Excited state dynamics in Zn phthalocyanines

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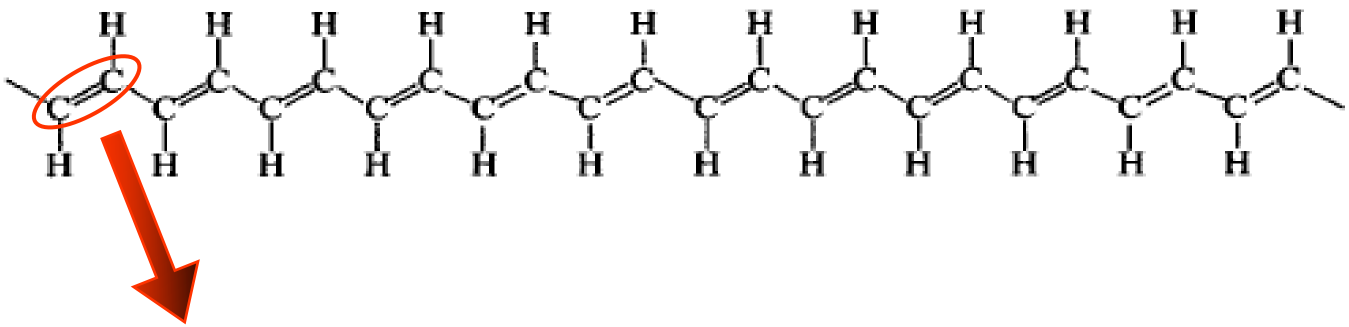
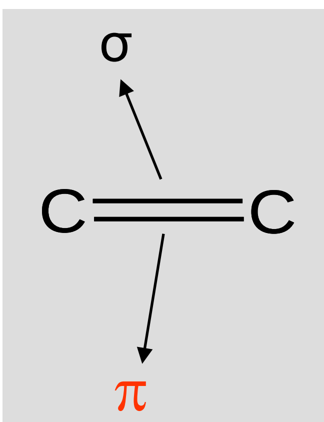
Organic materials

- Flexibility to tune the nonlinear optical response by manipulating the molecular structure

- π-conjugated structures

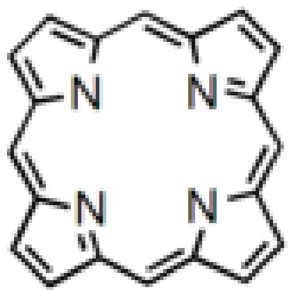




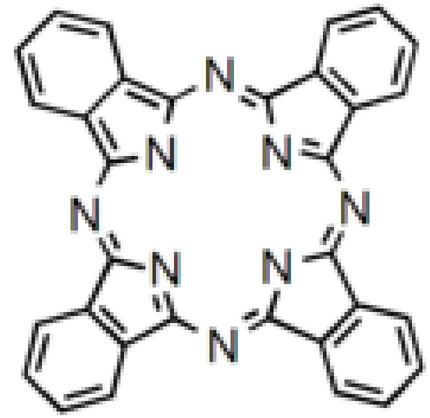
π - conjugated system: delocalized electrons

high optical nonlinearities

Macrocycles



porphyrin



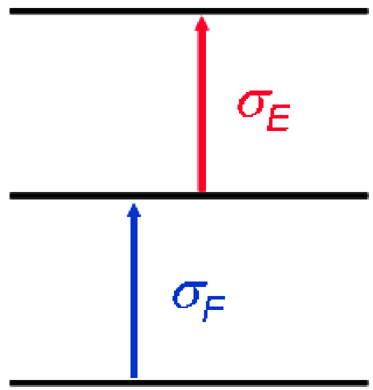
phthalocyanine

•Macrocyclic organic compounds such as porphyrins and phthalocyanines exhibit large optical nonlinearities

•Present intense reverse saturable absorption (RSA)

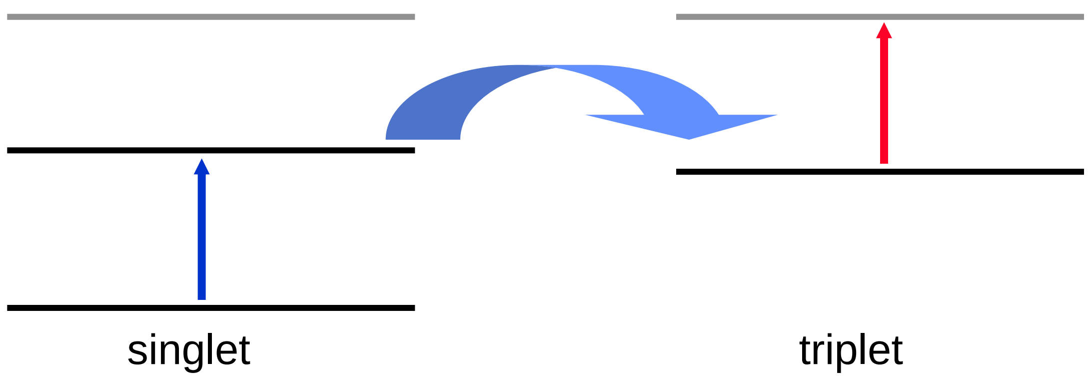
Reverse saturable absorption - (RSA)

The excited cross-section exceeds that of the ground state.



$$\sigma_E > \sigma_F$$

Usually, RSA follows from an intersystem crossing process from a higher excited singlet to an triplet state.



Applications

- Photodynamic therapy

Generation of singlet oxygen through the interaction of oxygen with triplet macrocycles

↓

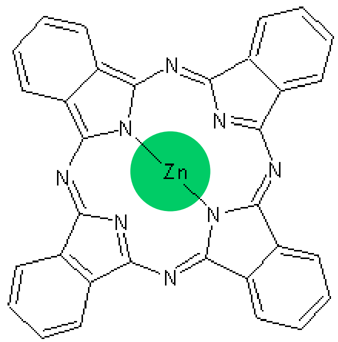
cytotoxic

- Optical limiting

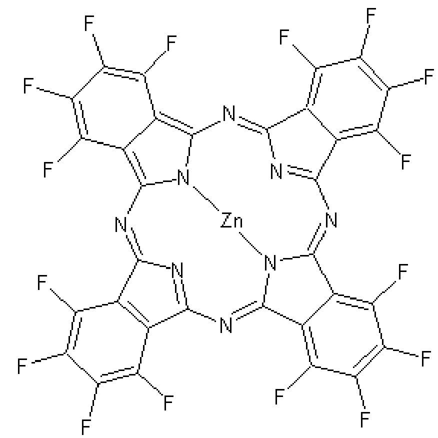
To protect eye and sensors from intense laser pulses

Samples

One way to screening materials for a specific application is through the knowledge of their excited state properties, which can be obtained using nonlinear optical techniques.



