Optical nonlinearities in organic materials: a special look at some bio-photonic materials

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www.photonics.if.sc.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

Institute of Physics of São Carlos

IFSC

Professors: 80

Employers: 180
(technical and administration)

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

Several research areas in Physics and Material Sciences

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 interaction
- fs-laser microfabrication and micromachining
- Optical spectroscopy
- Optical storage

Outline

- Introduction and Motivation
- Experimental
- Results
  - Resonant optical nonlinearities in ***cytochrome c***
  - Two-photon absorption spectrum in ***all-trans retinal***
  - Two-photon absorption of ***carotenoids derivatives***
- Final remarks

Introduction/Motivation

• Organic materials may present high nonlinear optical processes

• Flexibility to tune the nonlinearity by manipulating the molecular structure

• Some biomaterials present, by nature, interesting optical and electrical properties

• ultrafast optical switching

• multi-photon absorption

• multi-photon fluorescence imaging

• microfabrication of devices for photonics and opto-electronics

• optical power limiting

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Experimental

We have been using three main techniques

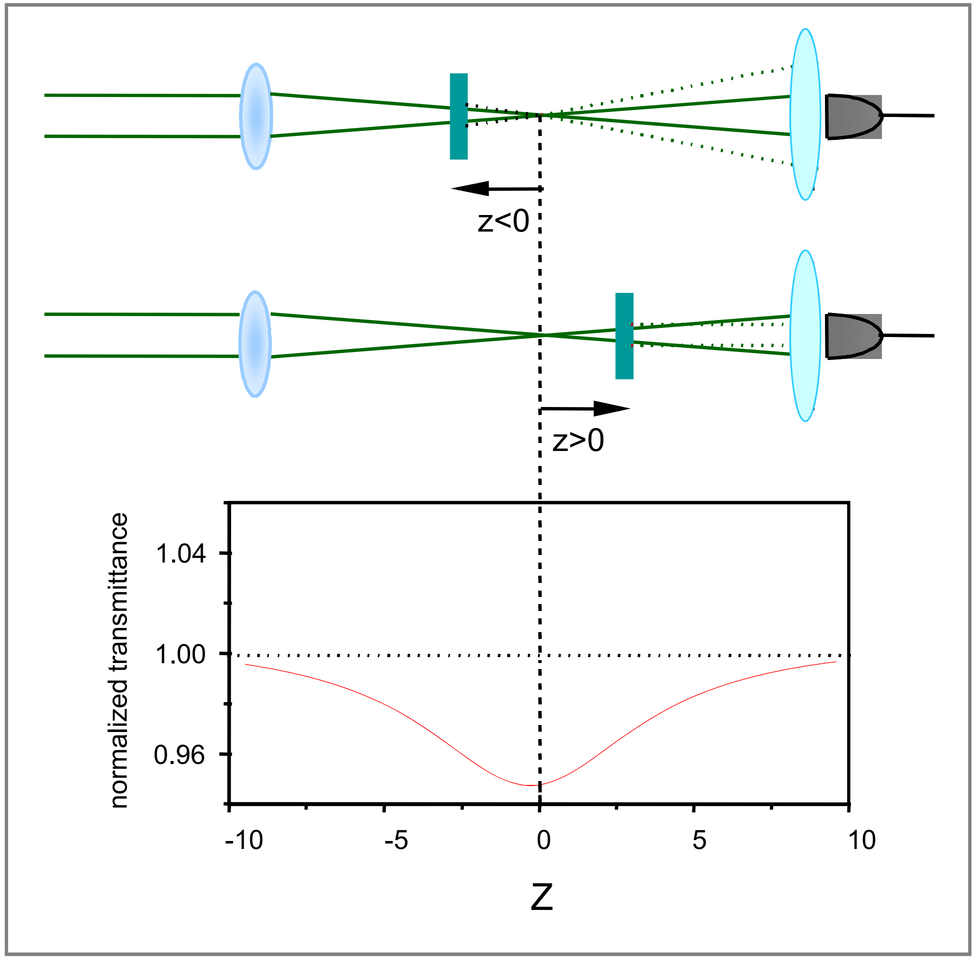
fs-laser Z-scan with the optical parametric amplifier

white light continuum Z-scan

Z-scan with pulse trains

Z-scan (nonlinear absorption)

open aperture Z-scan



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

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

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

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

150 fs laser system

Ti:Sapphire amplifier

775 nm

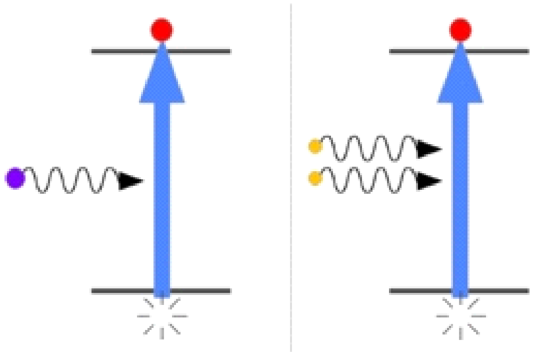
150 fs

800 μJ

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 ???

