Dynamics nonlinear optical properties in indocyanine green solutions

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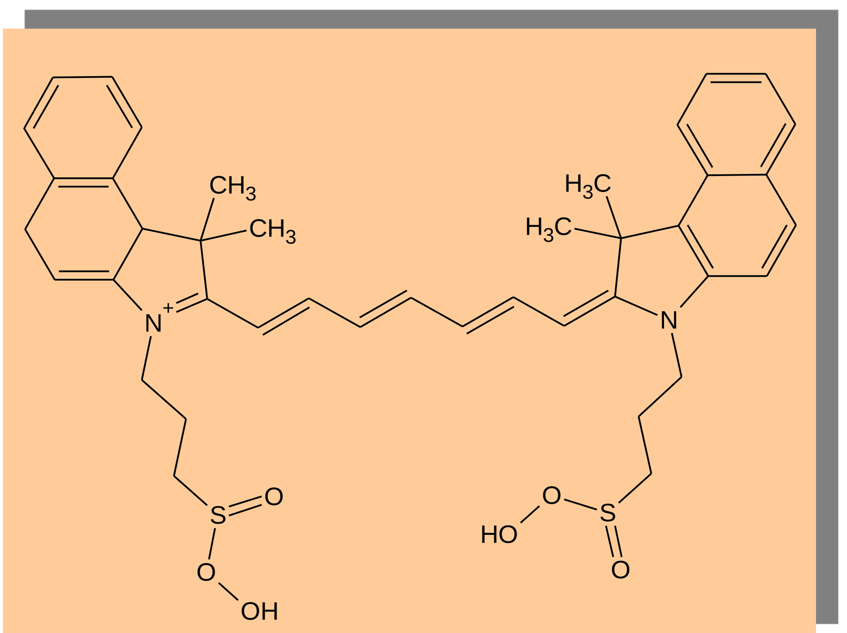
Abstract

In this work, we present a study of dynamic nonlinear of the Indocyanine Green diluted in distilled water and in DMSO solvents. We have used two configuration of the Z-scan technique to obtain the singlet and triplet dynamics, separately. The results obtained with both techniques have shown that the excited singlet and triplet cross sections of molecule in both solvents are extremely high in relation at ground singlet state. The results found exhibit a reverse saturated absorption and a fast intersystem crossing process. The high excited singlet and triplet states cross section and a high population in the triplet state does the indocyanine green to be a good sensitizer for photodynamic therapy and also a good molecule for fast optical limiting devices.

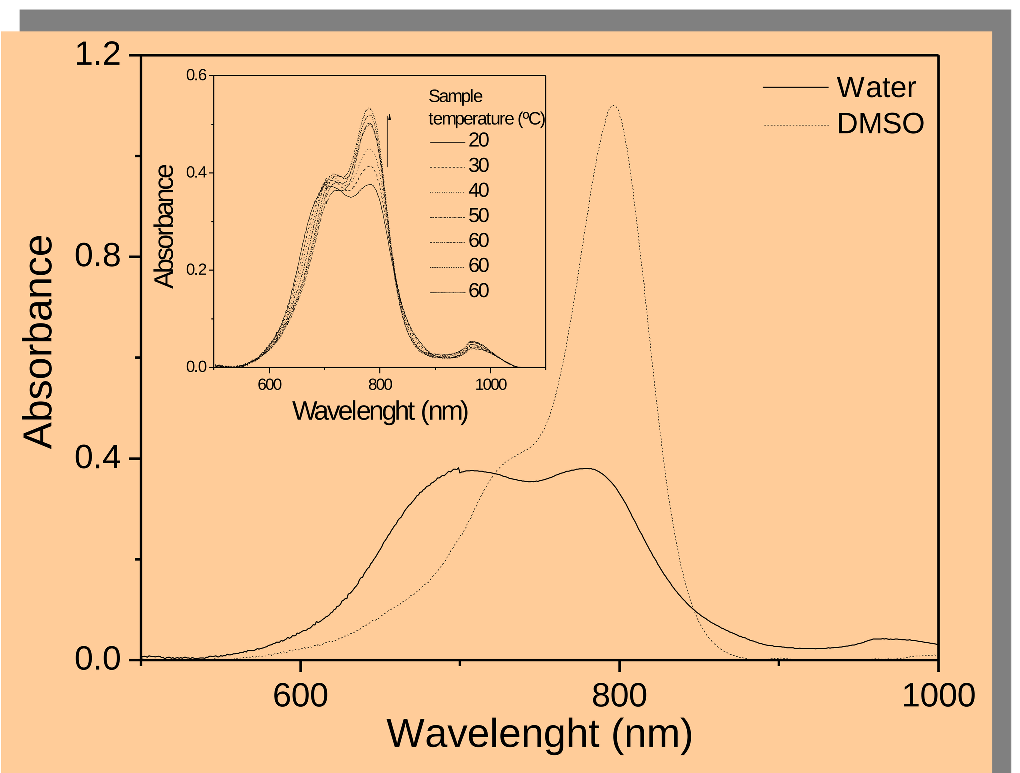
Indocyanine Green (ICG)

✓ Molecular structures



The organic dye Indocyanine Green (ICG) has many applications:
- as laser dye;
- as saturable absorber;
- for diagnosis ;
- for photo-dynamic therapy (PDT) of cancer;
- Optical limiting.