ZnPc, FePc, PdPc

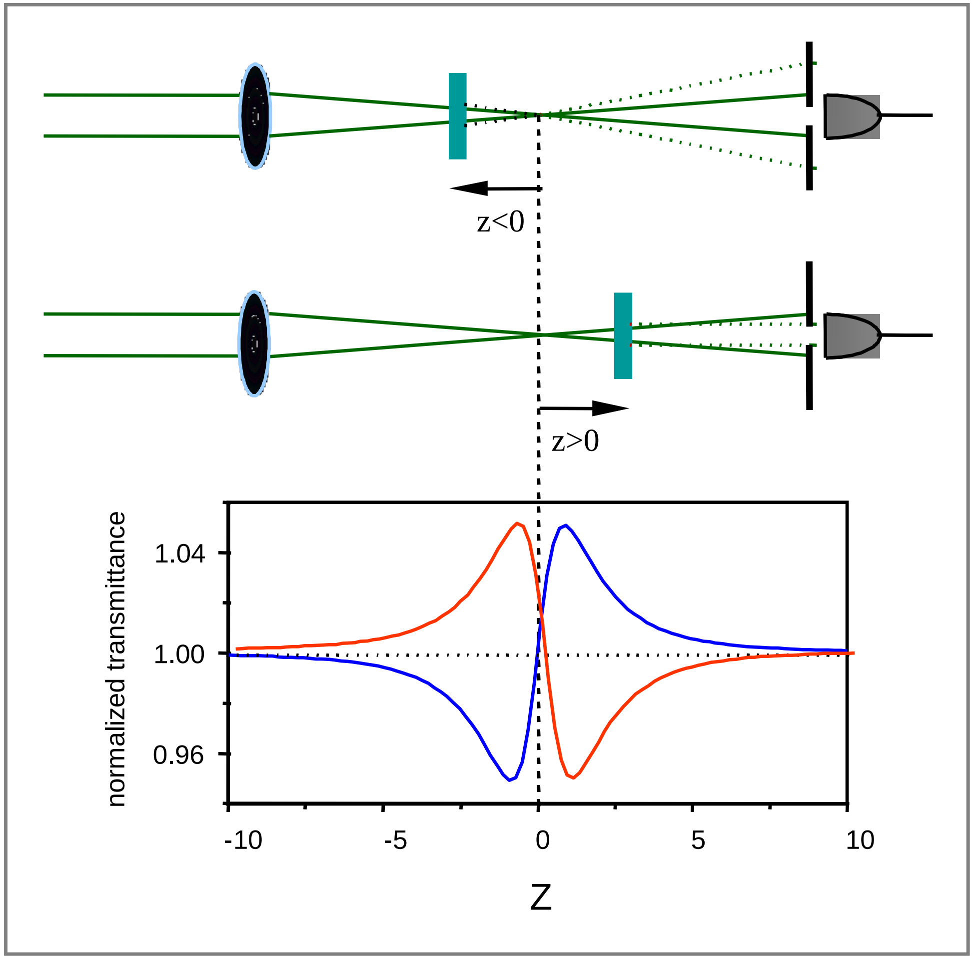


$F_{16}ZnPc$

Samples in DMSO solution

Z-scan technique

closed aperture Z-scan



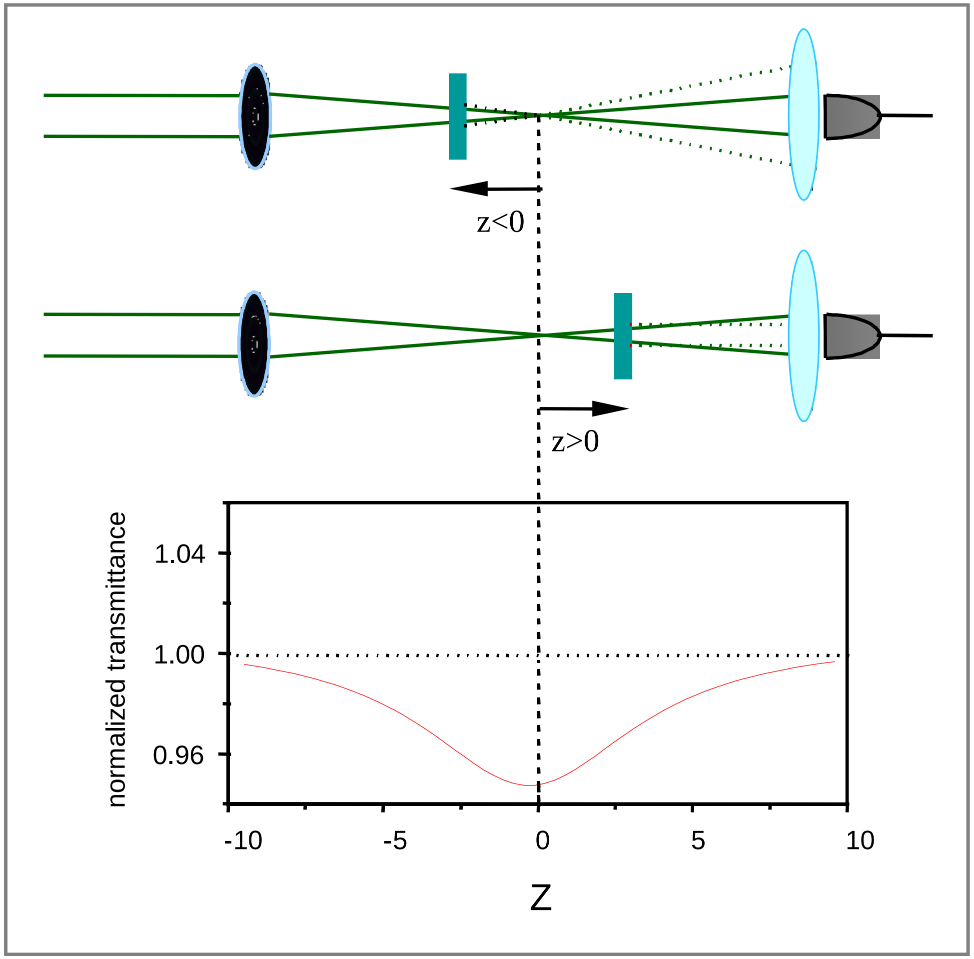
- Nonlinear refraction

$$n = n_0 + n_2 I$$

$$\Delta T \propto n_2 I$$

Z-scan technique

open aperture Z-scan



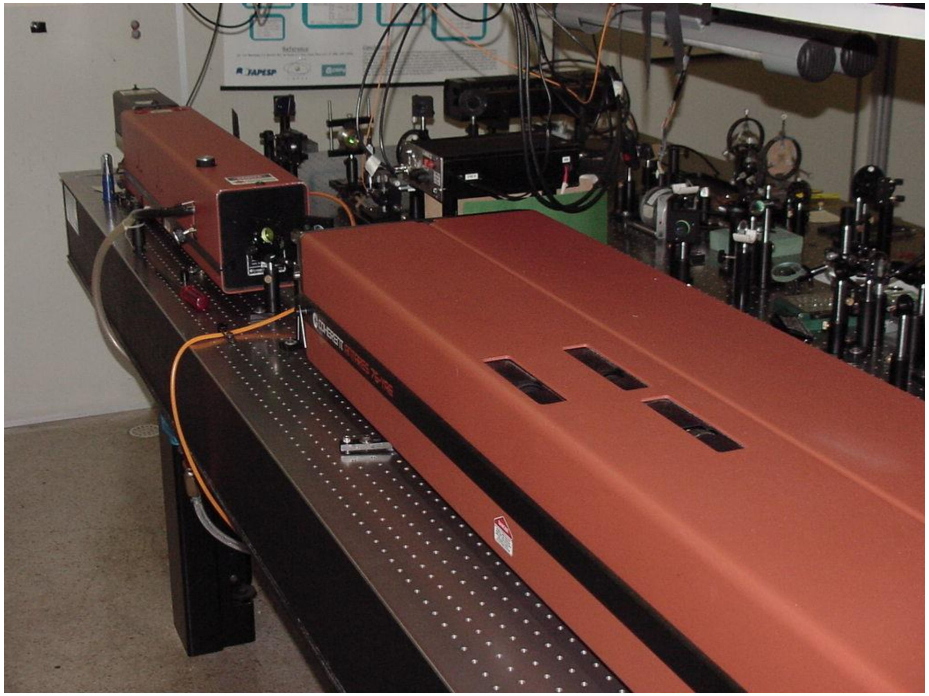
- Nonlinear absorption
  - Saturation of absorption
  - Reverse Saturation of abs
  - Two-photon absorption

