Supplementary material

An alternative method to determine the quantum yield of the excited triplet state using Laser Flash Photolysis

Iouri Evgenievitch Borissevitch[1,2,*], Eli Silveira-Alves Jr[3],

Claudio Gabriel Lemos Almeida[4], Guilherme Rocha Lino de Souza[5],

Svyatoslav Sergeevich Sokolov[6], Pablo José Gonçalves[2,3**]

[1]Departamento de Física, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Ribeirão Preto, Brazil.

[2]Instituto de Física, Universidade Federal de Goiás, Goiânia, Brazil.

[3]Instituto de Química, Universidade Federal de Goiás, Goiânia, Brazil,

[4]Escola de Engenharia Elétrica, Mecânica e de Computação, Universidade Federal de Goiás, Goiânia, Brazil.

[5]Instituto de Ciências Biológicas, Universidade Federal de Goiás – UFG, Goiânia – GO, Brazil.

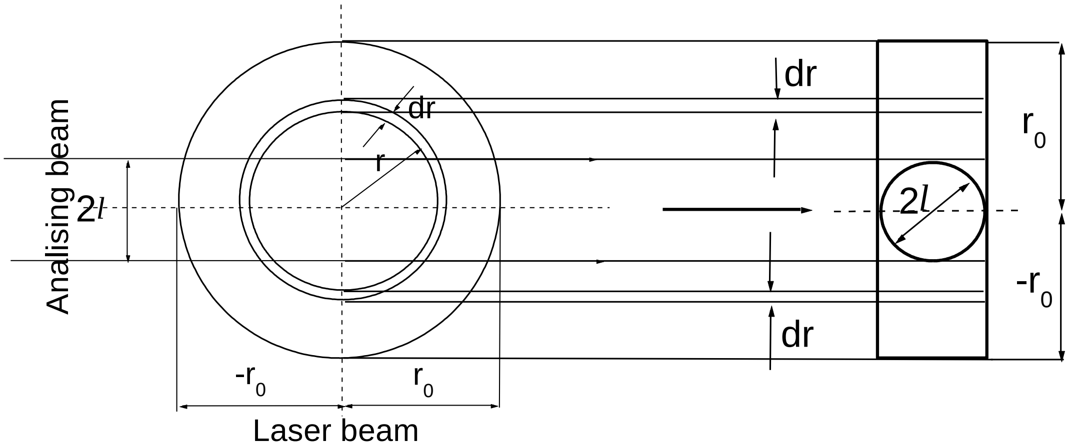
[6]B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine 47 Nauky ave, 61103 Kharkiv, Ukraine.

.

Authors to whom correspondence should be addressed:

*iourib@ffclrp.usp.br and **pablo@ufg.br

Supplementary material



SI-1: Scheme of propagation of the exciting and analyzing beams, used for calculation of φ_T value from spectroscopic data.

The number of exciting photons in the cylindrical volume element dV_r is

$$dn_{ex}(r,z) = GF(r,z)dV_r$$

where dV_r is equal to

$$dV_r = 4\pi lrdr$$

Here r is the cylinder radius, dr is its thickness and $2l$ is its height, were l is the radius of the analyzing beam.

$GF(r,z)$ is the spatial distribution of laser pulse intensity, which, taking into account the cylindrical symmetry of the pulse, is

$$GF(r,z) = C \times exp\left(-\frac{r^2}{2\zeta^2}\right)$$

The C value is determined from normalization by the volume

$$C\int_0^{2\pi} d\theta \int_0^{r_0} exp\left(-\frac{r^2}{2\zeta^2}\right) rdr \int_{-l}^{l} dz = 1$$

And

$$C = \frac{1}{4\pi l\zeta^2\left[1 - exp\left(-\frac{r^2}{2\zeta^2}\right)\right]}$$

Finally

$$dn_{ex} = \frac{n_{ex0}}{4\pi l\zeta^2\left[1 - exp\left(-\frac{r_0^2}{2\zeta^2}\right)\right]} exp\left(-\frac{r^2}{2\zeta^2}\right) \times 4\pi lrdr$$

or

$$dn_{ex} = \frac{n_{ex0}}{\zeta^2\left[1 - exp\left(-\frac{r_0^2}{2\zeta^2}\right)\right]} exp\left(-\frac{r^2}{2\zeta^2}\right) \times rdr$$

