Journal of Luminescence 158 (2015) 510–518

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Effect of triplet–triplet absorption on time-resolved phosphorescence

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A R T I C L E   I N F O

Article history:
Received 23 July 2014
Received in revised form
18 September 2014
Accepted 22 October 2014
Available online 30 October 2014

Keywords:
Luminescence decay law
Reabsorption
Phosphorescence
Triplet–triplet absorption
Coronene

A B S T R A C T

Molecular radiative transport, consisting in consecutive emission–absorption events by atoms or molecules of the same species, is studied in the case of excited-state absorption, a situation relevant to the phosphorescence of polycyclic aromatic hydrocarbons. This type of transfer differs in a number of ways from the better studied atomic resonance and molecular fluorescence cases, and leads to decays with a very distinctive form. A simple 1D model is introduced and used to discuss qualitatively the phosphorescence build-up and the phosphorescence decay in the presence of reabsorption. A new empirical phosphorescence decay law is also presented and justified on the basis of a phenomenological equation. The phosphorescence build-up and the phosphorescence decay in the presence of reabsorption are discussed and confronted with experimental results obtained for both normal and perdeuterated coronene.

1. Introduction

Radiative transport, i.e., a sequence of emission–absorption events by an ensemble of atoms or molecules of the same kind, also called radiative migration and radiation trapping, is a well known process in atomic resonance lines [1] and in molecular fluorescence [2]. Herein, we will concentrate on the molecular case. For low radiation densities and not too high temperatures the fraction of molecules in electronic excited states is usually very small and their contribution to absorption can be neglected. Molecular radiative transport is represented in Scheme 1 for a generic species A.

In this scheme, $I(t)$ is the time-dependent excitation, e.g. a short impulse or a step function, A_1^* represents the first generation of excited molecules (molecules directly excited by the radiation pulse), A_1 represents the second generation of excited molecules (molecules excited by photons emitted by first-generation molecules), α_1 is the average absorption probability by a ground state molecule of a photon emitted by a first-generation excited molecule, α_2 is the average absorption probability by a ground state molecule of a photon emitted by a second-generation excited molecule, k_r is the radiative rate constant, and k_{nr} is the non-radiative rate constant. In order to reach the detector, radiation generated within the sample has to avoid internal absorption. Radiation originating from first-generation molecules that escapes unimpeded is called primary emission, and has an exponential decay law, with the intrinsic lifetime of the species in question. The remaining emitted radiation is absorbed, and may or may not give rise to new photons (emission being in competition with nonradiative decay channels, see Scheme 1). If a new photon is emitted, it will face again the possibility of reabsorption. Emission reaching the detector from the second generation of molecules is therefore also depleted, but has a different decay law, owing to the different waiting times (convolution between two exponential decays) [1–4]. Because the spatial distribution of second-generation excited molecules does not usually coincide with that of the primary ones, the reabsorption (and escape) probabilities are in general different [2]. The decay law for radiative transport results from the contribution of many generations and is therefore complex and emission-wavelength and observation direction dependent [2–4]. For instance, excitation of an optically dense sample leads to a significant rise time if the decay is observed in a right angle geometry [2,4]. The rise time is longer for wavelengths within the absorption–emission overlap region, as these photons result, on the average, from a larger number of absorption–emission events [2,4]. Although a general theoretical framework for the radiative transport of fluorescence is possible [2,5], an accurate calculation of decay law parameters requires Monte-Carlo simulations [2,4].

Reabsorption of molecular phosphorescence is a much less studied process [6–9] and no general quantitative treatment or detailed experimental studies are available, although most of the main aspects have been identified at an early stage [6–9]. In the case of polycyclic aromatic hydrocarbons, reabsorption of molecular phosphorescence results from triplet–triplet (T–T) absorption, i.e. $T_n \leftarrow T_1$ radiative transitions, and not from absorption by

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http://dx.doi.org/10.1016/j.jlumin.2014.10.054
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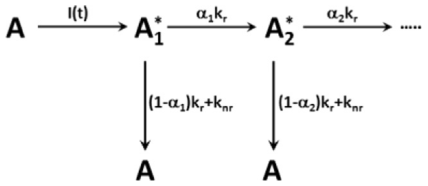

Scheme 1. Sequential emission-absorption events.

ground state molecules, owing to the forbidden nature of the $T_n \leftarrow S_0$ radiative transitions. In this way, all absorbing molecules are already in the T_1 state, and are generated in the first place by the external source, which completely determines the set of allowed sites for excitation diffusion. The excitation moves from one triplet, that returns to the ground state, to another, that undergoes the fast sequence $T_1 \rightarrow T_n \rightarrow T_1$ and thus remains unchanged, hence the elementary process for radiative transfer is $T_1 + T_1 \rightarrow S_0 + T_1$. The process may take place a number of times. In this mechanism there is no radiation imprisonment, only a peculiar type of inner filter effect, as the emitted photon is lost and does not reach the detector.

For sufficiently high concentrations (typically around 0.01 M), *nonradiative* transfer of the type $T_1 + T_1 \rightarrow S_0 + T_n$ (the final triplet state after relaxation being T_1) by the dipole–dipole mechanism [10,11] can also occur. Here, the phosphorescence decay is affected owing to an increase of the nonradiative decay rate. This process is sometimes called *long-range* triplet–triplet annihilation.

