High excited state cross-section of the indocyanine green solutions

Introduction

IFSC-USP
Fotônica

✓ **Study of nonlinear absorption dynamics on Indocyanine Green diluted in water and in DMSO.**

✓ **Two configuration of the Z-scan technique:**

- **single pulse Z-scan**
- **pulse train Z-scan**

  ⇒ to obtain the singlet and triplet dynamics, separately.

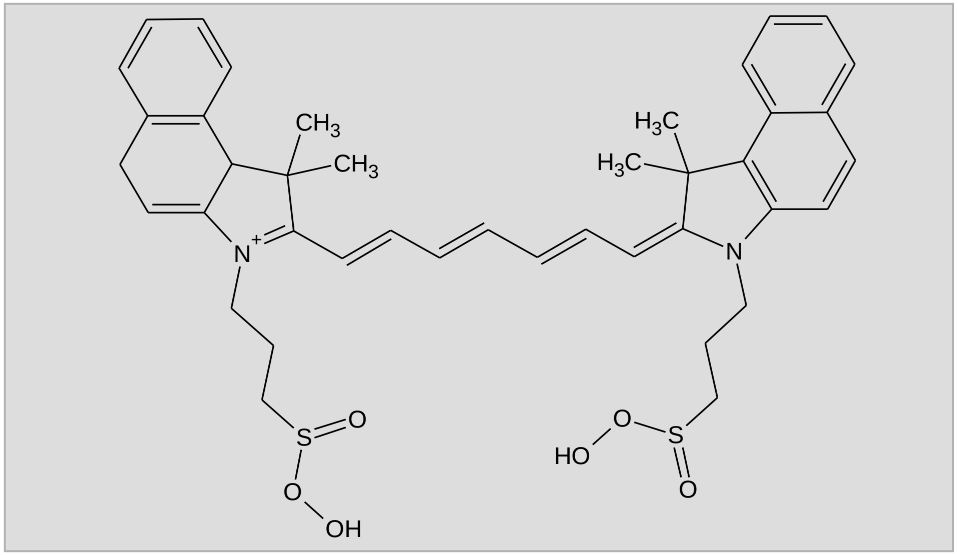
✓ **The results obtained with both techniques have shown that indocyanine green is a good sensitizer for photodynamic therapy, and also a good molecule for optical limiting devices.**

Introduction

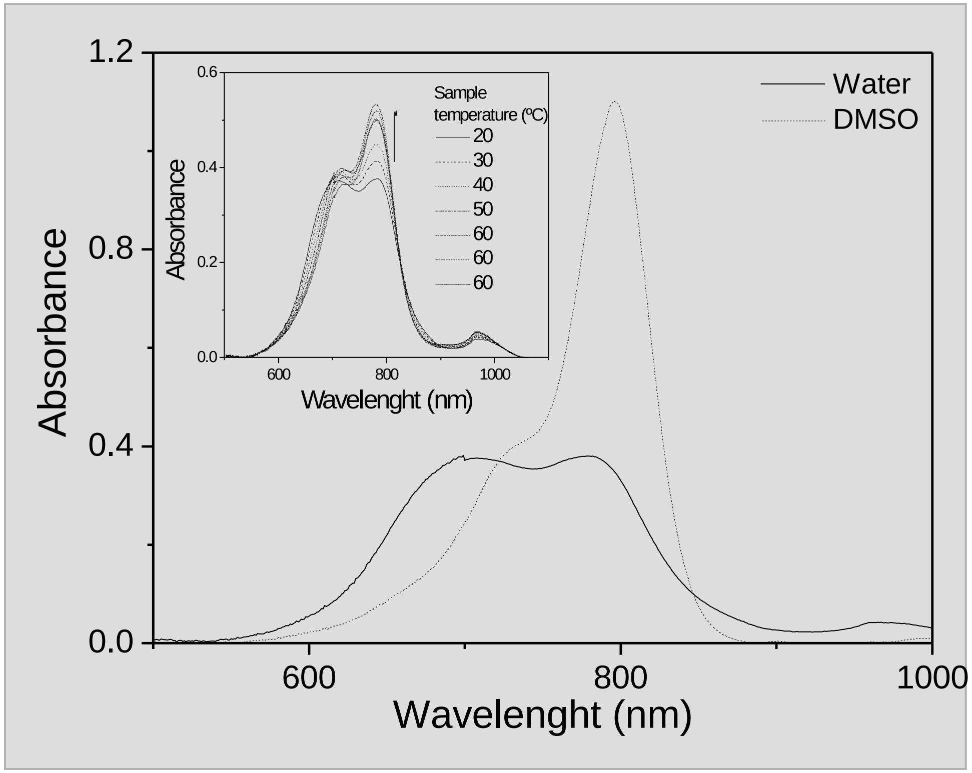
The organic dye Indocyanine Green (ICG) has many applications:

- ✓ laser dye;
- ✓ saturable absorber;
- ✓ diagnosis ;
- ✓ photo-dynamic therapy (PDT) of cancer;
- ✓ optical limiting.

