Optical nonlinearities in organic materials

Prof. Cleber R. Mendonca

http://www.fotonica.ifsc.usp.br

University of Sao Paulo - Brazil

students 77.000
52.000 undergrad.
25.000 grad.
employers 15.000
professors 6.000

- Sao Paulo
- Sao Carlos (9.000)
- Ribeirao Preto

University of Sao Paulo – in Sao Carlos

University of Sao Paulo – in Sao Carlos

University of Sao Paulo – in Sao Carlos Campus II (new Campus)

Instituto de Física de São Carlos

IFSC

Professors: 68

Employers: 160
(technical and administration)

Students: 450 (undergrad)
100 (master)
140 (phD)

Several research areas in Physics and Material Sciences

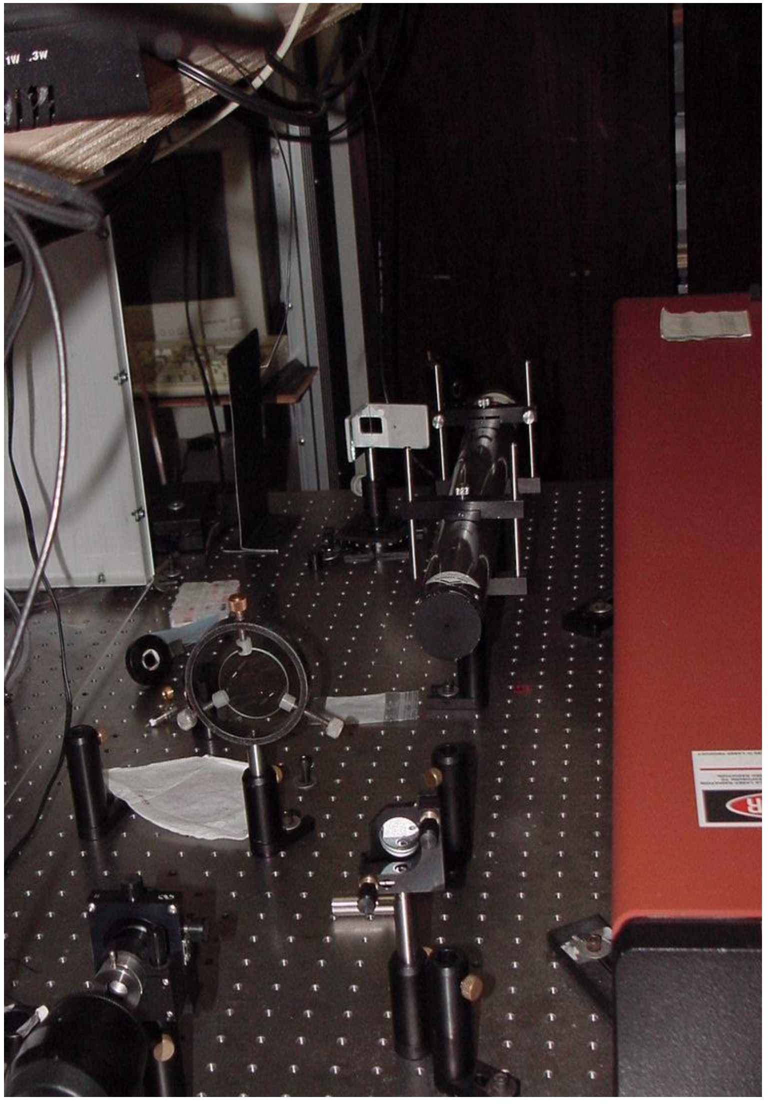
Grupo de Fotonica
Photonics Groups

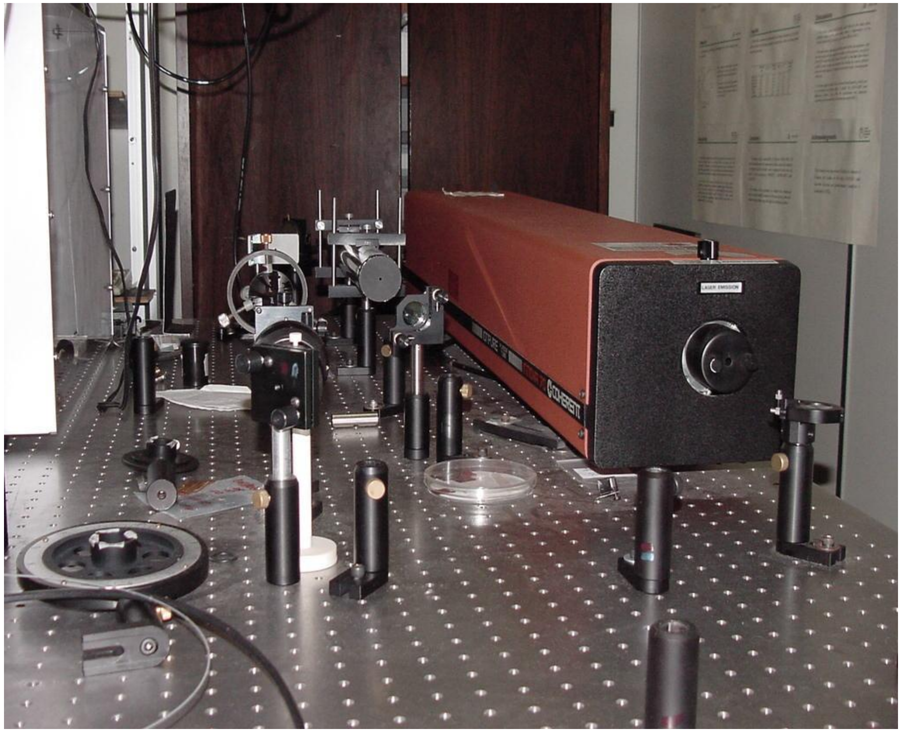
The purpose of the Photonics Group is to develop fundamental science and applied technology *in Optics and Photonics*

Some of the research areas

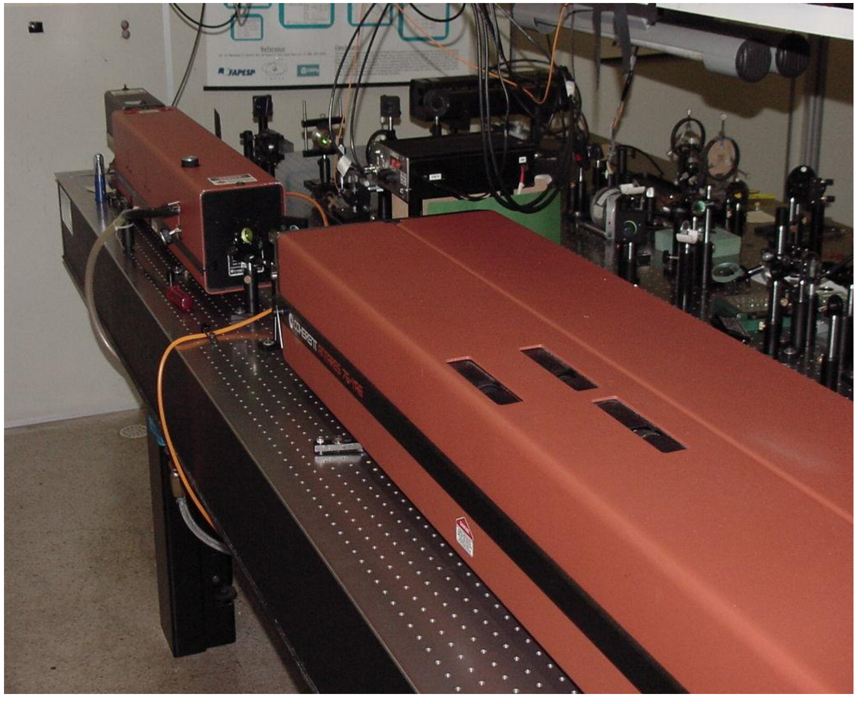
- Nonlinear optics
- Coherent control of light matter intercation
- fs-laser microfabrication and micromachining
- Optical spectroscopy
- Optical storage

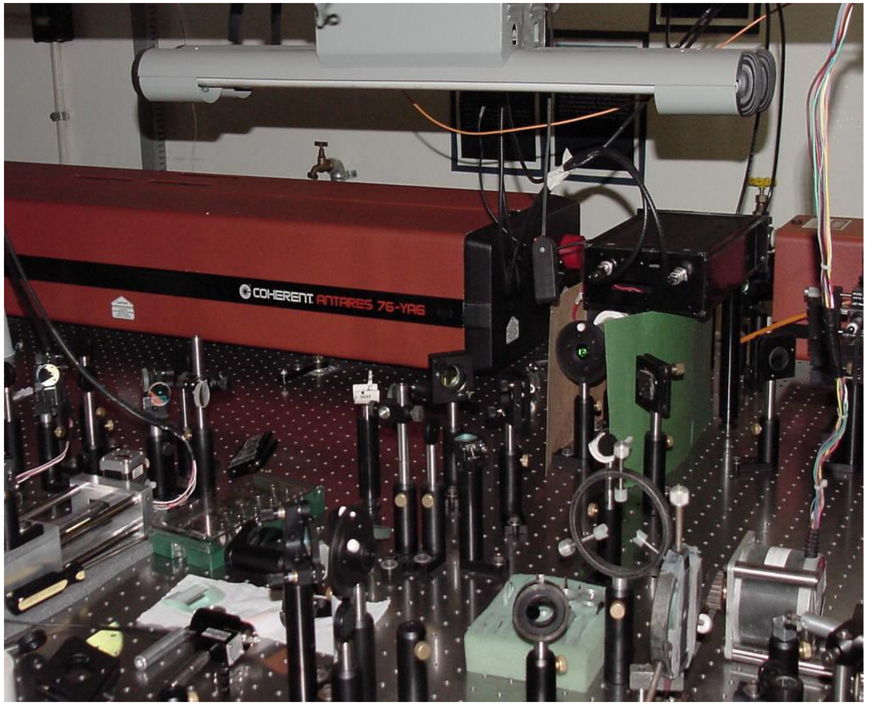
cw laser





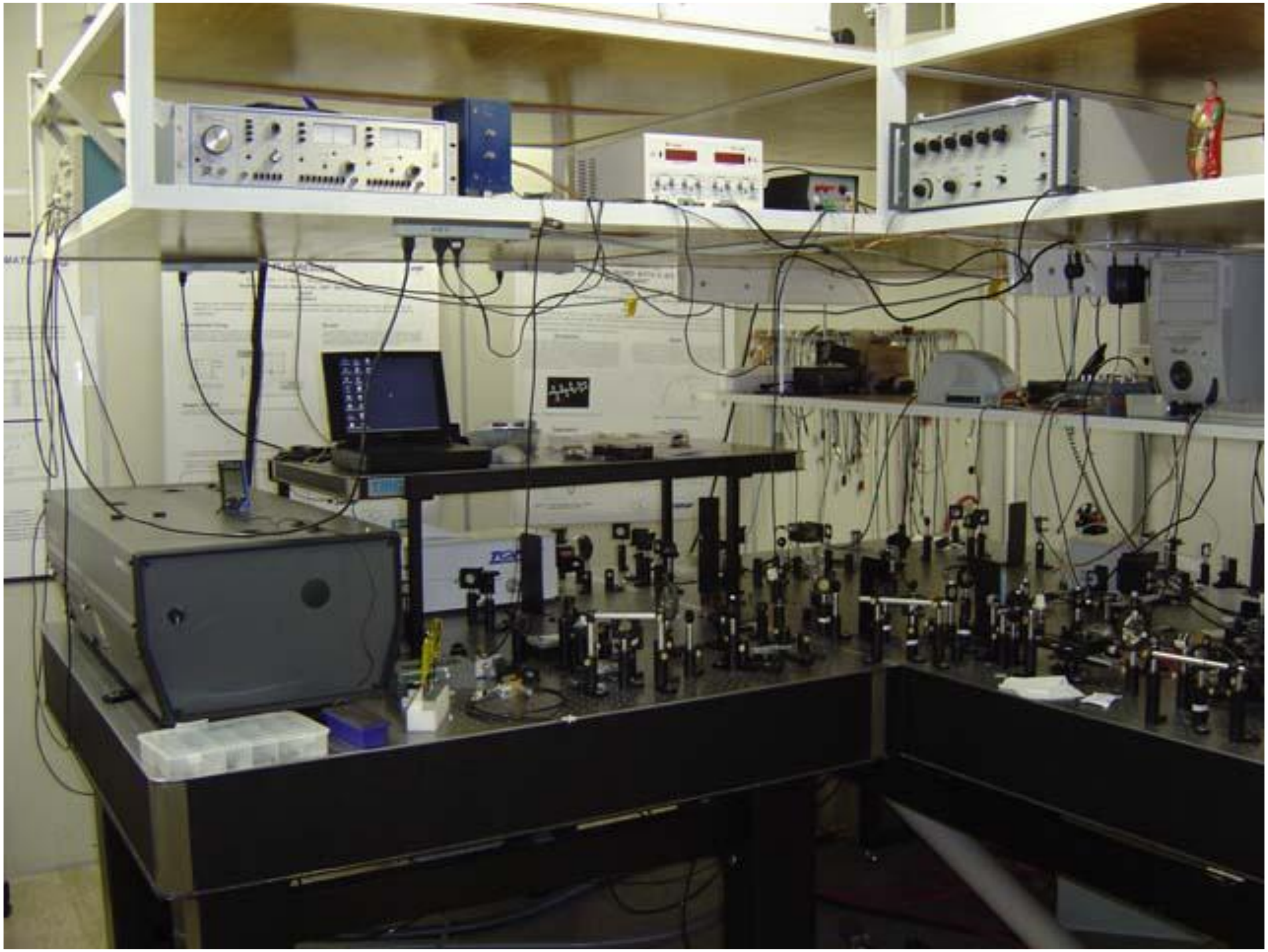
Picosecond laser





- ✓ Laser Nd:YAG Qswitched/modelocked
  - ✓ 532nm and 1064 nm
  - ✓ 100 ps

150-fs amplified laser system



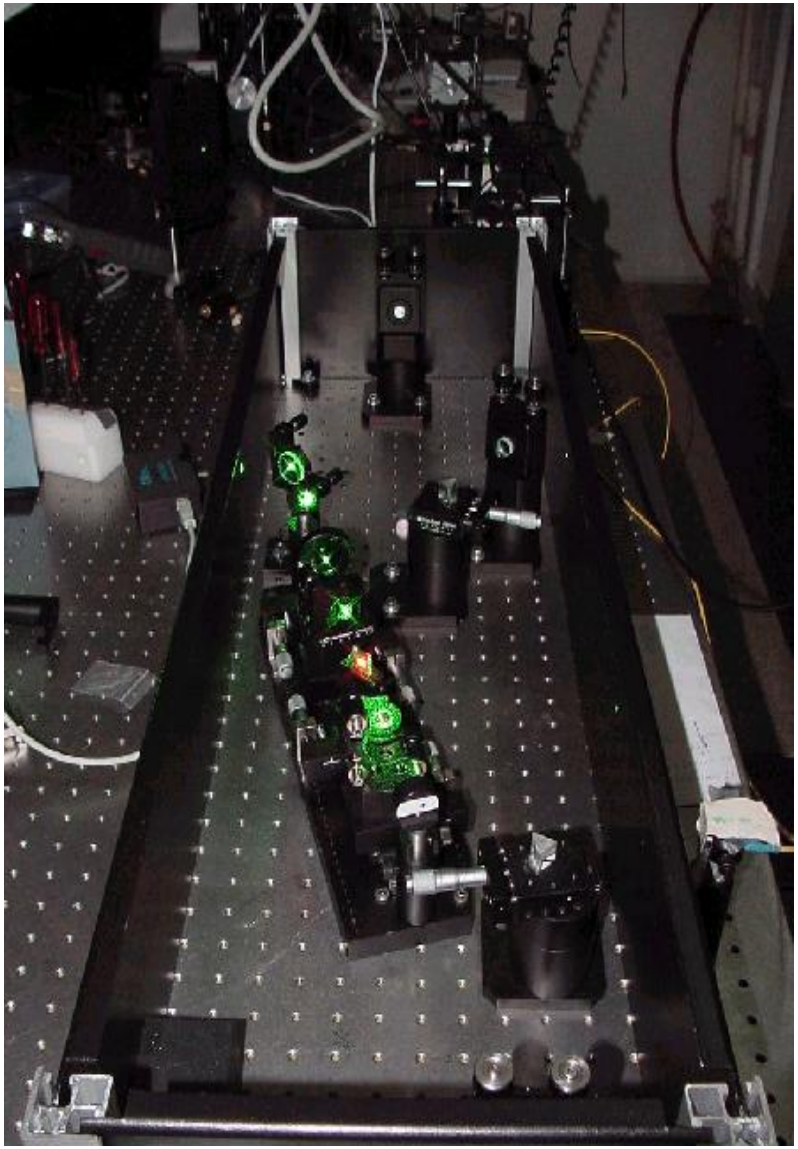
- ✓ *Amplificador Ti:safira*
  - ✓ *775 nm*
  - ✓ *150 fs*
  - ✓ *800 μJ*

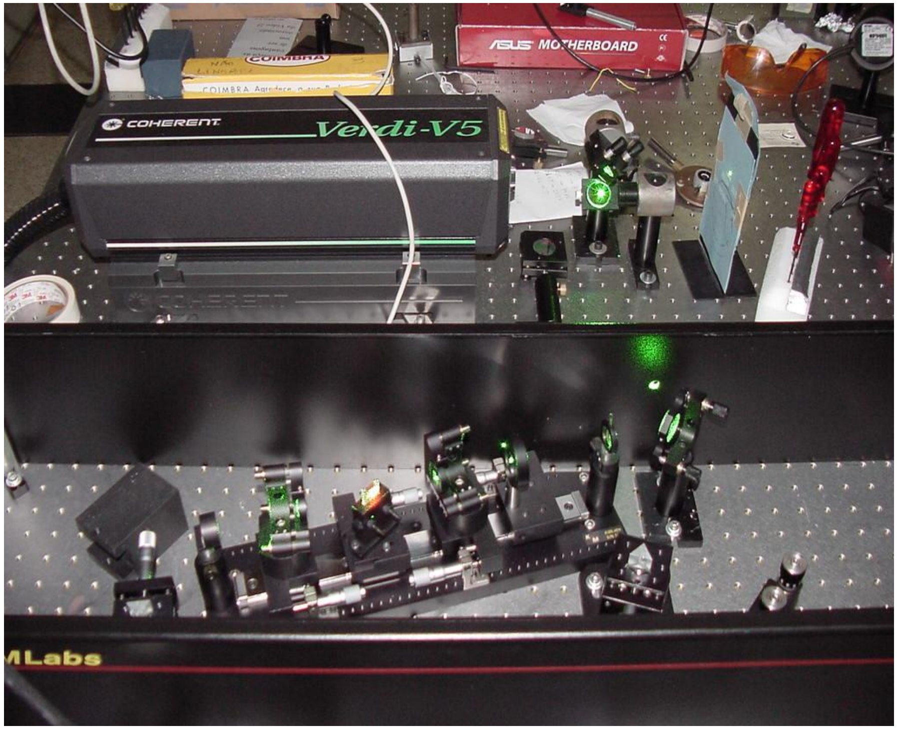
Optical Parametric Amplifier

TOPAS

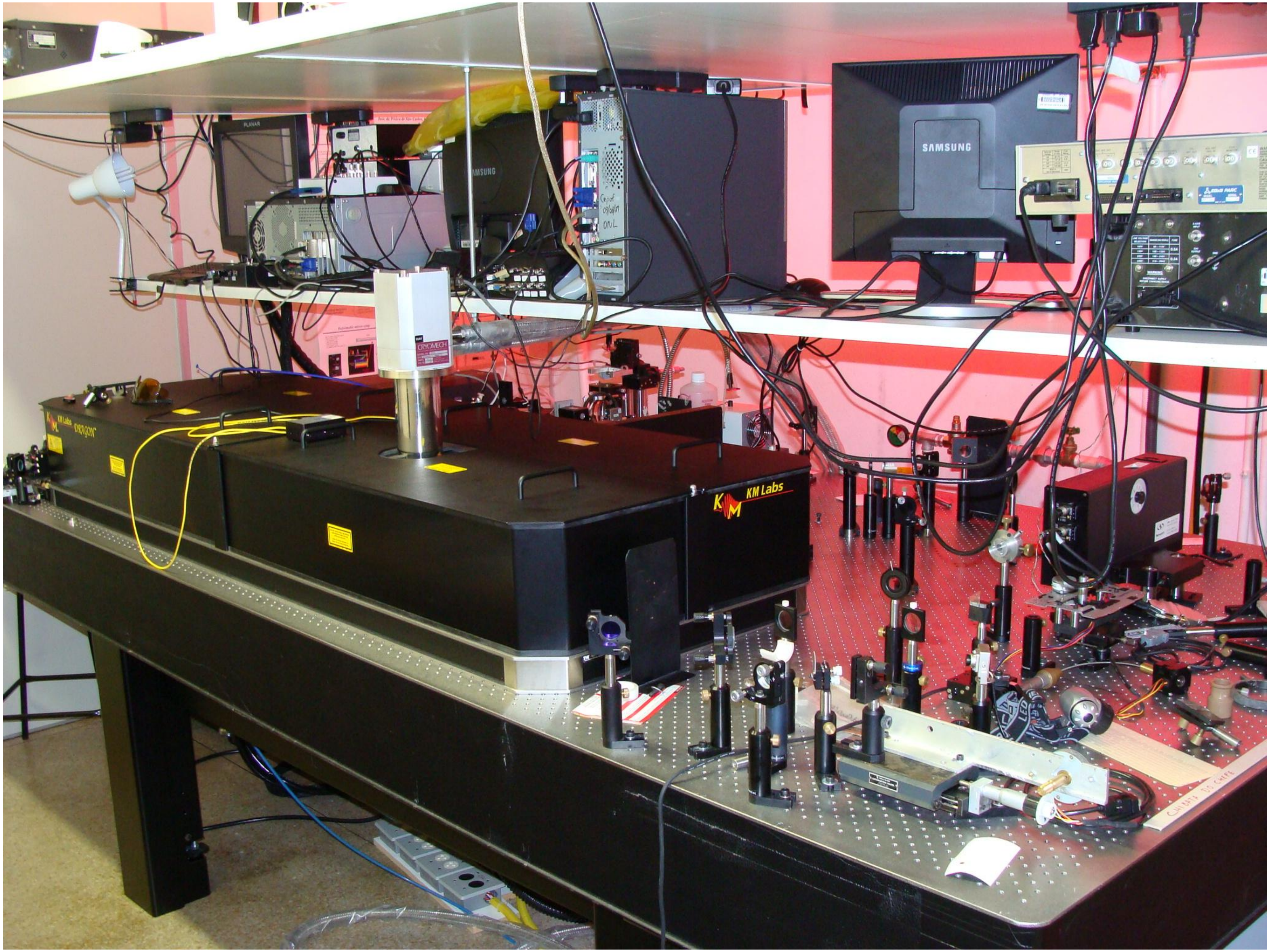
- ✓ pumped - Laser Clark
  - ✓ 460 - 2600 nm
  - ✓ ≈120 fs
  - ✓ 20-60 μJ

