

Short Communication

Radiative energy transfer: verification of a method of correction for the system pyrene-9,10-diphenylanthracene in benzene

J. M. G. MARTINHO, V. R. PEREIRA, A. GONÇALVES DA SILVA and J. C. CONTE

Centro de Química Física Molecular, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa codex (Portugal)

(Received August 3, 1984)

1. Introduction

Electronic energy transfer between organic fluorescent molecules in solution may occur by a radiative or a non-radiative mechanism. The radiative process consists of the absorption by the energy acceptor Z of the radiation emitted by the energy donor Y, and therefore modifies the intensities and fluorescence spectra of the donor. The non-radiative energy transfer occurs through a resonance process and can be studied using the fluorescence intensities of the donor.

The radiative process is often the dominant mechanism of energy transfer and cannot be neglected in studies of non-radiative transfer. Therefore it is very important to correct the fluorescence intensities for the radiative energy transfer process.

In an earlier publication [1] an expression was proposed to correct the fluorescence intensities of the donor for radiative transfer and also for the direct absorption of the exciting radiation by the acceptor for the geometrical arrangement (measurements in reflection) depicted in Fig. 1.

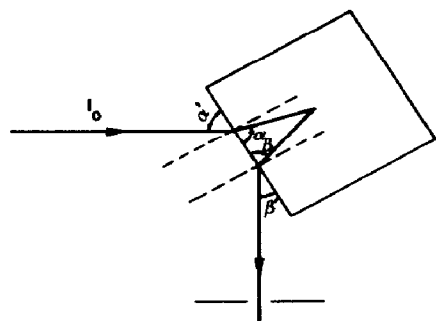


Fig. 1. Experimental arrangement used in the reflection measurements.

The experimental fluorescence intensities I_Y^t and the corrected intensities are related by

$$I_Y^t = I_Y \frac{\mu_Y(\bar{\nu}_{exc})c_Y \sin \beta}{\{\mu_Y(\bar{\nu}_{exc})c_Y + \mu_Z(\bar{\nu}_{exc})c_Z\} \sin \beta + \mu_Z(\bar{\nu}_{em}^Y)c_Z \sin \alpha} \times \left(1 - \exp \left[-\delta \frac{\{\mu_Y(\bar{\nu}_{exc})c_Y + \mu_Z(\bar{\nu}_{exc})c_Z\} \sin \beta + \mu_Z(\bar{\nu}_{em}^Y)c_Z \sin \alpha}{\sin \beta} \right] \right) \quad (1)$$

where c_Y and c_Z are the concentrations of the donor and of the acceptor respectively, μ_Y and μ_Z are the molar absorption coefficients of Y and Z ($\mu = 2.303\epsilon$, where ϵ is the molar extinction coefficient), $\bar{\nu}_{exc}$ and $\bar{\nu}_{em}$ are the frequencies of the exciting radiation and the emitted radiation, δ is the thickness of the sample and α and β are the angles depicted in Fig. 1. The exciting beam and the detected beam make the angles α' and β' respectively with the face of the cell, which are related to the angles α and β by the Snell refraction law

$$\frac{\cos \alpha'}{\cos \alpha} = \frac{\cos \beta'}{\cos \beta} = n$$

where n is the refractive index of the solvent.

The aim of this communication is to verify that this simple expression is a very good approximation for the correction of the experimental fluorescence intensities in the energy transfer process from pyrene to 9,10-diphenylanthracene in benzene.

2. Results and discussion

The experimental fluorescence spectra of degassed solutions of pyrene and 9,10-diphenylanthracene in benzene were obtained using a home-built spectrofluorometer which has been described previously [2]. In Fig. 2 we present the variation of the experimental intensities of the excited pyrene monomer at different concentrations c_Y of pyrene for different concentrations c_Z of 9,10-diphenylanthracene.

The kinetics scheme that takes into account all the photophysical processes that occur in this system has already been studied [3] and for the intensities of the excited pyrene monomer it gives

$$I_{MY} = I_0 q_{MY} \frac{\Gamma_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} \quad (2)$$

where I_0 is the intensity of the exciting radiation, q_{MY} is the quantum efficiency of the pyrene monomer, σ_{ZY}^m and σ_{ZY}^d are the Stern-Volmer constants for the non-radiative energy transfer process of the excited monomer and the excimer respectively and

$$\Gamma_Y = c_{hY}(1 + \gamma_Y \sigma_{ZY}^d c_Z)$$

where c_{hY} (the half-value concentration for the excited monomer-excimer equilibrium of pyrene) and γ_Y are characteristic constants for pyrene in benzene.