The number of absorbed photons in accordance with the Lambert-Beer law is:

$$dn_{abs} = dn_{ex}(r,z)[1 - exp(-\sigma_{01}N_0 2l)]$$

where σ_{01} is a cross section of the $S_0 \rightarrow S_1$ transition at the excitation wavelength, N_0 is a number of PS molecules per a volume unit, and

$$dn_{abs} = \frac{n_{ex0}[1 - exp(-\sigma_{01}N_0 2l)]}{\zeta^2\left[1 - exp\left(-\frac{r_0^2}{2\zeta^2}\right)\right]} exp\left(-\frac{r^2}{2\zeta^2}\right) rdr$$

When the radius of the analyzing beam $l \ll r_0$, the problem can be considered as a one-dimensional one, and the elementary absorbance can be written as:

$$dA = \sigma_S N_S dr + \sigma_T N_T dr$$

where σ_S and σ_T are cross sections of $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_2$ transitions at the analyzing wavelength and $N_S = \frac{dn_S}{dV_r}$ and $N_T = \frac{dn_T}{dV_r}$ are numbers of the PS molecules in the S_1 and T_1 states per the volume unit, respectively.

Taking into account that $N_S + N_T = N_0$ we obtain

$$d(\Delta A) = d(A - A_0) = (\sigma_T - \sigma_S)N_T dr = (\sigma_T - \sigma_S)\frac{dn_T}{4\pi l r dr}dr = (\sigma_T - \sigma_S)\frac{dn_T}{4\pi l r}$$

where $A_0 = \int_{-r_0}^{r_0} \sigma_S N_0 dr$ is the absorbance of the sample before the exciting pulse action.

Using the definition of the triplet state quantum yield as $\varphi_T = \frac{dn_T}{dn_{abs}}$, we obtain after integration

$$\Delta A = (\sigma_T - \sigma_S)\int_{-r_0}^{r_0} \frac{dn_T}{4\pi l r} = \frac{\varphi_T(\sigma_T - \sigma_S)}{4\pi l}\int_{-r_0}^{r_0} \frac{dn_{abs}}{r}$$

$$\Delta A = \frac{\varphi_T(\sigma_T - \sigma_S)}{4\pi l} \times \frac{[1 - exp(-\sigma_{01}N_0 l)]}{\zeta^2\left[1 - exp\left(-\frac{r_0^2}{2\zeta^2}\right)\right]} \times \int_{-r_0}^{r_0} exp\left(-\frac{r^2}{2\zeta^2}\right)dr$$

$$\Delta A = \varphi_T\frac{n_{ex0}(\sigma_T - \sigma_S)}{2\pi l} \times \frac{[1 - exp(-\sigma_{01}N_0 l)]}{\zeta^2\left[1 - exp\left(-\frac{r_0^2}{2\zeta^2}\right)\right]} \times \int_{0}^{r_0} exp\left(-\frac{r^2}{2\zeta^2}\right)dr$$

$$\Delta A = \varphi_T\frac{n_{ex0}(\sigma_T - \sigma_S)}{2\pi l} \times \frac{[1 - exp(-\sigma_{01}N_0 l)]}{\zeta^2\left[1 - exp\left(-\frac{r_0^2}{2\zeta^2}\right)\right]}\sqrt{\frac{\pi}{2}}\zeta \times erf\left(-\frac{r^2}{2\zeta^2}\right)$$

$$\Delta A = \varphi_T\frac{n_{ex0}(\sigma_T - \sigma_S)}{2\sqrt{2\pi}l\zeta} \times \frac{[1 - exp(-\sigma_{01}N_0 l)]}{\left[1 - exp\left(-\frac{r_0^2}{2\zeta^2}\right)\right]} \times erf\left(-\frac{r^2}{2\zeta^2}\right)$$

where

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^{x^2} \exp(-t^2)dt = \frac{1}{\sqrt{\pi}}\int_0^{x^2} \exp(-t)\frac{dt}{\sqrt{t}}$$

is the error integral with the argument $x = \frac{r_0}{\sqrt{2}\zeta}$.

And as a result

$$\varphi_T = \frac{2\sqrt{2\pi}l\zeta}{n_{ex0}(\sigma_T - \sigma_S)} \times \frac{\left[1 - exp\left(-\frac{r_0^2}{2\zeta^2}\right)\right]}{[1 - exp(-\sigma_{01}N_0 l)]erf\left(\frac{r_0}{\sqrt{2}\zeta}\right)} \times \Delta A$$