15-fs laser

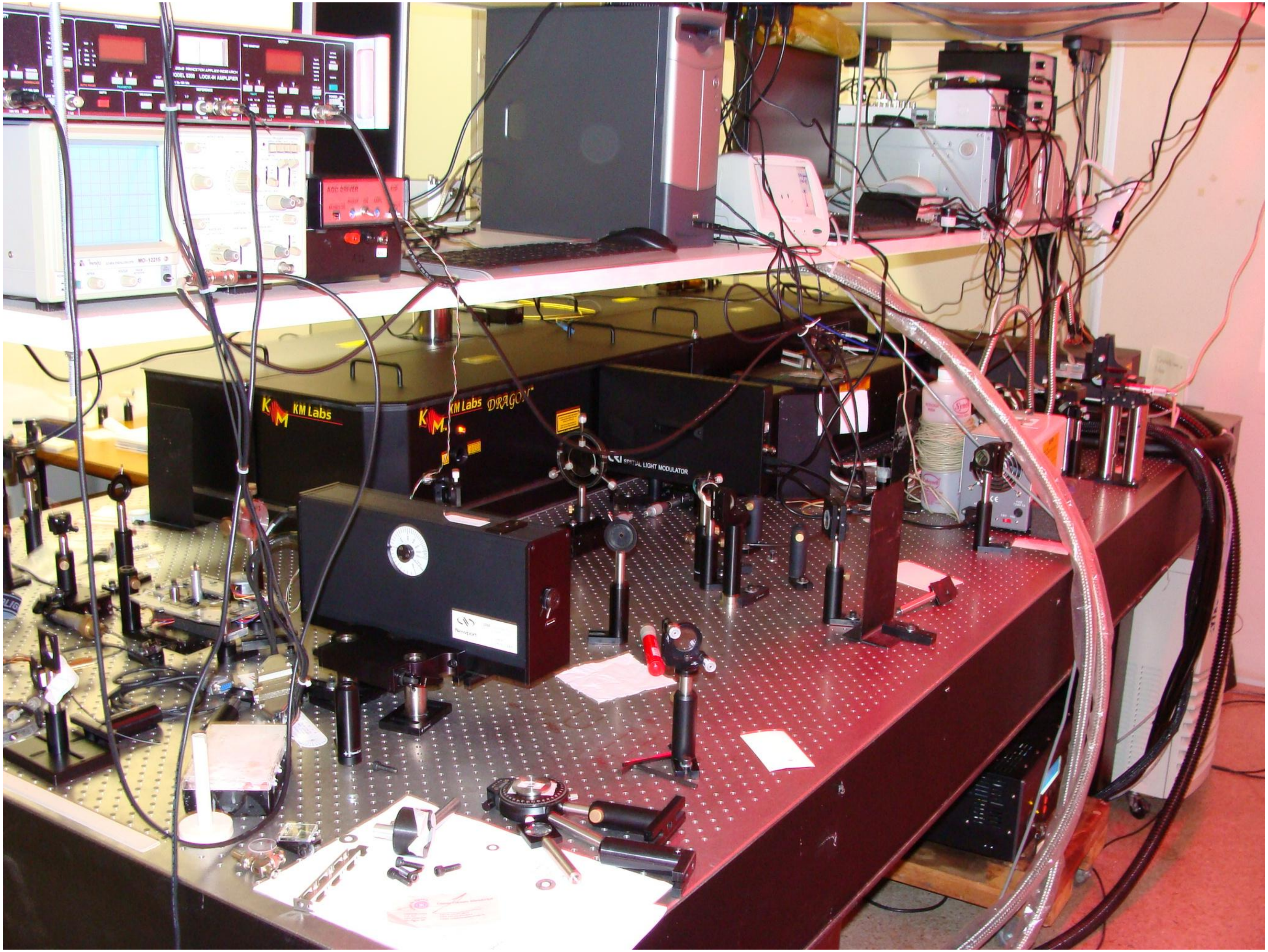




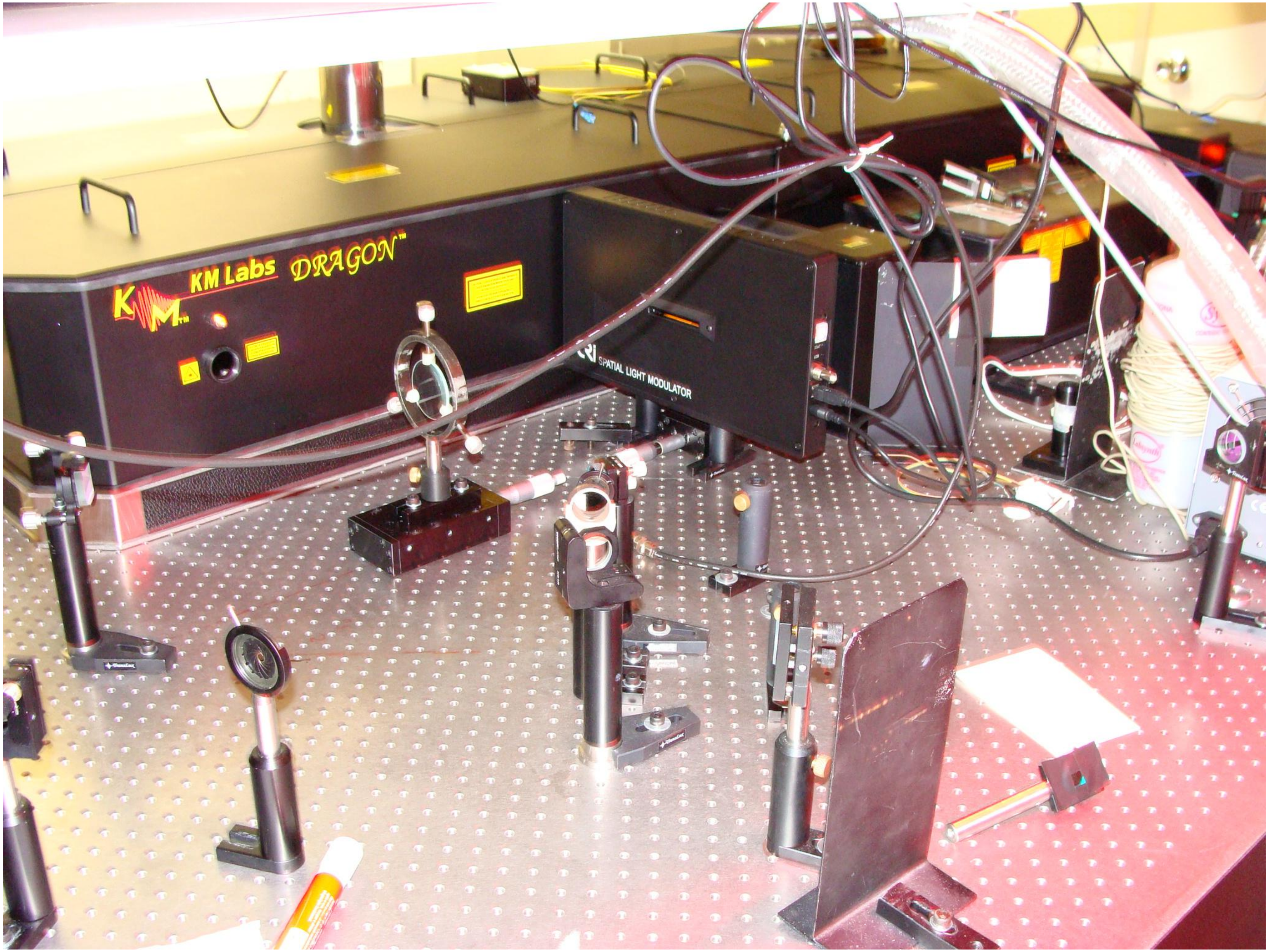
40-fs amplified laser system



40-fs amplified laser system



40-fs amplified laser system



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Outline

introduction to nonlinear optics

nonlinear optics in organic materials

experimental methods

examples of some results

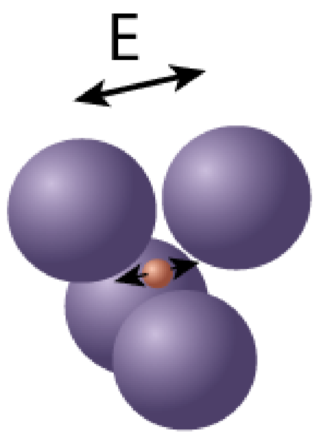
Linear optics vs Nonlinear optics

Optics is a branch of physics that describes the behavior and properties of light and the interaction of light with matter. Explains optical phenomena.

Nonlinear Optics

The branch of optics that describes optical phenomena that occur when very intense light is used

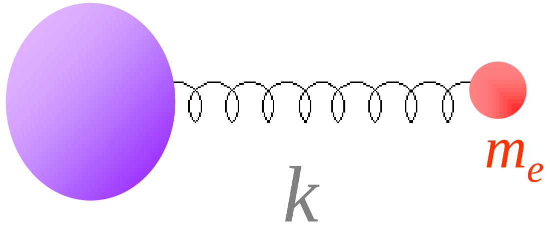
Linear optics



harmonic oscillator

$$E_{rad.} << E_{inter.}$$

electron on a spring



oscillation frequency

$$\omega_0 = \sqrt{\frac{k}{m_e}}$$

Linear optics

electron on a spring

$$F_{binding} = -m_e\omega_o^2 x$$

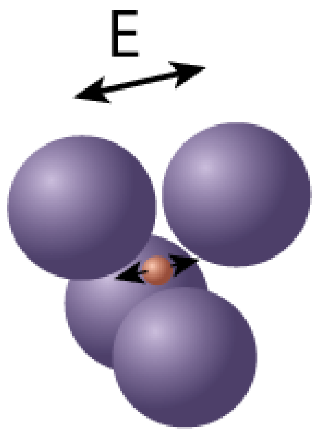
$$F_{damping} = -m_e\gamma\frac{dx}{dt}$$

$$F_{driving} = -eE = -eE_o e^{-i\omega t}$$

equation of motion

$$m\frac{d^2x}{dt^2} = \sum F$$

Linear optics



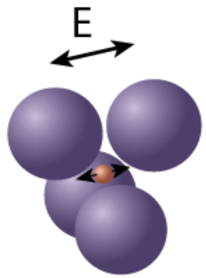
harmonic oscillator

$$m\frac{d^2x}{dt^2} + m\gamma\frac{dx}{dt} + m\omega_o^2 x = -eE$$

Steady state: electron oscillates at driving frequency

$$x(t) = x_o e^{-i\omega t} \qquad x_o = -\frac{e}{m}\frac{1}{(\omega_o^2 - \omega^2) - i\gamma\omega}E_o$$

Linear optics



Oscillating dipole

$$p(t) = -e\,x(t) = \frac{e^2}{m}\frac{1}{(\omega_o^2 - \omega^2) - i\gamma\omega}E_o e^{-i\omega t}$$

Polarization oscillator

$$P(t) = \left(\frac{Ne^2}{m}\right)\sum_j \frac{f_j}{(\omega_j^2 - \omega^2) - i\gamma_j\omega}E(t) \equiv \epsilon_o \chi_e E(t)$$

linear response

$$P = \chi E$$

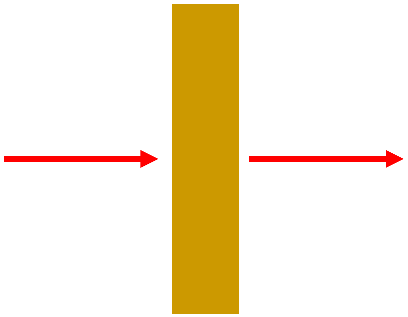
Linear optical process

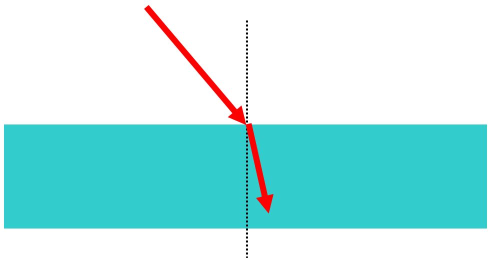
absorption

refraction

α_0 does not depend on light intensity

n_0 does not depend on light intensity

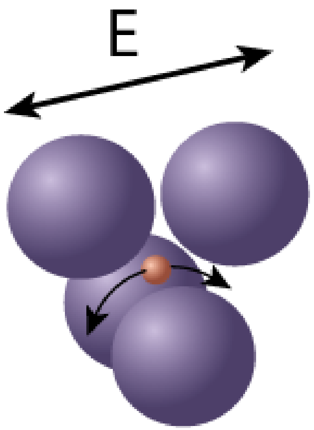




absorption of 10 %

index of refraction 1.3

Nonlinear optics



anharmonic oscillator

high light intensity

$$E_{rad.} \sim E_{inter.}$$

nonlinear polarization response

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots$$

Nonlinear optics

nonlinear expansion of the polarization

$$\vec{P} = \chi^{(1)} . \vec{E} + \chi^{(2)} : \vec{E}\vec{E} + \chi^{(3)} \vdots \vec{E}\vec{E}\vec{E} + \ldots$$

linear processes

SHG

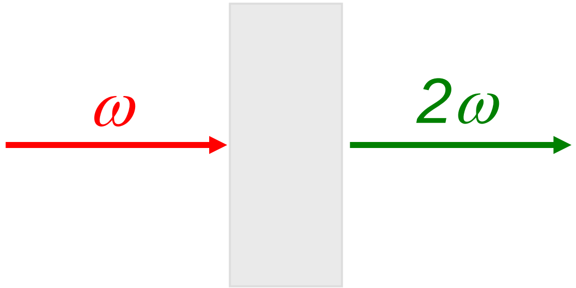
THG

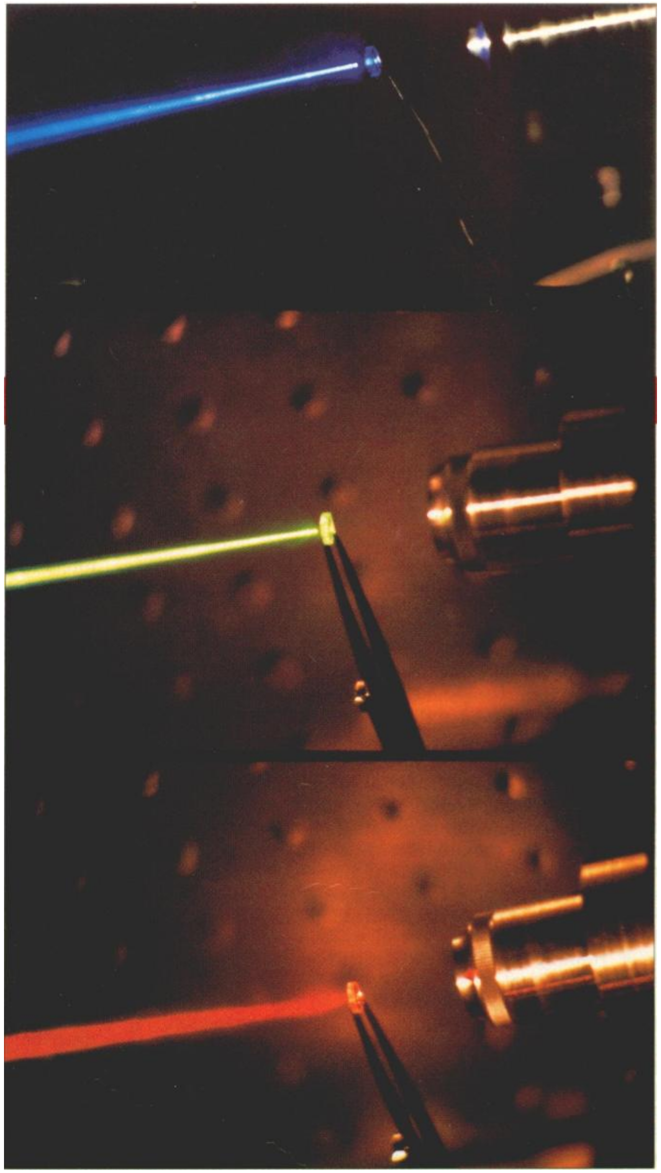
Kerr effect

Nonlinear Optics

Second order processes $\chi^{(2)}$

Second Harmonic Generation





Nonlinear Optics

in medium with inversion symmetry

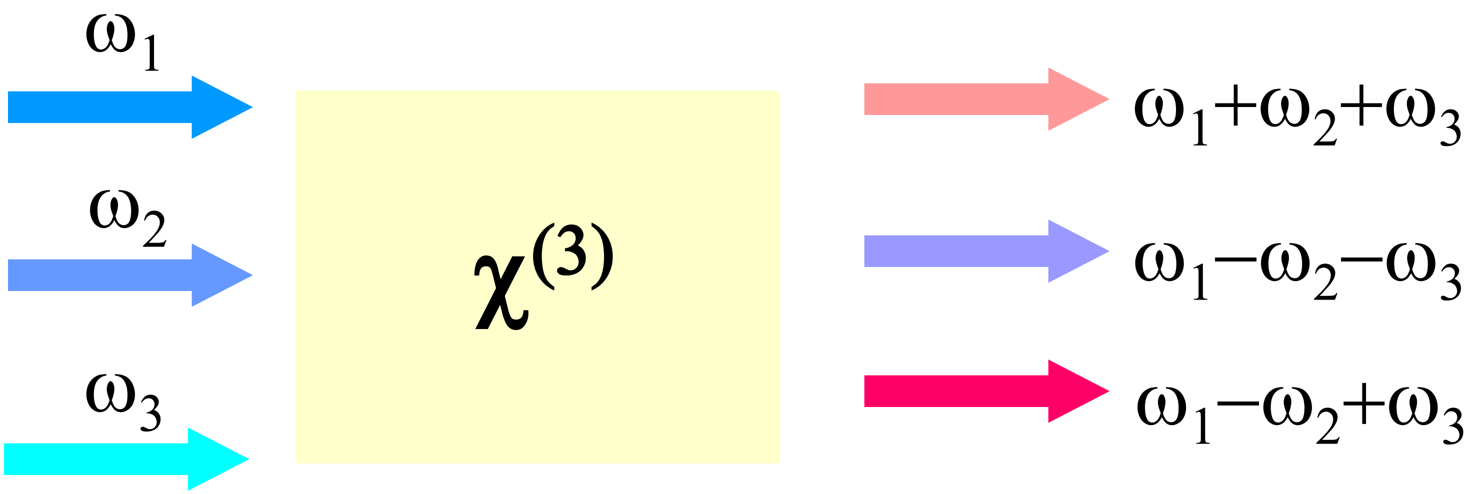
$$\vec{P}^{(2)} = \overleftrightarrow{\chi}^{(2)} : \vec{E}\,\vec{E} \quad \Rightarrow \quad -\vec{P}^{(2)} = \overleftrightarrow{\chi}^{(2)} : (-\vec{E})(-\vec{E})$$

and consequently

$$\chi^{(2)} = -\chi^{(2)} = 0$$

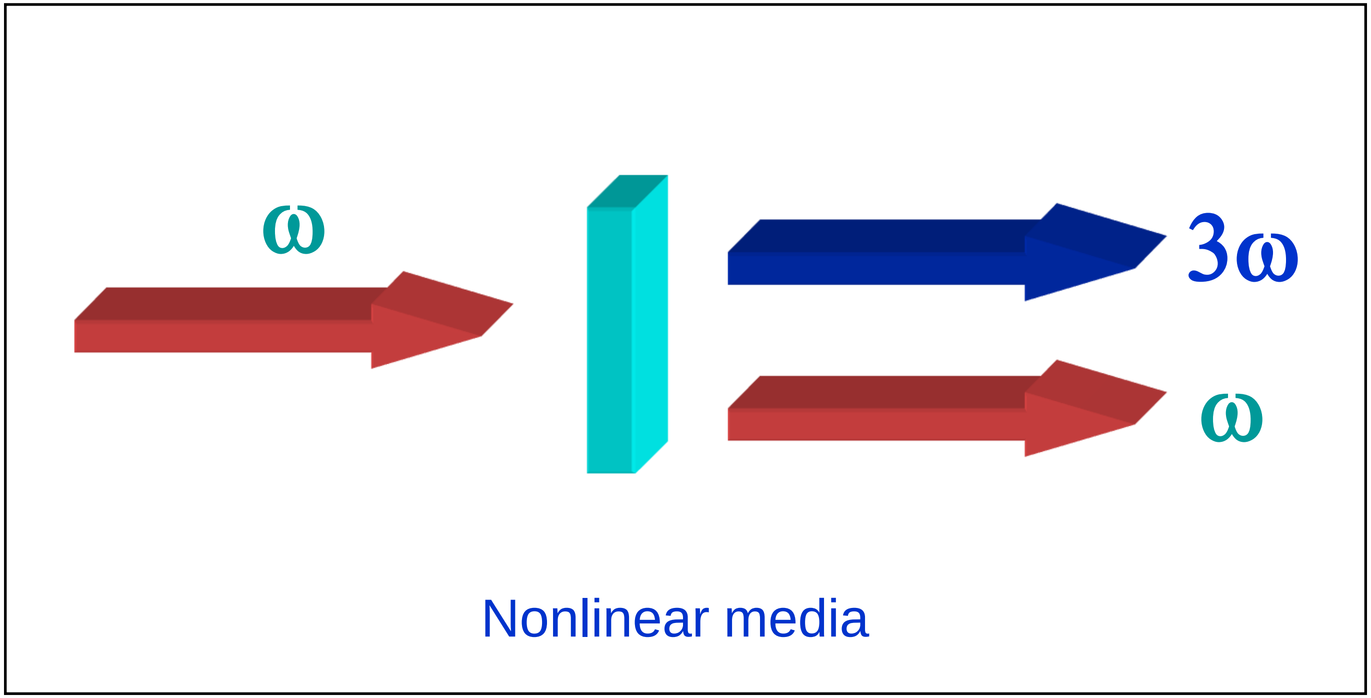
Nonlinear Optics

Third order processes $\chi^{(3)}$



- If $\omega_1 = \omega_2 = \omega_3$
  - Third harmonic generation: 3ω
  - Self phase modulation: ω

Third Harmonic Generation $\chi^{(3)}$



Nonlinear Optics

$$\chi^{(2)} = 0 \quad \Rightarrow \quad \chi^{(3)}$$ Third order processes

Nonlinear polarization

$$P = \chi^{(1)}E + \chi^{(3)}E^3 + \ldots$$

Third order polarization

$$P^{(3)}(t) = \chi^{(3)}E(t)E^*(t)E(t) = \chi^{(3)}I(t)E(t)$$

Nonlinear Optics

consequently

$$P = P^{(1)} + P^{(3)} = (\chi^{(1)} + \chi^{(3)} I)E \equiv \chi_{eff} E$$

and

$$n = \sqrt{\epsilon} = \sqrt{1 + \chi_{eff}} \approx \sqrt{1 + \chi^{(1)}} + \frac{1}{2} \frac{\chi^{(3)} I}{\sqrt{1 + \chi^{(1)}}} = n_o + n_2 I$$