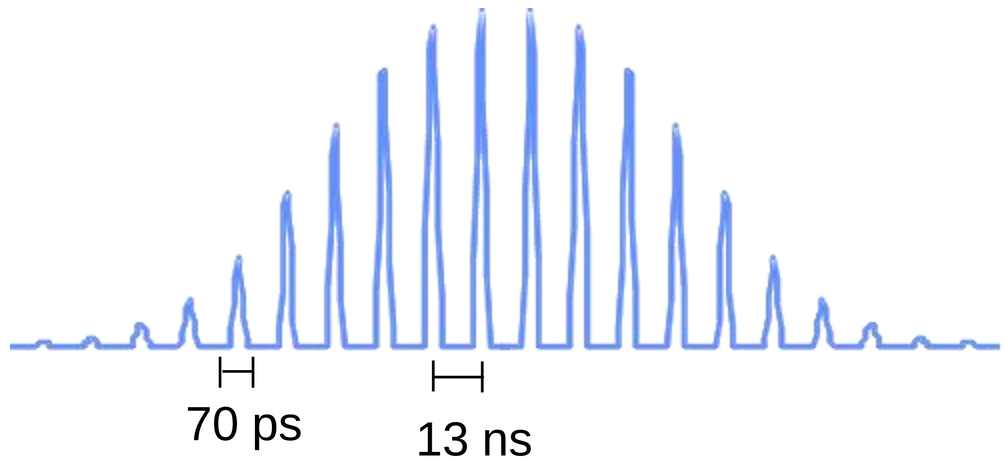
$$\alpha(I) = \alpha_0 + \beta I$$

$$\Delta T \propto \beta I$$

Dynamic of these processes

Z-scan with pulse trains

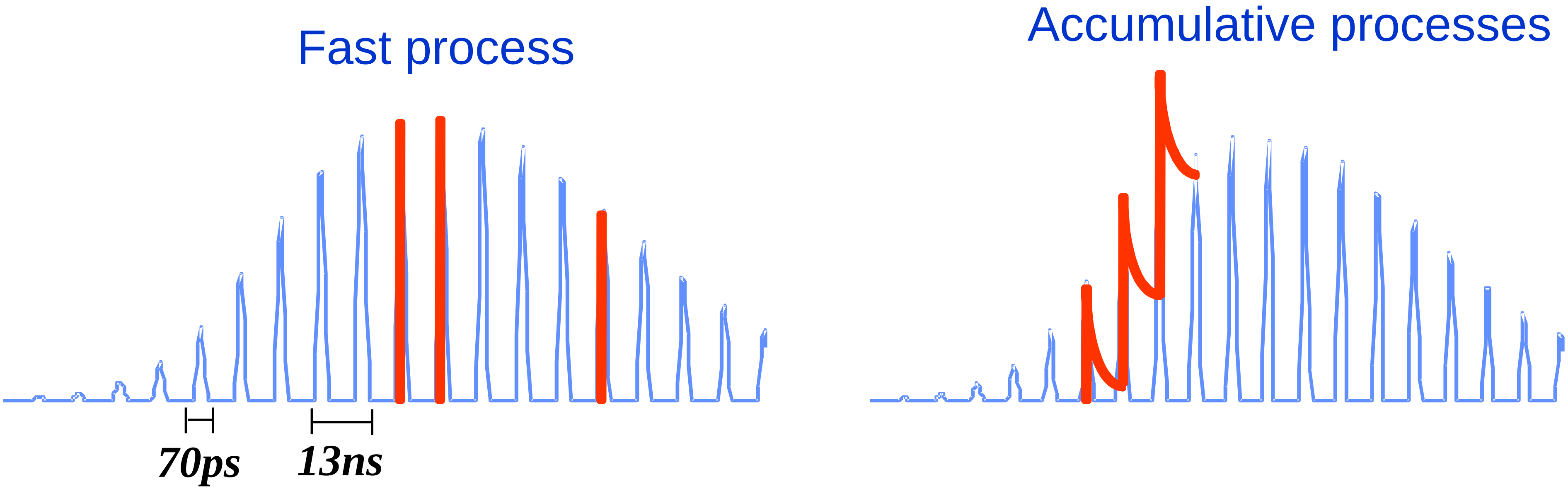




- Nd:YAG Q-switched/modelocked laser
  - 532nm and 1064 nm
  - 70 ps

Pulse train Z-scan

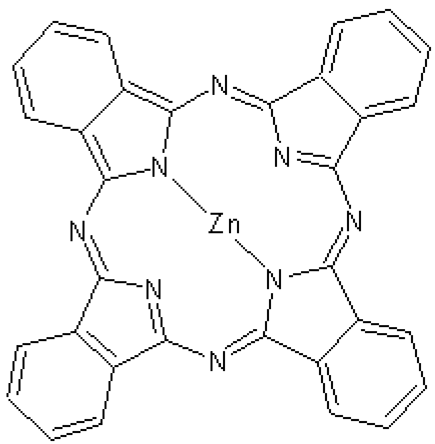
Allows the discrimination between fast and accumulative contributions

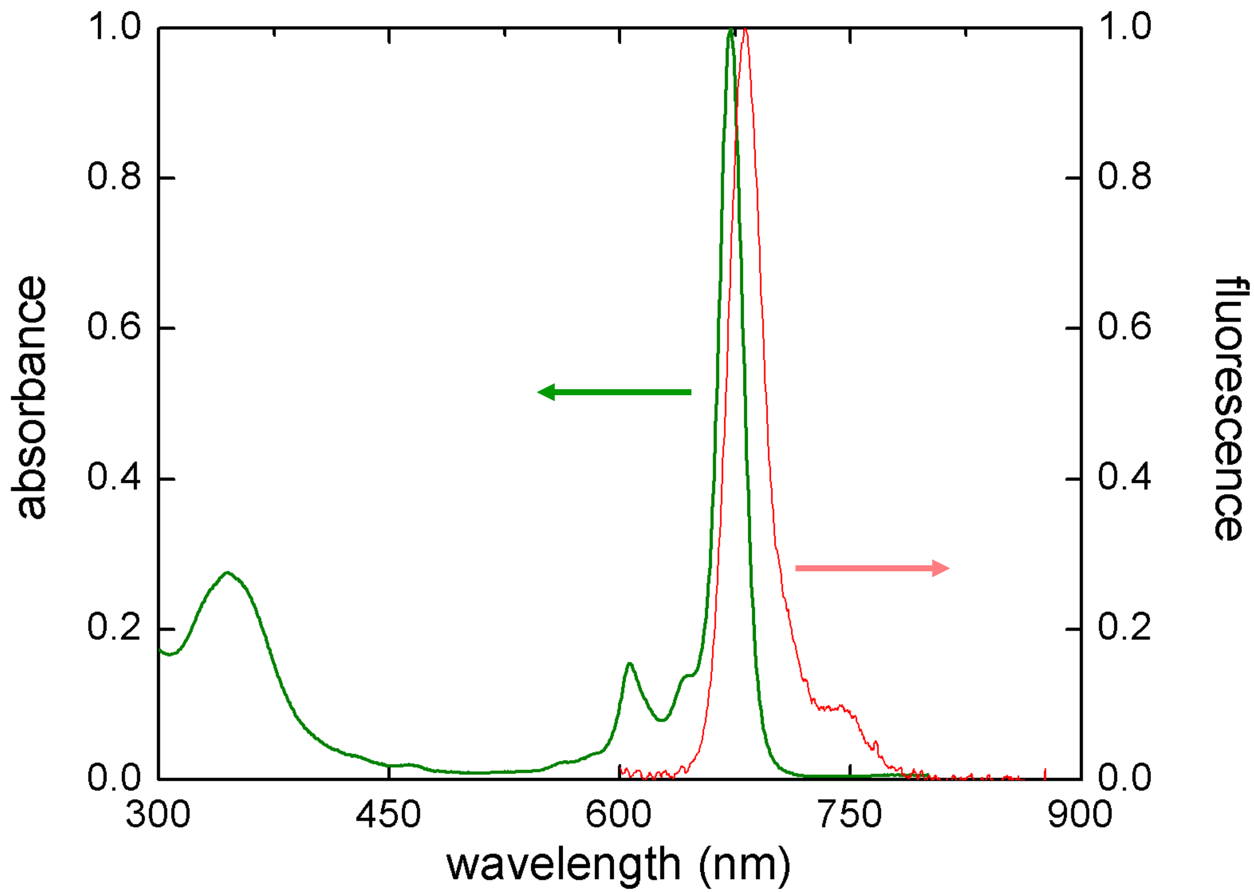


Dynamic of the nonlinear response

Nonlinear absorption dynamics

Zn phtalocyanine
(ZnPc)