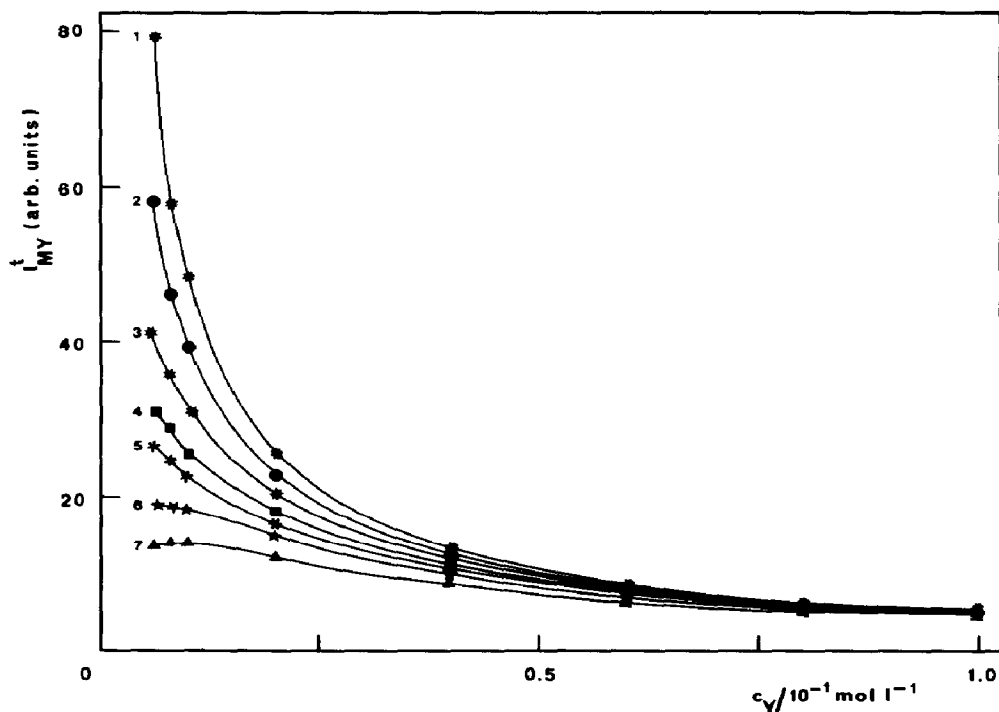


Fig. 2. Experimental intensities I_{MY}^t of the excited pyrene monomer as a function of donor concentration c_Y : curve 1, $c_Z = 0$; curve 2, $c_Z = 0.40 \times 10^{-3} \text{ mol l}^{-1}$; curve 3, $c_Z = 0.96 \times 10^{-3} \text{ mol l}^{-1}$; curve 4, $c_Z = 1.6 \times 10^{-3} \text{ mol l}^{-1}$; curve 5, $c_Z = 2.0 \times 10^{-3} \text{ mol l}^{-1}$; curve 6, $c_Z = 2.8 \times 10^{-3} \text{ mol l}^{-1}$; curve 7, $c_Z = 4.0 \times 10^{-3} \text{ mol l}^{-1}$.

From eqn. (2) we can see that, for all the acceptor concentrations c_Z , the intensities of the excited pyrene monomer decrease with increasing concentration c_Y . From the experimental values of I_{MY}^t , presented in Fig. 2, we can see an anomalous behaviour for high values of c_Z .

In Fig. 3 we present the corrected values of the intensities obtained using eqn. (1) with $\alpha' = 60^\circ$, $\beta' = 30^\circ$ and the molar extinction coefficients of pyrene and 9,10-diphenylanthracene obtained from the absorption spectra. The correction is particularly important for low values of c_Y since the depth of penetration of the exciting radiation is large and it can be noticed that the corrected values adhere to the variation predicted by eqn. (2).