Kerr media

$$n = n_0 + n_2 I$$

Nonlinear Optics

Third order processes $\chi^{(3)}$

$$n_2 \approx \chi^{(3)}$$

Kerr media:

$$n = n_0 + n_2 I$$

Index of refraction depends on the light intensity

Self phase modulation

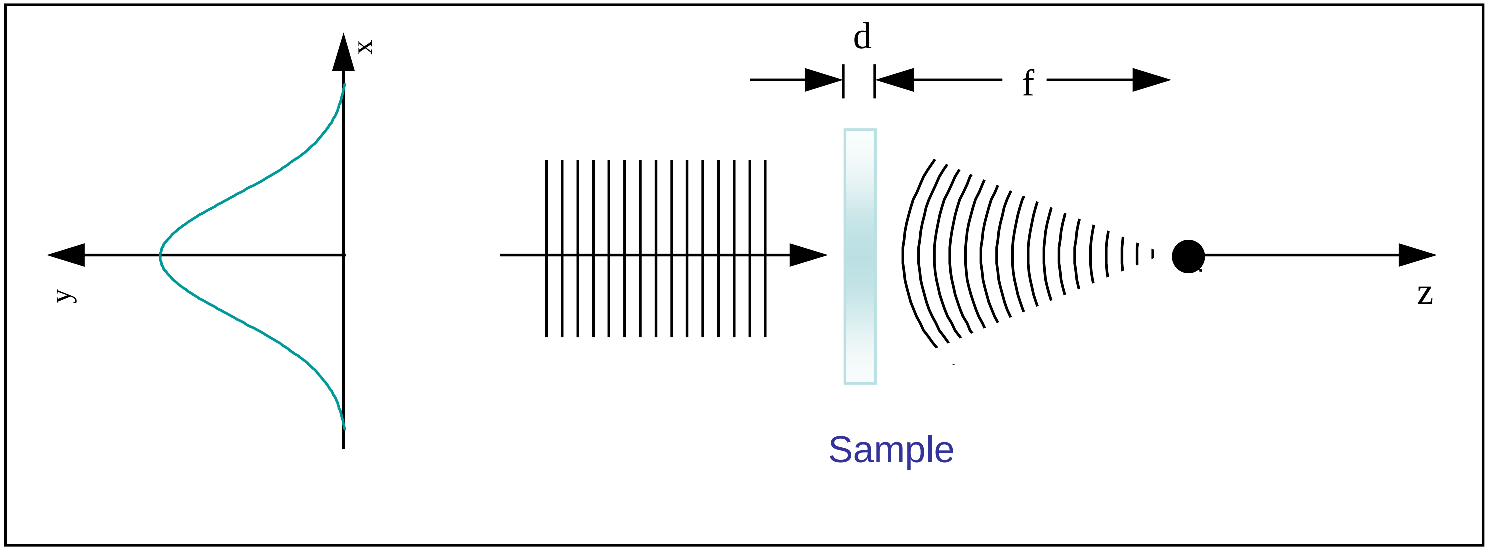
Kerr media:

$$n = n_0 + n_2 I$$

centre symmetric: $\chi^{(2)} = 0$

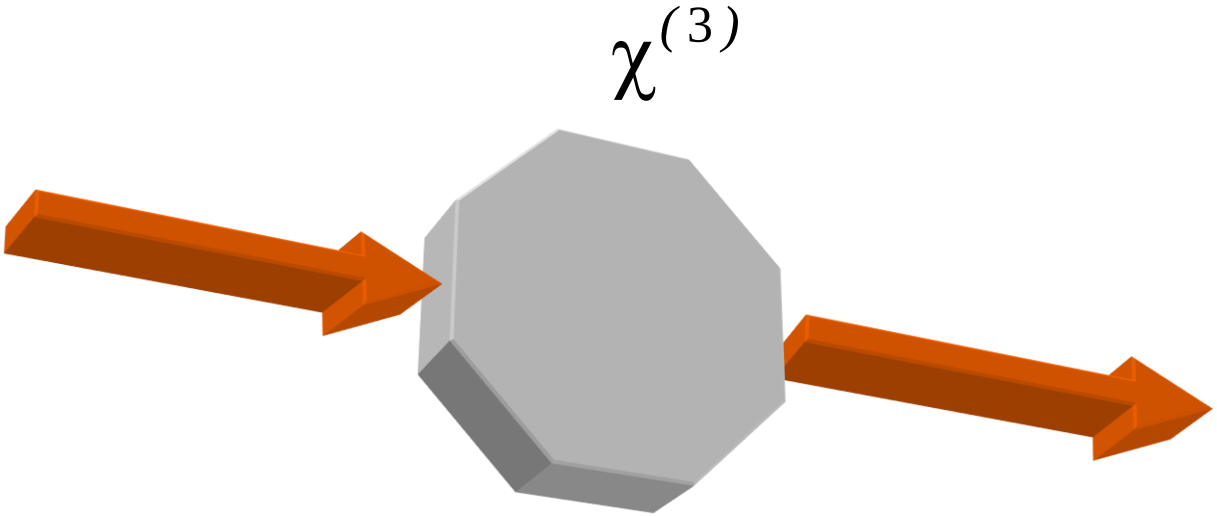
$$P_{NL} = \chi^{(3)} E^3$$

$n_2 > 0$ Material behaves as a convergent lens



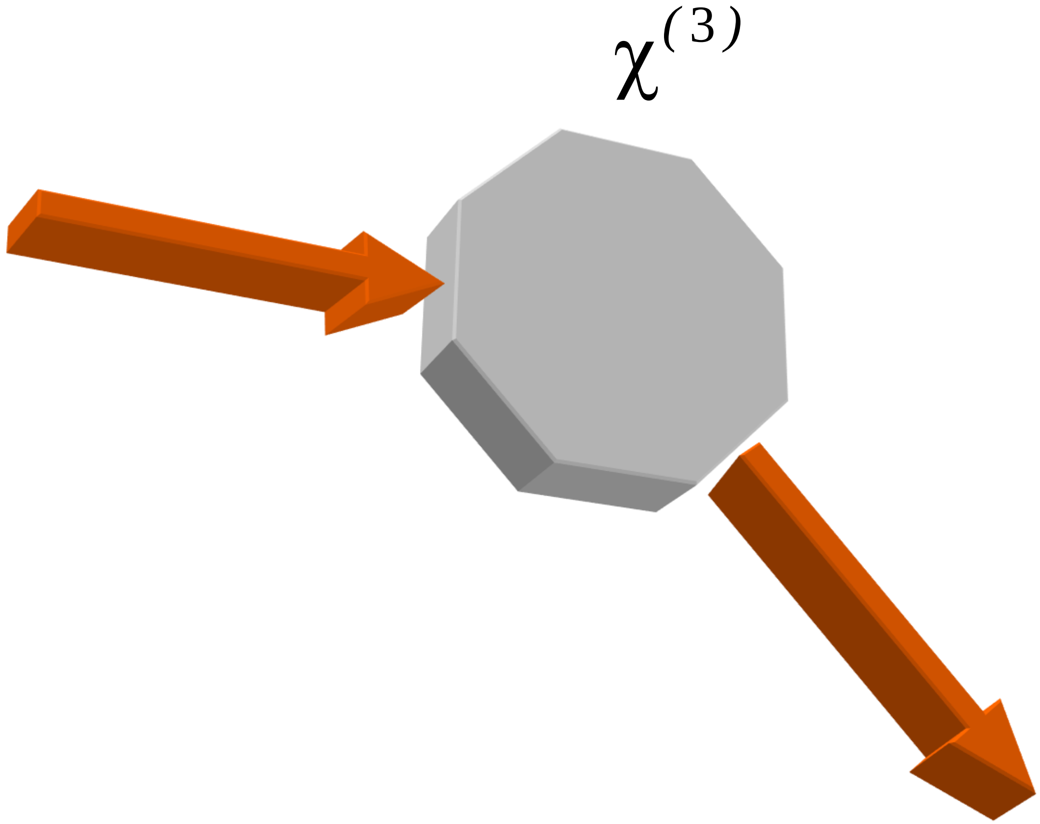
Optical switching

• low intensity



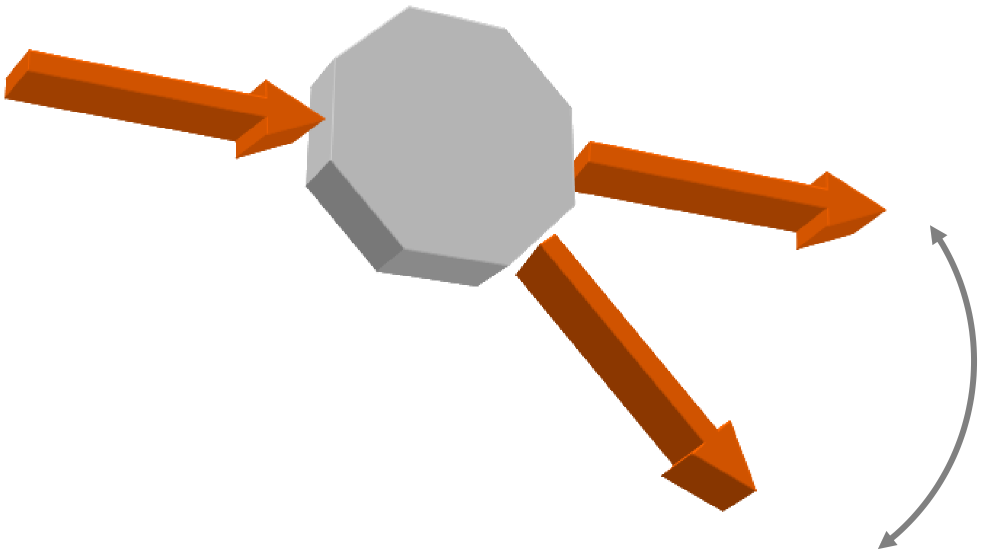
Optical switching

• high intensity



Self action process

Optical switching



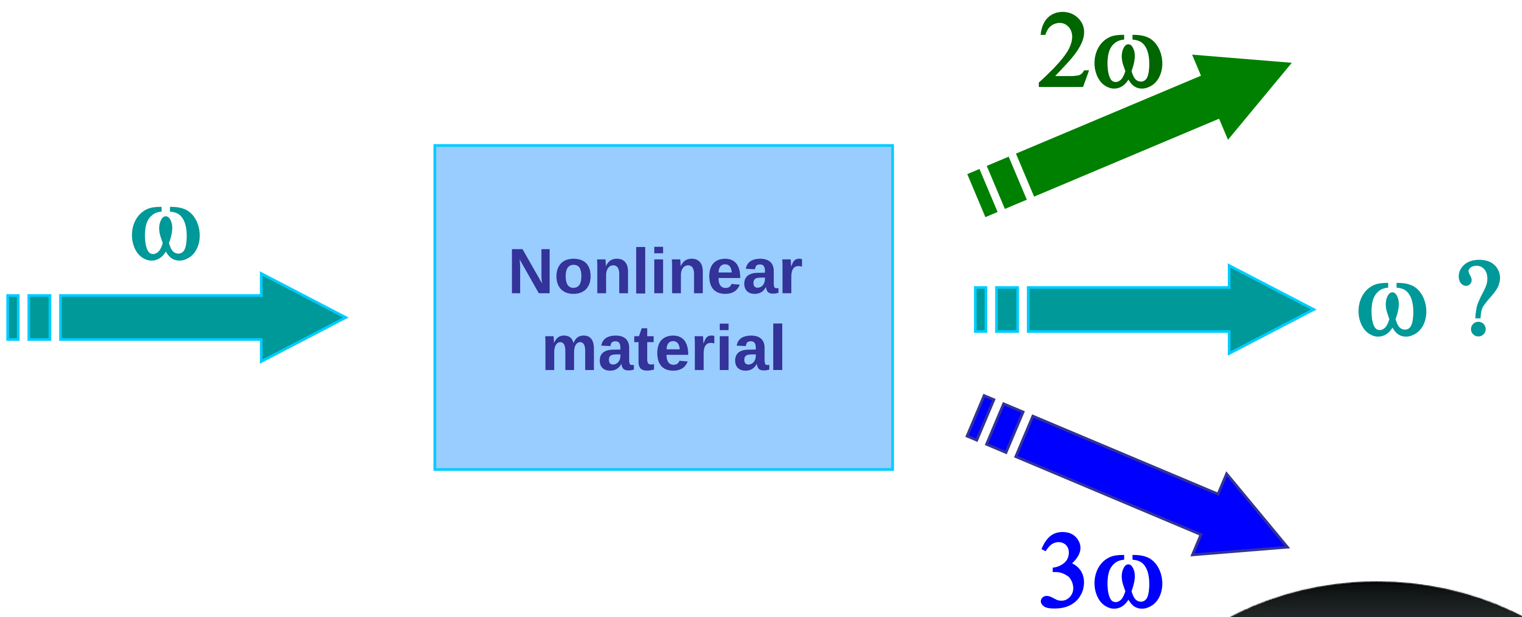
response time: 10^{-15} s

response time *1×10^{-9}* *1×10^{-15}*

1GHz → 1 THz

1 million times faster

Nonlinear optics



- Intense light induced nonlinear response in the material
- Material change the light in a nonlinear way

Self action effect

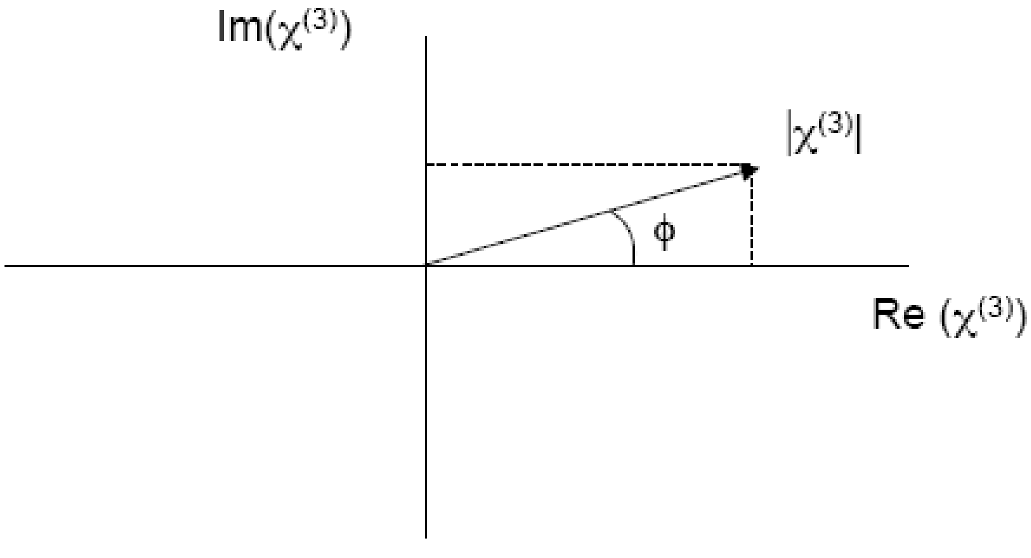
Nonlinear Optics

$\chi^{(3)}$ is a complex quantity

$$\chi^{(3)} = \mathrm{Re}\,(\chi^{(3)}) + i\,\mathrm{Im}(\chi^{(3)})$$

Related to intensity dependent refractive index

Related to two-photon absorption



Third order processes: $\chi^{(3)}$

Refractive process:

$$n = n_0 + n_2 I$$

- self-phase modulation
- lens-like effect

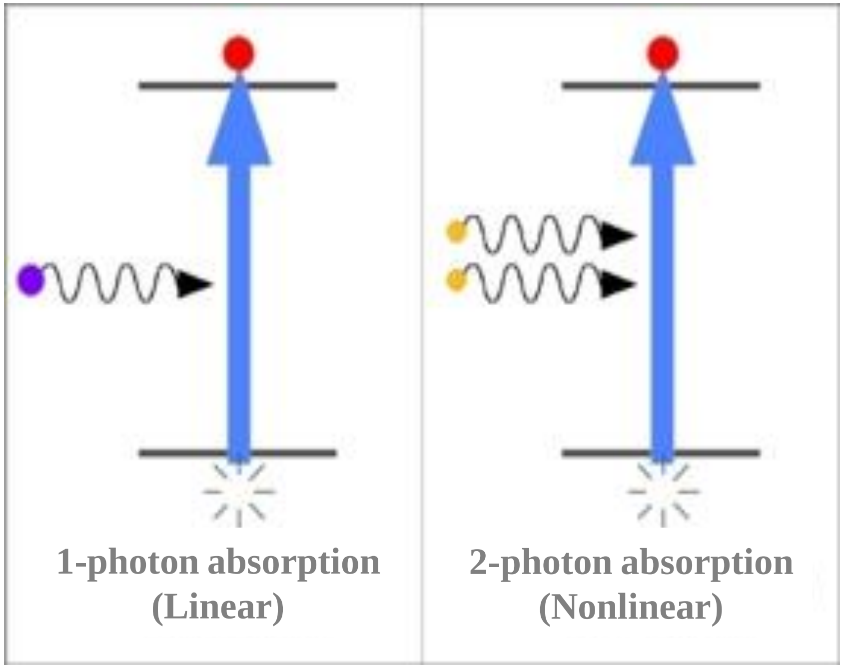
Absorptive process:

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

- nonlinear absorption
- two-photon absorption

Two-photon absorption (2PA) process

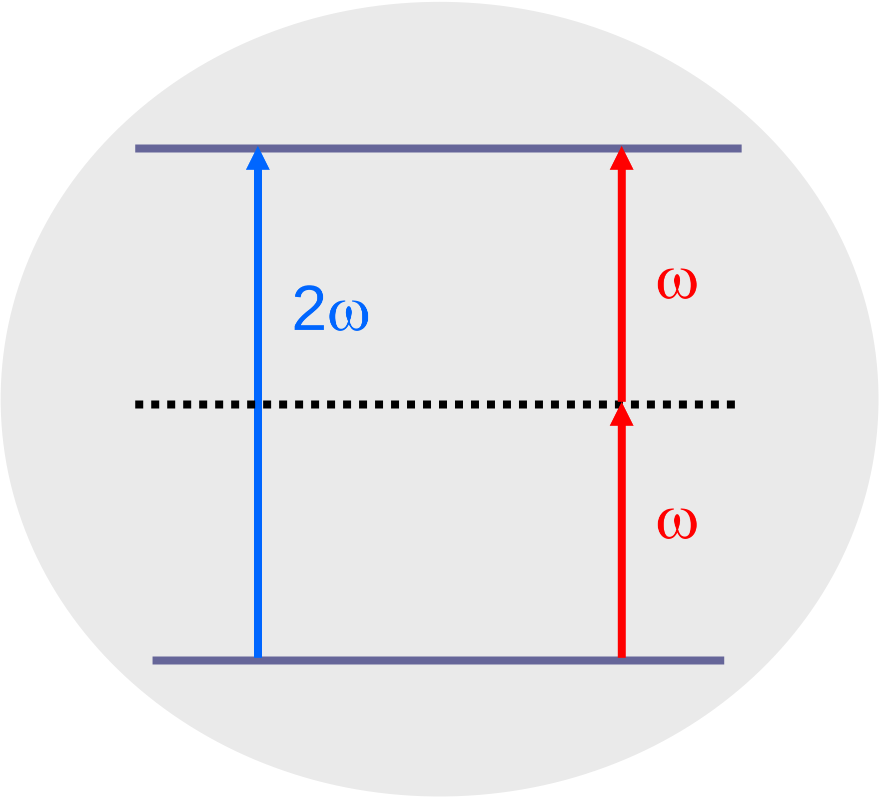
Phenomenon does not described for the Classical Physics and does not observed until the development of the Laser.



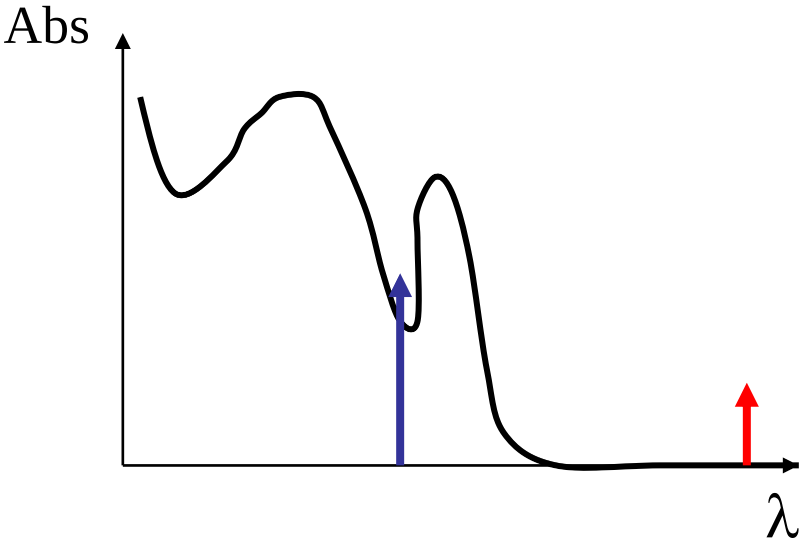
Theoretical model: Maria Göppert-Mayer, 1931

Two photons from an intense laser light beam are simultaneously absorbed in the same “quantum act”, leading the molecule to some excited state with energy equivalent to the absorbed two photons.

two-photon absorption



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



Applications:

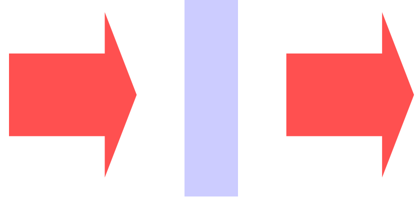
optical limiting

fluorescence microscopy

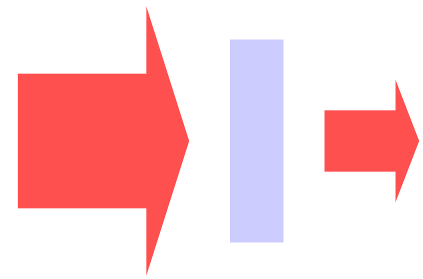
microfabrication

optical limiting

low intensity



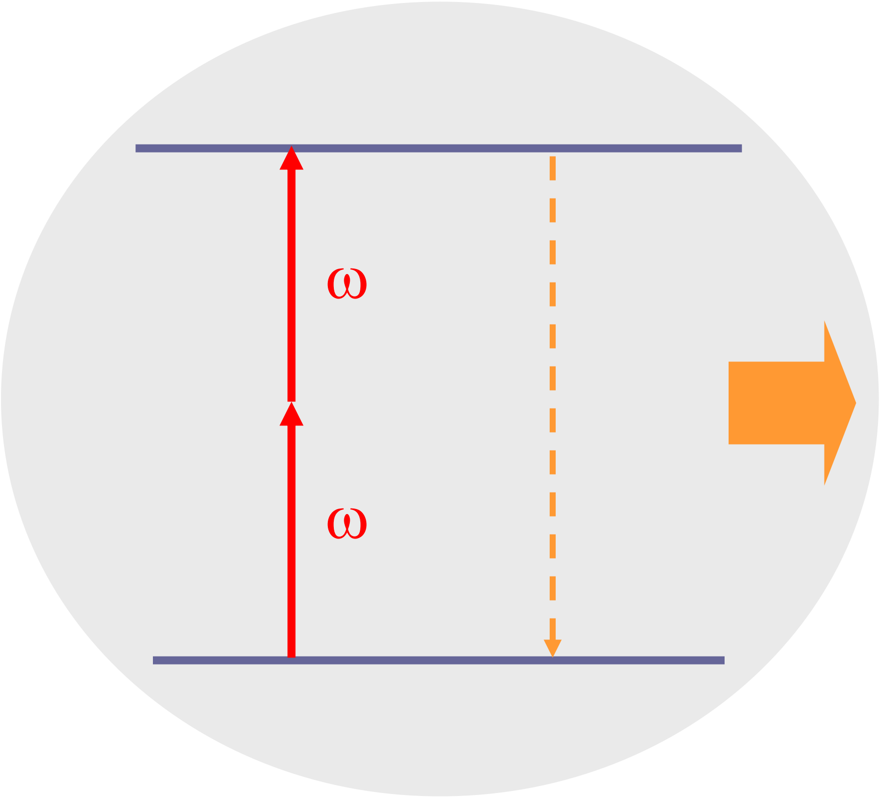
high intensity



To protect eye and sensors from intense laser pulses

two-photon fluorescence

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

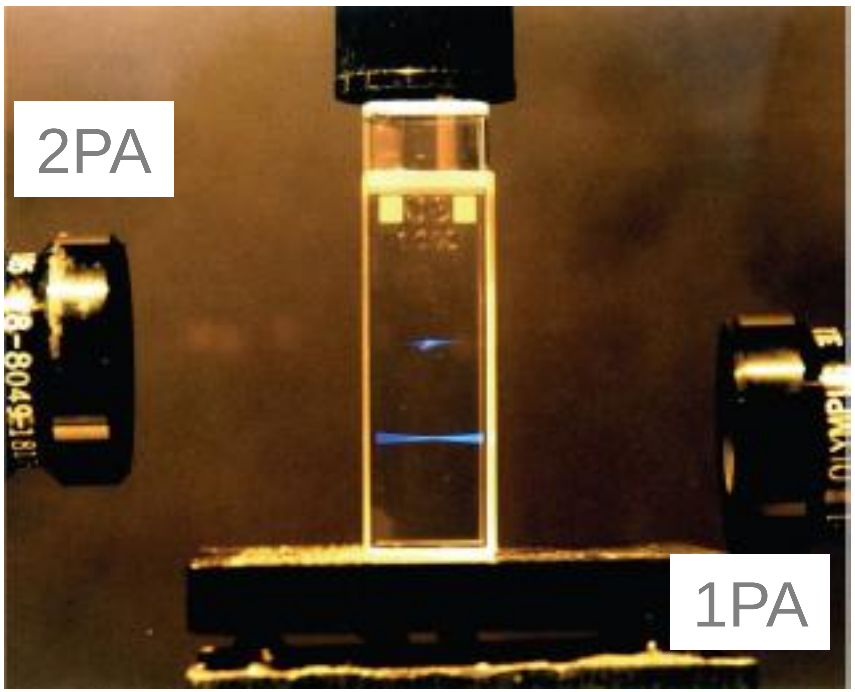


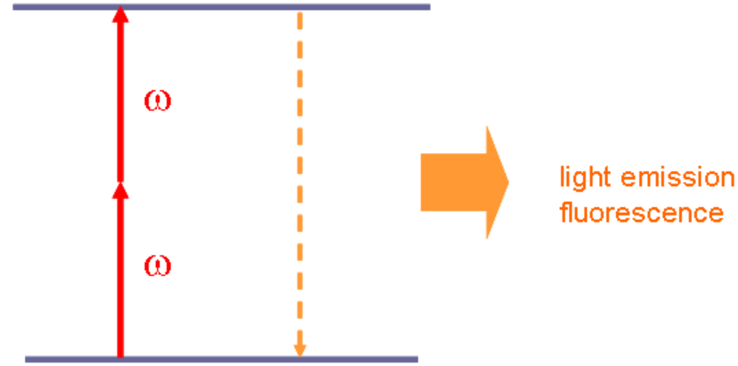
light emission
fluorescence

$$\text{TPA rate constant} \propto \delta I^2$$

localization of the excitation with 2PA

dilute solution of fluorescent dye





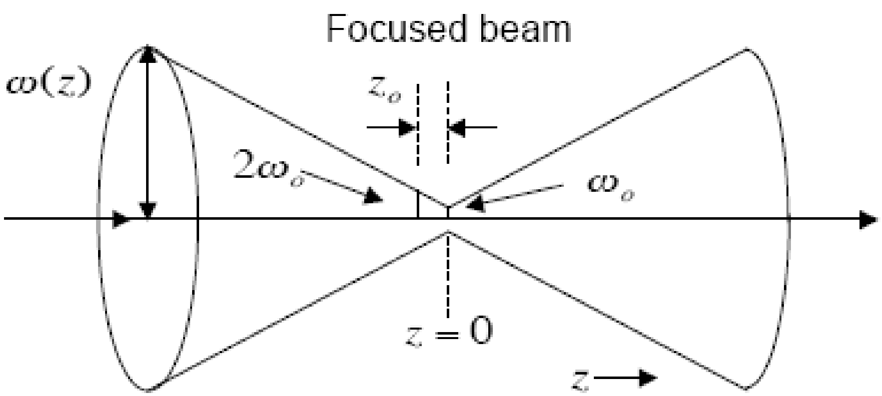
$$\mathrm{TPA} \propto \delta I^2$$

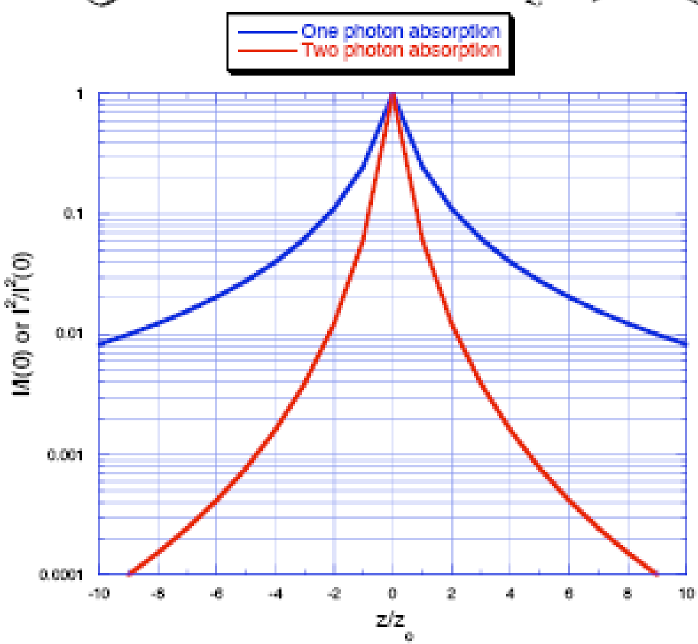
$$I \sim \frac{1}{z^2}$$

$$\Rightarrow TPA \sim \frac{1}{z^4}$$

spatial confinement of excitation

excitation profile along z





Radius, area and intensity of focused beam

$$\omega(z) = \omega_0 \left(1 + \frac{z}{z_0} \right)$$

$$A(z) = \pi\omega^2 = \pi\omega_0^2 \left(1 + \frac{z}{z_0} \right)^2$$

$$I(z) = \frac{E}{At} \propto \frac{1}{A} = \frac{1}{\pi\omega_0^2 \left(1 + \frac{z}{z_0} \right)^2}$$

Normalized excitation rates

(ignoring beam attenuation)

one photon

$$\frac{I(z)}{I(0)} = \left(1 + \frac{z}{z_0} \right)^{-2}$$

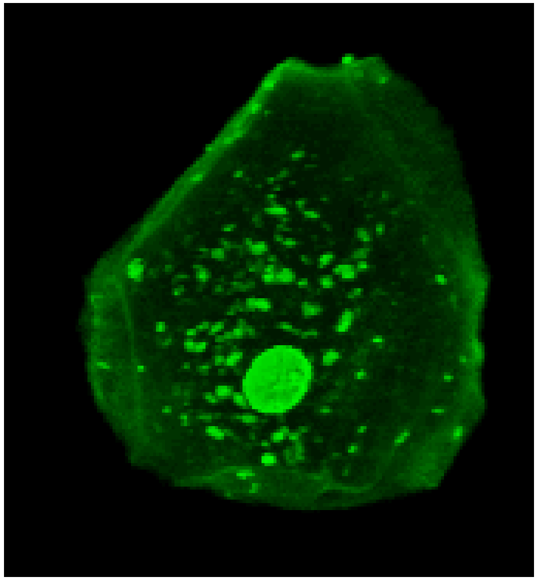
two photon

$$\frac{I(z)}{I(0)} = \left(1 + \frac{z}{z_0} \right)^{-4}$$

two-photon fluorescence microscopy

- Microscopy by two-photon fluorescence

3D image of a cell



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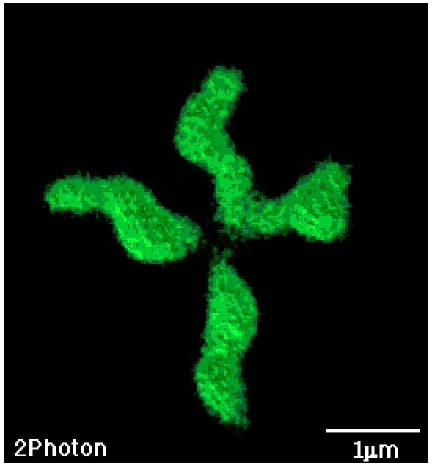
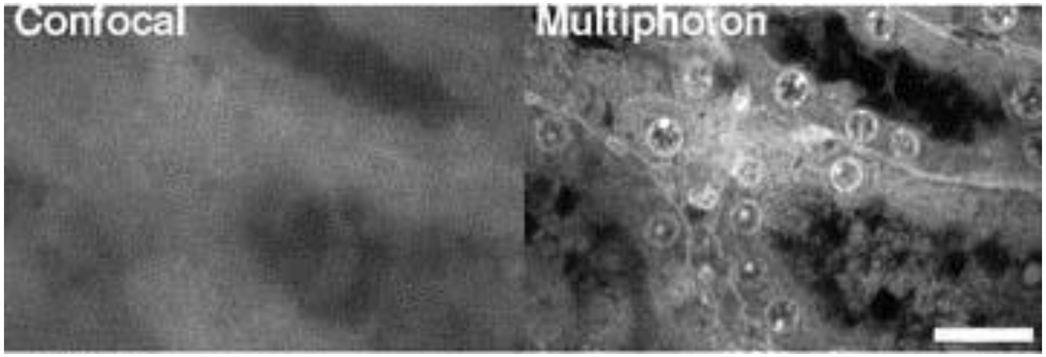
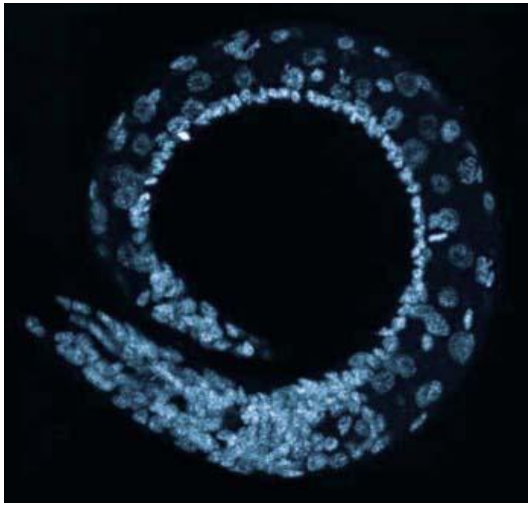
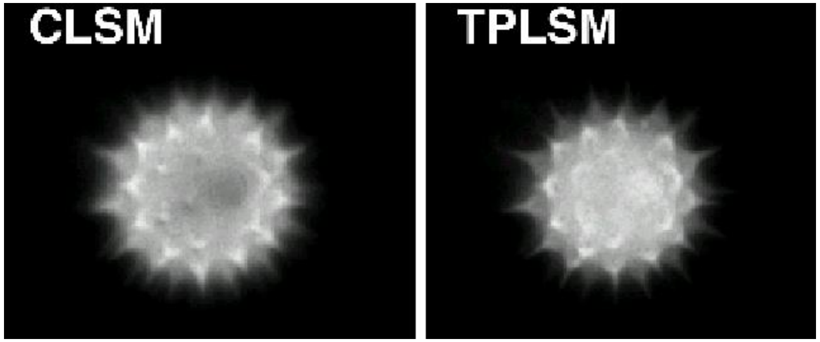


Human chromosome

Two-photon fluorescence microscopy





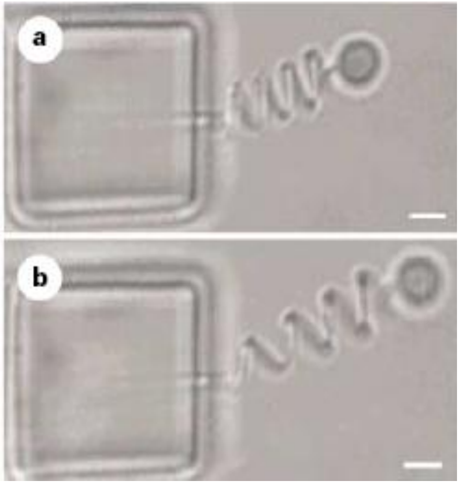


Fluorescent marker ⇒ fluorophores

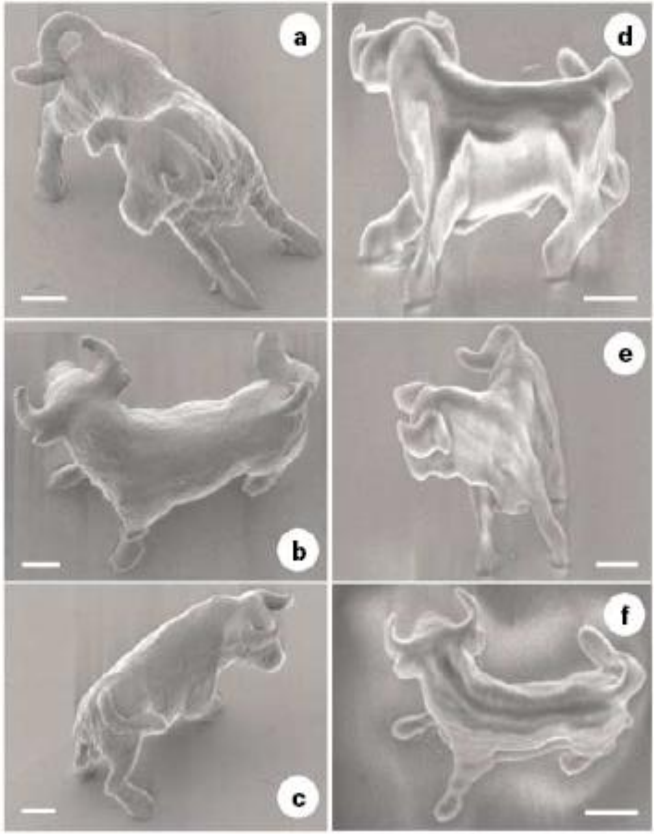
microfabrication

- **Two-photon polymerization**

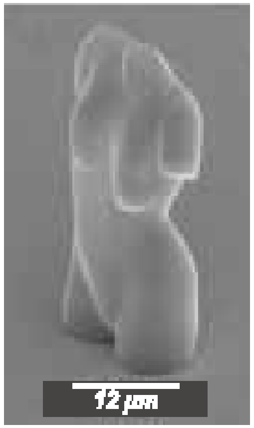
Nature 412, 697-698 (2001)



oscillator



Bull

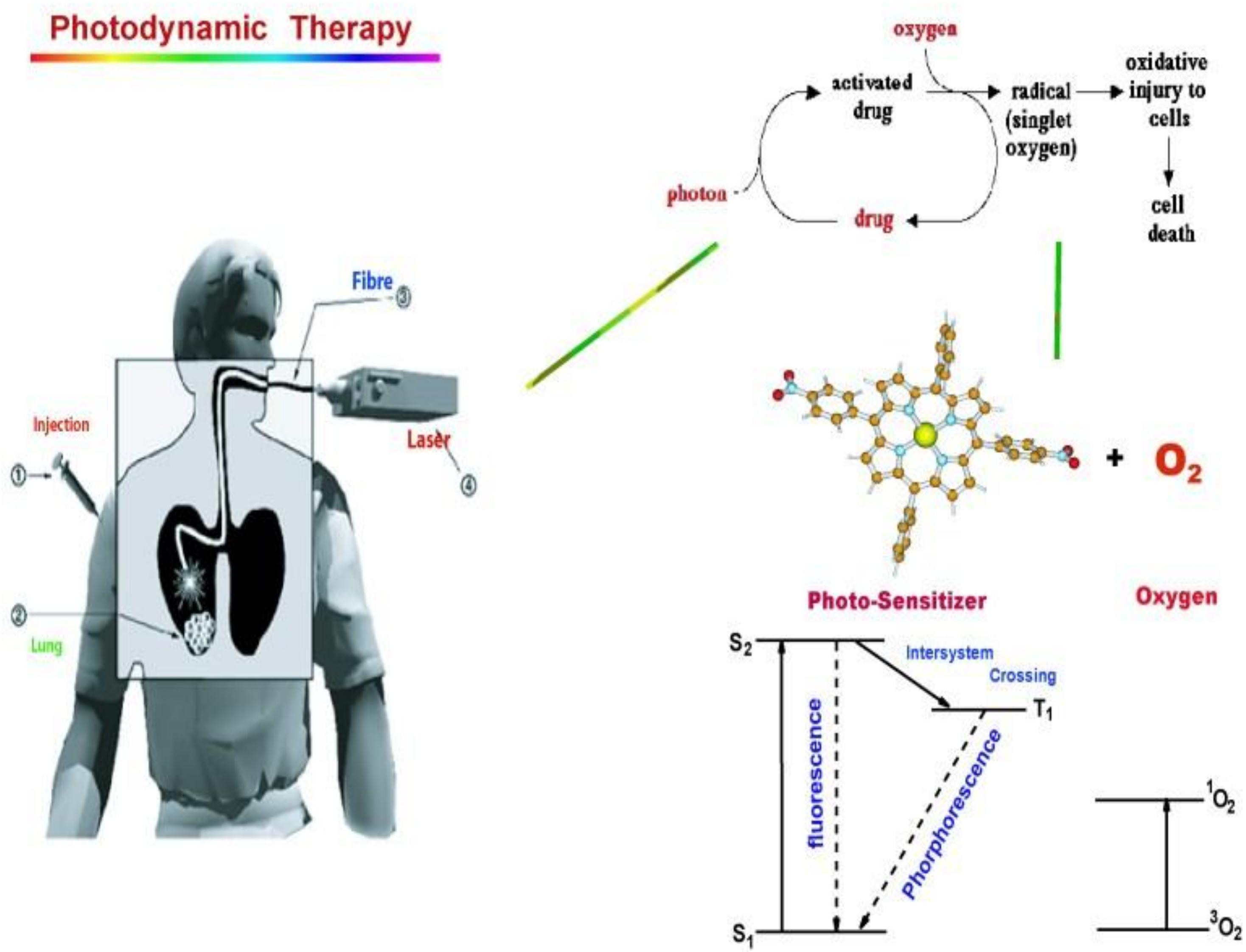


Venus statue
Two-photon polymerization

Opt. Exp. 12, 5521-5528 (2004)

two-photon photodynamic therapy

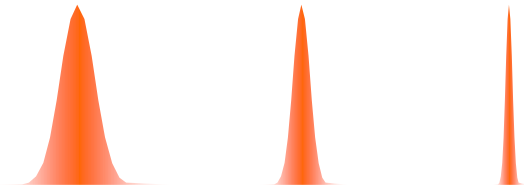
- PDT via dois fótons



Real applications in nonlinear optics

Very intense light: femtosecond pulses

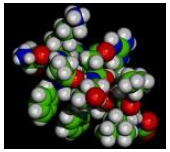
Ti:Sapphire lasers



100 fs 50 fs 20 fs

1 fs = 10^{-15} s

1 fs → 1s



Laser intensities ~ 100 GW/cm^2

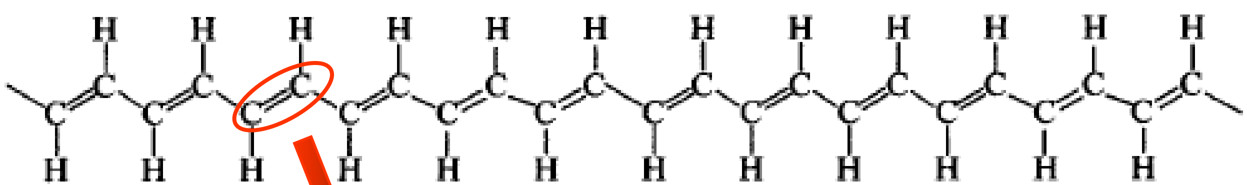
1 x 10^{11} W/cm^2

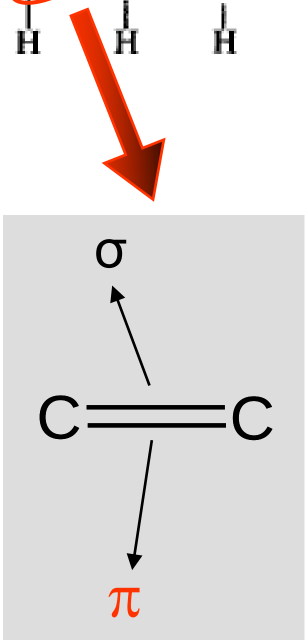
Laser pointer: 1 mW/cm^2 (1 x10^{-3} W/ cm^2)

Organic materials

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

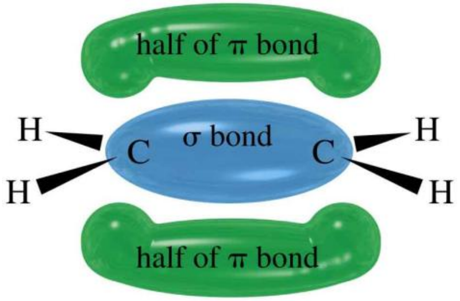
- π-conjugated structures





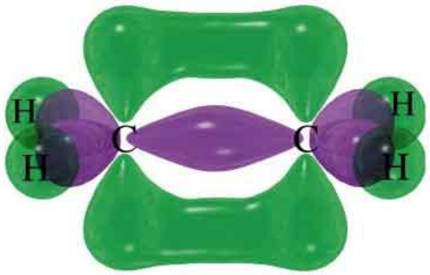
Conjugation: alternation of single and doubles bonds between carbon atoms

π-conjugation



σ bond: forms a strong chemical bond; localized

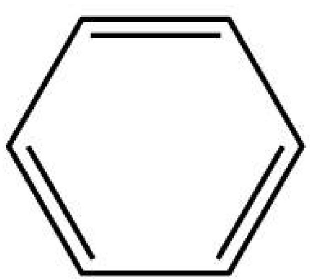
π bond: weaker bond; out of the C atoms axis



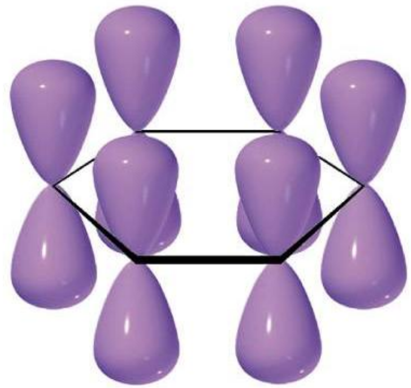
"Free electrons" that are easier to move under an applied electric filed

π-conjugation

benzene



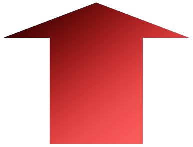
p-orbitals



π delocalization
(π-electron cloud)