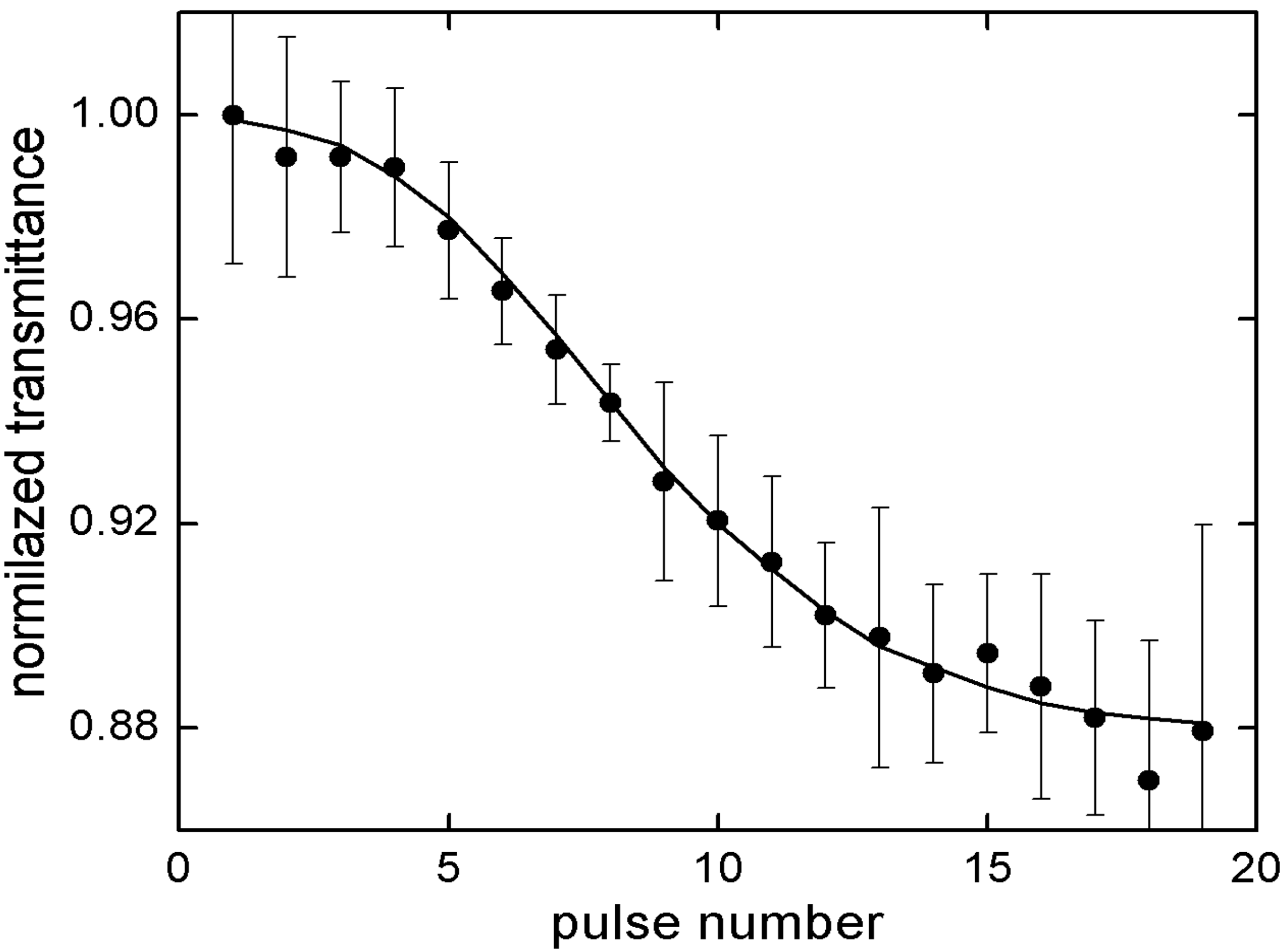


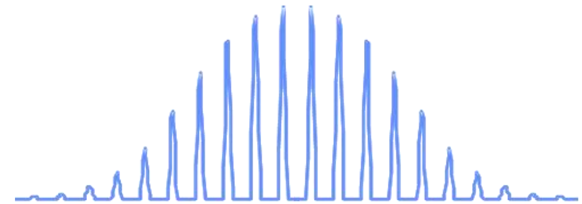


✓ $\sigma_{01} = 0.5 \times 10^{-17}$ cm^2
✓ $\tau_f = 4.3$ ns

Fluorescence excited at 532 nm

Pulse train Z-scan





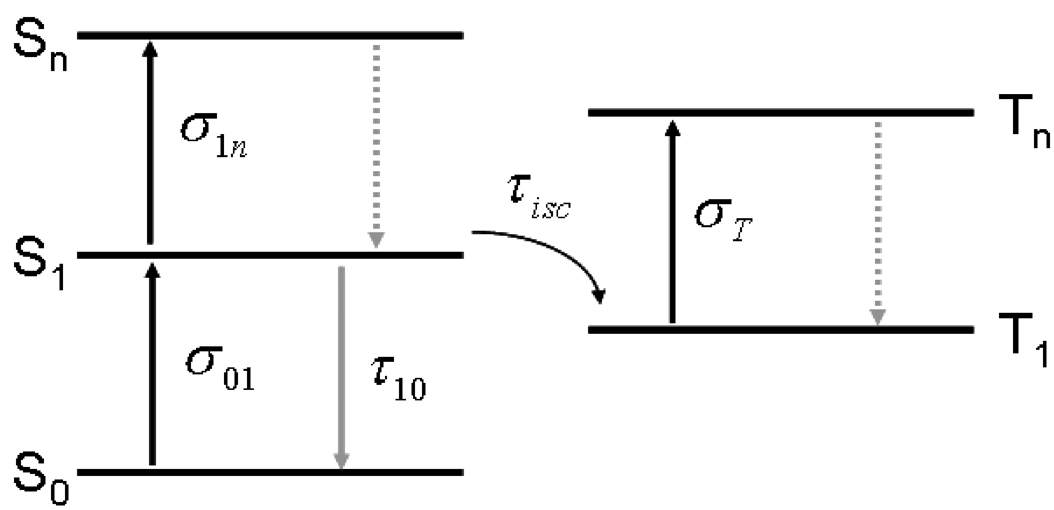
I_{peak} ~ 60 MW/cm^2

acummulative effect

Pulse train Z-scan

Modeling the nonlinear absorption

$$\begin{cases} \dfrac{dn_{S_0}}{dt} = -n_{S_0} W_{01} + \dfrac{n_{S_1}}{\tau_{10}} \\ \dfrac{dn_{S_1}}{dt} = n_{S_0} W_{01} - \dfrac{n_{S_1}}{\tau_{10}} - \dfrac{n_{S_1}}{\tau_{isc}} \\ \dfrac{dn_{T_1}}{dt} = \dfrac{n_{S_1}}{\tau_{isc}} \\ \tau_f^{-1} = \tau_{isc}^{-1} + \tau_{10}^{-1} \end{cases}$$