Nonlinear absorption spectrum

Optical parametric amplifier

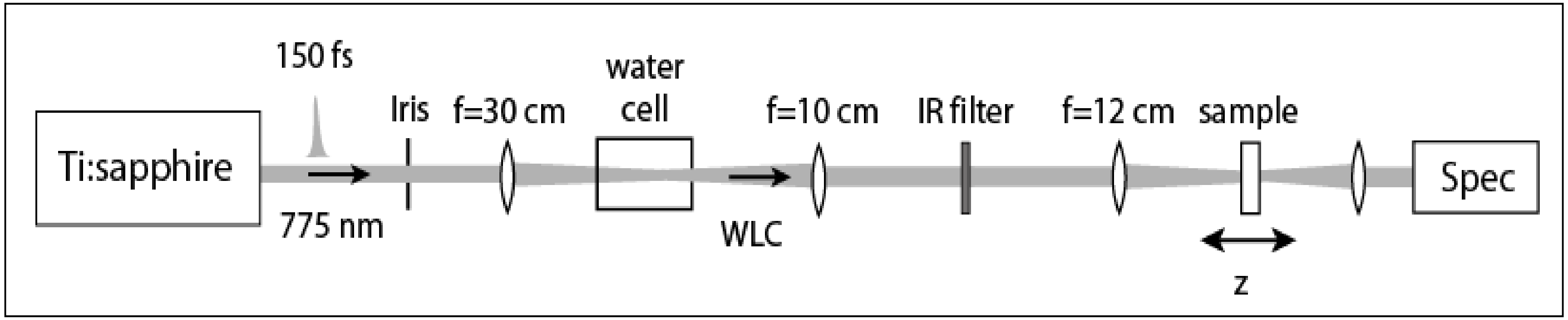
460 - 2600 nm

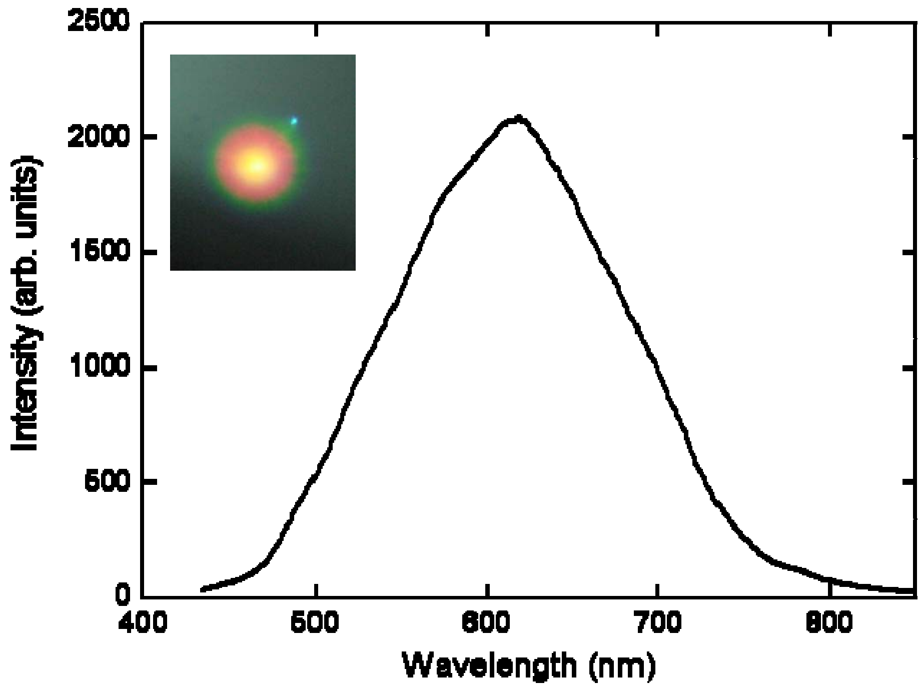
$\approx$ *120 fs*

20-60 μJ

White light continuum Z-scan

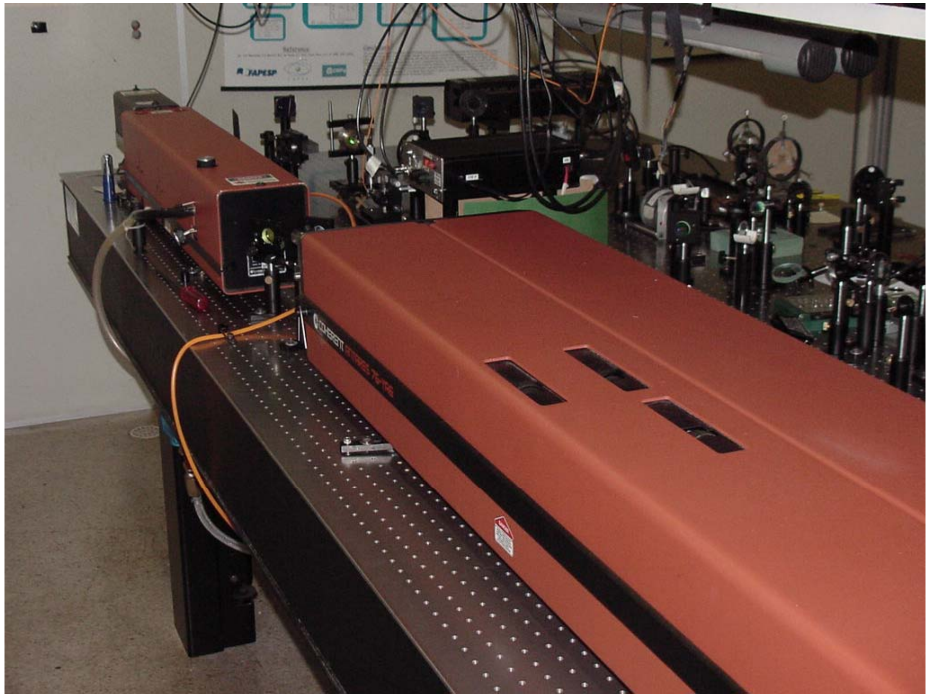
To get the spectral response of the nonlinearity