π bond in conjugated system: delocalized electrons

high optical nonlinearities

 $\chi^{(3)}$

Research

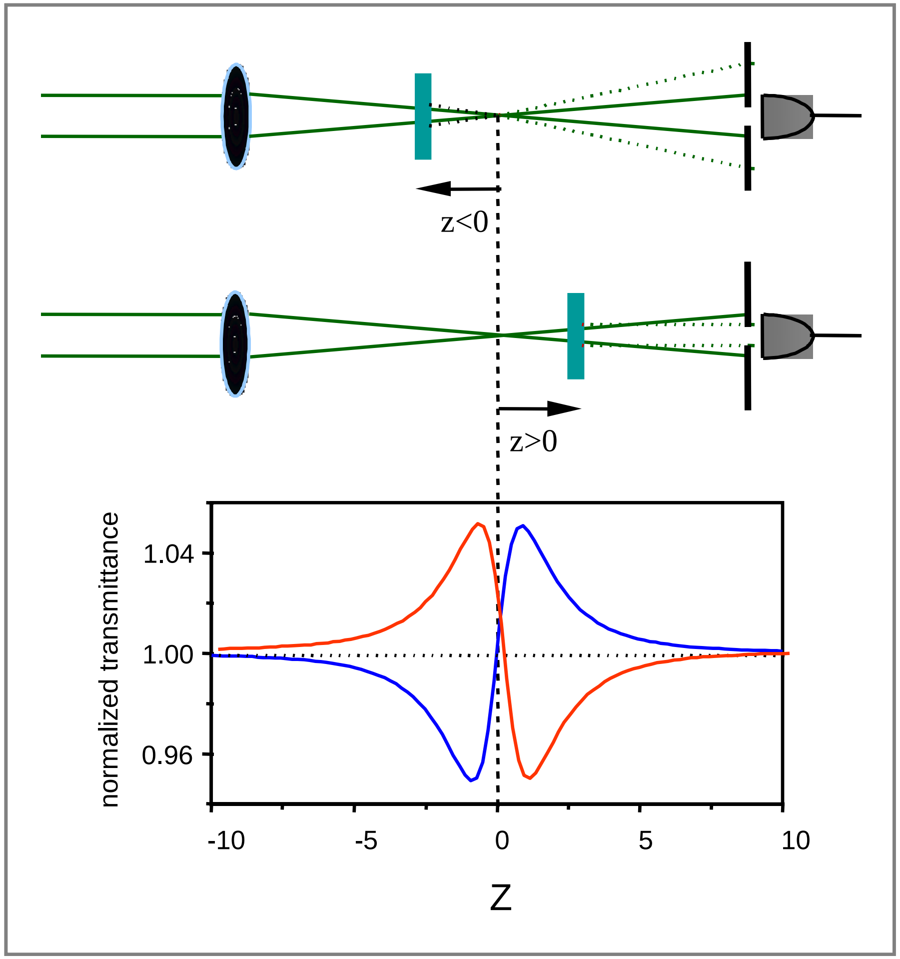
- Understanding the physical principles behind two-photon absorption

- Understanding the relationship between molecular structure and two-photon absorption

- Developing molecules with high optical nonlinearities that can be used for application

Z-scan

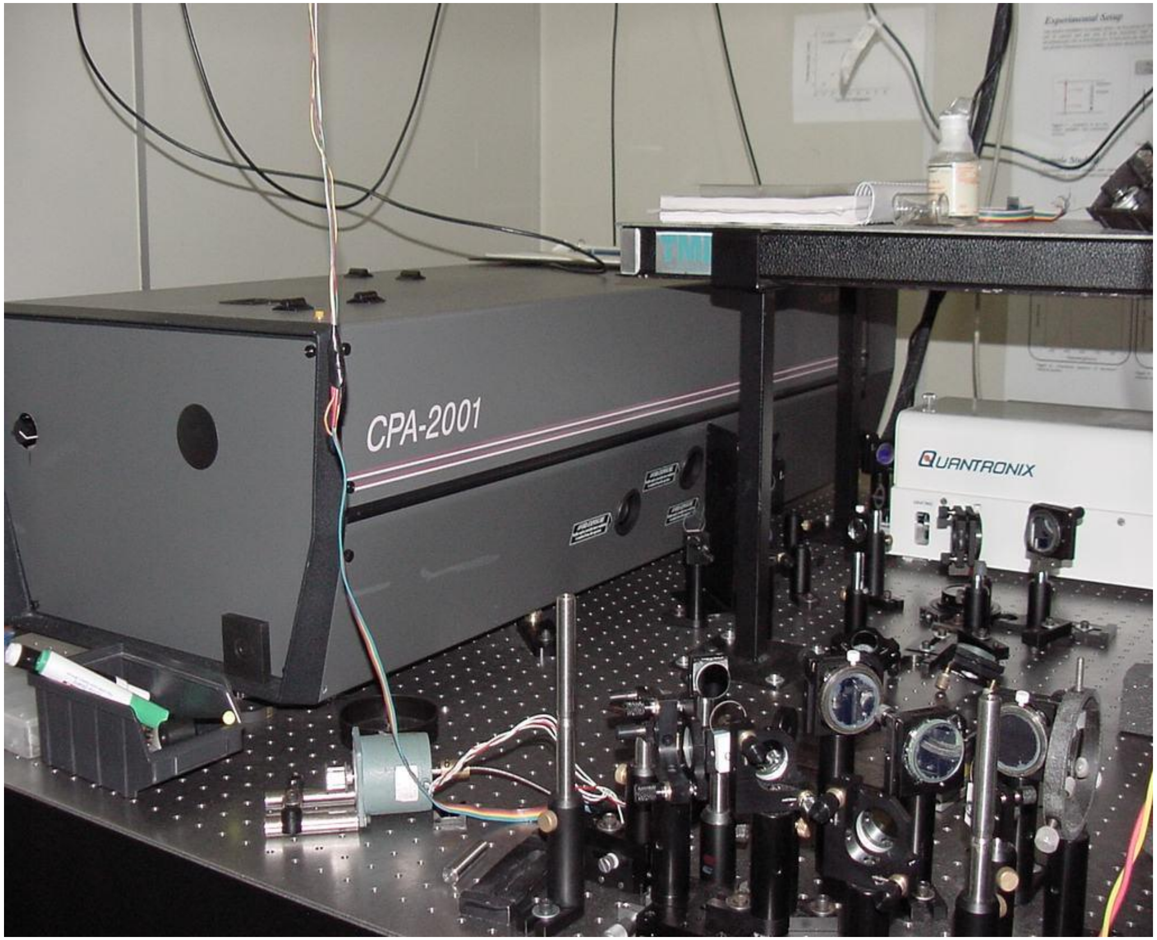
closed aperture Z-scan



$$n = n_0 + n_2 I$$

$$\Delta T \propto n_2 I$$

150 fs laser system



Ti:Sapphire amplifier

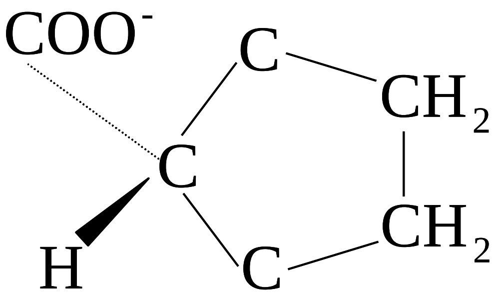
775 nm

150 fs

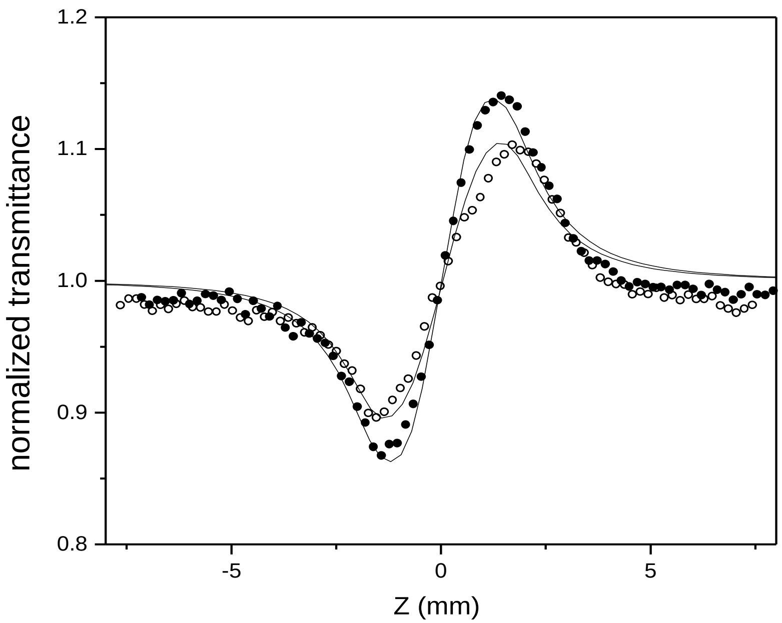
800 μJ

Nonlinear refraction

Aminoacids



L-Proline



$$\Delta T_{pv} = 0.406\Delta\Phi_0 = 0.406\left(\frac{2\pi}{\lambda} n_2 I_0 L\right)$$

150 fs 100 GW/cm^2

775 nm

$$n_2 \propto \chi^{(3)}$$

microscopic to macroscopic nonlinearities

Molecular

$$\mu = \mu_0 + \alpha E + \beta E^2 + \gamma E^3 + \ldots$$

Material

Electro-optic effect

Intensity dependent refraction

$$P = P_o + \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots$$

For weakly interacting molecules

$$\chi^{(3)} = \gamma N L^4$$

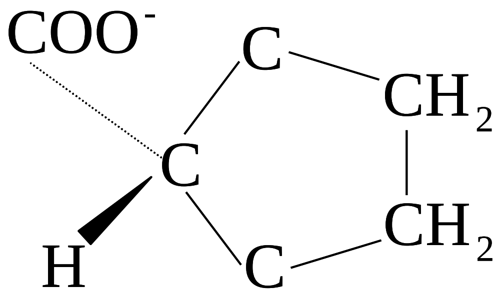
Number density

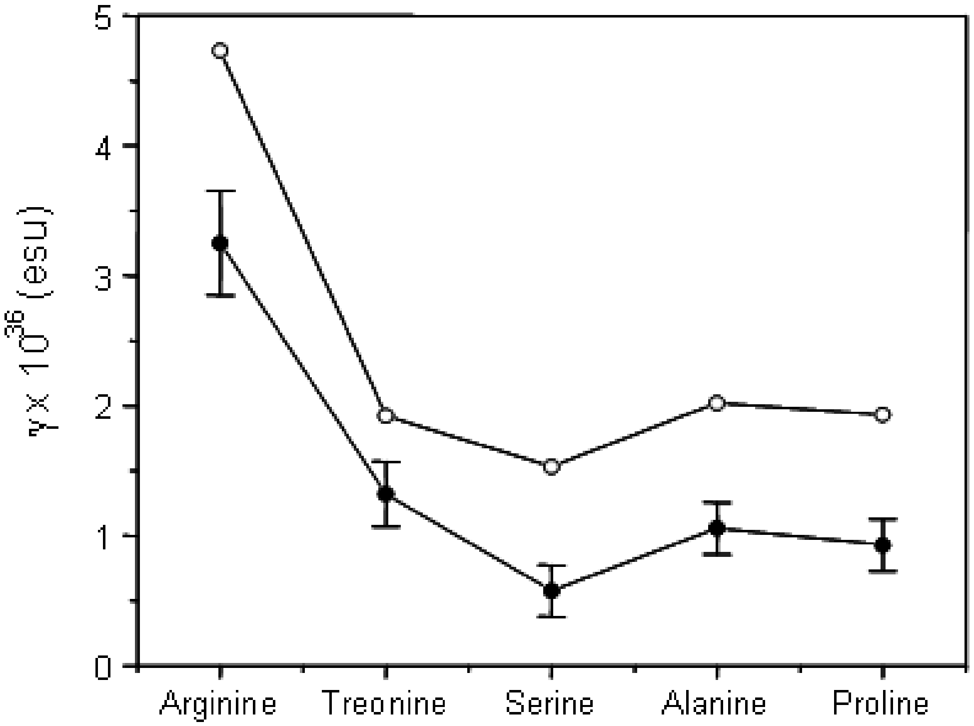
Local field factor

$(n^2 + 2)/3$

Nonlinear refraction

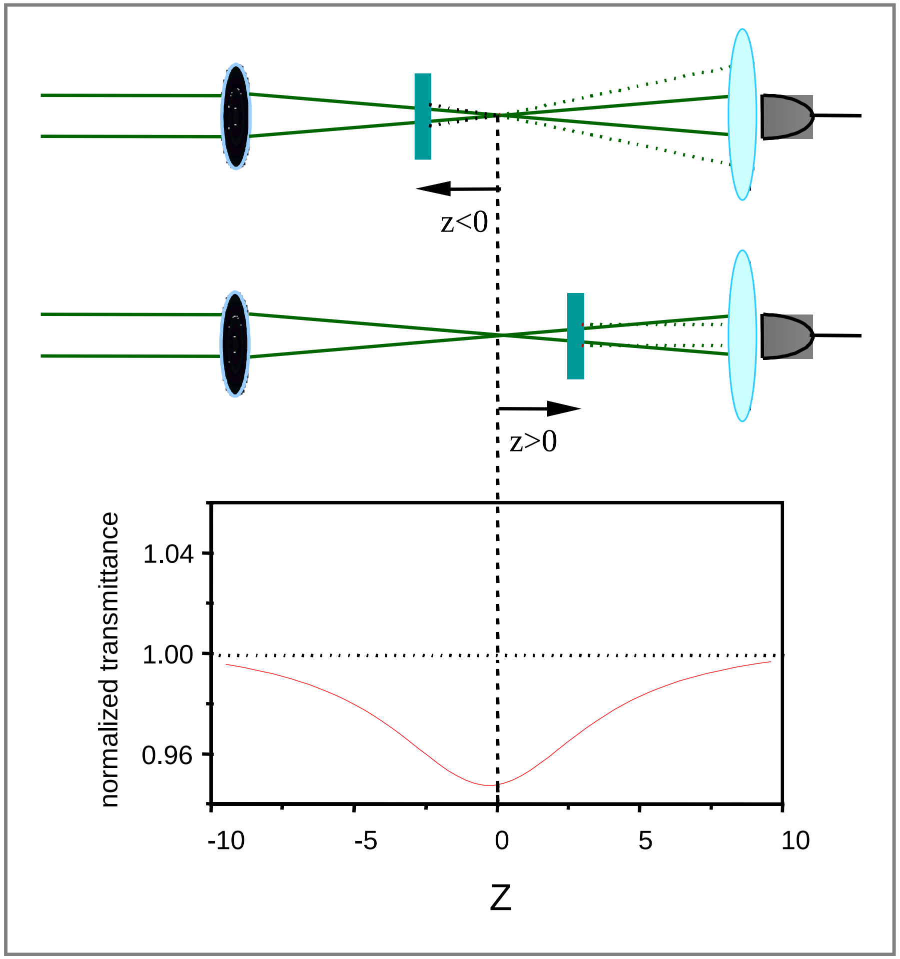
L-Proline





Z-scan (nonlinear absorption)

open aperture Z-scan



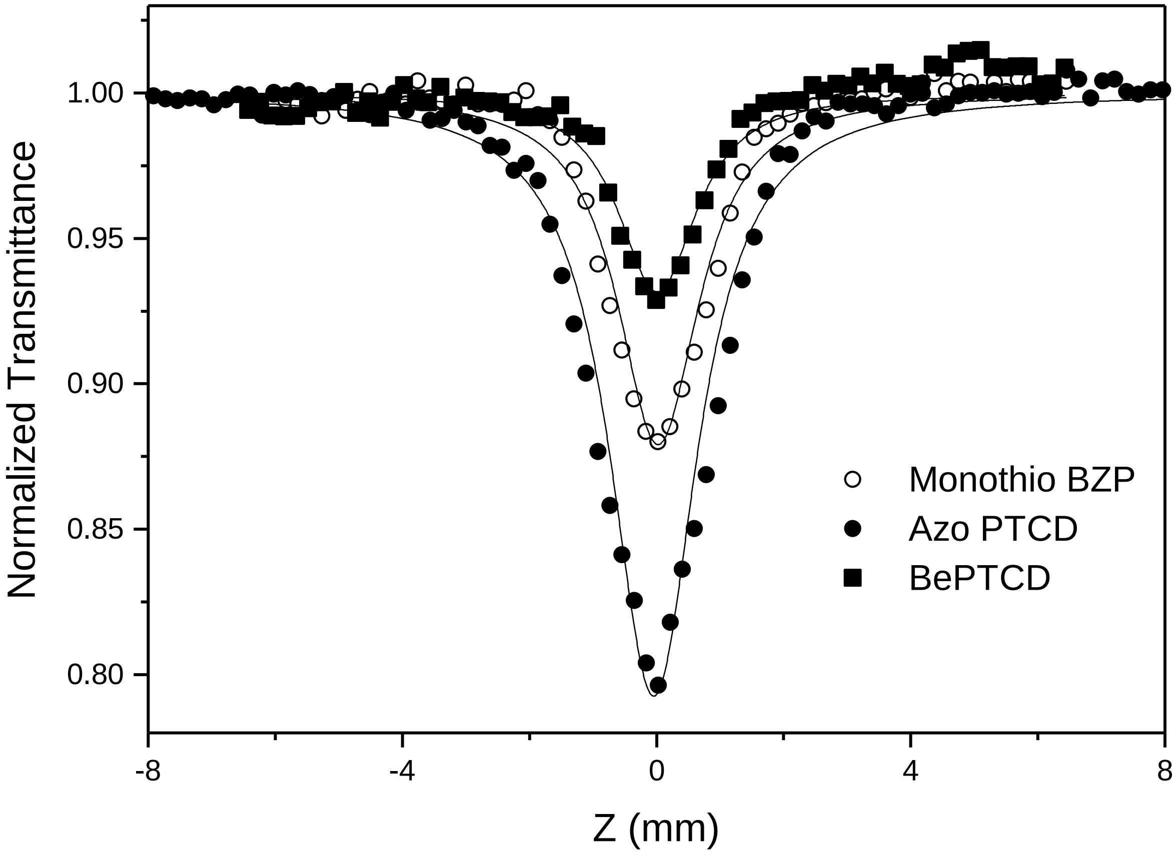
$$\alpha(I) = \alpha_0 + \beta I$$

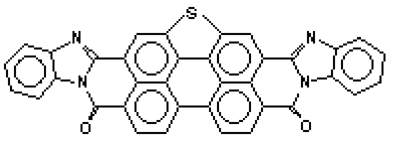
$$\Delta T \propto \beta I$$

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}$$

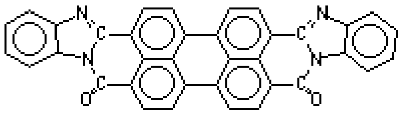
$$q_0(z,t) = \beta I_0 L / \left(1 + z^2 / z_0^2\right)$$

Nonlinear absorption

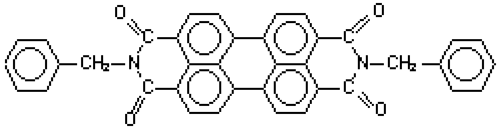




Monothio BZP



AzoPTCD

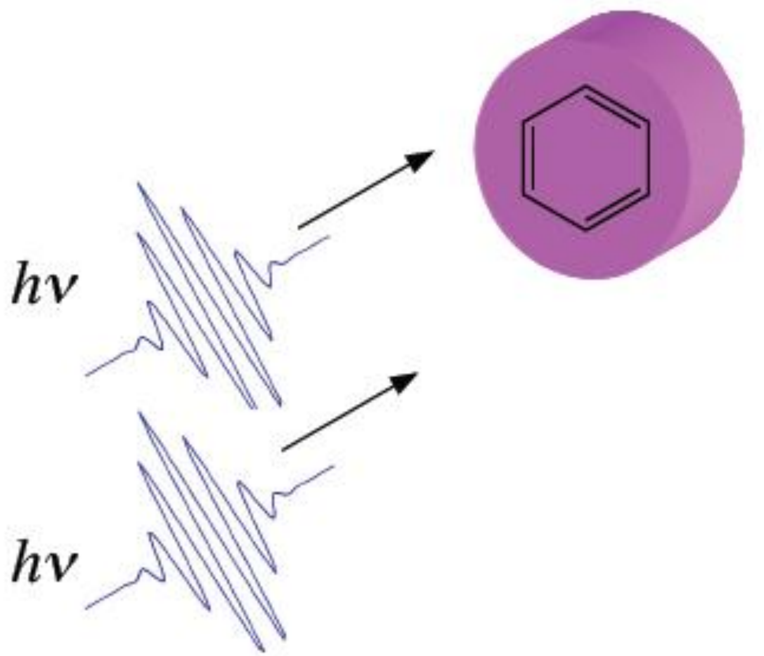


BePTCD

775 nm

two-photon absorption cross-section

A pair of photon incident on a molecule



For two-photon absorption to occur, a pair of photons must be incident within a cross sectional area and within the lifetime of the virtual sate, $\tau \sim 10^{-15}$ s

Relation between molecular TPA cross section and TPA absorption coefficient

$$\delta = \frac{h\nu\beta}{N}$$

Representative values for TPA transitions:

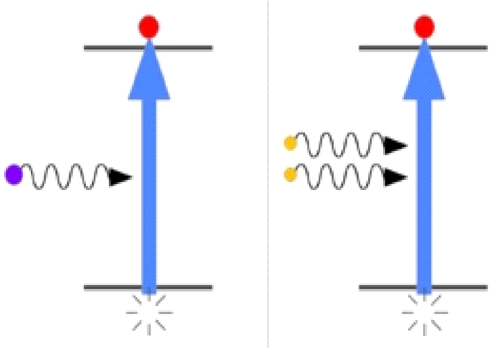
δ = 10 to 1000 x 10^{-50} cm^4 s $photon^{-1}$

β = 10 to 100 cm GW^{-1} for a neat material

Nonlinear spectrum

nonlinear absorption

$$\alpha = \alpha_0 + \beta\, I$$



nonlinear refraction

$$n = n_0 + n_2 I$$

intense laser (ultra short pulses)

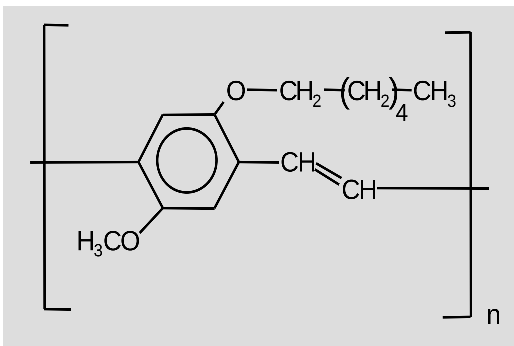
discrete λ s

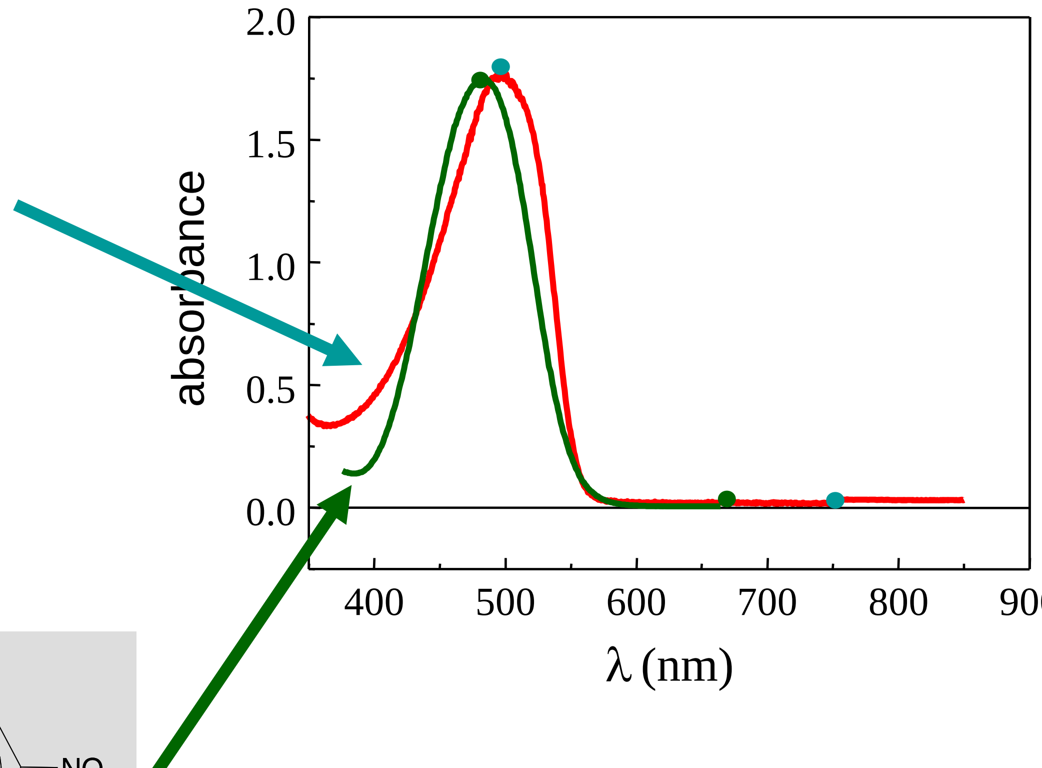
$\delta(\lambda)$ $n_2(\lambda)$

nonlinear spectrum ???