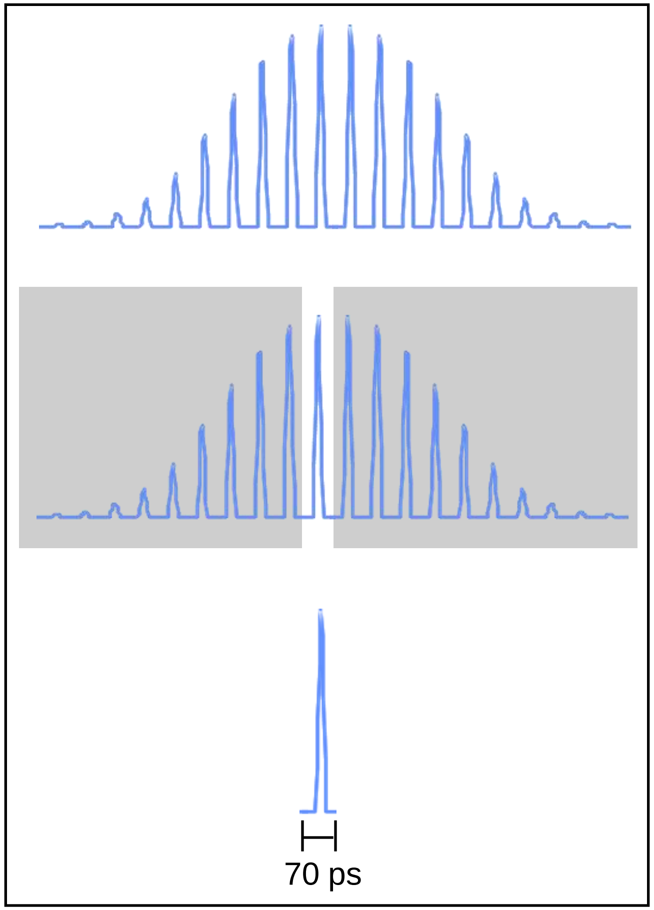
$$\alpha(t) = N\left\{ n_0(t)\sigma_{01} + n_1(t)\sigma_{1n} + n_{T_1}(t)\sigma_T \right\}$$