✓ Absorption linear



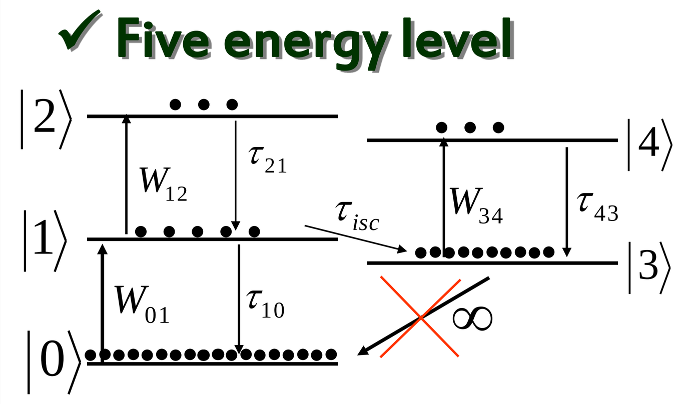
UV-Vis absorption spectrum, obtained with a Cary-17A spectrometer , of ICG diluted in water (solid line) and in DMSO (dash line) for a concentration of the 2x10[16] molecules/cm[3].

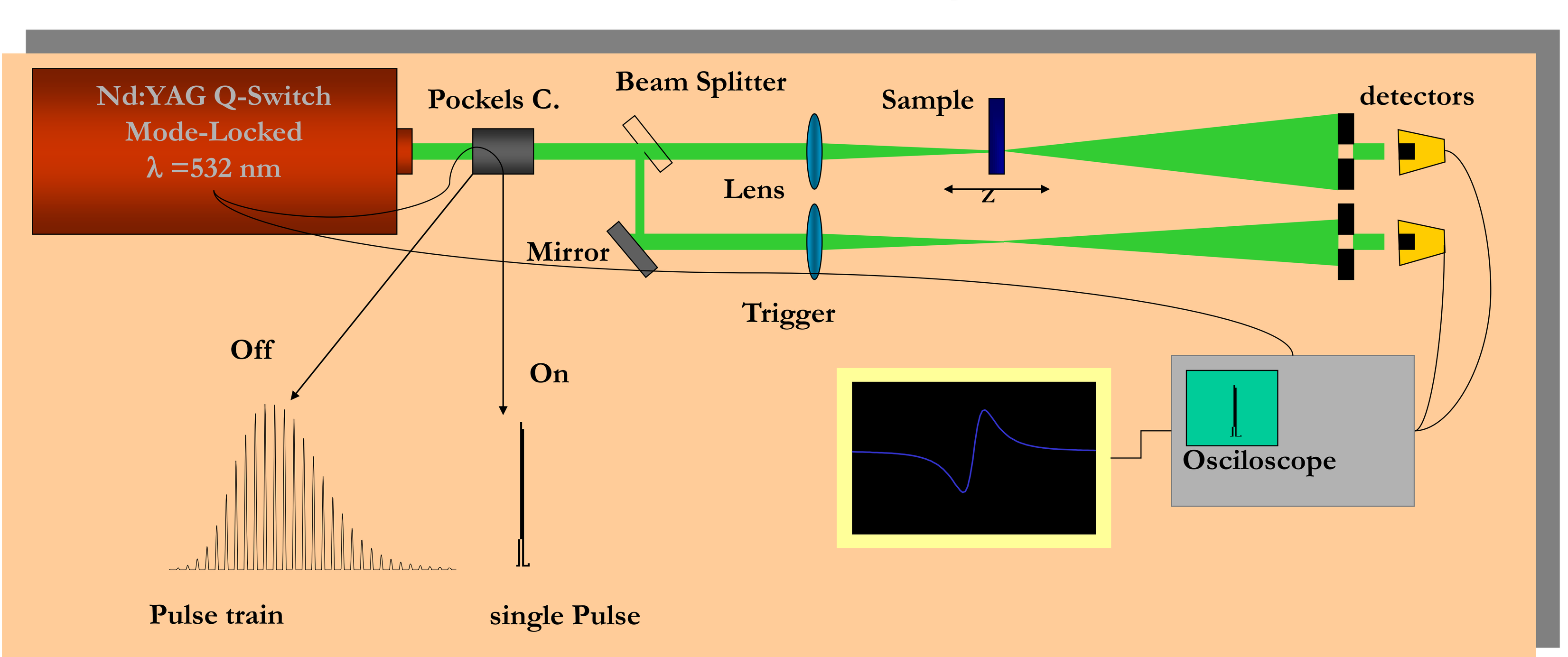
For temperatures low that 60ºC, this optical process is reversible and for temperatures higher than 60ºC it does not recovery the initial absorption. This can be associated with sample degradation. Due to this thermal behavior, we have just done the nonlinear measurements in the room temperature.