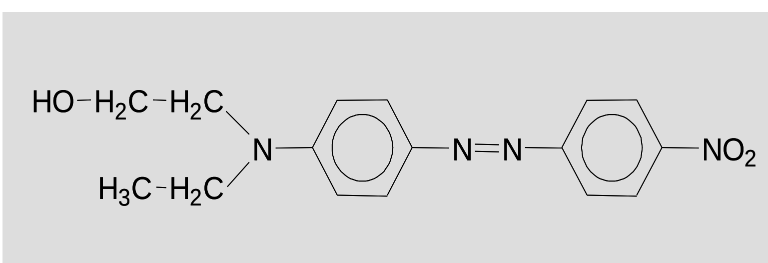
Linear absorption spectrum

MeH-PPV





DR1



Nonlinear absorption spectrum

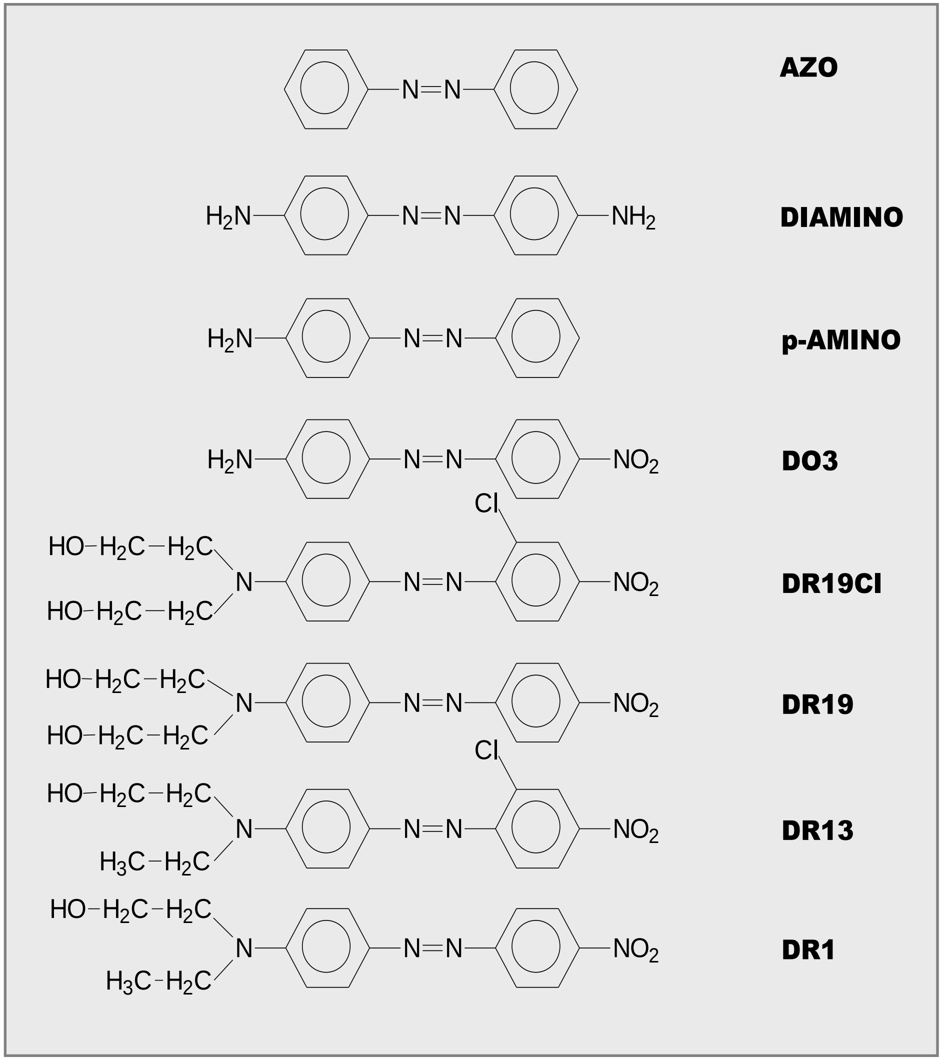
Optical parametric amplifier

460 - 2600 nm

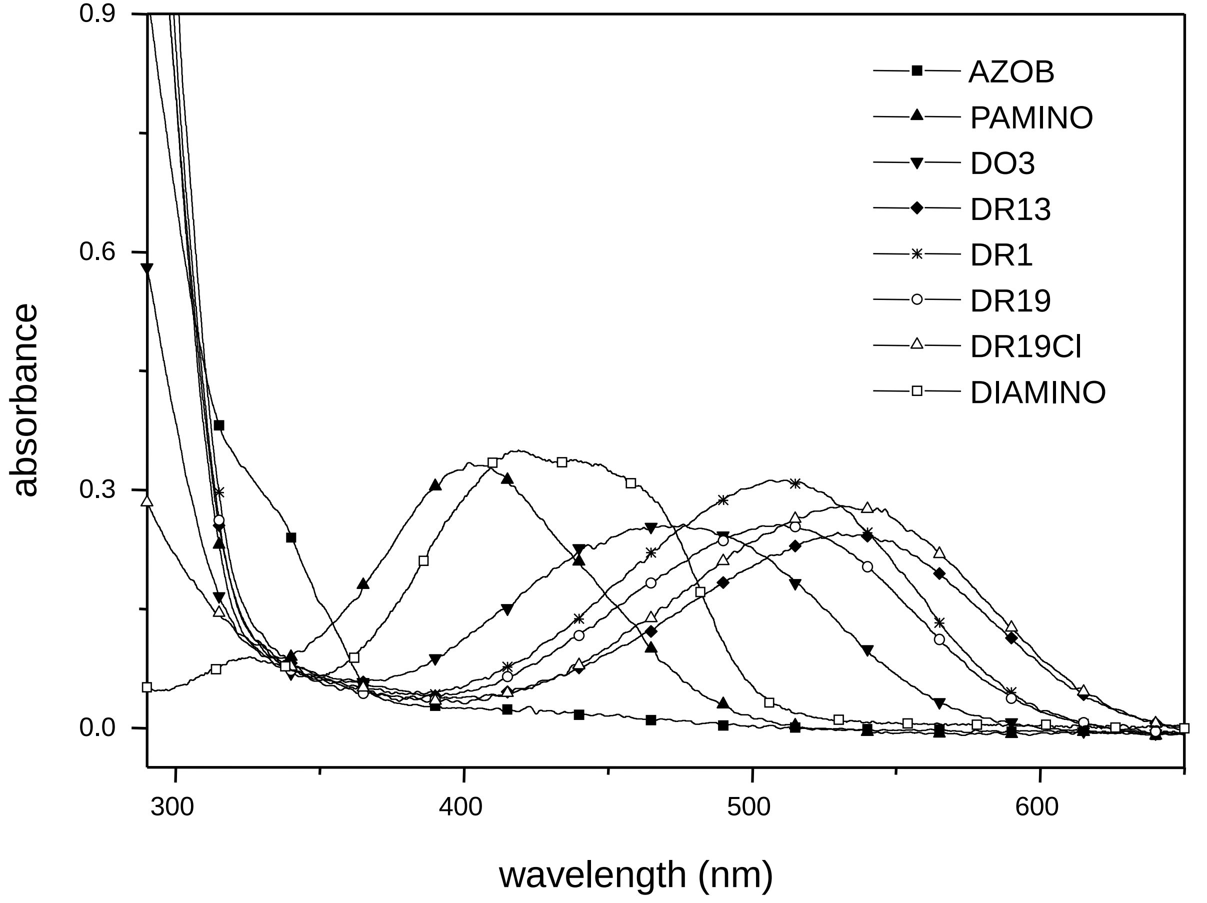
$\approx$ *120 fs*

20-60 μJ

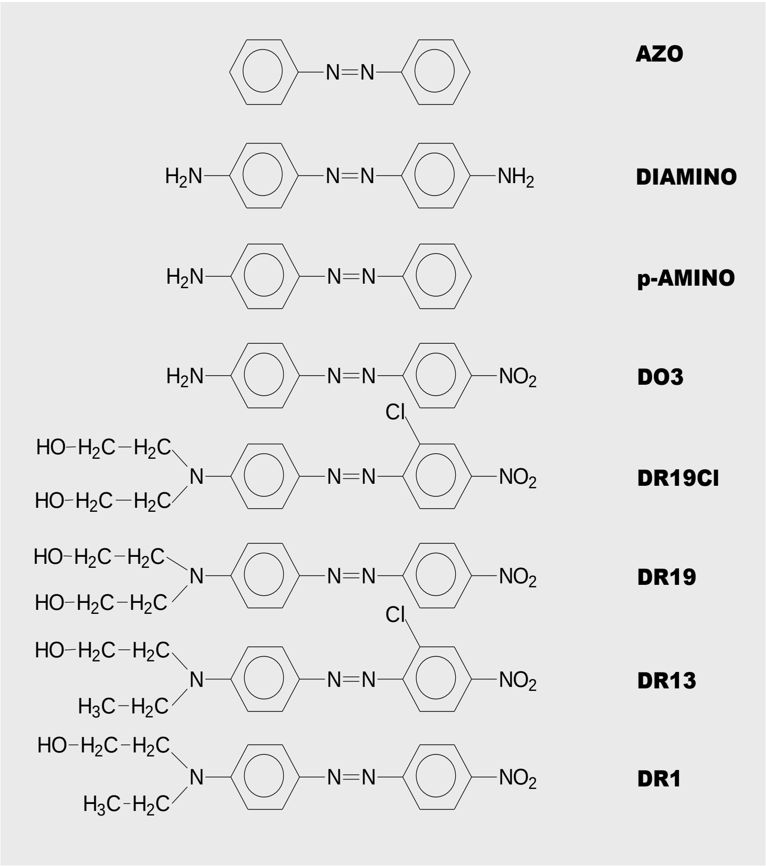
Azoaromatic samples

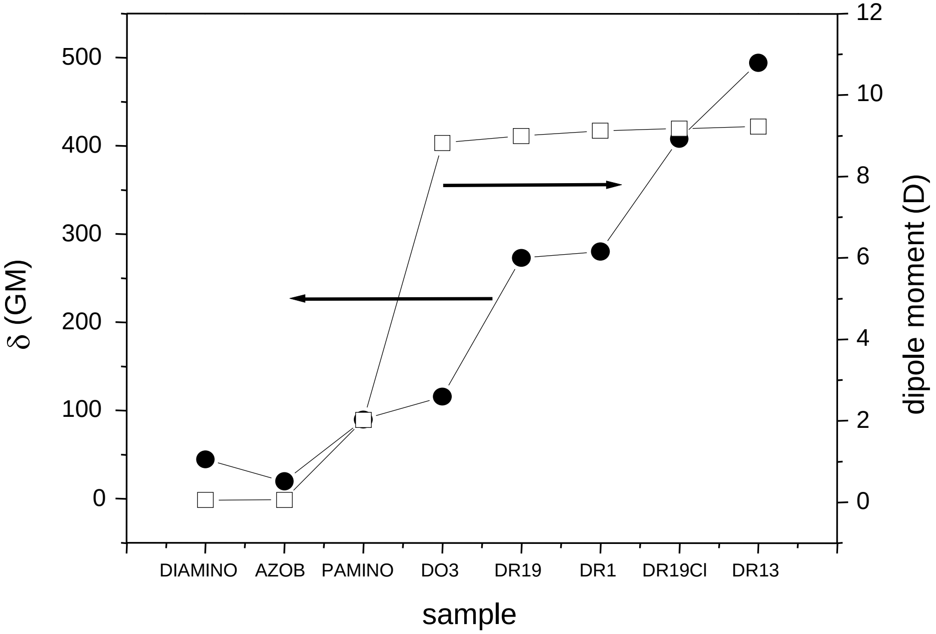


Linear absorption of azoaromatic compounds



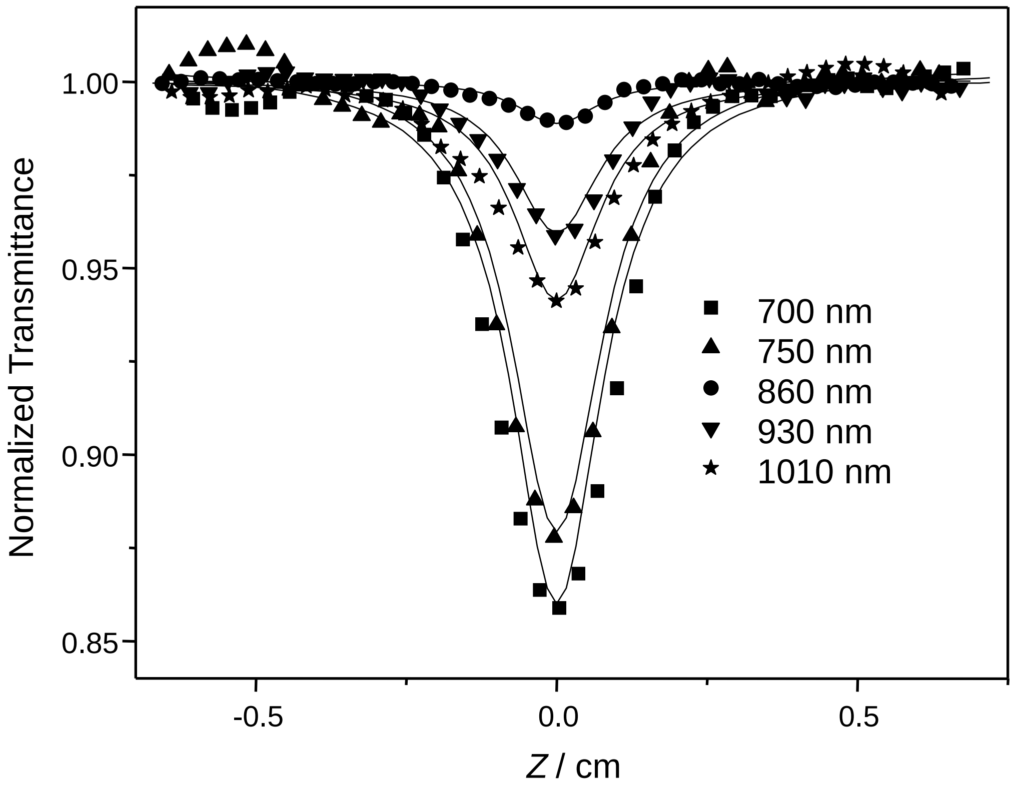
Two-photons absorption



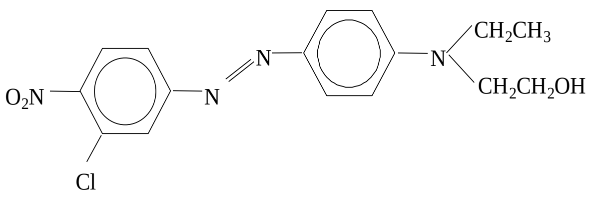


775 nm

Two-photon absorption



DR13

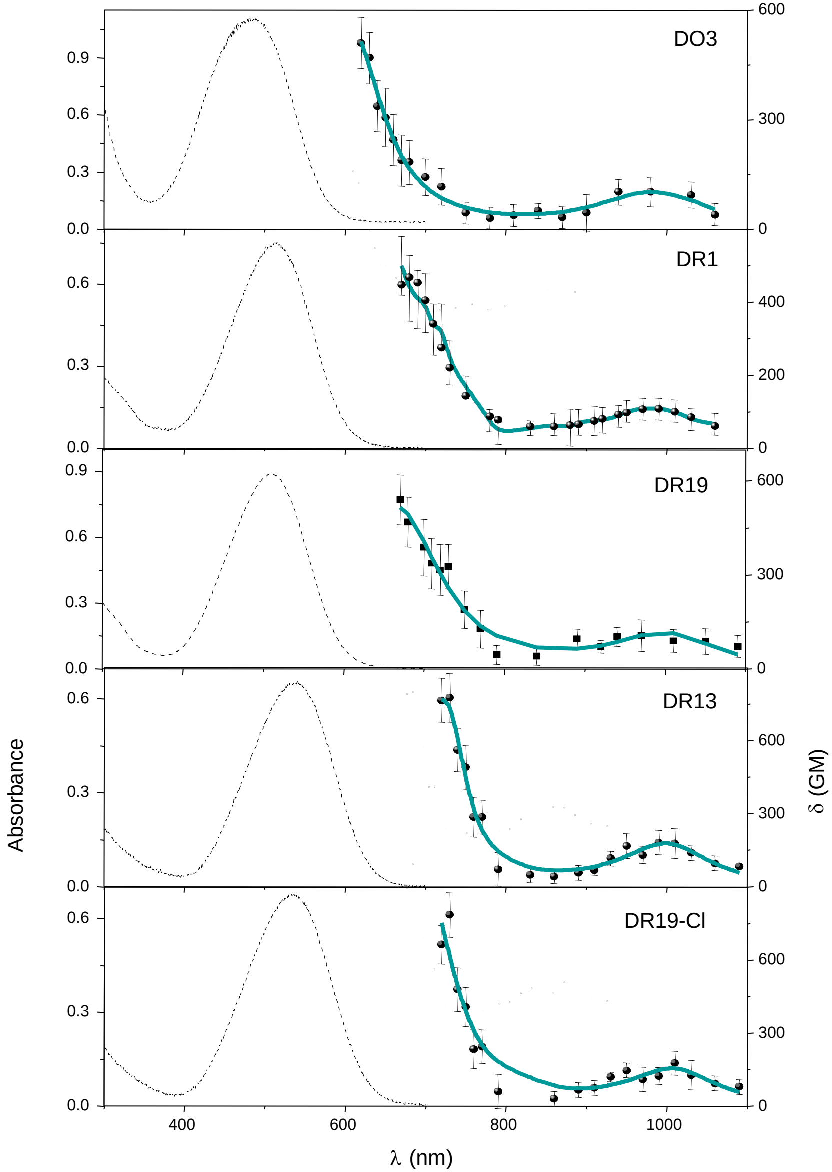


$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}$$

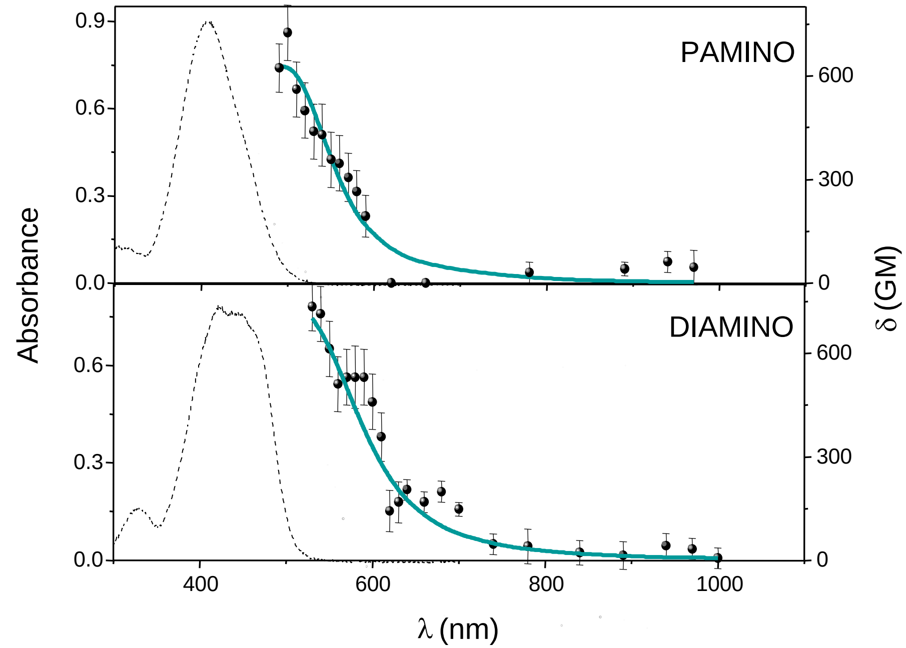
$$\alpha = \alpha_0 + \beta I$$

β: two-photon absorption coefficient

Psuedostilbenos

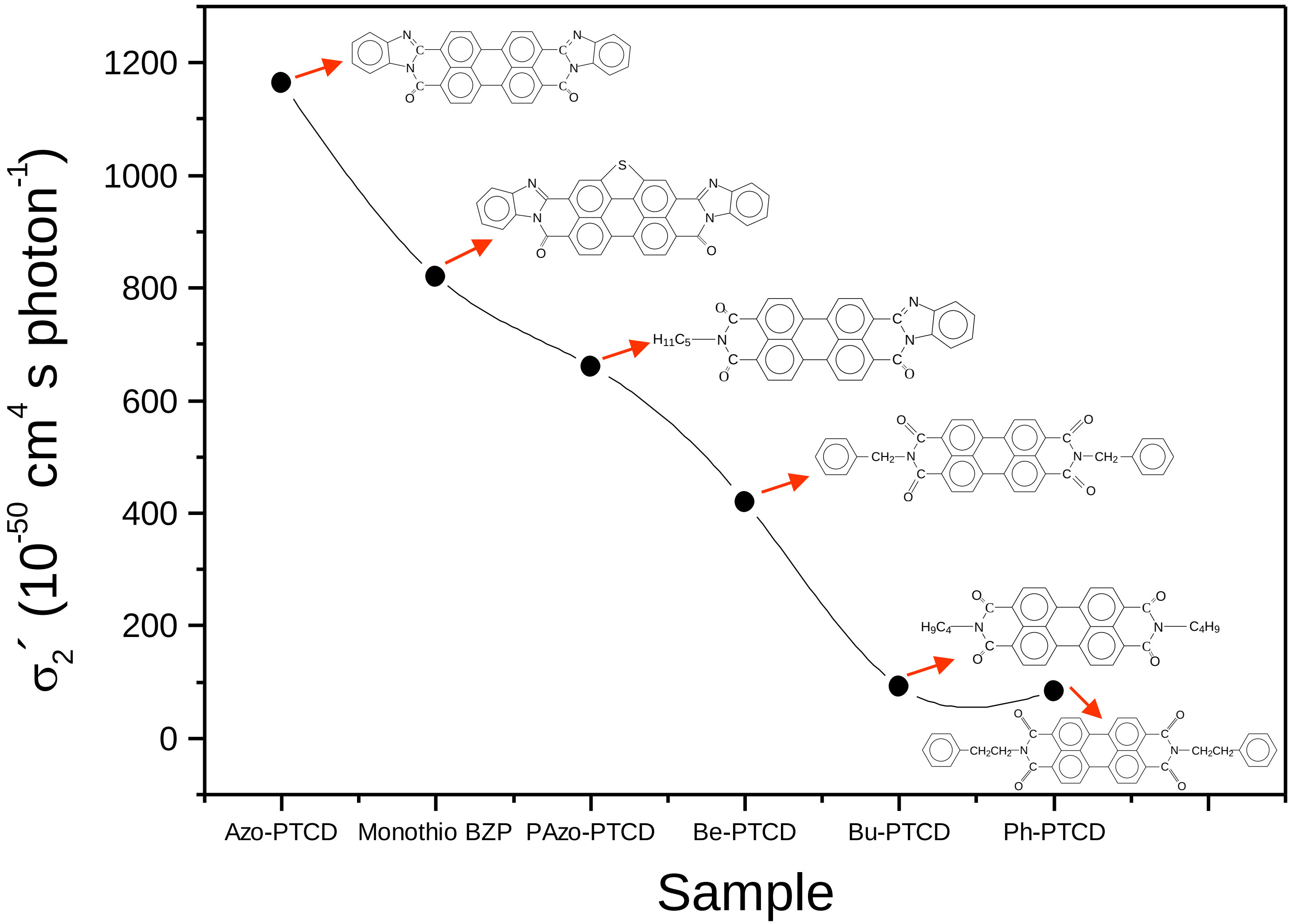


Aminoazobenzenos



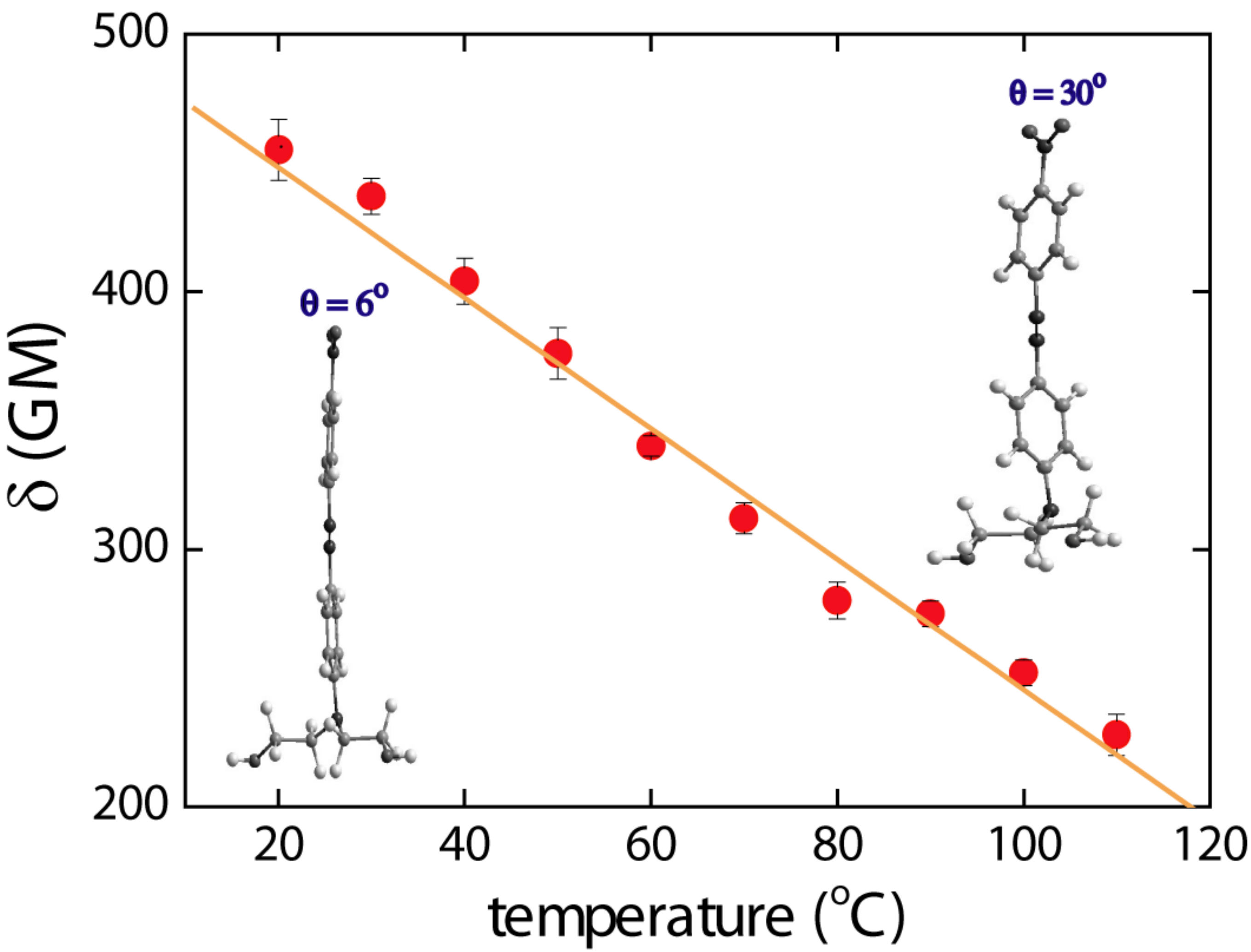