For even higher concentrations (typically around 0.1 M) a significant fraction of molecules is so close that the exchange interaction is now operative. In this way, for high excitation intensities *short-range* triplet–triplet annihilation, $T_1 + T_1 \rightarrow S_0 + S_1$, eventually preceded by triplet energy migration, $T_1 + S_0 \rightarrow S_0 + T_1$, comes into play [10,11]. The phosphorescence decay is affected and delayed fluorescence may be observed.

Unlike atomic and molecular fluorescence reabsorption, phosphorescence reabsorption depends significantly on the excitation intensity, which determines the number and spatial distribution of triplets.

A third and equally striking difference results from the instability of the triplet state: the reabsorption probability is not constant, as the T–T absorption contribution to the optical thickness of the medium continuously decreases with time, after the excitation pulse: for sufficiently long times, the phosphorescence absorption probability becomes negligible.

A fourth difference with respect to the other reabsorption mechanisms is the lack of correlation between the absorption and the emission spectra. For atomic resonance radiation, absorption and emission spectra overlap to a large extent [12,13]; In the case of molecular fluorescence, Stokes law applies and (at least) the low energy portion of the fluorescence spectrum never overlaps the absorption spectrum [2,4]; However, in the case of phosphorescence there is no correlation between the (T–S) emission and the T–T spectra, hence overlap can be quite extensive, moderate (with intermediate portions or any of the edges of the emission spectrum free from overlap), or entirely negligible, see e.g. Ref. [9].

In this work, radiative transfer of phosphorescence owing to triplet–triplet absorption is studied both theoretically and experimentally. The general equations are presented at the beginning. A simple 1D model is introduced and used to discuss qualitatively the phosphorescence build-up and the phosphorescence decay in the presence of reabsorption. A new empirical phosphorescence decay law is also presented and justified on the basis of a phenomenological equation. The theoretical predictions are next confronted with experimental results obtained for both normal and perdeuterated coronene. The main conclusions are summarized at the end.

2. Experimental section

2.1. Materials

Perdeuterated coronene (high purity, 98% atom %D) was purchased from CDN Isotopes. Normal coronene (sublimed 99%) and toluene (spectroscopic grade) were purchased from Sigma-Aldrich. The cyclic polyolefin Zeonex 480R (average $M_w \approx 480{,}000$, pellets) was a donation from Zeon Chemicals L.P.

2.2. Methods

The coronene-containing films (25 μm thickness) were prepared by dissolving coronene (ca. 1.5 mg) and the polymer (100 mg) in toluene (0.9 g) and then by coating a quartz plate with the viscous solution at room temperature. After complete solvent evaporation, the plate containing the clear film was placed in a quartz cell that was degassed with an Alcatel Drytel 100 turbomolecular pump (final pressure: ca. 3×10^{-7} atm), the cell being sealed afterwards. The final concentration of coronene in the film, determined from the absorption spectrum, was 2.0×10^{-3} M in all cases. Absorption spectra were recorded on a UV-3101PC UV–vis–NIR spectrophotometer (Shimadzu, www.shimadzu.com). Fluorescence and phosphorescence spectra and phosphorescence decays were obtained with a Fluorolog F112A fluorimeter (Spex, www.jobinyvon.com) in right-angle configuration. Emission spectra were corrected for the spectral response of the optics and photomultiplier. For phosphorescence decays, excitation and emission wavelengths were always 340 nm and 560 nm, respectively, and the (broadband) excitation and emission slits were 18 nm and 4.5 nm, respectively. In some experiments excitation intensity was varied using a set of neutral density filters from Optics Balzers. The maximum excitation intensity, corresponding to absence of filters (denoted 100 in the arbitrary units used in this work) was about 2.7 mW/cm^2. Time-resolved fluorescence intensity decays were obtained by the single-photon timing method with laser excitation, with the set-up described in Ref. 14. Measurements at 77 K were performed with a liquid nitrogen cryostat (Oxford DN1704) connected to an ITC-4 temperature controller.

3. Results and discussion

3.1. Phosphorescence decay law

In the case of phosphorescence, it is the triplet state molecules that are responsible for reabsorption. Following pulsed excitation, their concentration continuously decreases with time. In this way, the reabsorption probability also decreases continuously and approaches zero for sufficiently long times. As a consequence, the phosphorescence decay asymptotically approaches an exponential one governed by the intrinsic phosphorescence lifetime, τ_P. This characteristic trait of phosphorescence reabsorption leads to a unique type of decay law.

The average photon escape probability, γ, cannot be analytically evaluated except for simple models. Consider triplet molecules uniformly distributed in a slab, with concentration C_T, and with a decadic molar absorption coefficient ε_T at the phosphorescence emission wavelength. Let the x-axis be normal to the slab delimiting planes, located at $x=0$ and $x=l$, (Scheme 2).

If the photon is emitted at $0 < x' < l$, along the x-direction (1D model, hence no slant trajectories are allowed), the probability of