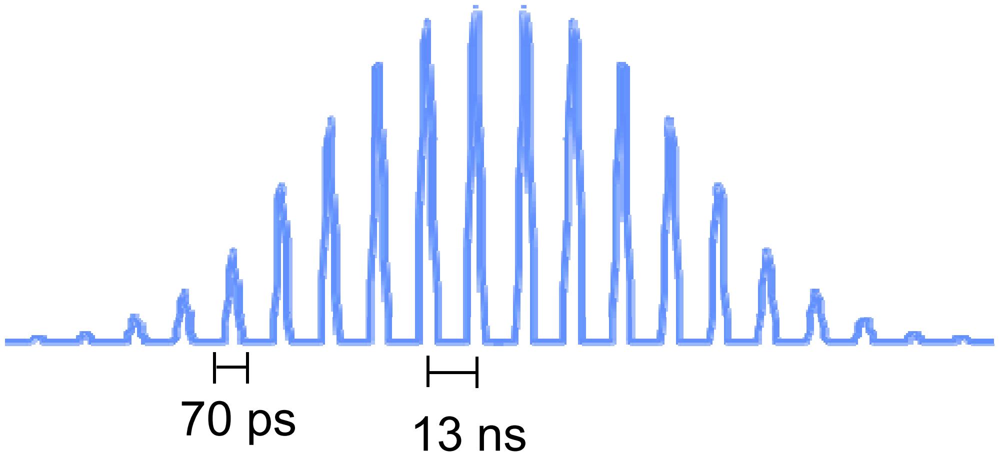




WLC chirp ~ 4 ps

Z-scan with pulse trains

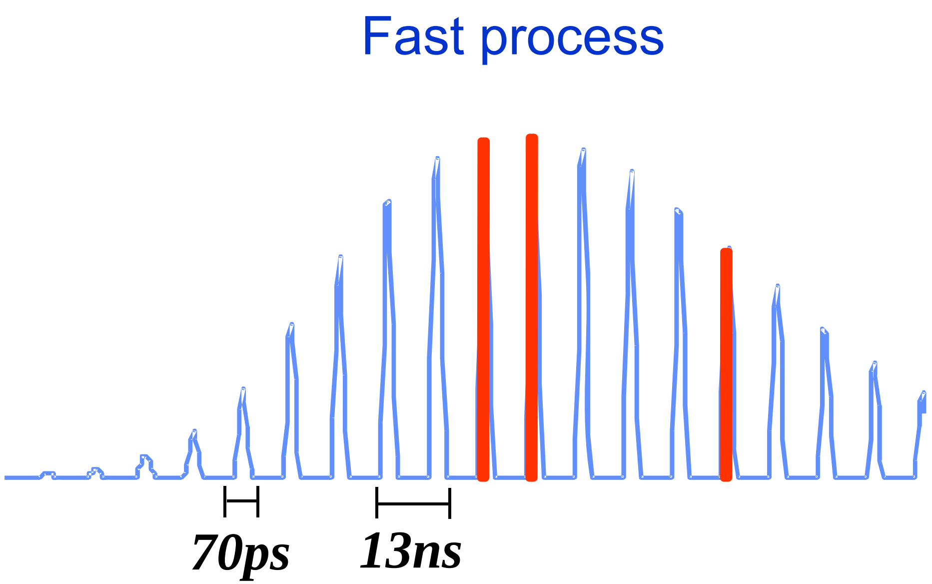


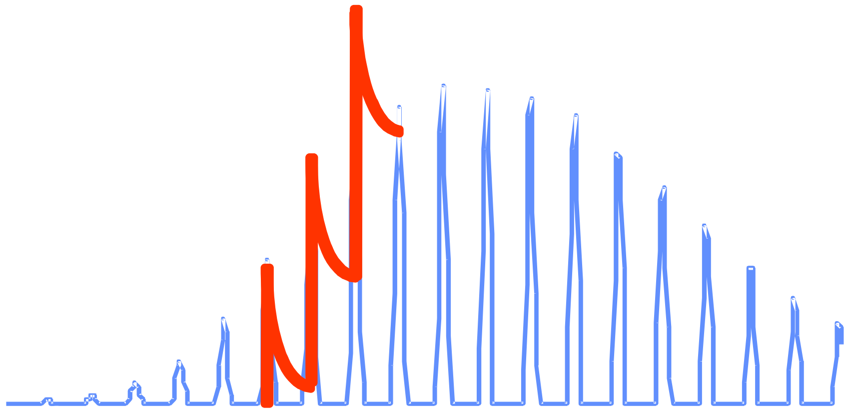


- Nd:YAG Q-switched/modelocked laser
  - 532 nm and 1064 nm
  - 70 ps

Pulse train Z-scan

Allows the discrimination between fast and accumulative contributions





Dynamic of the nonlinear response

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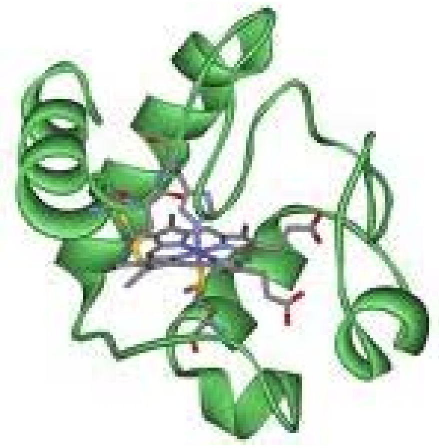
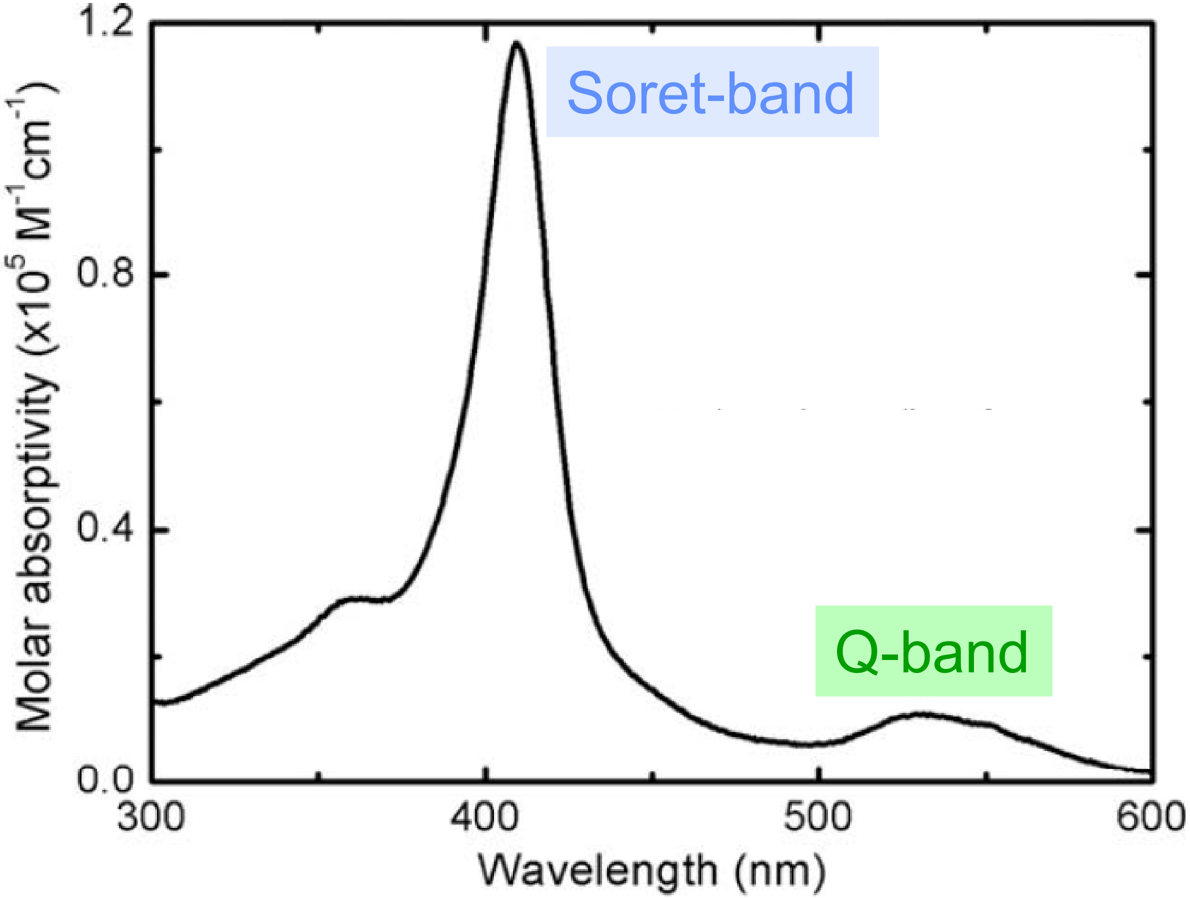
cytochrome c

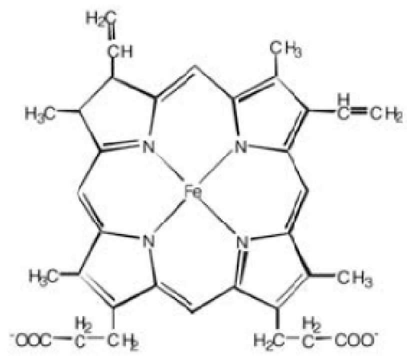


- Photoactive protein that mediates biological process
  - cell apoptosis
  - cellular regeneration upon laser therapy
  - electron transfer in cells mitochondria