To verify the validity of the method of correction we have also presented in Fig. 3 the variations (full line) predicted by eqn. (2) with the parameters $c_{hY} = 8.5 \times 10^{-4} \text{ mol l}^{-1}$, $\gamma_Y = 0.77$ (obtained from the decay curves [3] of solutions of pyrene in benzene) and the Stern-Volmer rate constants $\sigma_{ZY}^m = 3.7 \times 10^3 \text{ l mol}^{-1}$ and $\sigma_{ZY}^d = 1.1 \times 10^2 \text{ l mol}^{-1}$ (also obtained from the decay curves of pyrene in solutions of pyrene and 9,10-diphenylanthracene in benzene [3]).

The differences between the corrected experimental intensities and the "theoretical intensities" are less than 10%. Similar results were obtained

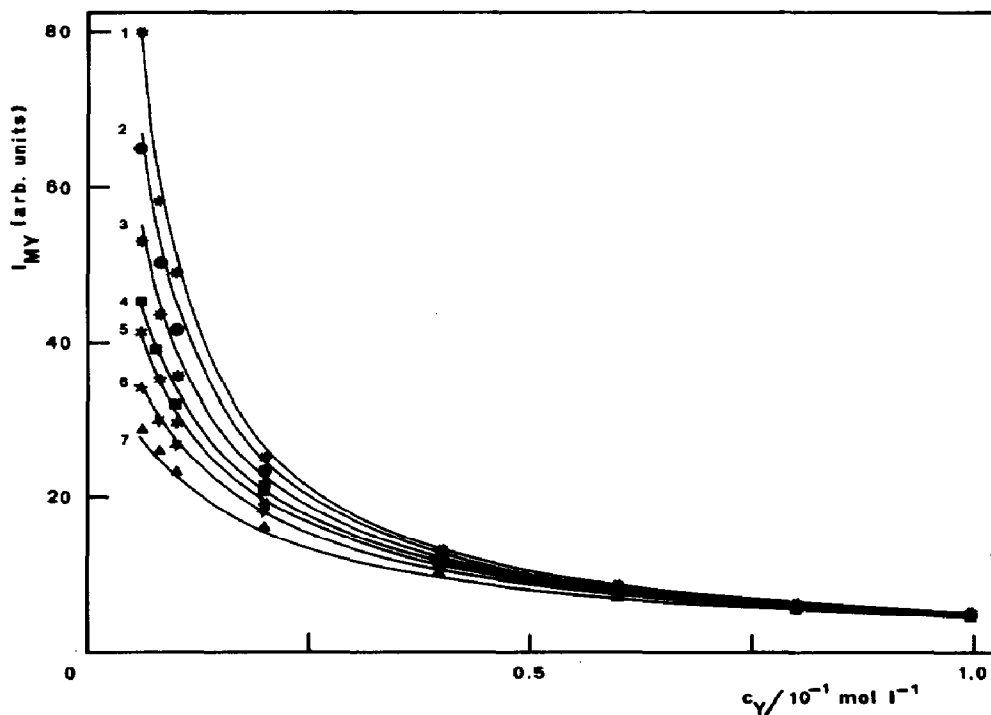


Fig. 3. Intensities I_{MY} of the excited pyrene monomer as a function of donor concentration c_Y . The curves are labelled as in Fig. 2. The symbols represent the intensities corrected using eqn. (1) and the curves were calculated using eqn. (2).

for the correction of the experimental fluorescence spectra of aromatic molecules for the reabsorption process [4, 5], with equations identical with eqn. (1).

All the parameters used to calculate the "theoretical curves" from eqn. (2) were obtained from a different set of experiments, and the Stern-Volmer rate constants thus obtained were not modified by the radiative process. We conclude that expression (1) is a very good correction for the radiative energy transfer process in reflection measurements.

- 1 J. C. Conte and J. M. G. Martinho, *J. Lumin.*, 22 (1981) 273.
- 2 J. M. G. Martinho and J. C. Conte, *J. Lumin.*, 22 (1981) 285.
- 3 J. M. G. Martinho and J. C. Conte, *J. Chem. Soc., Faraday Trans. 2*, 78 (1982) 975.
- 4 W. H. Melhuish, *J. Phys. Chem.*, 65 (1961) 229; *Natl. Bur. Stand. (U. S.), Spec. Publ.*, 378 (1973) 137.
- 5 I. Lopes Arbeloa, *J. Photochem.*, 14 (1980) 97.