three fitting parameters

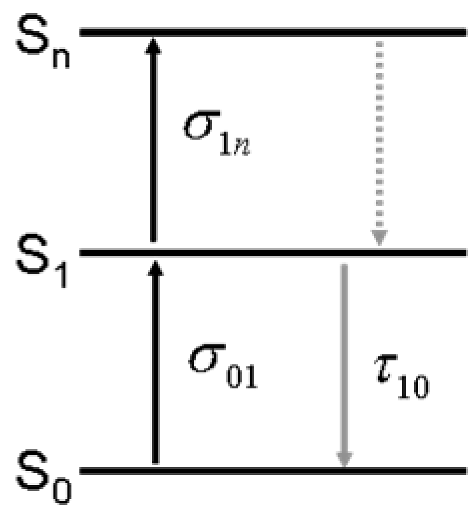
σ_{1n} σ_T τ_{isc}

Single pulse Z-scan

Single-pulse selection using a Pockell cell



As the pulse duration is 70 ps, we do not observe the triplet state

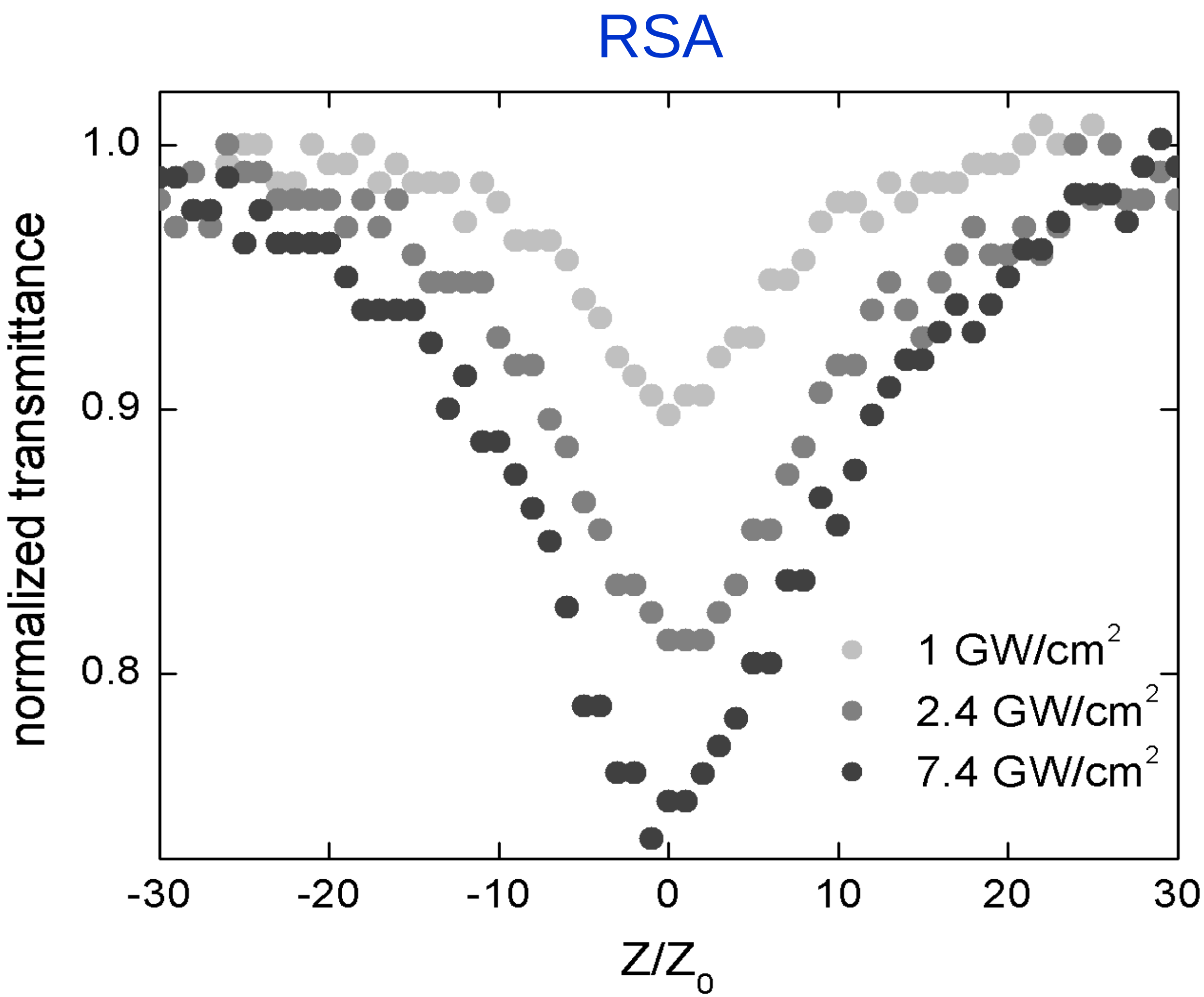


one fitting parameter

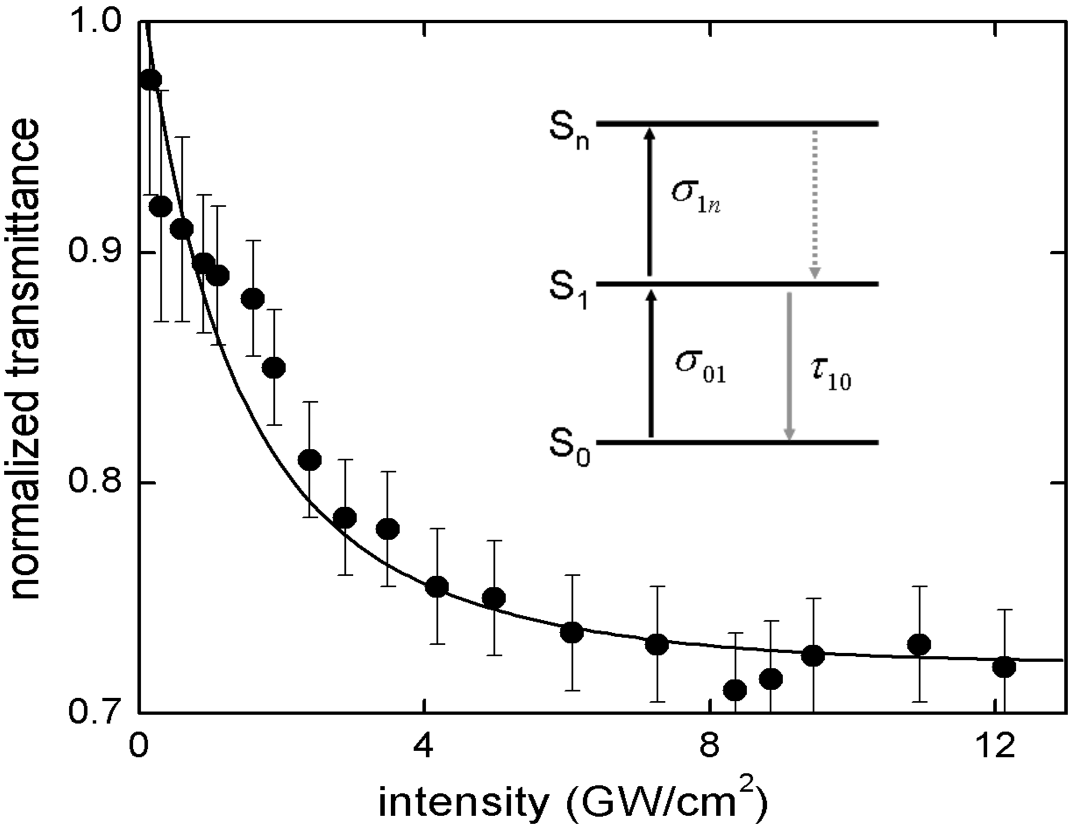
σ_{1n}

Single pulse Z-scan

We perform regular Z-scan measurements with the single pulse



Single pulse Z-scan



$$\frac{dn_{S_0}}{dt} = -n_{S_0} W_{01} + \frac{n_{S_1}}{\tau_{10}}$$

$$\frac{dn_{S_1}}{dt} = n_{S_0} W_{01} - \frac{n_{S_1}}{\tau_{10}}$$

$$\tau_f = \tau_{10}$$

$$\alpha(t) = N\left\{ n_0(t)\sigma_{01} + n_1(t)\sigma_{1n} \right\}$$

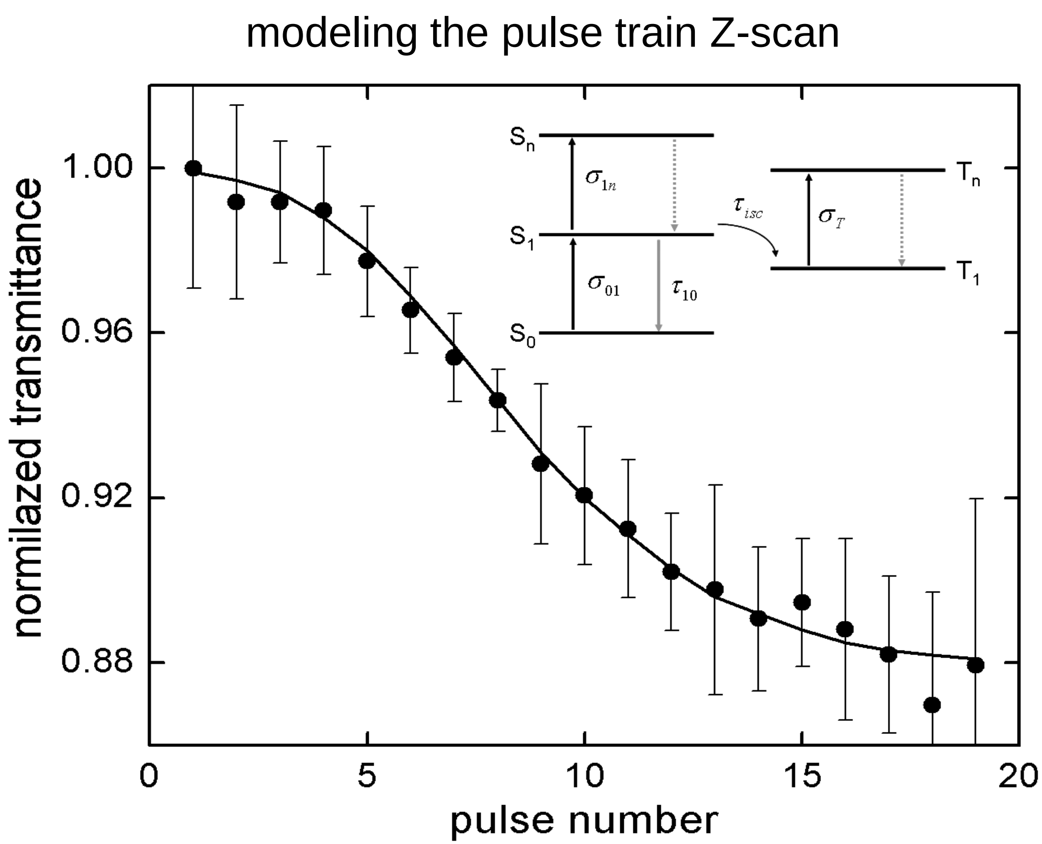
known parameter

✓σ_{01} = 0.5 x 10^{-17} cm^2
✓τ_f = 4.3 ns

determined parameter

✓σ_{1n} = 1.6 x 10^{-17} cm^2

Pulse train Z-scan



$$\begin{cases} \dfrac{dn_{S_0}}{dt} = -n_{S_0} W_{01} + \dfrac{n_{S_1}}{\tau_{10}} \\ \dfrac{dn_{S_1}}{dt} = n_{S_0} W_{01} - \dfrac{n_{S_1}}{\tau_{10}} - \dfrac{n_{S_1}}{\tau_{isc}} \\ \dfrac{dn_{T_1}}{dt} = \dfrac{n_{S_1}}{\tau_{isc}} \\ \tau_f^{-1} = \tau_{isc}^{-1} + \tau_{10}^{-1} \end{cases}$$

$$\alpha(t) = N\left\{ n_0(t)\sigma_{01} + n_1(t)\sigma_{1n} + n_{T_1}(t)\sigma_T \right\}$$

known parameter

- ✓ σ_{01} = 0.5 x 10^{-17} cm^2
- ✓ σ_{1n} = 1.6 x 10^{-17} cm^2
- ✓ τ_f = 4.3 ns

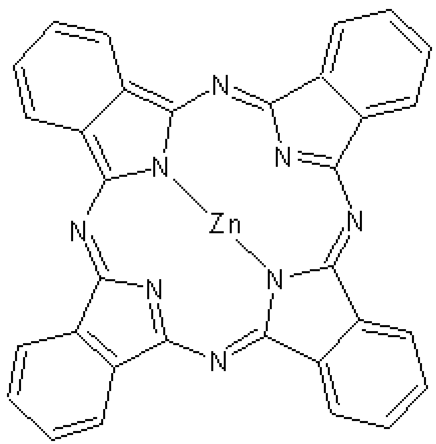
determined parameter

- ✓ σ_T = 1.3 x 10^{-17} cm^2
- ✓ τ_{isc} = 8.9 ns

Nonlinear absorption dynamics

Pulse train Z-scan

ZnPc



λ = 532 nm

- σ_{01} = 0.5 x 10^{-17} cm^2
- σ_{1n} = 1.6 x 10^{-17} cm^2
- σ_T = 1.3 x 10^{-17} cm^2
- τ_f = 4.3 ns
- τ_{isc} = 8.9 ns

