}{\left(\frac{2}{\beta v} - \tau\right)(1 - e^{-\beta L})} \qquad (4)$$

chosen so that $\int_0^\infty I(t)\, dt = 1$.

The effect of the absorption coefficient β at the excitation wavelength on the fluorescence decay is shown in Fig. 2 in terms of reduced parameters. For a small

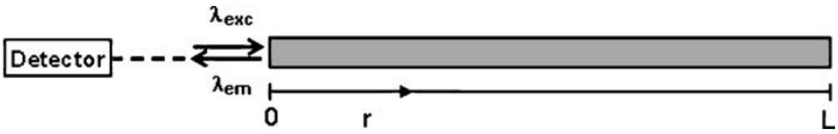

Fig. 1. Linear geometry model, with excitation and detection at the same side.

absorption coefficient ($\beta v\tau \ll 1$), the initial rising phase is clearly seen, with a rise-time τ. A break occurs at t_r, and from then on, the decay is single exponential, again with lifetime τ. As β increases, the break becomes less apparent, and the maximum of the decay occurs at times smaller than t_r. For a sufficiently large β, the decay is essentially single exponential from the very beginning.

For short lifetimes it results from Eq. (3) that a small rise period is followed by an exponential decay with lifetime $2/(\beta v)$, up to t_r, after which there is a very fast decay to zero. In the extreme cases of pure Mie or Rayleigh scattering (in the single scattering regime) the rise period is essentially nonexistent, there is an exponential decay up to t_r with an effective lifetime of $1/\beta v$, once resonance radiation will be attenuated by scattering in both the ingoing and outgoing paths, and a most abrupt drop to zero afterwards.

Finally, if we consider the very long lifetime case, one expects from Eq. (3) that, after the initial rising phase up to t_r, the intensity will decrease very slowly.

EXPERIMENTAL DECAYS

Experimental decays were recorded with the set-up described, approaching in Section 2, approaching the quasi-one-dimensional geometry treated above (Fig. 1) in Section 3.

Previous Results

The time dependence of the back scattered light obtained with a dilute colloidal dispersion of silica nanoparticles (Ludox, 38 nm radius, determined by dynamic light scattering) in water (3×10^{-4} g/ml) was previously reported in [4], displaying a behaviour very close to the predicted by the theoretical model for a pure scattering system. A very brief rising period is followed by a first maximum corresponding to the reflection of the laser light beam at the first wall. Between this maximum and a second one delayed by 11.2 ns, and corresponding to the reflection of the laser light beam at the end wall of the tube, the signal profile is clearly exponential after 6 ns. The respective measured time constant is 5.3 ns, which corresponds to an extinction coefficient of 8.4×10^{-3} cm^{-1}, according to the model presented. This was shown to be in good agreement with the value directly measured by static light scattering (7.3×10^{-3} cm^{-1}) that leads to a time constant of 5.9 ns. An abrupt drop of the signal after the second reflection is finally observed, as predicted.

The time evolution of the fluorescence for Rhodamine 101 in ethanol samples (3×10^{-8} M) reported in [4] also displayed the predicted behaviour according to the model for an intermediate lifetime and clearly showed the effect of absorption coefficient variation by the use of two different excitation wavelengths. With excitation at 320 nm, the observed curve resembles the curve shown in Fig. 2 for negligible absorption ($\beta v\tau/2 = 0$): a first phase of rising intensity is clearly seen, up to a time of 11.9 ns, at which the intensity starts to decay exponentially, with a lifetime of 4.3 ns, which is the known fluorescence lifetime of Rhodamine 101. The rising portion, when fitted with a sum of two exponentials (Eq. (3)) of which one fixed at the intrinsic lifetime (4.3 ns) gives identical and symmetrical amplitudes, and a second lifetime of 457 ns,

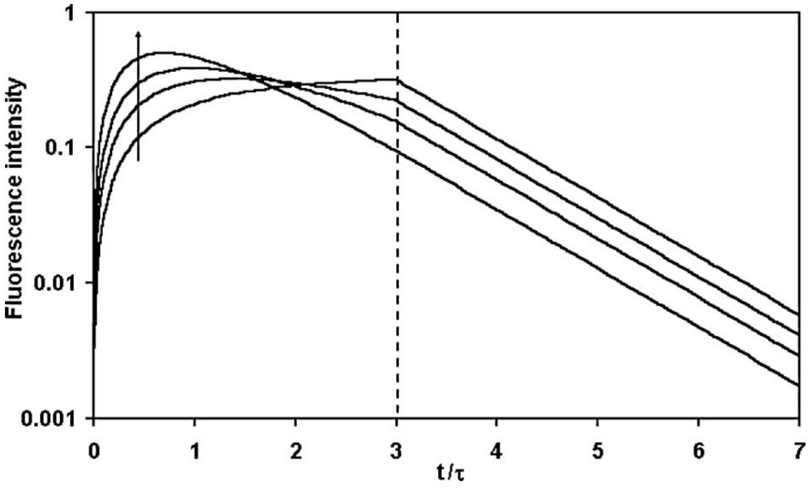

Fig. 2. Time evolution of the fluorescence intensity according to Eq. (3), with $t_r/\tau = 2L/(v\tau) = 3$. Curves vary with the dimensionless parameter $\beta v\tau/2$ according to the arrow. $\beta v\tau/2$ takes the values 0, 0.5, 1 and 2.