$$\delta(\nu) \propto \frac{\nu^2}{(\nu_{i0}-\nu)^2+\Gamma_{i0}^2}\left[\frac{A_1}{(\nu_{f_1 0}-2\nu)^2+\Gamma_{f_1 0}^2}+\frac{A_2}{(\nu_{f_2 0}-2\nu)^2+\Gamma_{f_2 0}^2}\right]$$

Two-photon absorption of perylenes



Correlation between molecular structure and the nonlinear response

Planarity of the π-bridge

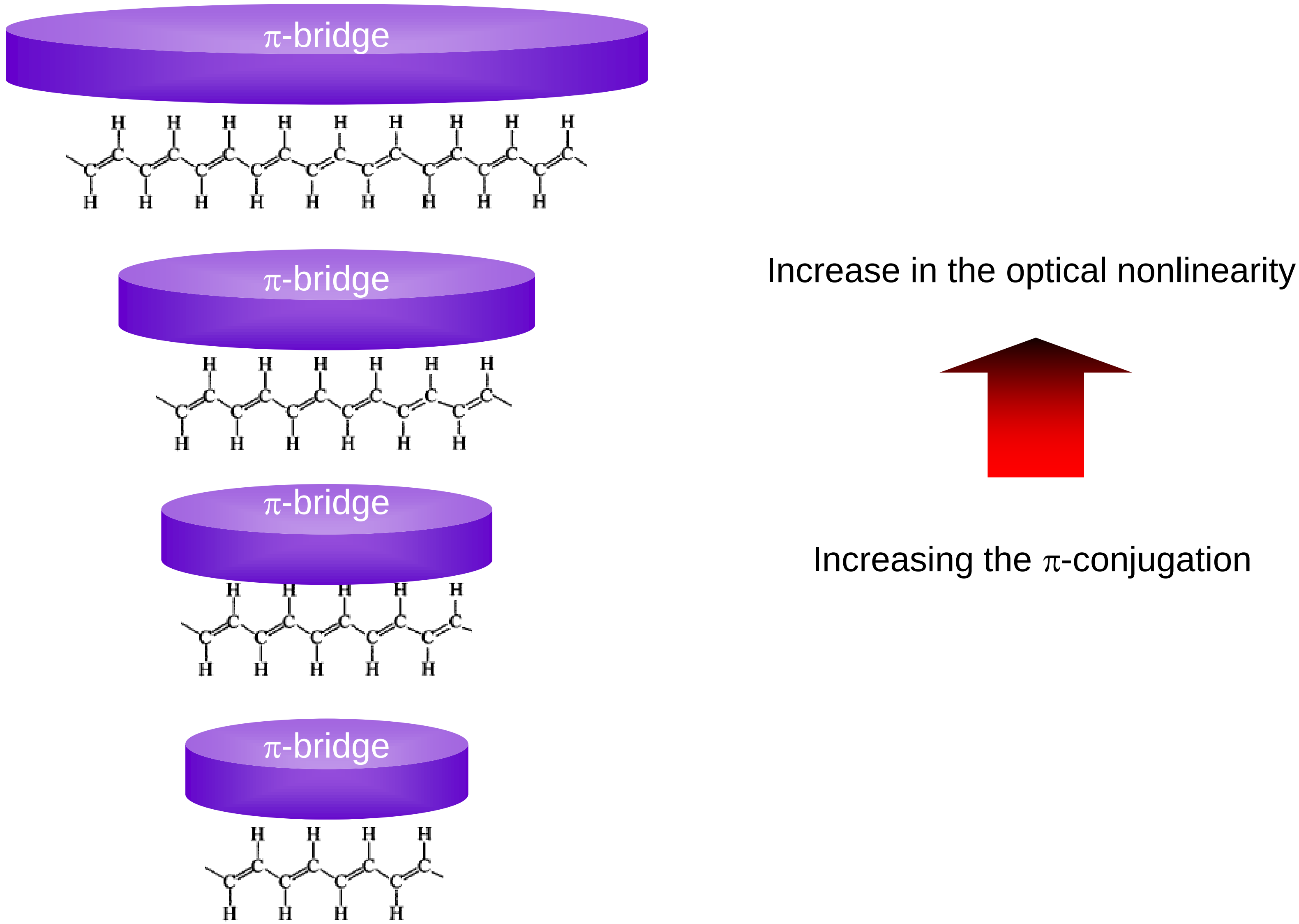


Thermally induced torsion in the molecular structure

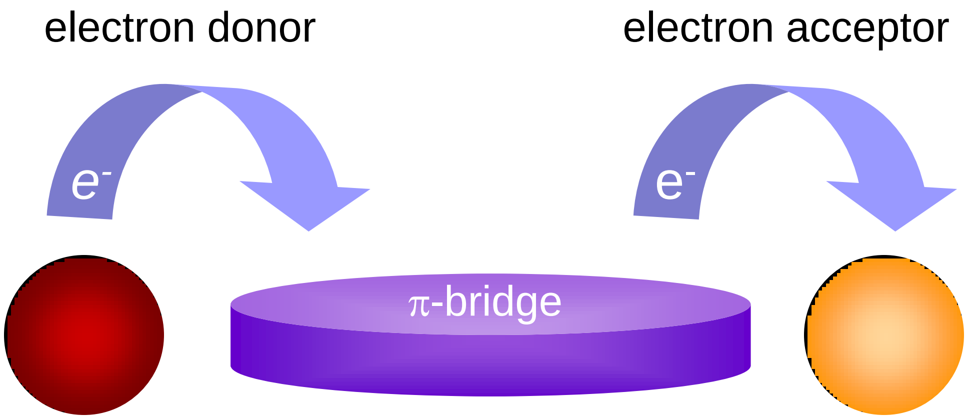
Molecular design strategy

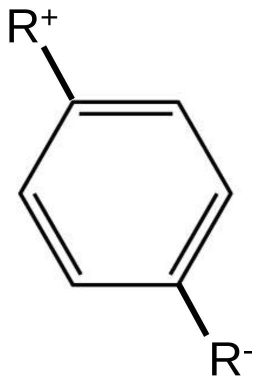
- Increasing the molecular conjugation
- Adding charged groups to the molecule
- Keep molecular planarity

Increasing the conjugation



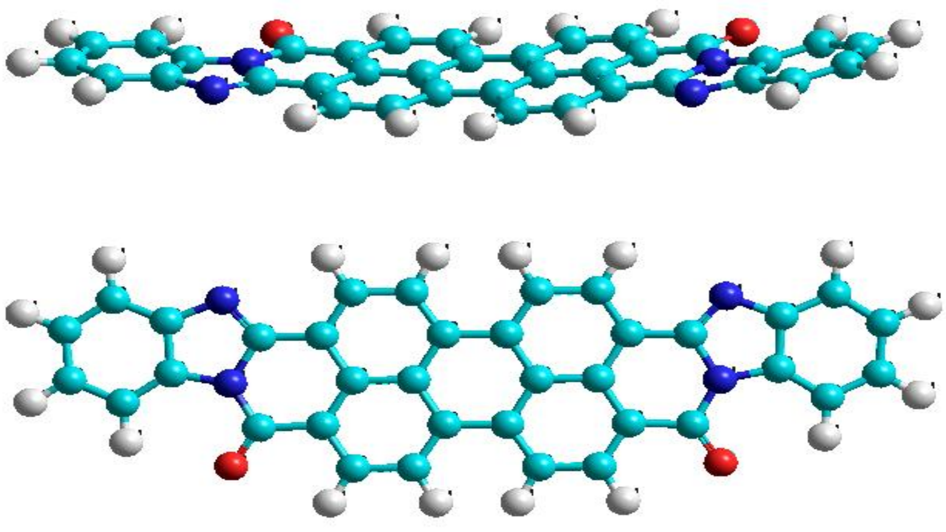
Donor and acceptor groups





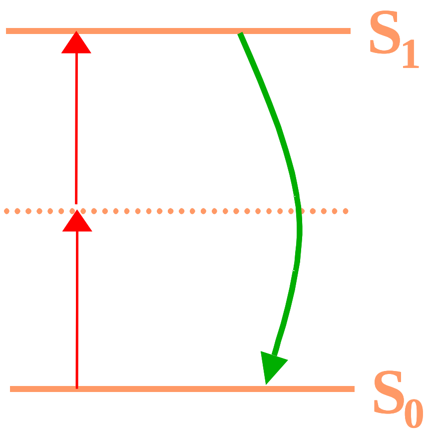
Incorporating electron donor and acceptor groups in a predictable way leads to an enhancement of the optical nonlinearity

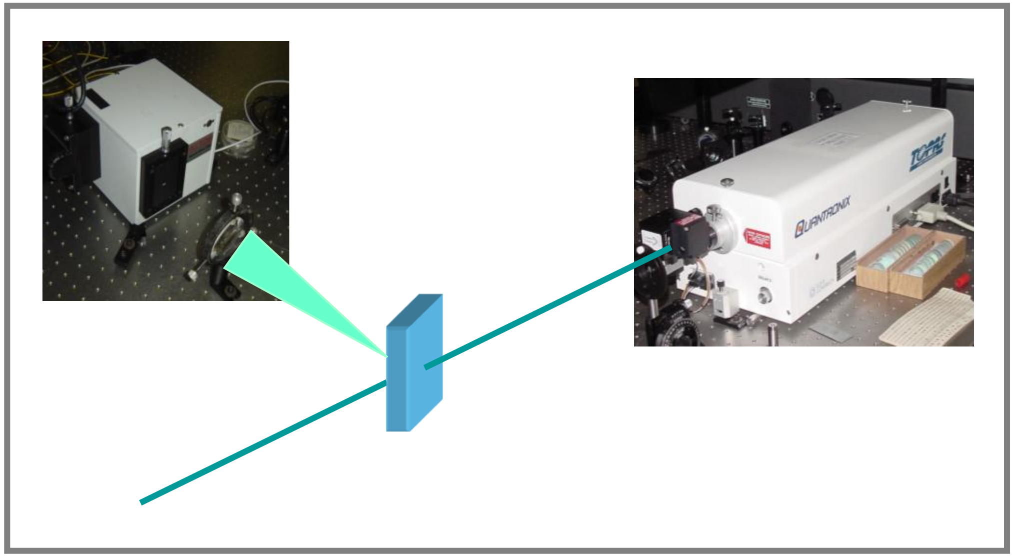
Planarity of the π-bridge



Perylene compounds are very planar molecules, which explains its high optical nonlinearities