cross-section rate

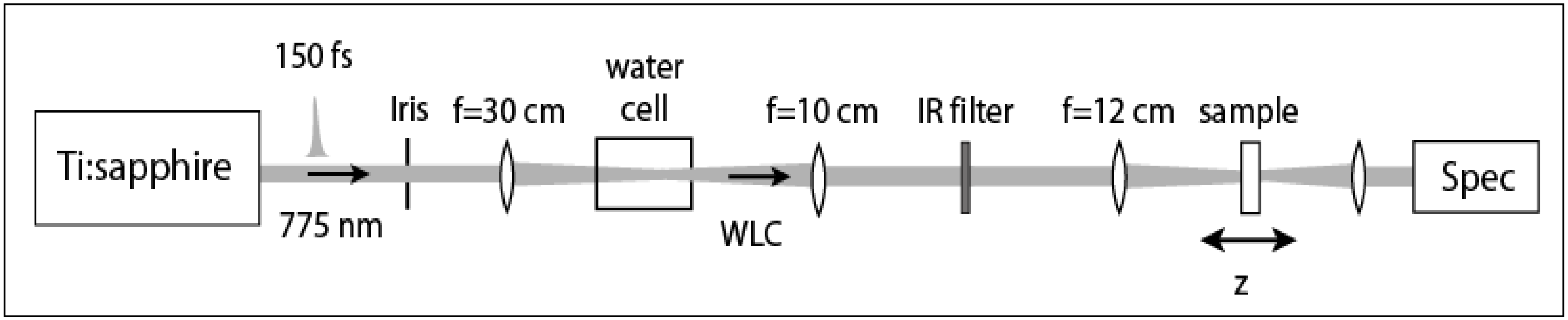
$$\sigma_E/\sigma_{01} \sim 3$$

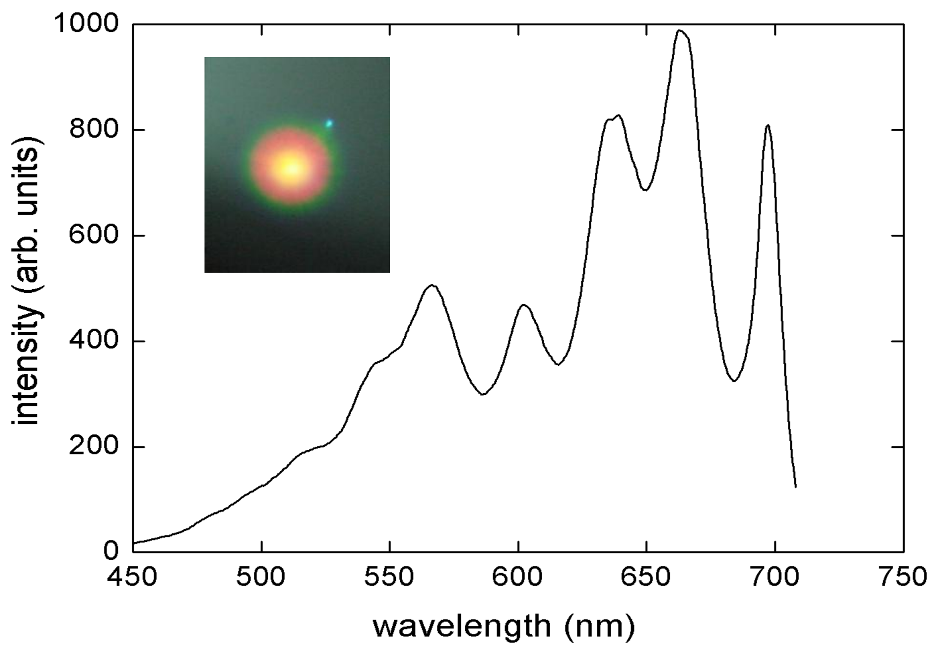
triplet quantum efficiency

$$\phi_T = \tau_f/\tau_{isc} = 0.48$$

White light continuum Z-scan

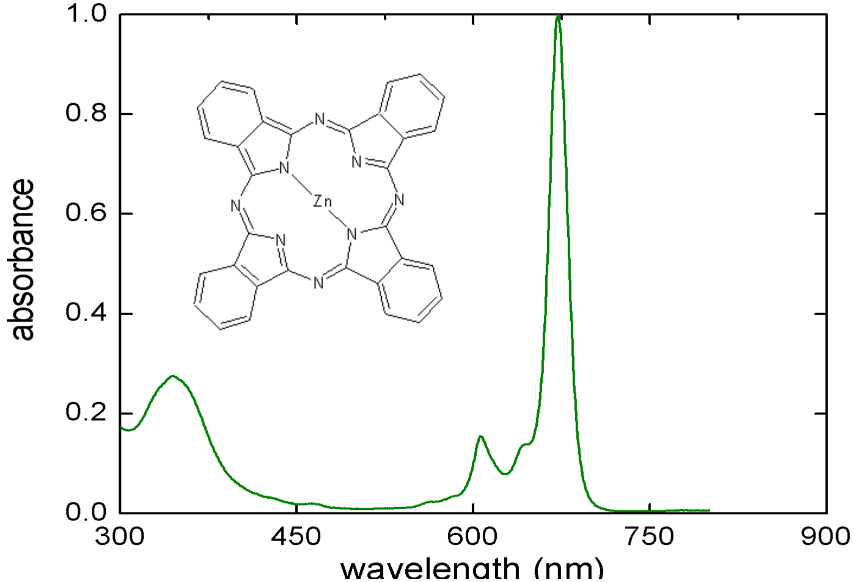
To get the spectral response of the nonlinearity