in reasonable agreement with a predicted value of 407 ns (yielding $\beta v\tau/2 = 0.0094$). When selecting a second excitation wavelength, 575 nm, for which the absorption coefficient is 37 times higher than at 320 nm, the first phase of the decay changes significantly, with the maximum shifted to shorter times, while the point at which the decay become single exponential (ca. 12.4 ns) remains essentially the same, in accord with the behaviour expected and displayed in Fig. 2. The first phase of the decay, when fitted with a sum of two exponentials (Eq. (3)) of which one fixed at the intrinsic lifetime (4.3 ns) gives identical and symmetrical amplitudes, and a second lifetime of 6.2 ns (implying $\beta v\tau/2 = 0.66$), in fair agreement with the expected value of 11.0 ns.

A Long Lifetime Molecule: Coronene

In this work we specifically report on a solution of coronene in ethanol, studied to address the case of a long lifetime. The fluorescence lifetime of the solution, measured in a 1 cm quartz cell, is 26.2 ns. This value is significantly lower than the published fluorescence lifetime for coronene in polar solvents, 320 ns [5], owing to the quenching effect of dissolved oxygen. But even with this lifetime, the time evolution of the fluorescence in response to flash excitation at 300 nm (Fig. 3) is close to the expected from the model. A first phase of rising intensity is again observed, up to around 12 ns, after which a constant intensity is almost attained, corresponding to a slow exponential decay, with a lifetime of 26.2 ns (lifetime of coronene in ethanol). The inset in Fig. 3 shows the rising part of the decay fitted with a sum of two exponentials (Eq. (3)), one fixed at the intrinsic lifetime (26.2 ns). The fitted function displays the correct trend, giving identical and symmetrical amplitudes, and a second lifetime of 16.3 ns. Experimental results obtained for this system (long lifetime) complete the study initiated with silica nanoparticles (zero lifetime) and Rhodamine 101 (intermediate lifetime), showing that the fluorescence decay law obtained for a linear geometry accounts well for the main features of the observations under the described circumstances.

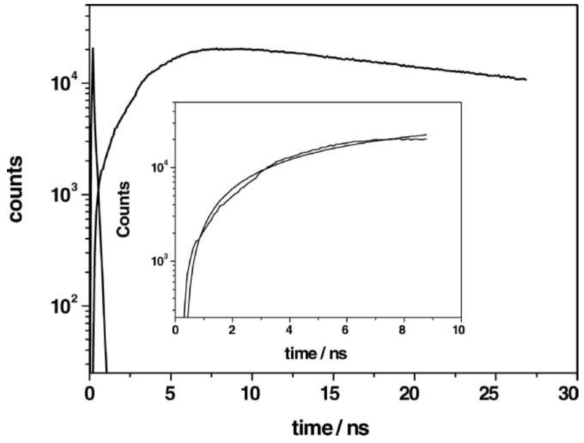

Fig. 3. Time evolution of fluorescence at 446 nm in response to excitation at 300 nm, for a coronene solution in the set-up shown in Fig. 1. The inset shows the two-exponential fit.

CONCLUSIONS

The effect of the time of flight of the photons on fluorescence decays was addressed. Fluorescence decay laws were given for two model geometries (spherical and linear) [4]. Experimental results for systems with a fluorescence lifetime in different ranges were obtained for the linear geometry, and analysed according to the developed model. It was shown that the model accounted well for the main features of the observations, the inclusion of photon propagation times being thus essential for a correct description of the fluorescence decays under the described circumstances. The measurements carried out also show that from the time dependence of fluorescence one can in principle determine the absorption or scattering coefficients of the sensed medium. While the systems studied were fairly large (in the meter range) and the time scales were in the nanosecond range, it seems clear that radiation propagation times cannot also be neglected in millimetre-sized systems when times shorter than a few picoseconds are concerned.

ACKNOWLEDGMENTS

This work was supported by Fundação para a Ciência e a Tecnologia (FCT, Portugal) within project POCTI/34836/FIS/2000. S.P.B. was supported by a doctoral grant from FCT.

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