✓ *Molecular structure*



Linear Absorption



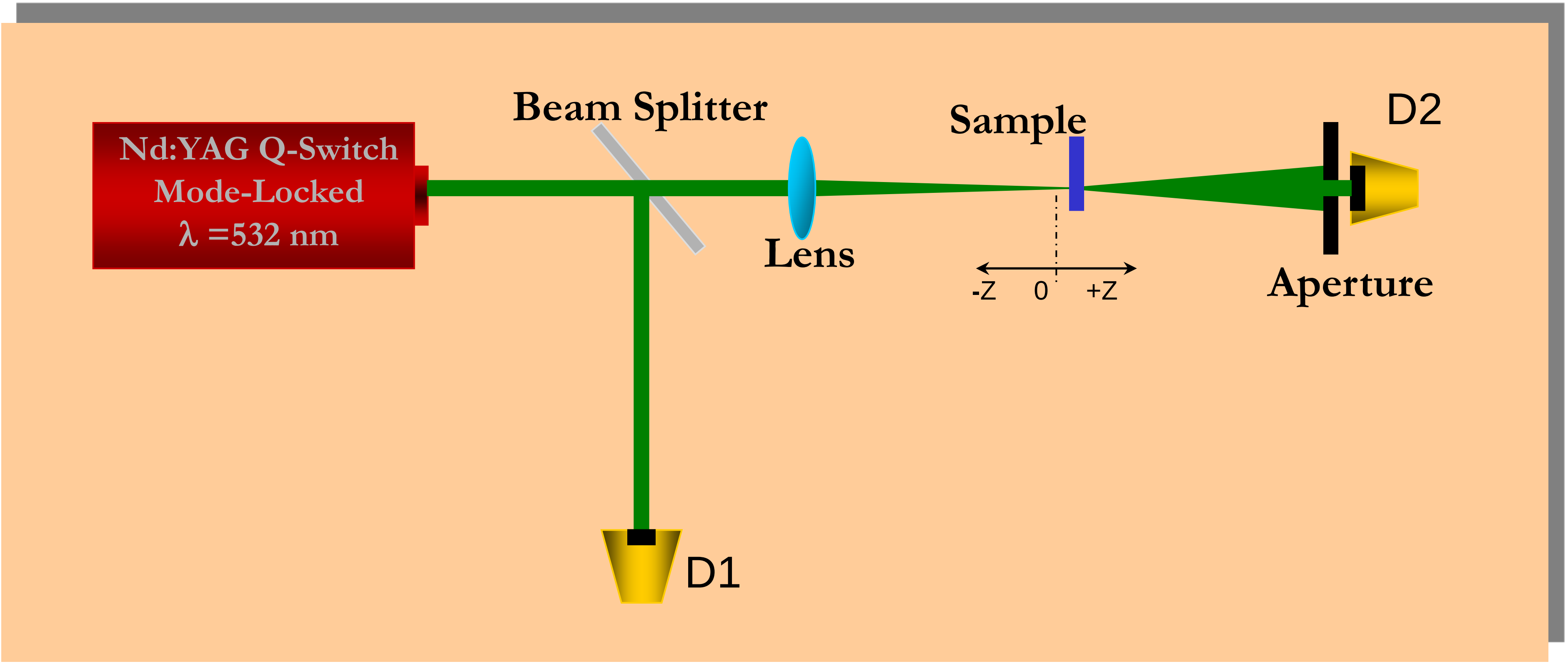
ICG diluted: in water (solid line) and in DMSO (dash line)

Concentration: $N_0 = 2x10^{16}$ molecules/cm^3.