Linear absorption

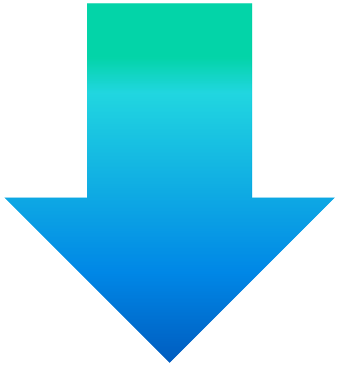


Absorption bands associated with the heme group

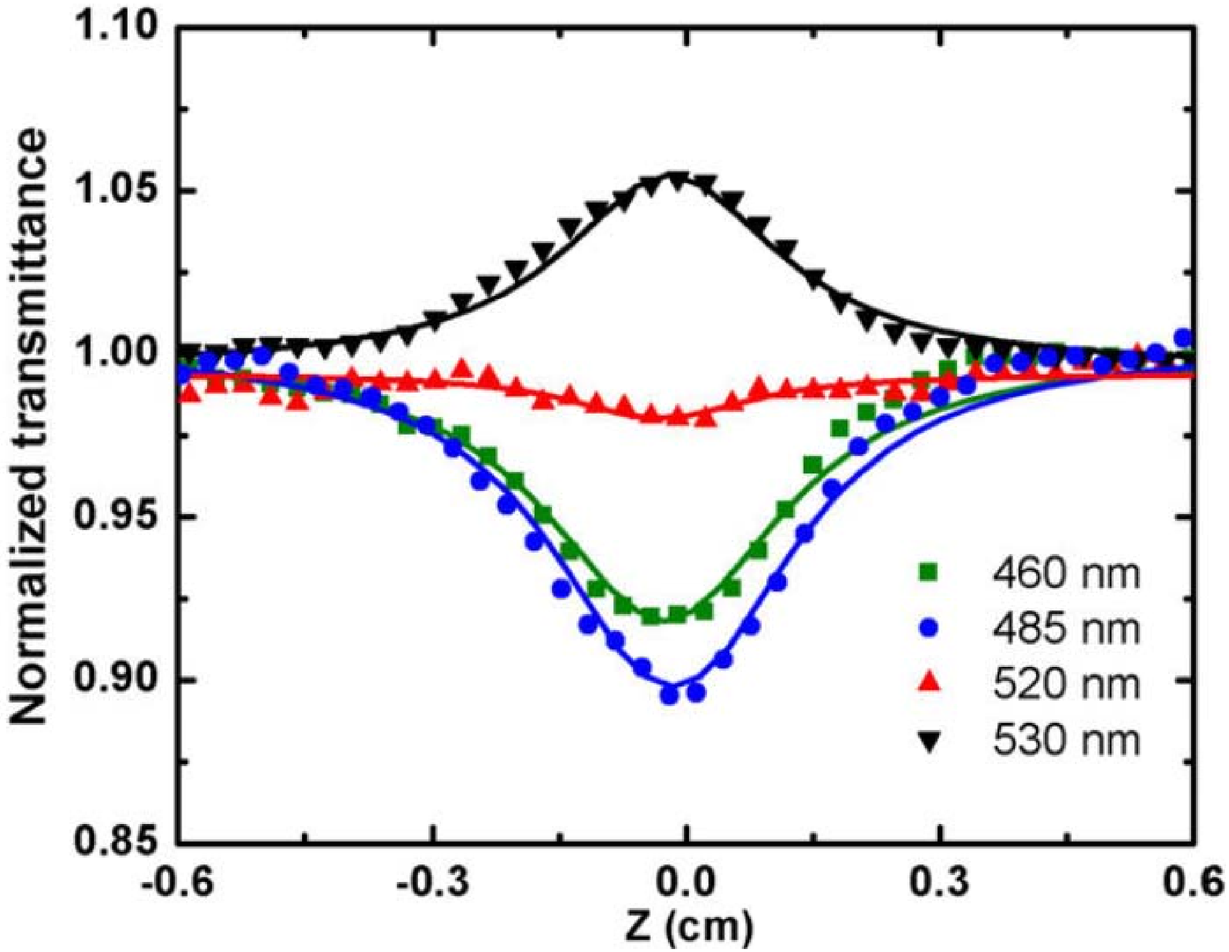


Z-scan measurements

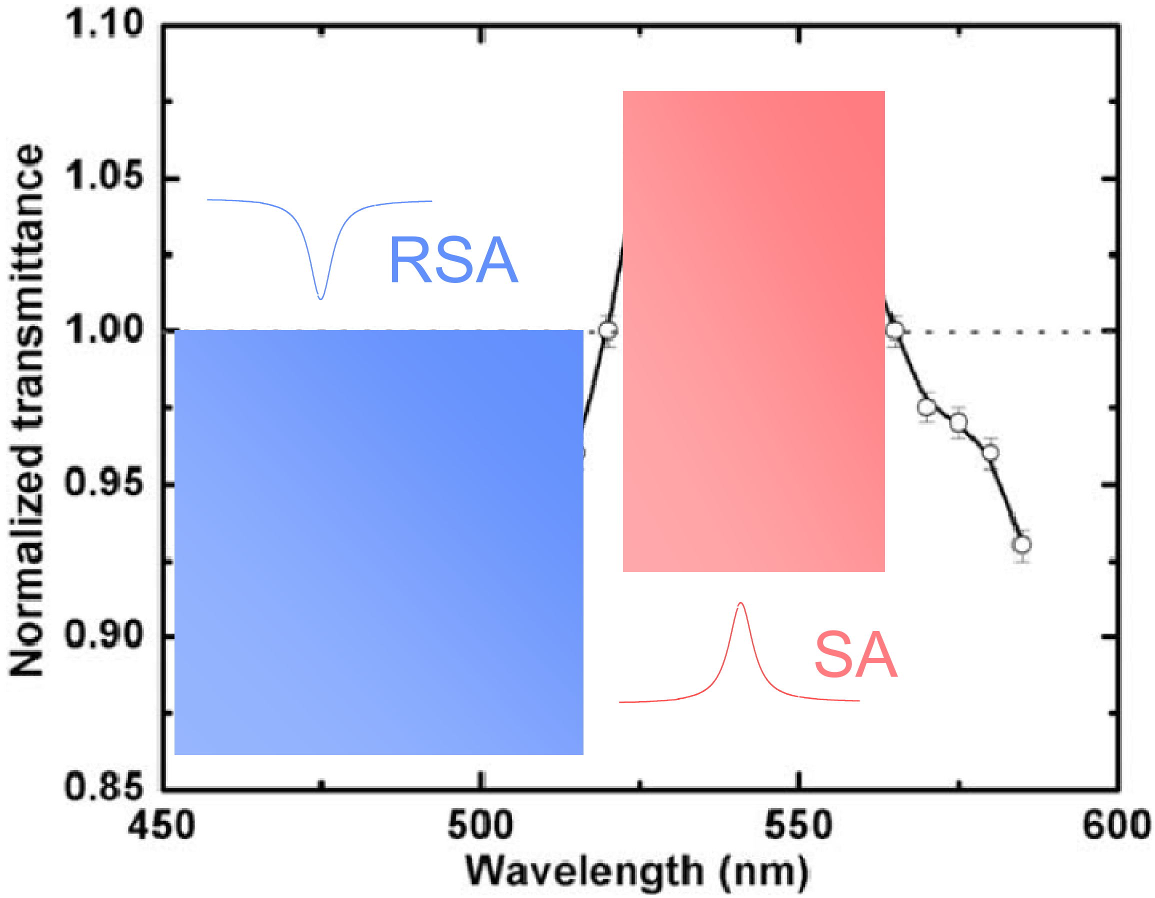
Saturable absorption



Reverse saturable absorption



Resonant nonlinear absorption spectrum

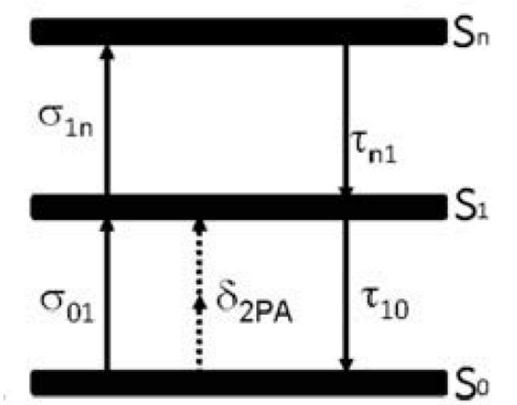


for λ> 570 nm

SA + 2PA

Nonlinear spectrum

three-level energy diagram



$$\frac{dn_{S_0}(t)}{dt} = -n_{S_0}(t)W_{01}(\lambda) + n_{S_1}(t)/\tau_{10} - n_{S_0}(t)W_{2PA}(\lambda) \quad (1)$$