✓ Z-Scan experimental setup

The excitation of the sample was made at 532 nm, being the double frequency of a laser Nd:YAG Q-switched and mode-locked (*Antares* Coherent). The characteristic pulse laser delivering from *Antares* contains a pulse train with about 20 pulses, separated by 13 ns and with 100 ps of FWHM. This pulse configuration was used in PTZ-scan. For a single pulse Z-scan, the pulse train pass into a Pockels cell sandwiched between two crossed polarizes, and when a Pockel cell is turn on a single pulse is extracted of the pulse envelope.

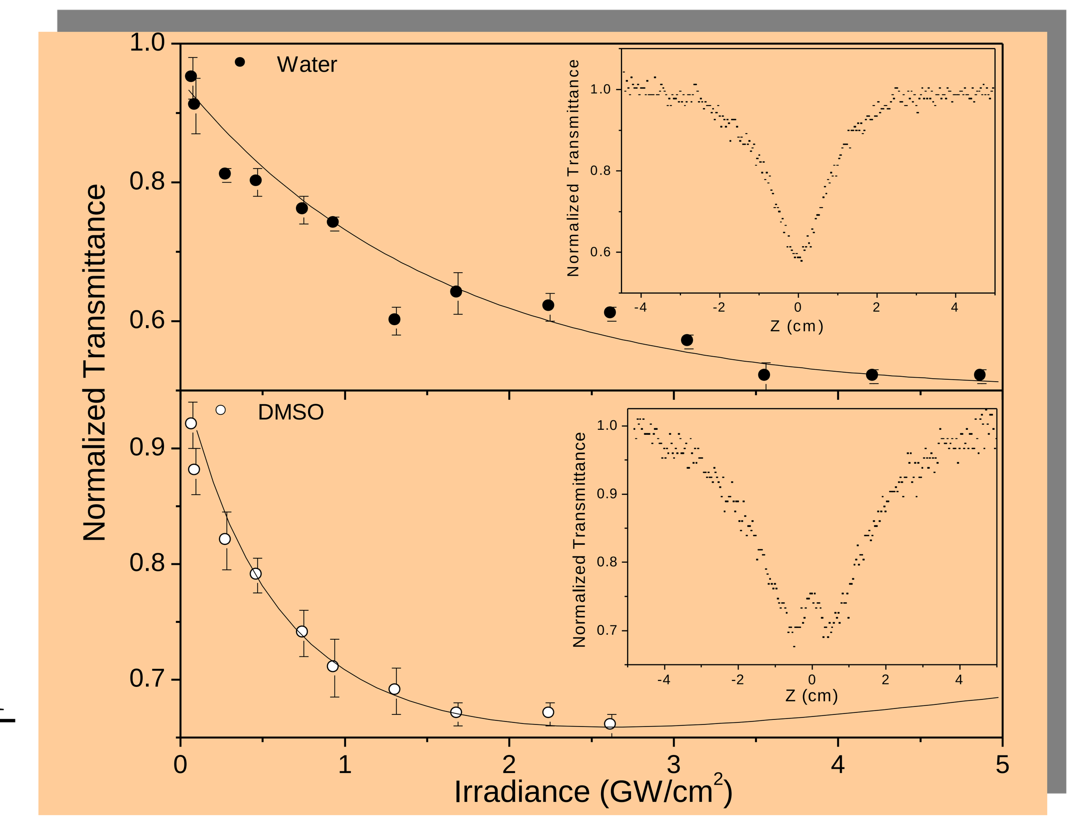
✓ Five energy level





✓ Z-scan results

Normalized transmittance as a function of pulse irradiance for ICG in water (solid circles) and DMSO (open circles). The fit are obtained by rate equations that describe three–energy-level diagram (red box)