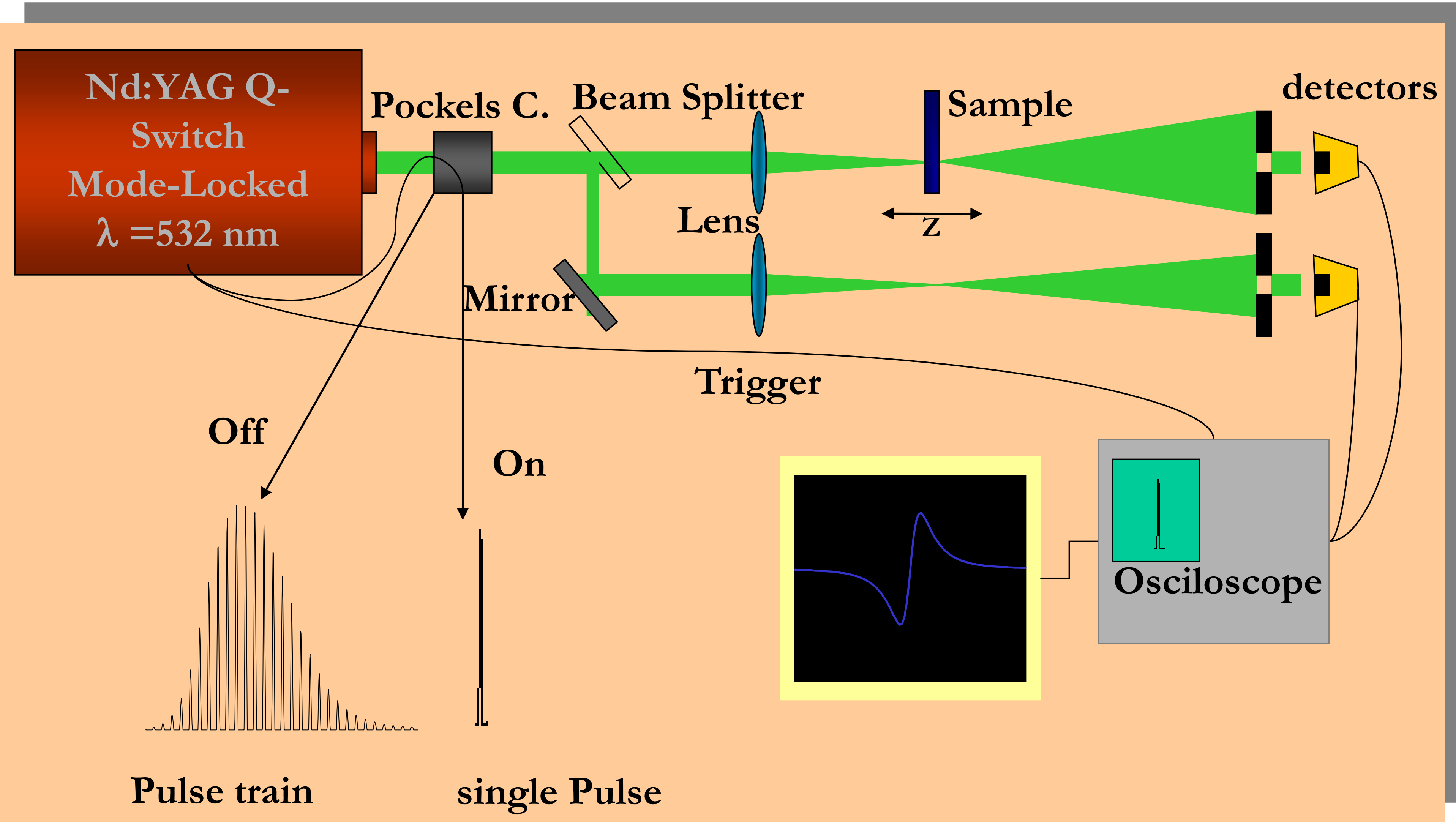
For temperatures: < 60ºC $\Rightarrow$ the optical process is reversible

> 60ºC it does not recovery the initial absorption. This can be associated with sample degradation.