$$\frac{dn_{S_1}(t)}{dt} = n_{S_0}(t)W_{01}(\lambda) + n_{S_0}(t)W_{2PA}(\lambda) - n_{S_1}(t)W_{1n}(\lambda) - n_{S_1}(t)/\tau_{10} + n_{S_n}(t)/\tau_{n1} \quad (2)$$

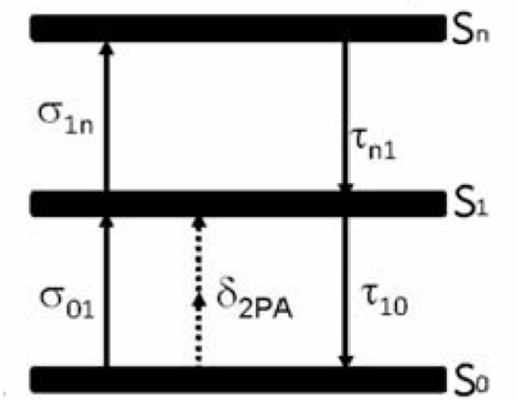
$$\frac{dn_{Sn}(t)}{dt} = n_{S_1}(t)W_{1n}(\lambda) - n_{S_n}(t)/\tau_{n1} \quad (3)$$

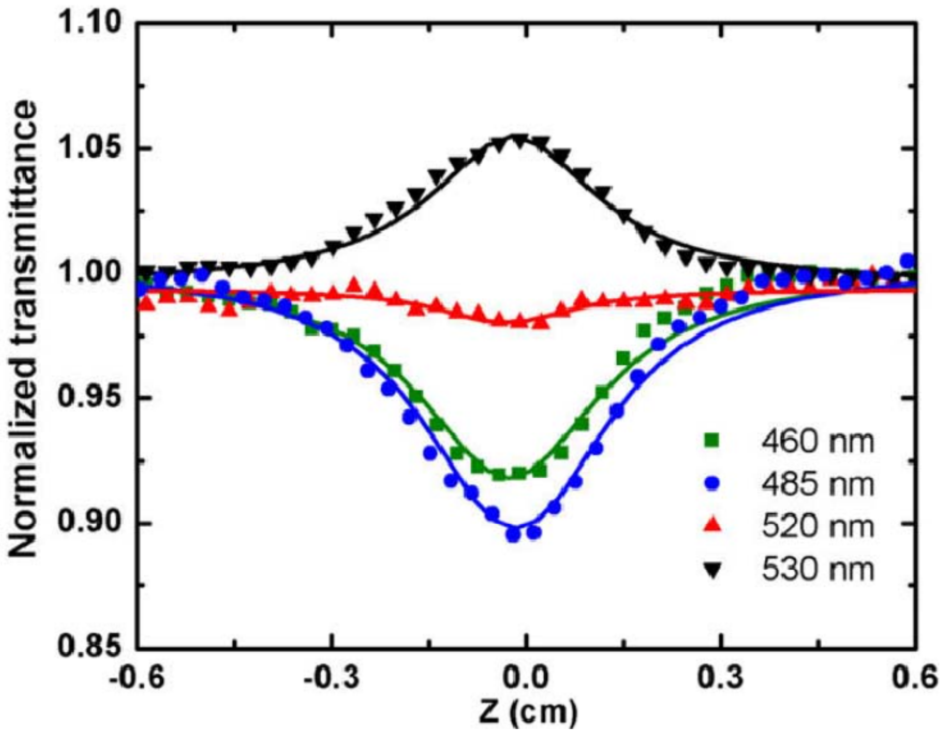
Transmitted intensity during the fs-pulse interaction

$$\frac{dI}{dz} = -\sigma_{01} I n_{S_0}(t) - \sigma_{1n} I n_{S_1}(t) - \beta\, I^2$$