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

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

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

$$\frac{dn_3}{dt} = -W_{34}n_3 + \frac{n_4}{\tau_{43}} + \frac{n_1}{\tau_{isc}}$$

$$\frac{dn_4}{dt} = W_{34}n_3 - \frac{n_4}{\tau_{43}}$$

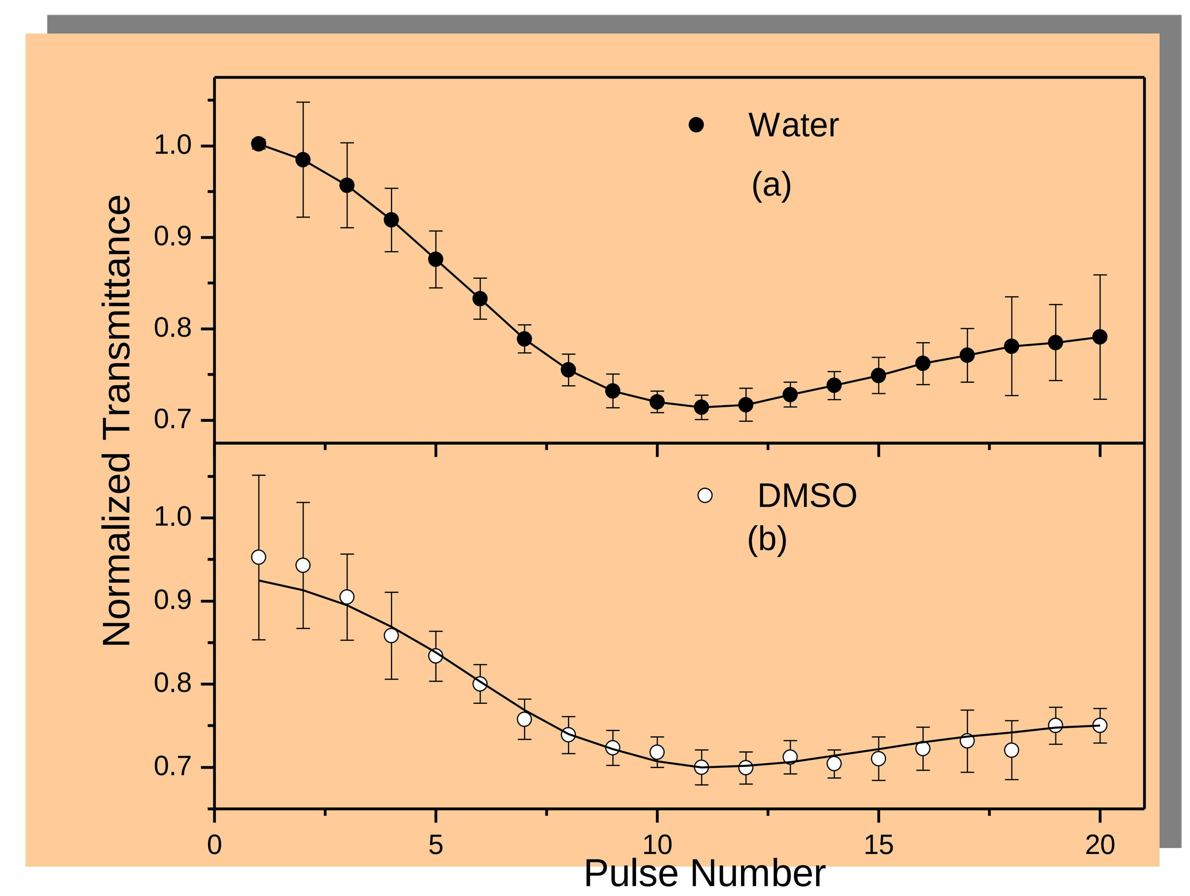
$$W_{01} = \frac{\sigma_{01}I(t)}{h\nu} \quad W_{12} = \frac{\sigma_{12}I(t)}{h\nu} \quad W_{34} = \frac{\sigma_{34}I(t)}{h\nu}$$

The values of excited state cross-section were $\sigma_{12}=(13\pm1)\times10^{-7}cm^2$ for water and $\sigma_{12}=(12\pm1)\times10^{-7}cm^2$ and 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 and 75 times larger for DMSO. The result indicates that ICG can be a good candidate for optical limiting.

✓ Pulse train (PTZ-scan) Z-scan results

Normalized transmittance along of the complete Q-switch envelope for water in a and for DMSO in b, both with same intensity of $I=0,63GW/cm^2$. The fit are obtained by rate equations that describe five–energy-level diagram.

The intersystem crossing time for water of $\tau_{isc}=1ns$ and 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. We also found, with this procedure, the absorption cross-section of the triplet state that were $\sigma_T=(9\pm1)\times10^{-7}cm^2$ and $\sigma_T=(7\pm1)\times10^{-7}cm^2$, respectively for water and DMSO solvents.



✓ Conclusion

The results obtained with both techniques have shown that the excited singlet and triplet cross sections of ICG in both solvents are extremely high in relation to the ground state. If 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 the 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 section and a high population in the triplet state makes ICG a good candidate for photodynamic therapy and optical limiting devices.