Two-photon excited fluorescence

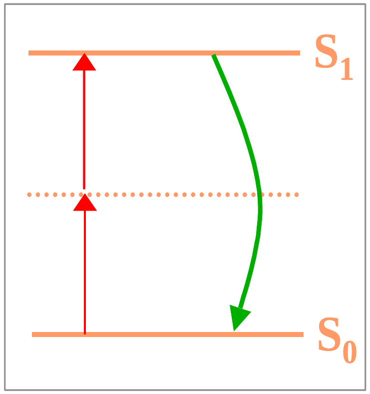




$$\frac{dN_2}{dt} \approx N_1 \delta I^2$$

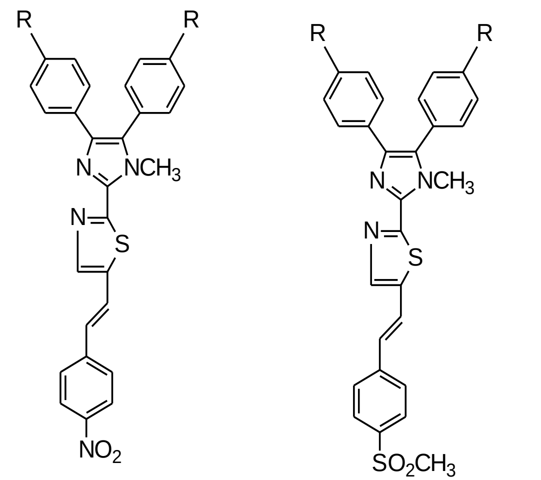
$$F \approx I^2$$

Multi-photon excited fluorescence



$$\frac{dN_2}{dt} \approx N_1 \delta I^2$$

$$F \approx I^2$$

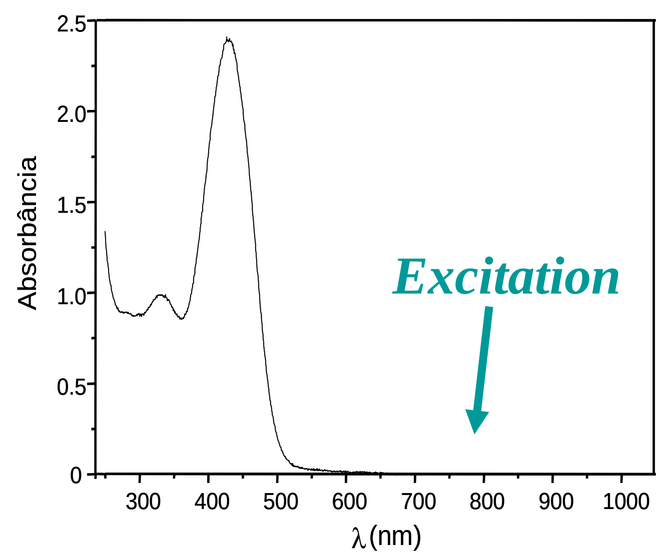


1 **2** **3**
R = H, CH_3, OCH_3

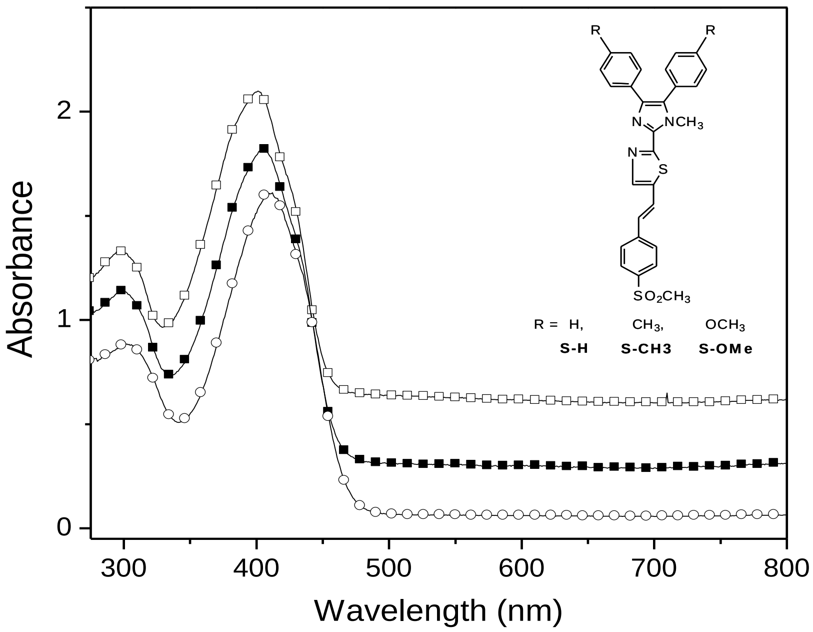
4 **5** **6**
R = H, CH_3, OCH_3

NITRO **SULFONIL**

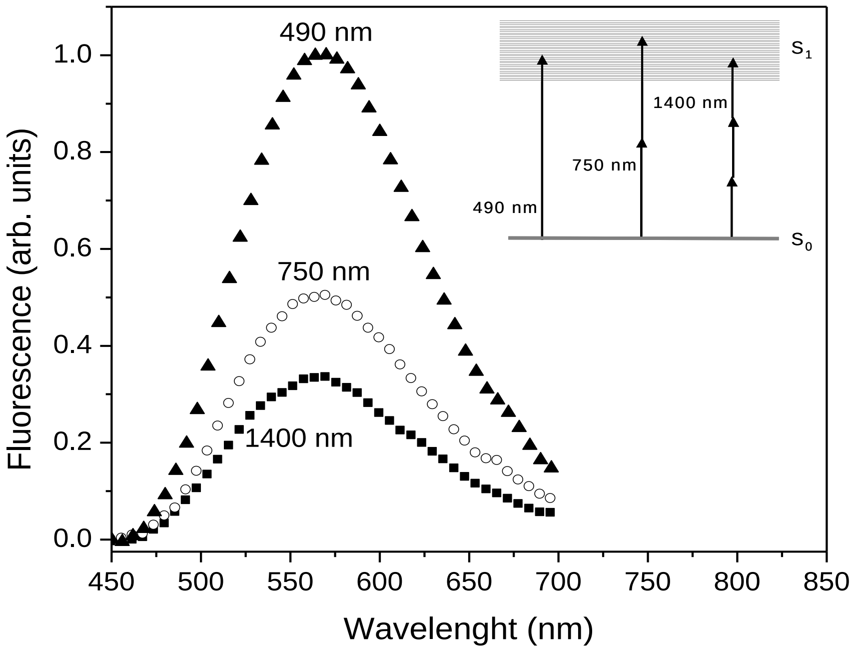
Y-shaped



Fluorescence excited by two and three photons

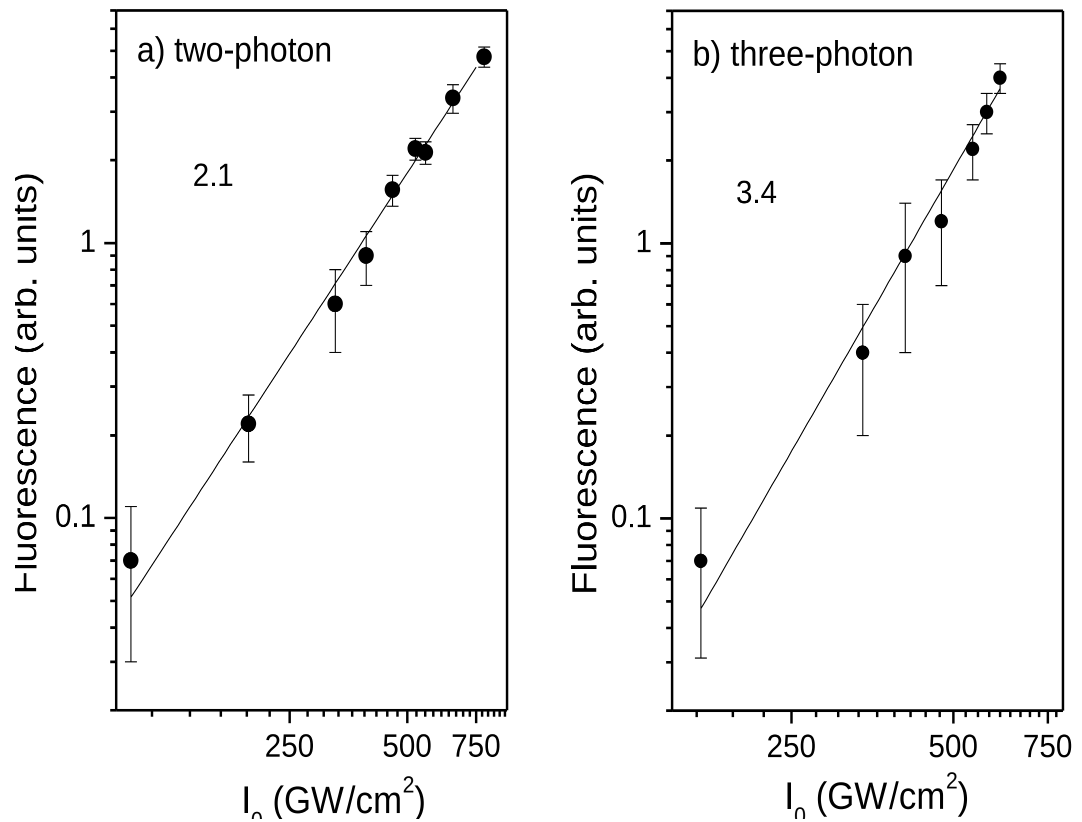


Absorption



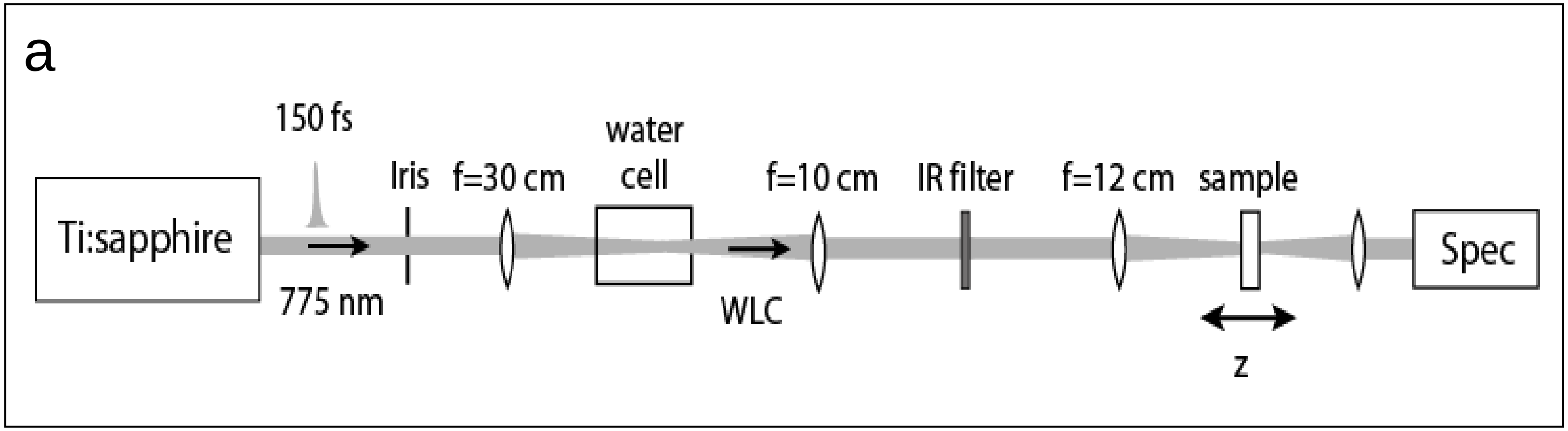
Fluorescence

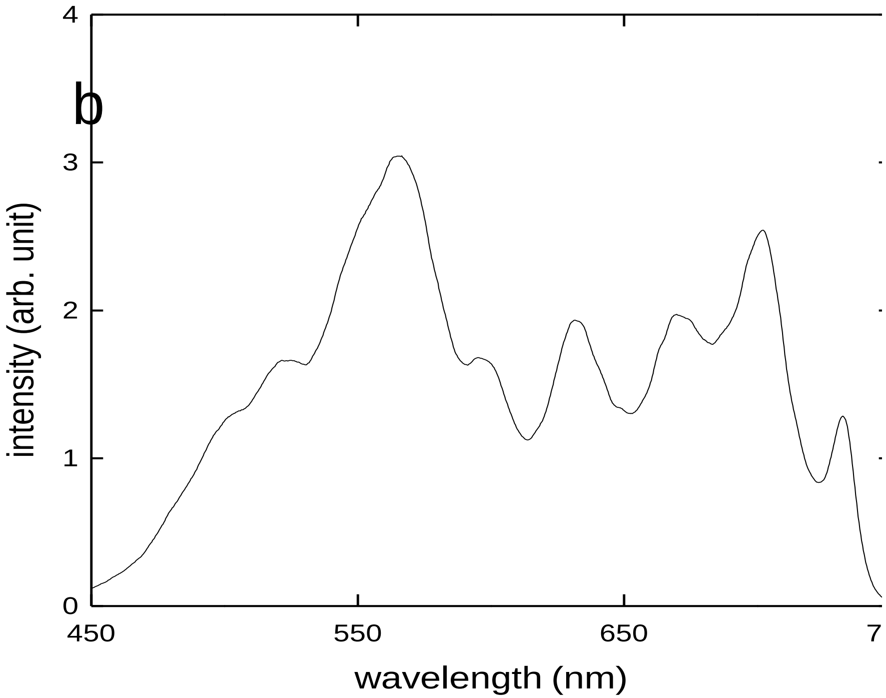
Two-photon excited fluorescence

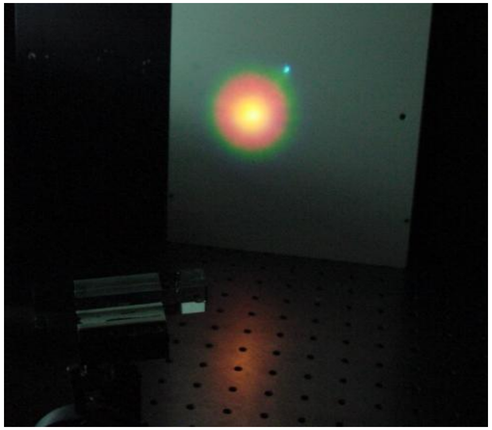


Sample	***N*** *(10^{18} molecules/cm^3)*	*σ_2 (10^{-50} cm^4 s) @ 750 nm*	*σ_3 (10^{-78} cm^6 s^2) @ 1400 nm*
S-H	3.2	500	4.5
S-CH3	2.6	1450	5.6
S-Ome	2.4	1550	7.3

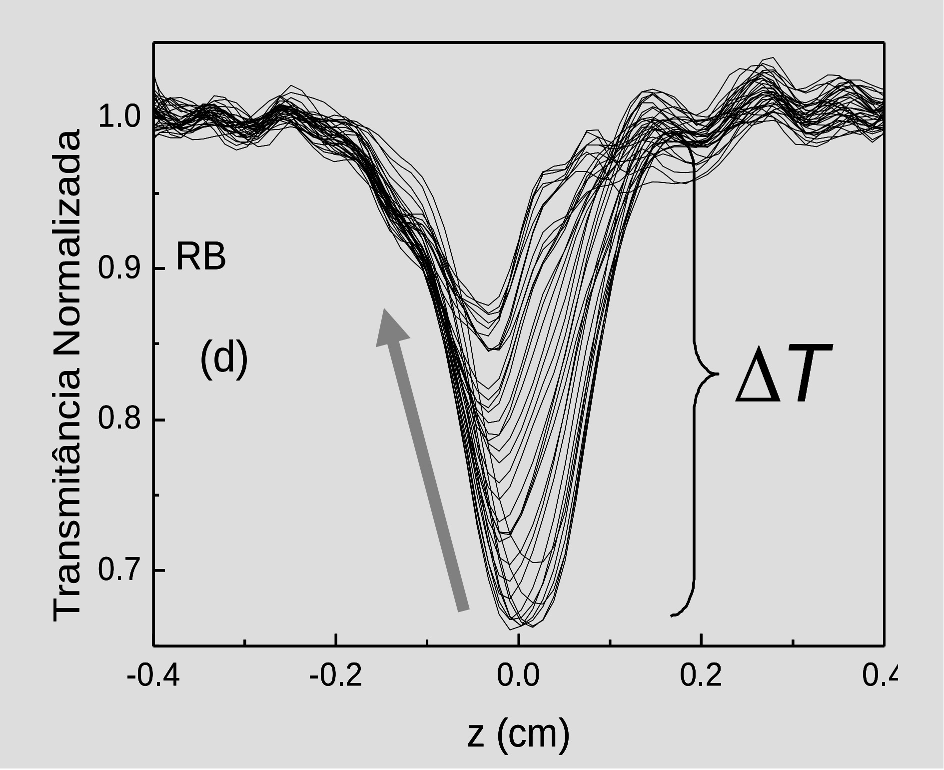
White light continuum Z-scan

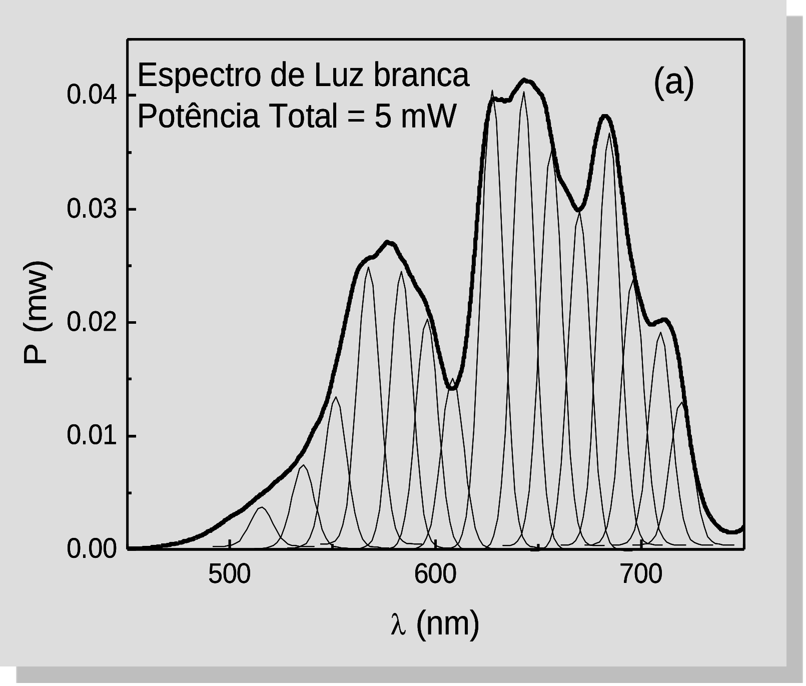






White light continuum Z-scan

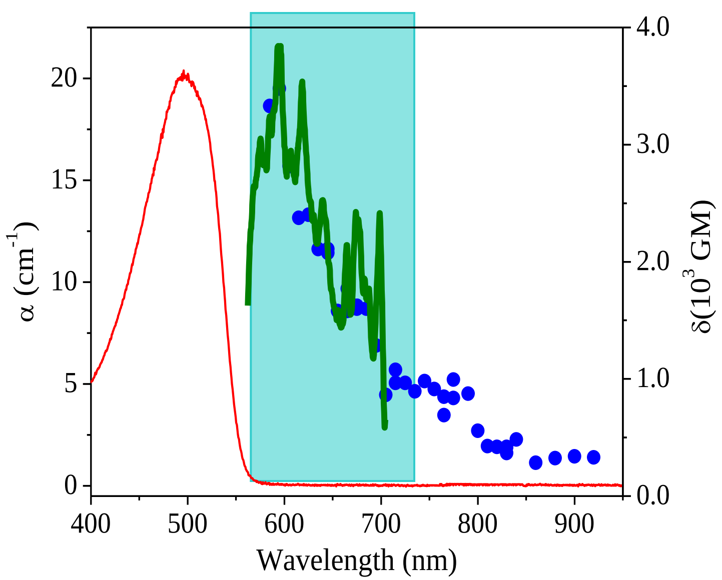




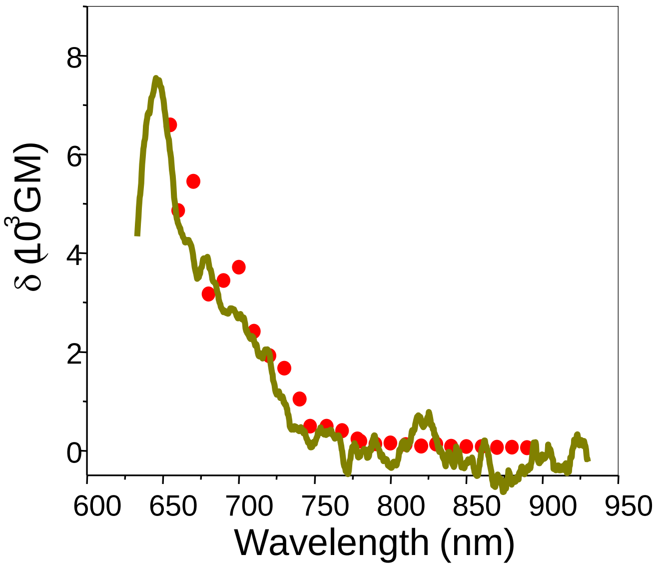
White light continuum Z-scan

Non resonant effects

MeH-PPV



Perylenes derivatives

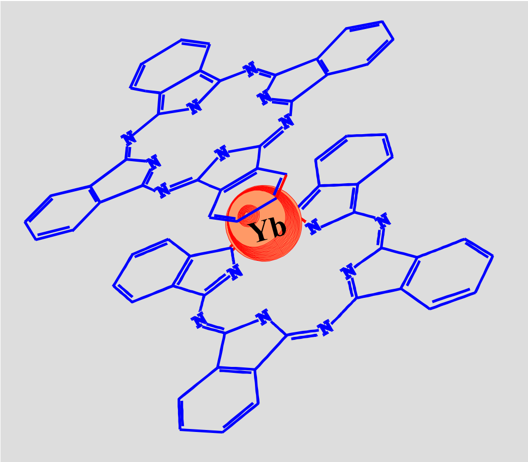


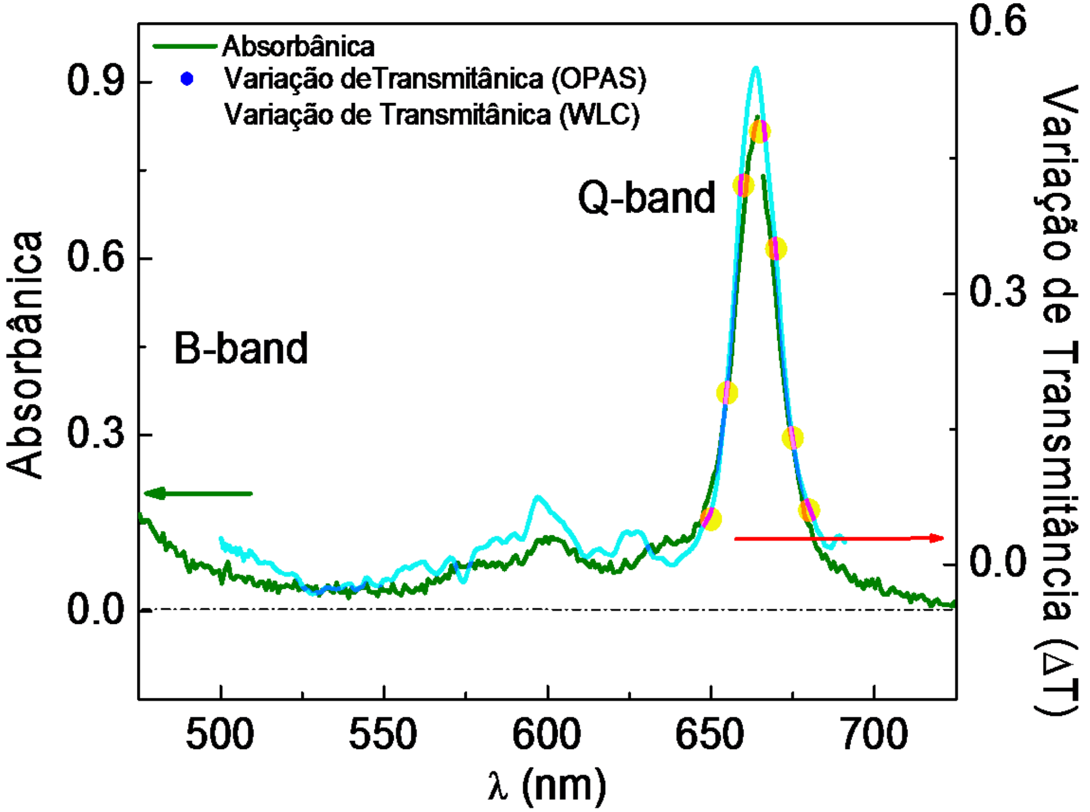
each measurement takes only a few minutes

White light continuum Z-scan

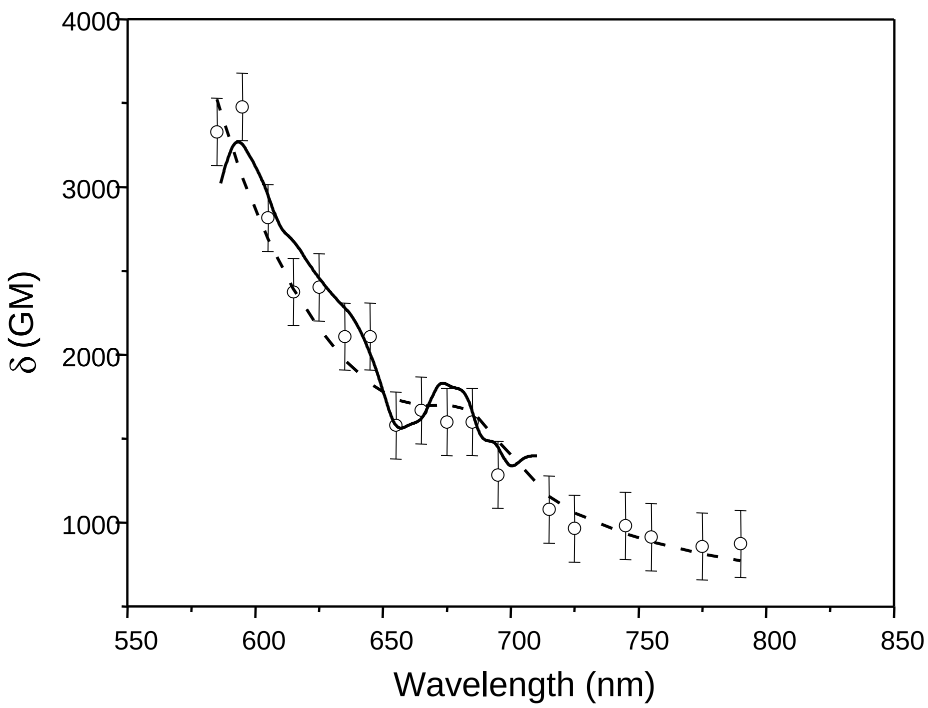
Resonant effects

Bisftalocianina de Yb





White light continuum Z-scan



Two-photon absorption

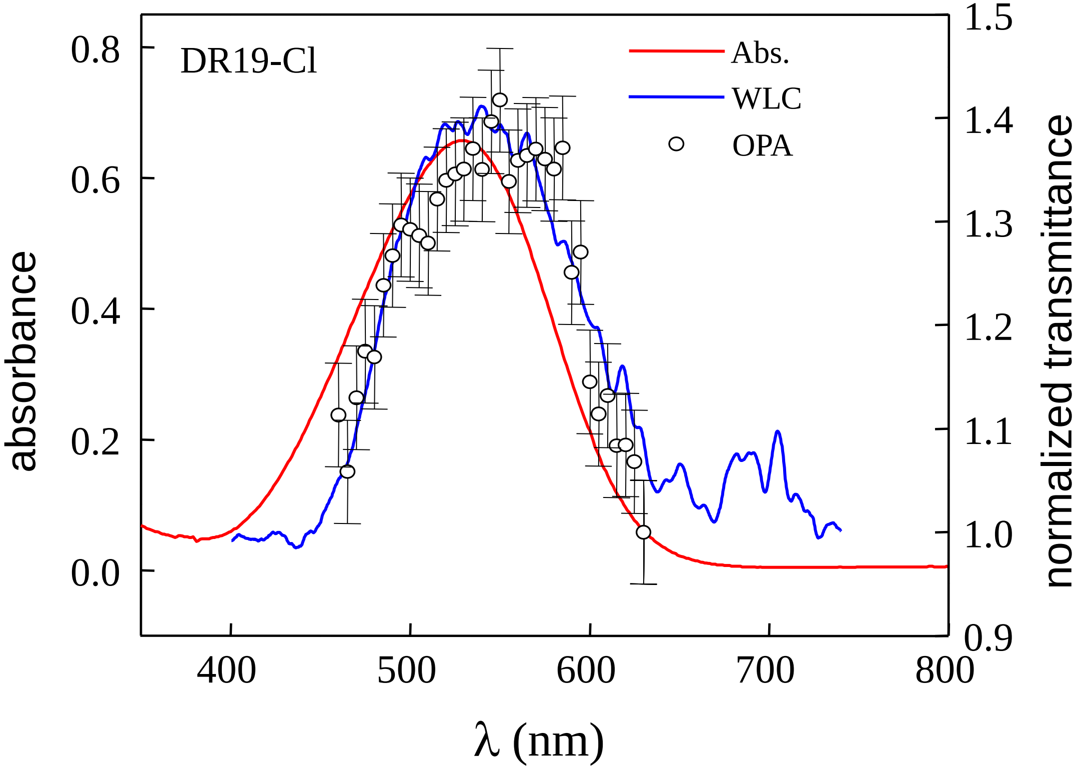
MEH-PPV

Circles : discrete Z-scan measurements

Dashed line: theoretical model

Solid line: Degenerate two-photon absorption cross-section spectra obtained from WLC Z-scan

White light continuum Z-scan



Resonant nonlinearities

saturated absorption

Thank you !

http://www.fotonica.ifsc.usp.br

http://www.photonics.ifsc.usp.br

IFSC-USP

Fotônica