Nonlinear spectrum

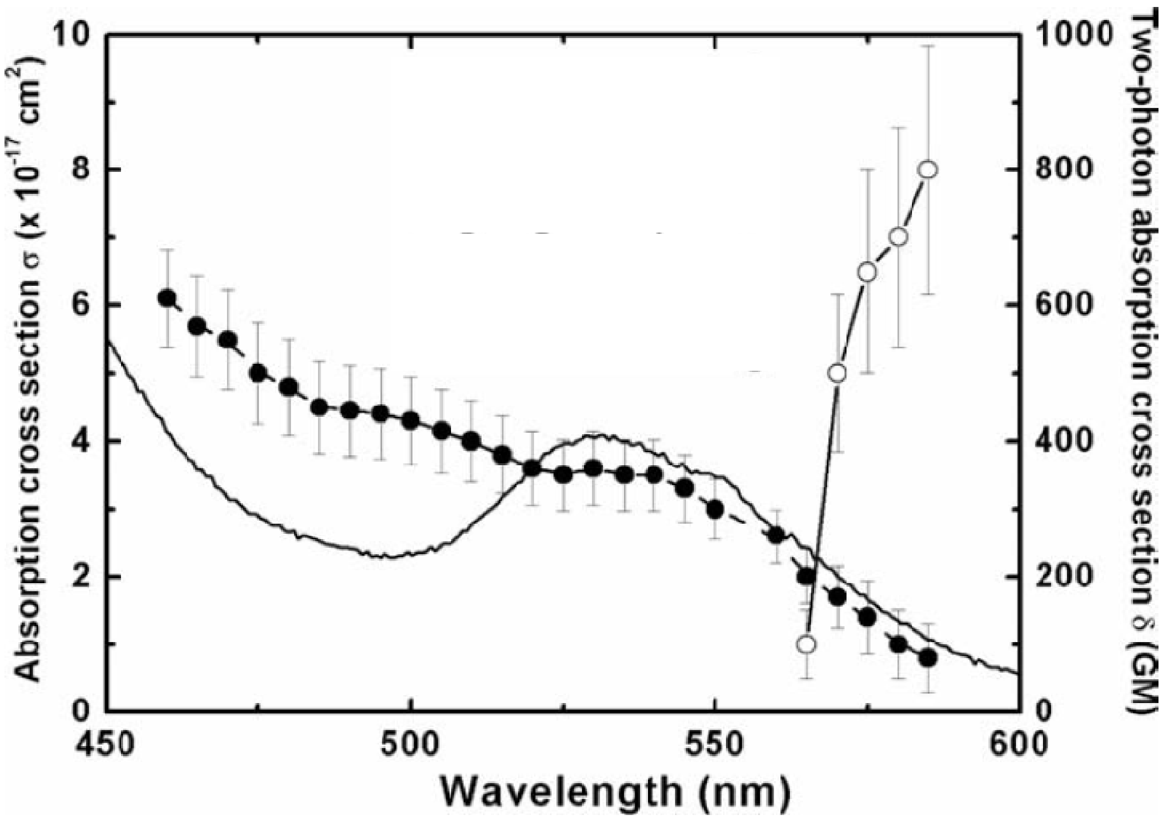
three-level energy diagram





the Z-scan curves can be fitted allowing the excited state cross-section determination

Nonlinear spectrum



Solid circles (●)
excited state abs. cross-section

Open circles (○)
2PA cross-section

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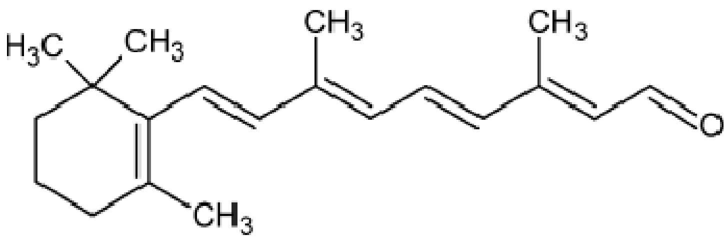
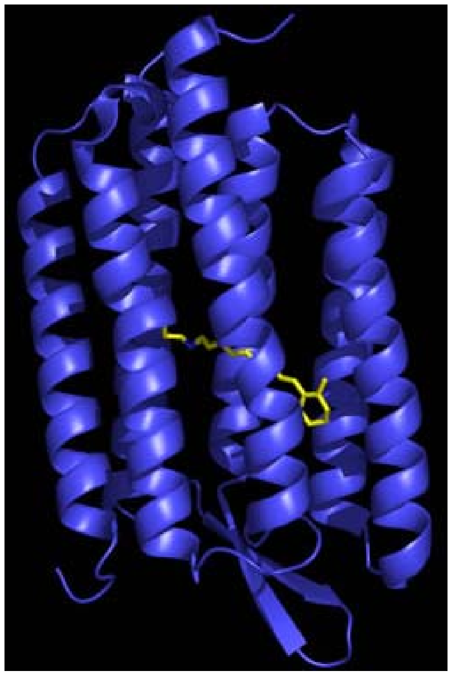
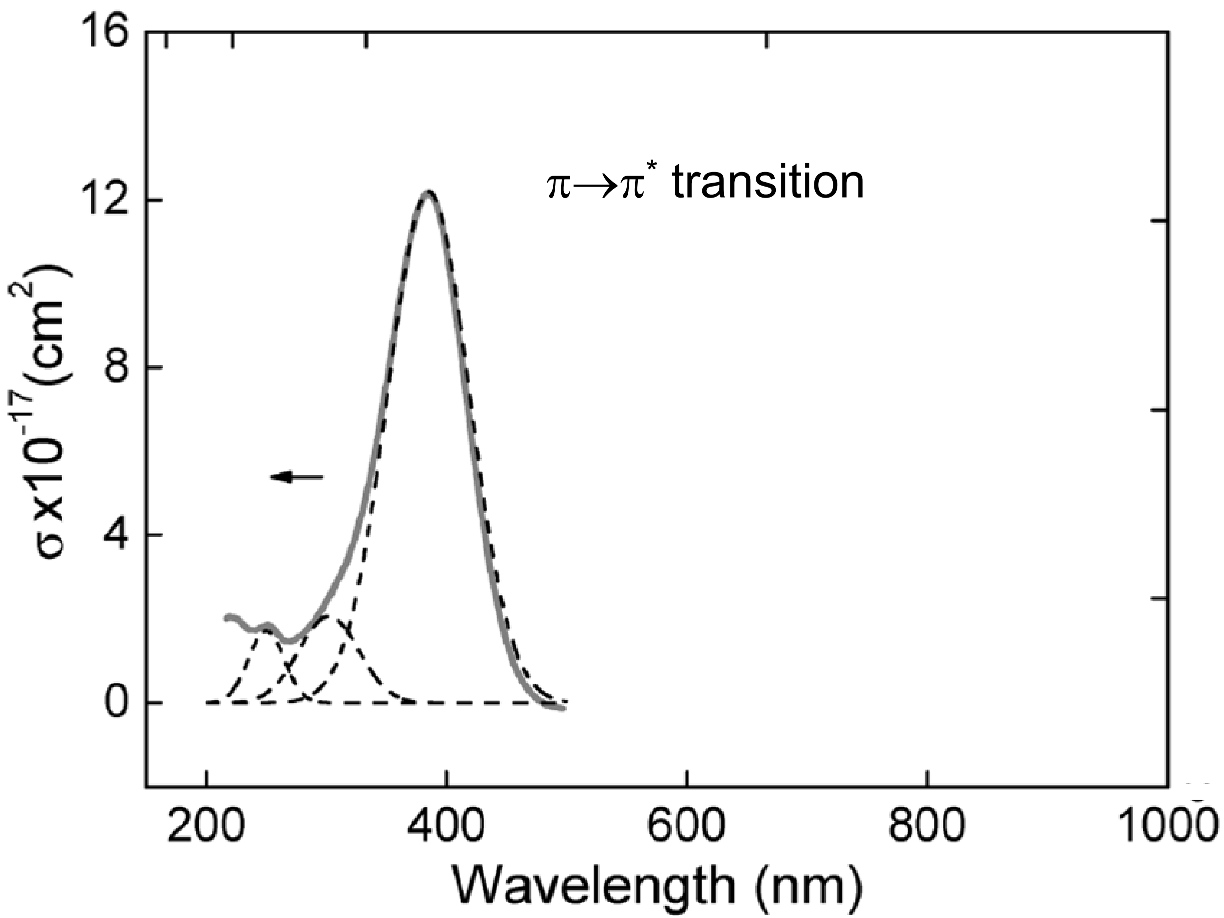
all-trans retinal