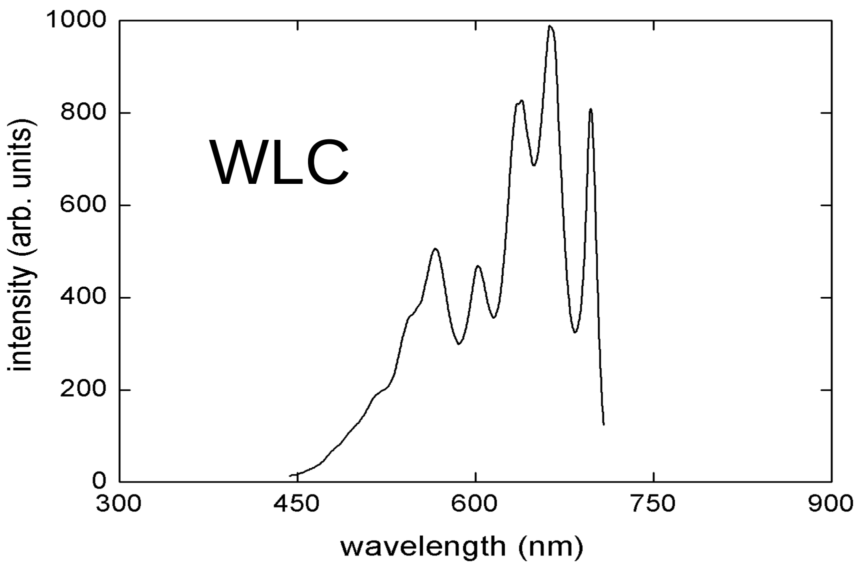




WLC chirp ~ 4 ps

White light continuum Z-scan

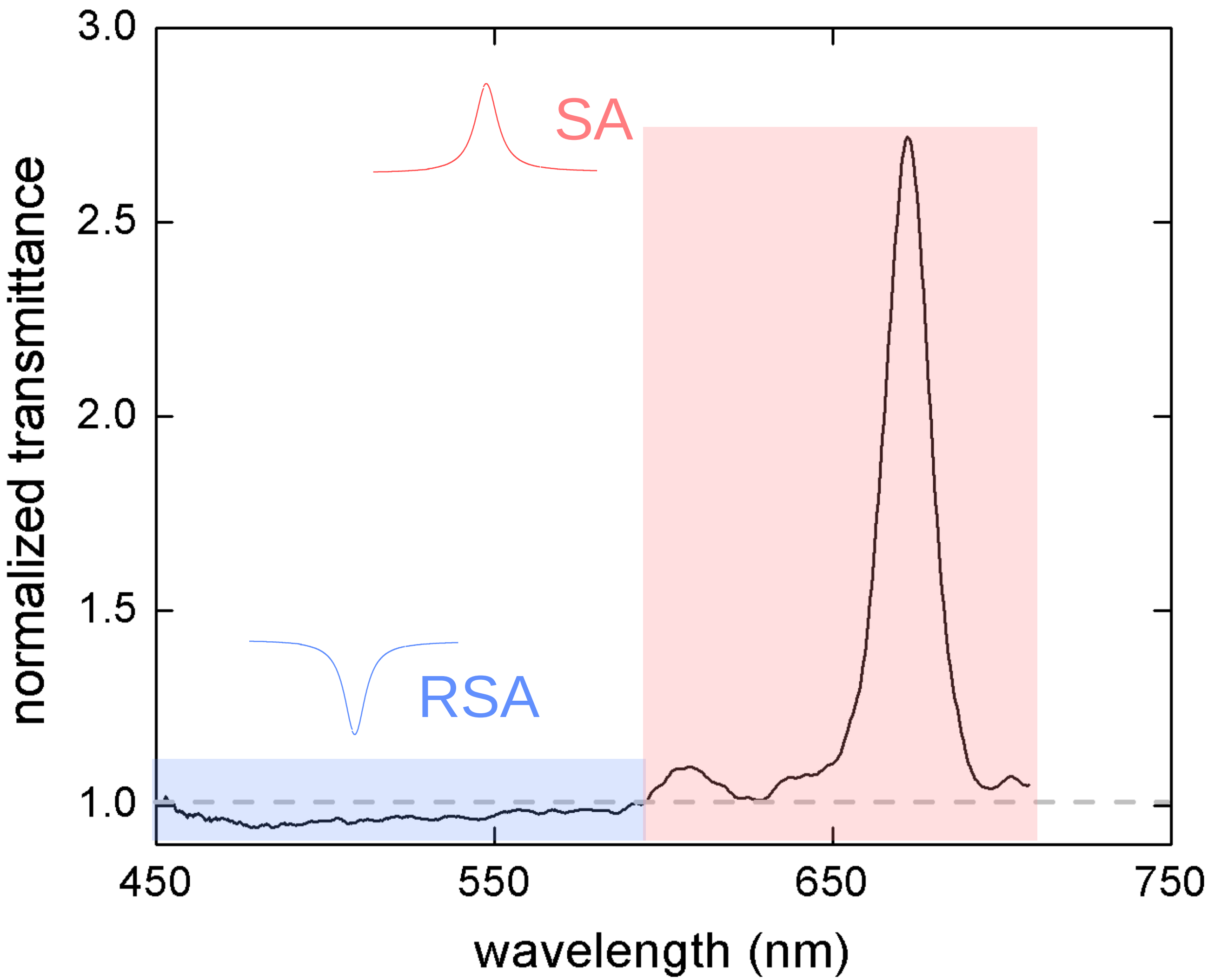




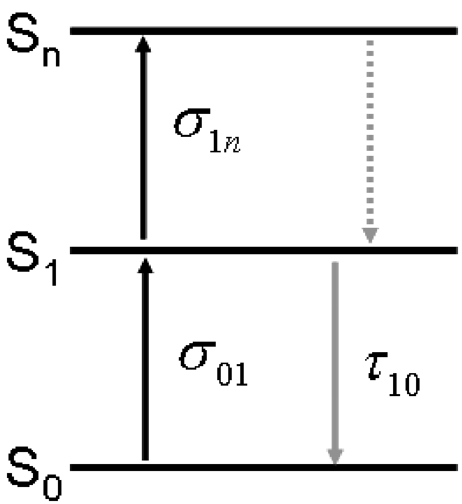
Red portion of the WLC excites ZnPc

Blue portion of the WLC probes the excited state

White light continuum Z-scan



White light continuum Z-scan



$$\frac{dn_0(t)}{dt} = -n_0(t)W_{01}(\lambda) + \frac{1-n_0(t)}{\tau_{10}}$$

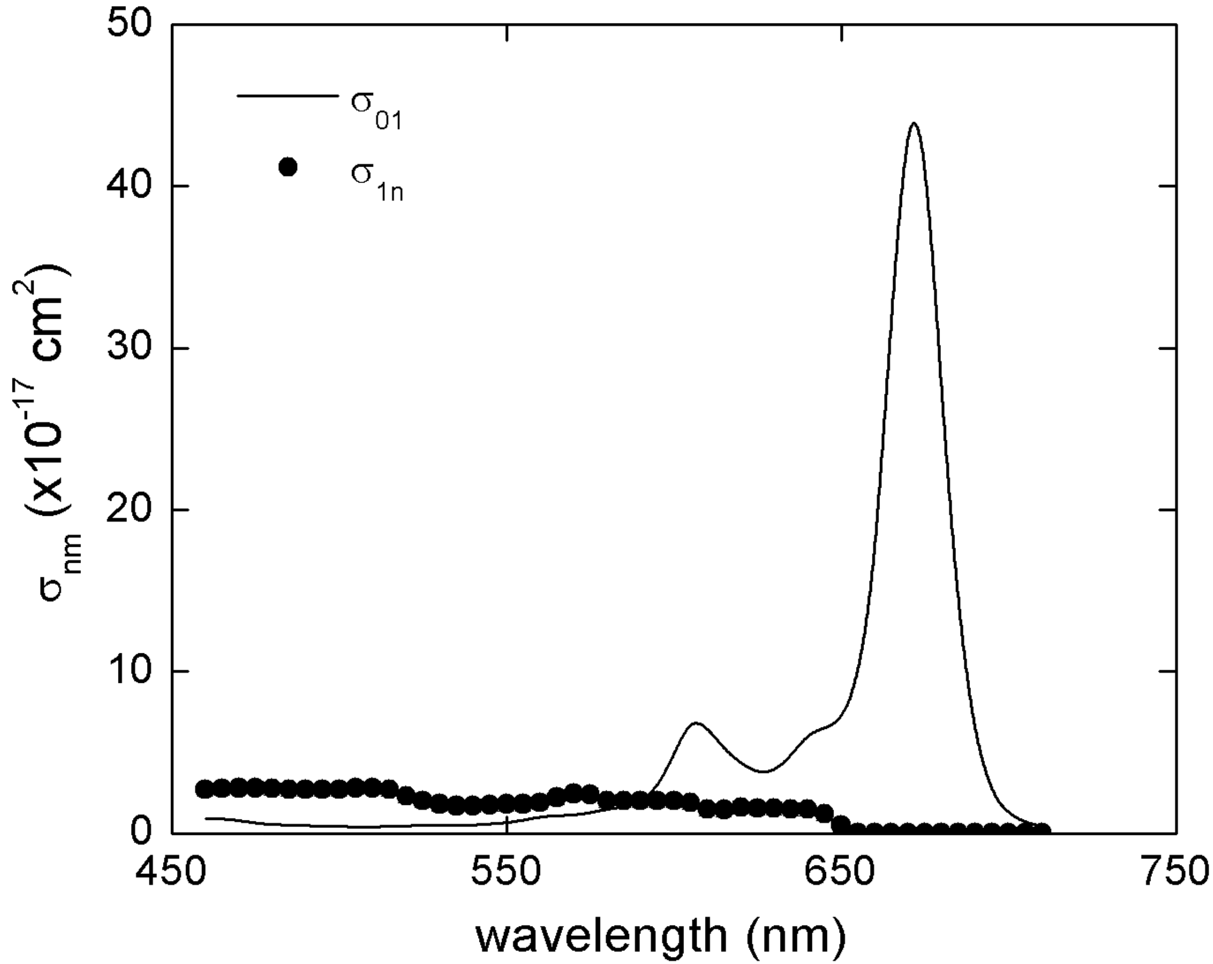
$$n_1(t) = 1 - n_0(t)$$

$$W_{01}(\lambda) = \sigma_{01}(\lambda)\, I/h\nu$$

$$\alpha(\lambda,t) = N\left[n_0(t)\sigma_{01}(\lambda) + n_1(t)\sigma_{1n}(\lambda)\right]$$

Here we use the WLC spectral profile and the absorption spectrum of the sample

White light continuum Z-scan



The value at 532 nm agrees with the one obtained with the pulse train Z-scan

Conclusion and Perspectives

We were able to determine the excited state (singlet and triplet) spectroscopic parameters of ZnPc using the pulse trains Z-scan technique

By employing the WLC Z-scan we determined the excited state cross-section spectrum (singlet state)

We now intend to apply the same techniques to the other Pc´s

We also intend to perform two-photon absorption measurements in these Pc

Acknowledgments

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