Z-scan technique

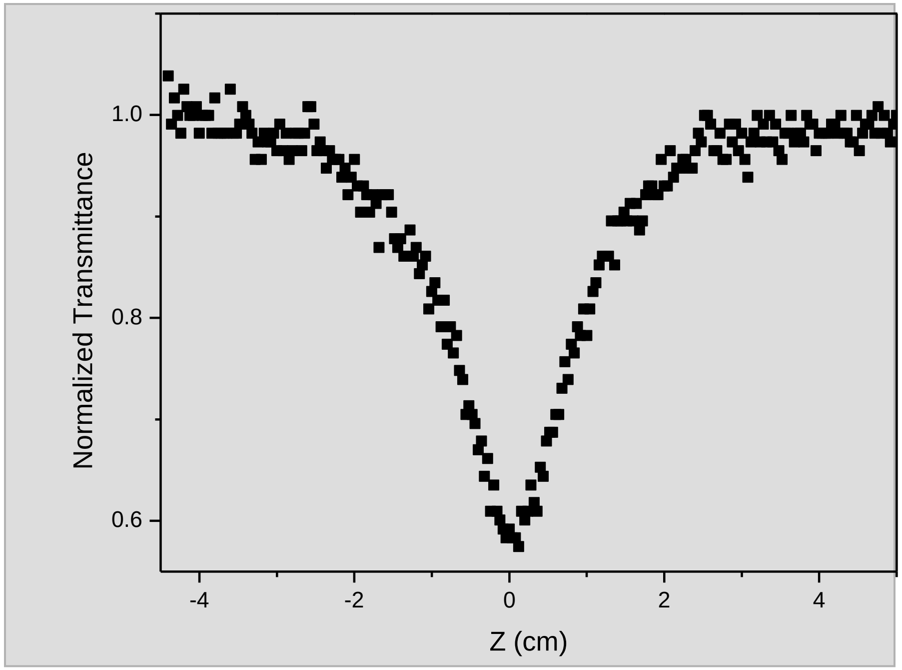


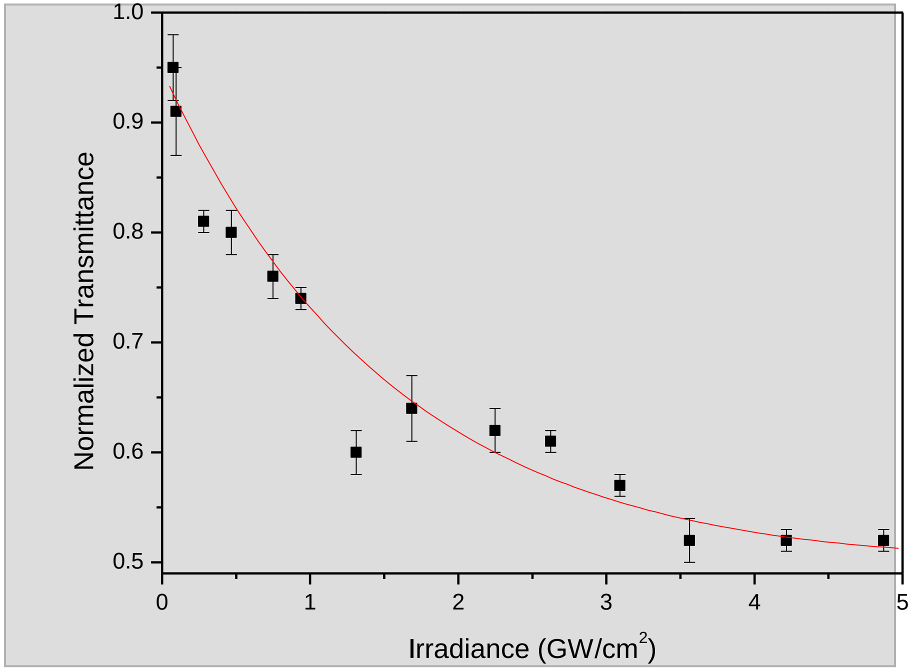
Pulse Train (PTZ-scan) Z-scan technique



Results (Z-scan)