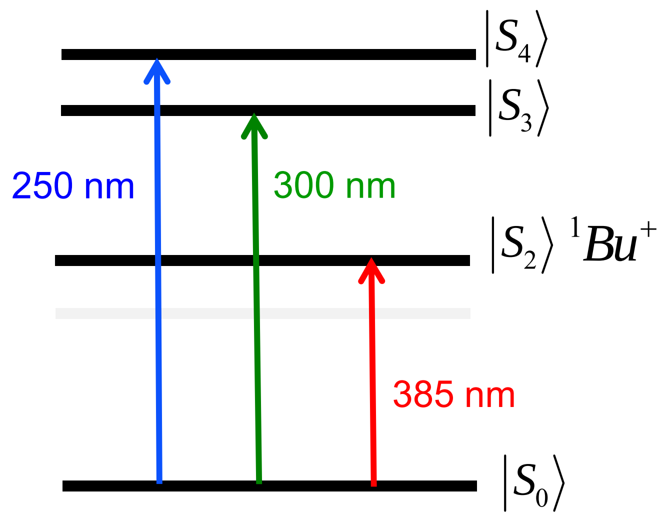


- light transduction in nervous impulse
- optoelectronics devices: ultrafast isomerization in bacteriorhodopsin

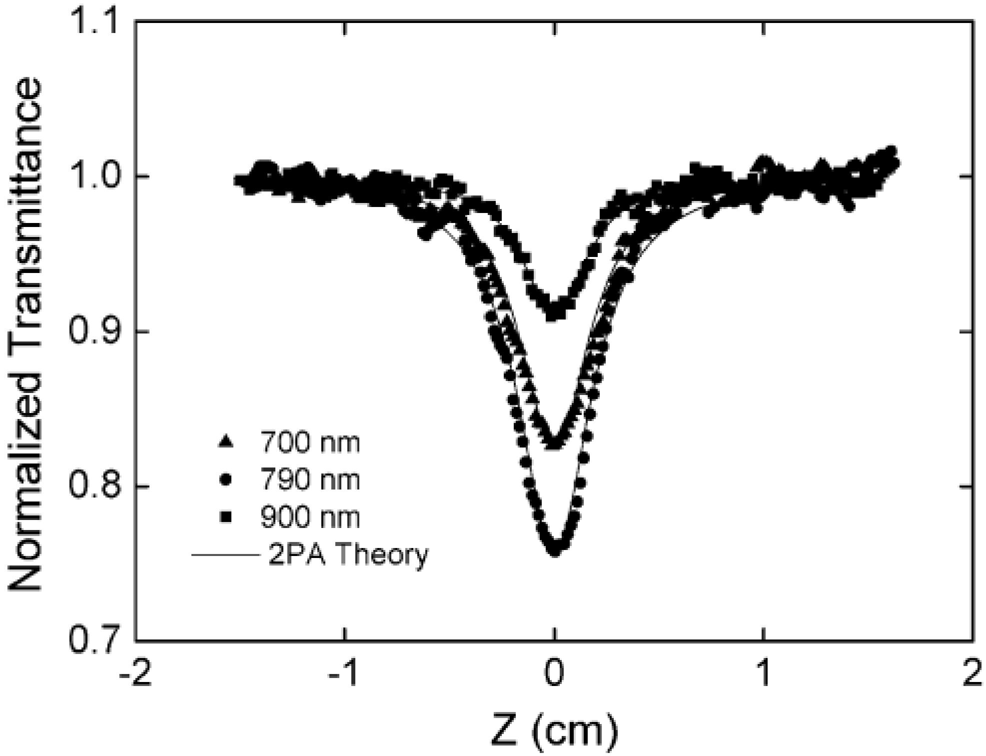


Linear absorption





Z-scan measurements



$$T(z) = \frac{1}{\sqrt{\pi}q_o(z,0)} \int_{-\infty}^{\infty} \ln[1 + q_o(z,0)e^{-\tau^2}]\, d\tau$$