✓ *Water*



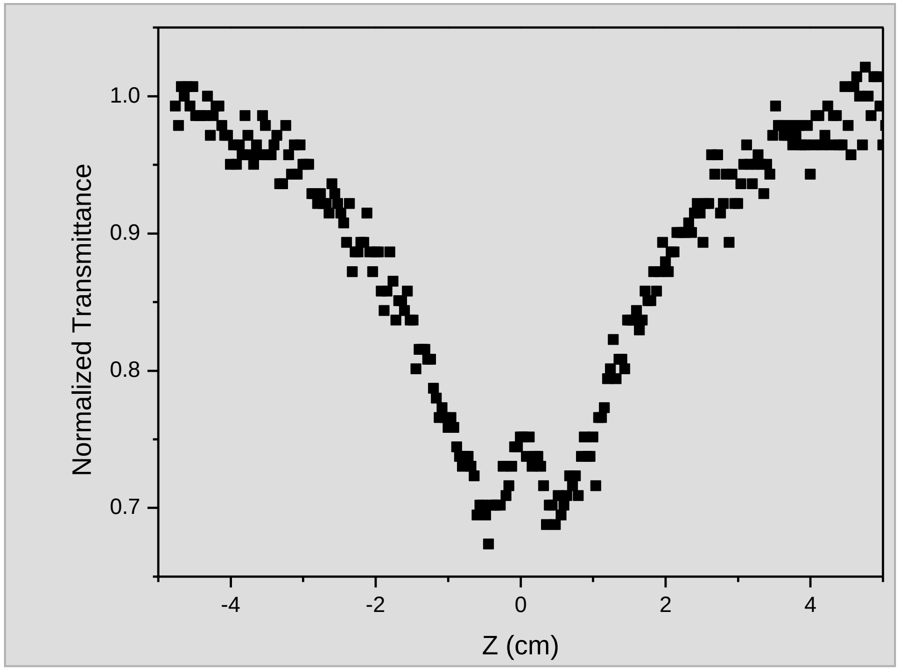


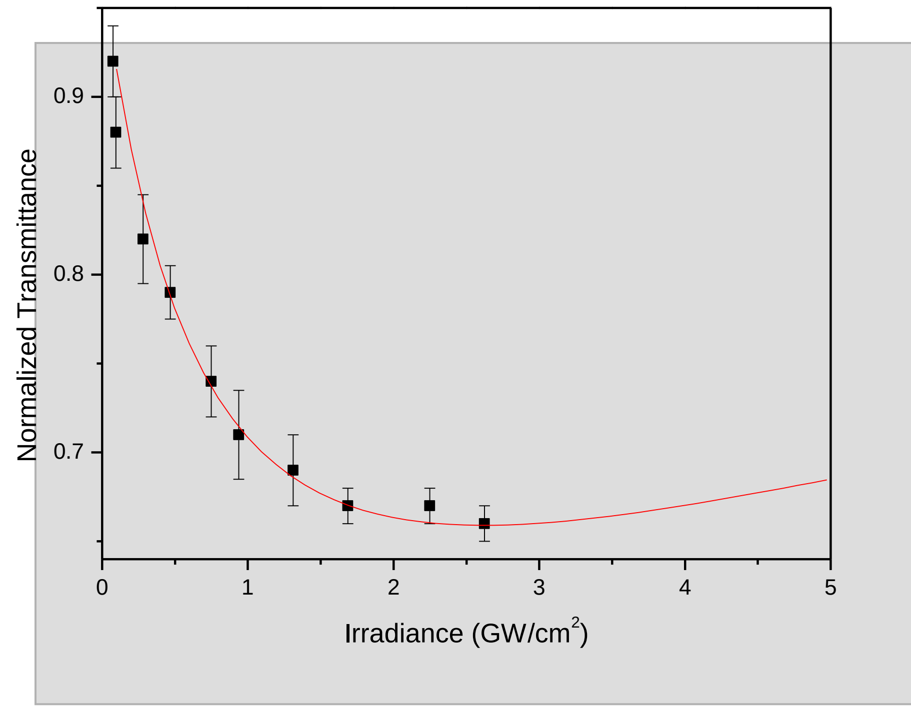
The fit was obtained by rate equations describing a three–energy-level diagram. Saturation effect of the TN is due to the accumulation of molecules in the singlet excited state and to the depleting of the ground state.

Fluorescence time:
Water = 20 ps

Results (Z-scan)

✓ DMSO





Fluorescence time:
DMSO = 800 ps

In DMSO ⇒ saturation occurs for low intensities due to the smaller fluorescence time of the first excited state.
This implies that for the same pulse irradiance, more population is accumulated in singlet excited state to ICG-DMSO, which causes a premature saturation of RSA effect. With more molecules excited in the first state, it is more probable that transitions will occurs to the second excited state, that present no absorption cross-section.

Results (Z-scan)

Rate equations:

$$\frac{dn_0}{dt} = -w_{01}n_0 + \frac{n_1}{\tau_{10}}$$

$$\frac{dn_1}{dt} = +w_{01}n_0 - w_{12}n_1 - \frac{n_1}{\tau_{10}} + \frac{n_2}{\tau_{21}}$$

$$\frac{dn_2}{dt} = +w_{12}n_1 - \frac{n_2}{\tau_{21}}$$

$$w_{01} = \frac{\sigma_{01}I(t)}{h\nu} \qquad w_{12} = \frac{\sigma_{12}I(t)}{h\nu}$$

Excited state cross-section:

- ✓ **Water of $\sigma_{12}=(13\pm1)\times10^{-7}cm^2$**
- ✓ **DMSO of $\sigma_{12}=(12\pm1)\times10^{-7}cm^2$**

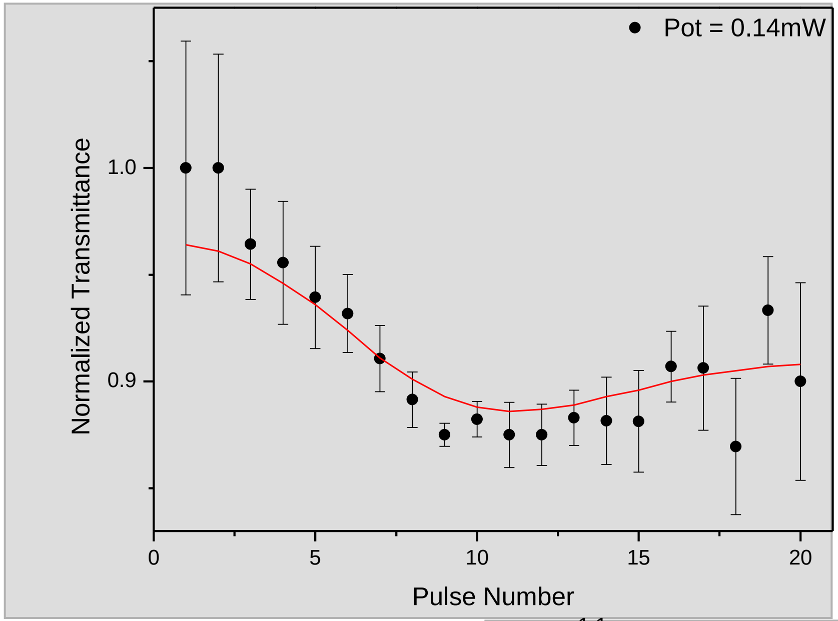
Compared with the ground state cross section (for water $\sigma_{01}=0,27\times10^{-7}cm^2$ and for DMSO $\sigma_{01}=0,16\times10^{-7}cm^2$) is approximately:

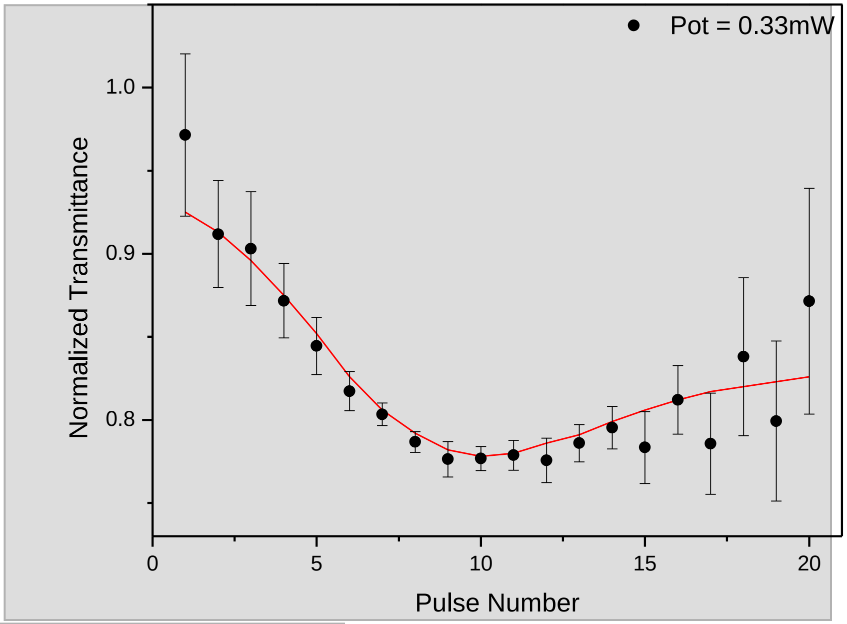
- ✓ **50 times larger for water**
- ✓ **75 times larger for DMSO**

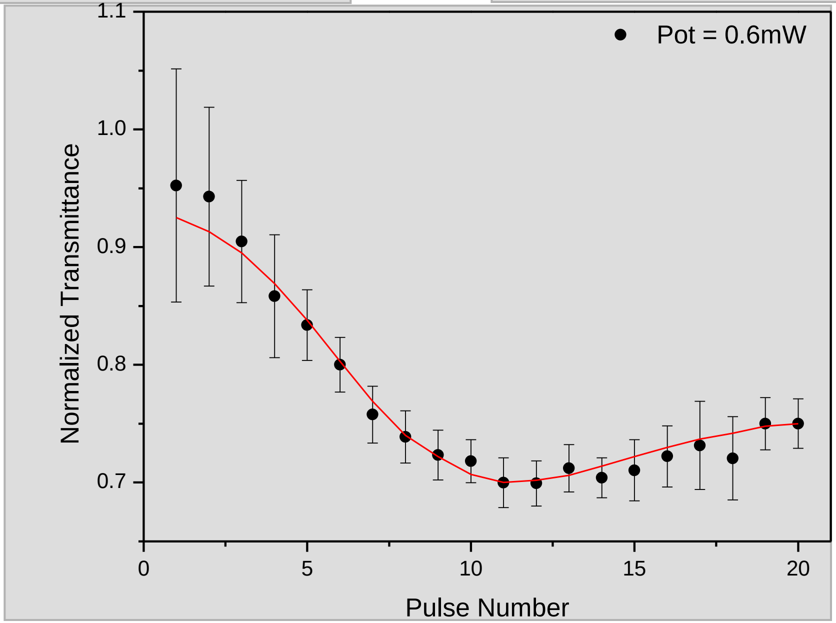
The result indicates that ICG can be a good candidate for optical limiting.

Results (PTZ-scan)

✓ *Water*



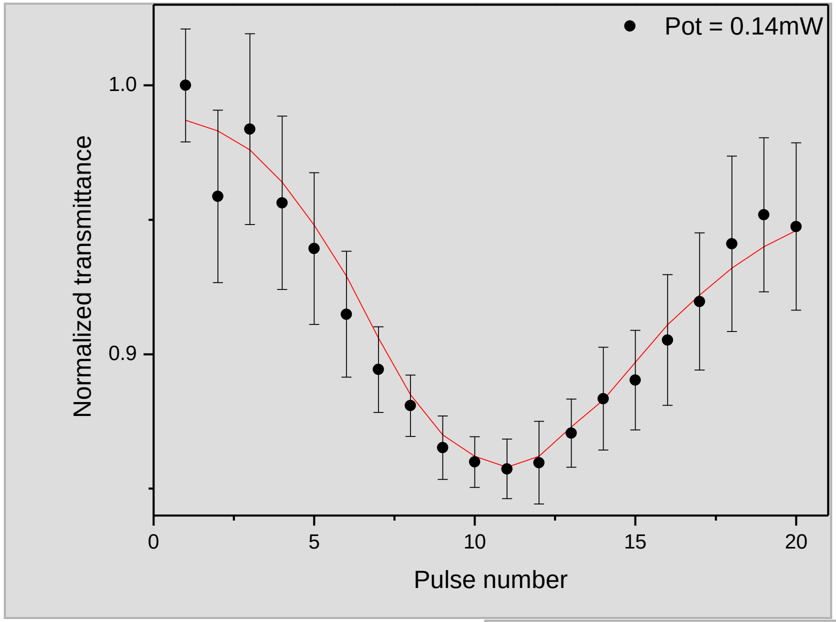


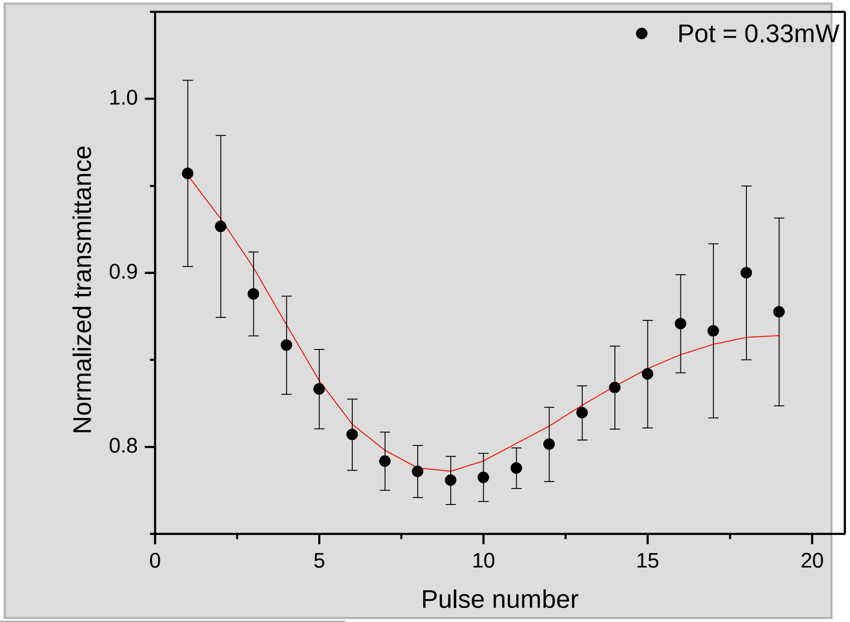


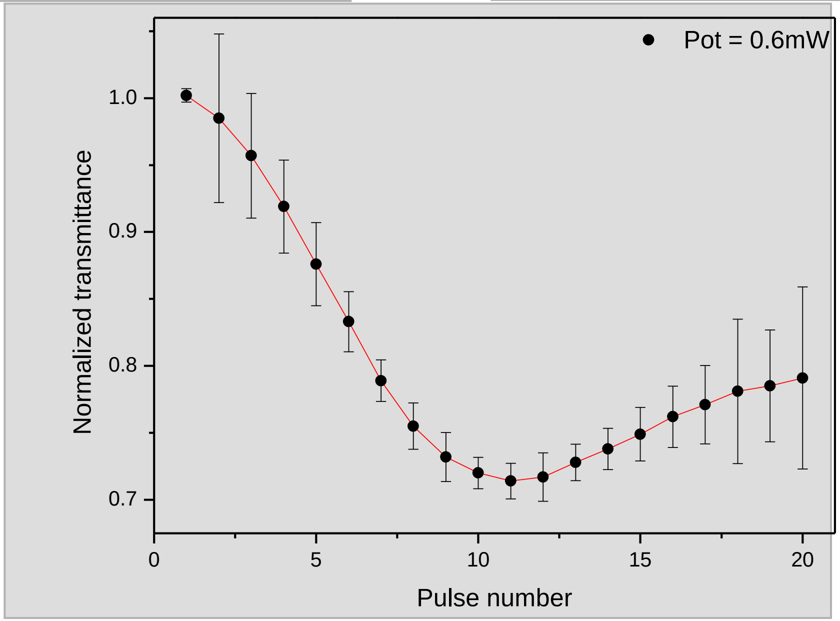
Fitting using five-level energy model

Results (PTZ-scan)

✓ DMSO







Fitting using five-level energy model

Results (PTZ-scan)

Rate equations:

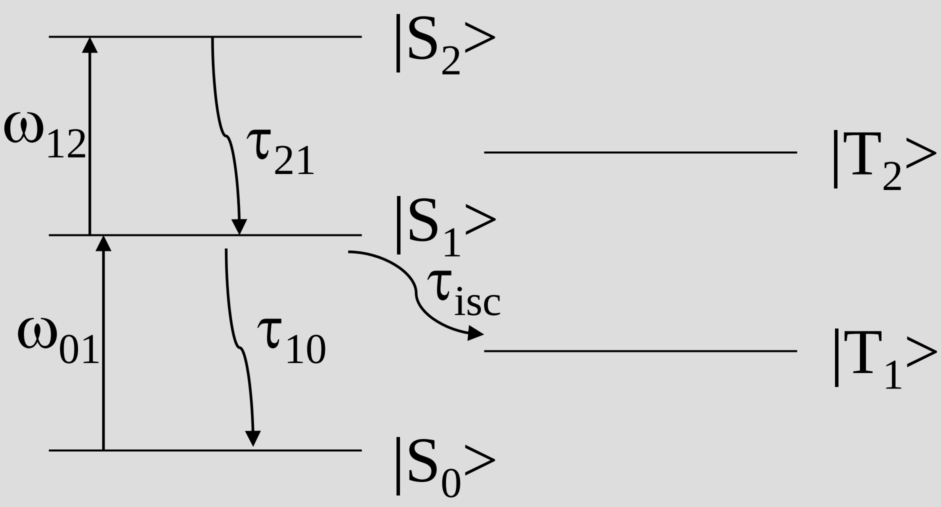
$$\frac{dn_0}{dt} = -w_{01}n_0 + n_1\left(\frac{1}{\tau_f} - \frac{1}{\tau_{isc}}\right)$$

$$\frac{dn_1}{dt} = w_{01}n_0 - n_1\left(\frac{1}{\tau_f} - \frac{1}{\tau_{isc}}\right)$$

$$\frac{dn_{T_1}}{dt} = \frac{n_1}{\tau_{isc}}$$

$$\frac{1}{\tau_f} = \frac{1}{\tau_{10}} + \frac{1}{\tau_{isc}}$$

Five-level energy diagram



where τ_f is the fluorescence lifetime
τ_{isc} is the intersystem crossing time

Results (PTZ-scan)

Intersystem crossing time:

- ✓ **water of $\tau_{isc}=1ns$**
- ✓ **DMSO of $\tau_{isc}=9ns$**

The values of the intersystem crossing time are short. These short times are due to an efficient singlet-triplet conversion, which indicate that the indocyanine green is suitable to be applied as a PDT sensitizer.

Absorption cross-section of the triplet state:

- ✓ **Water of $\sigma_T=(9\pm1)\times10^{-7}cm^2$**
- ✓ **DMSO of $\sigma_T=(7\pm1)\times10^{-7}cm^2$**

Conclusions

✓ **The results obtained exhibit a reverse saturated absorption and a fast intersystem crossing lifetime.**

✓ **Excited singlet and triplet cross-sections of ICG in both solvents are extremely high in relation to the ground state.**

✓ **Compared with de ground state, the singlet excited state present a value 50 times larger for water and 75 times larger for DMSO.**

✓ **In triplet state, this difference is lower than for singlet excited state. For this case, the values are 33 and 45 times larger for water and DMSO, respectively.**

✓ **The high singlet and triplet excited states cross-sections and the high population in the triplet state makes ICG a good candidate for photodynamic therapy and optical limiting devices.**