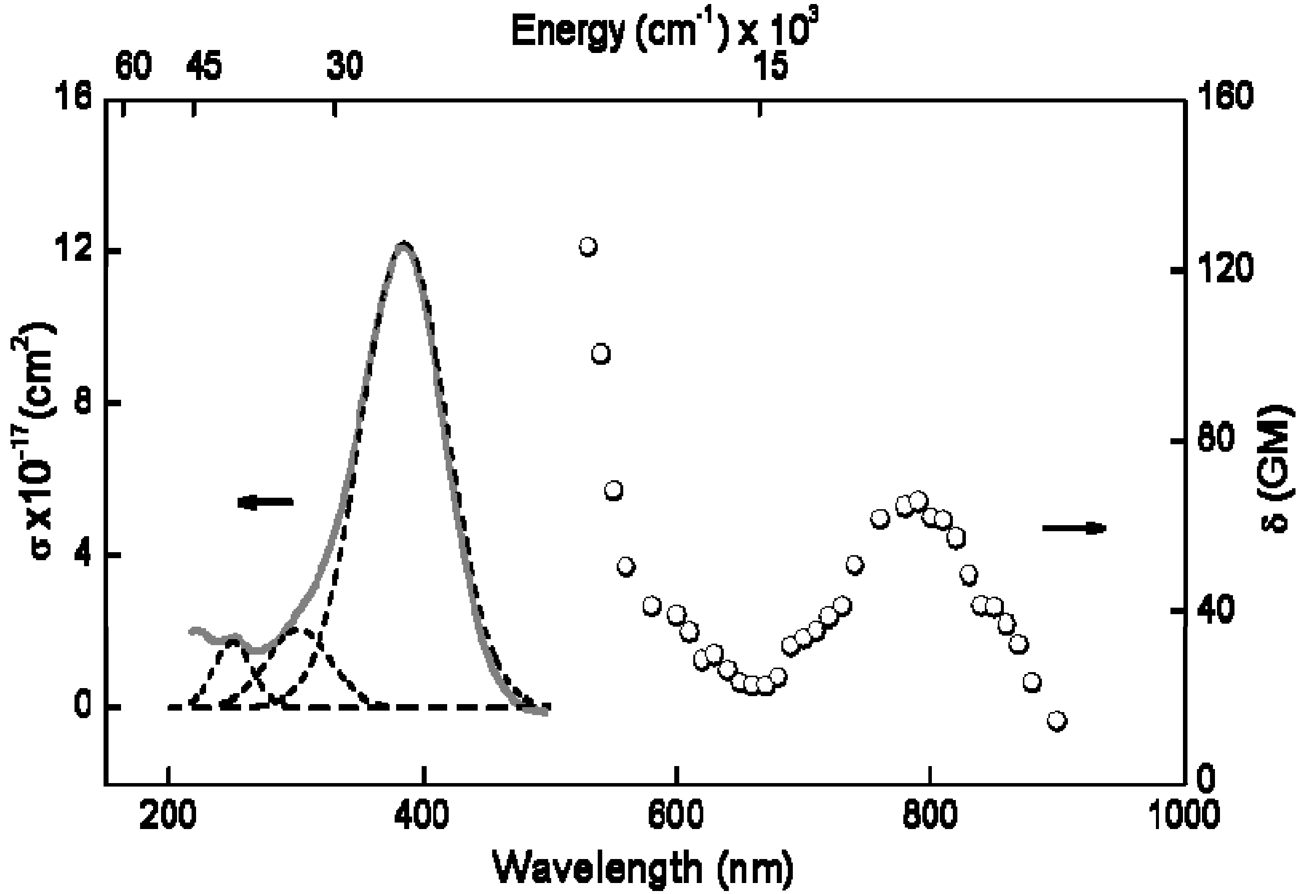
$$q_o = \beta I_o L(1 + (z^2/z_o^2))^{-1}$$

solid line: theoretical fitting

determine the 2PA cross-section

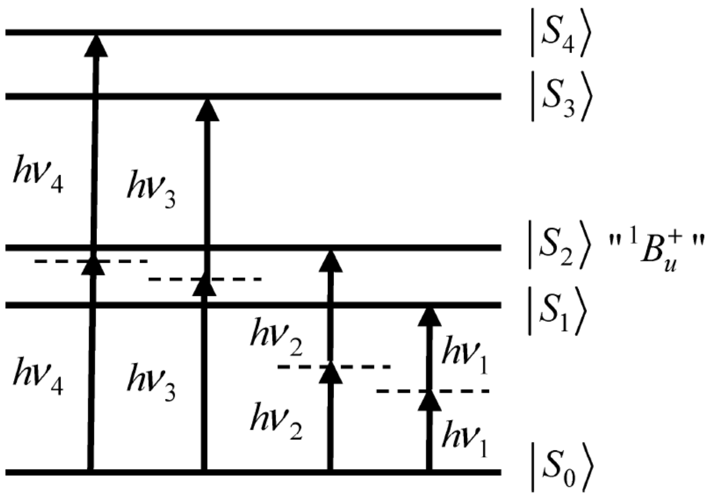
δ

Two-photon absorption spectrum



- peak at 790 nm
- resonant enhancement of NLO region

2PA: Sum-over-states model



for all-trans retinal there are several two-photon states (S_2 , S_3 and S_4)

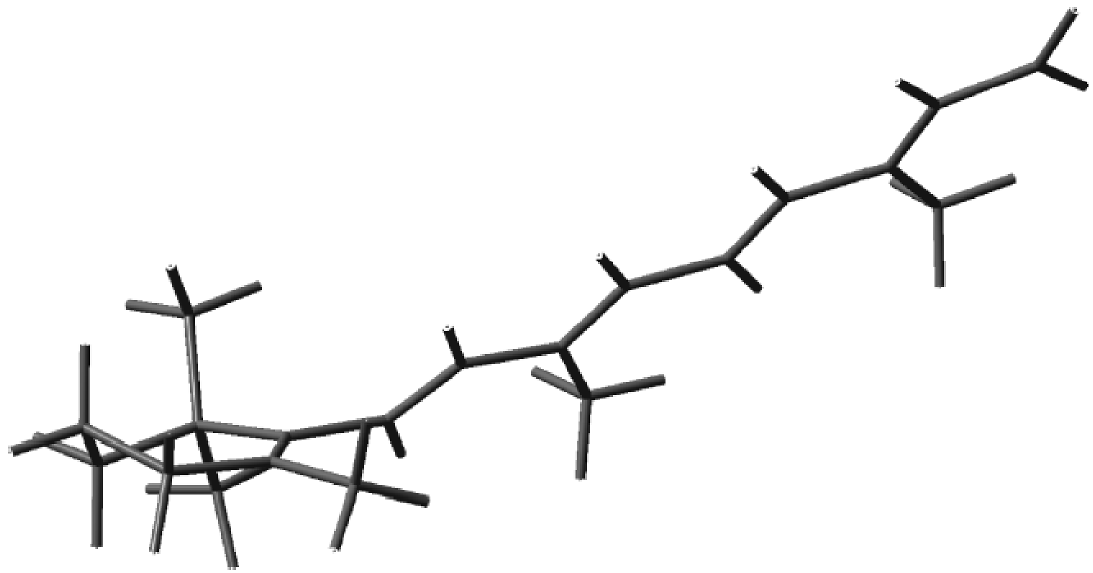
S_1 : state allowed only by 2PA

2PA cross-section at the laser frequency ν

$$\delta(\nu) = \frac{4}{5\pi}\frac{(2\pi)^4}{(hc)^2}\left\{\frac{|\mu_{01}|^2\Delta\mu_{01}{}^2\Gamma_{01}}{(\nu_{01}-2\nu)^2+\Gamma_{01}{}^2} + \frac{|\mu_{02}|^2\Delta\mu_{02}{}^2\Gamma_{02}}{(\nu_{02}-2\nu)^2+\Gamma_{02}{}^2} + \left[\frac{\nu^2}{(\nu_{02}-\nu)^2+\Gamma_{02}{}^2}\times\left(\frac{|\mu_{02}|^2|\mu_{23}|^2\Gamma_{03}}{(\nu_{03}-2\nu)^2+\Gamma_{03}{}^2} + \frac{|\mu_{02}|^2|\mu_{24}|^2\Gamma_{04}}{(\nu_{04}-2\nu)^2+\Gamma_{04}{}^2}\right)\right]\right\}$$

Quantum-chemical calculations

equilibrium geometry of all trans retinal



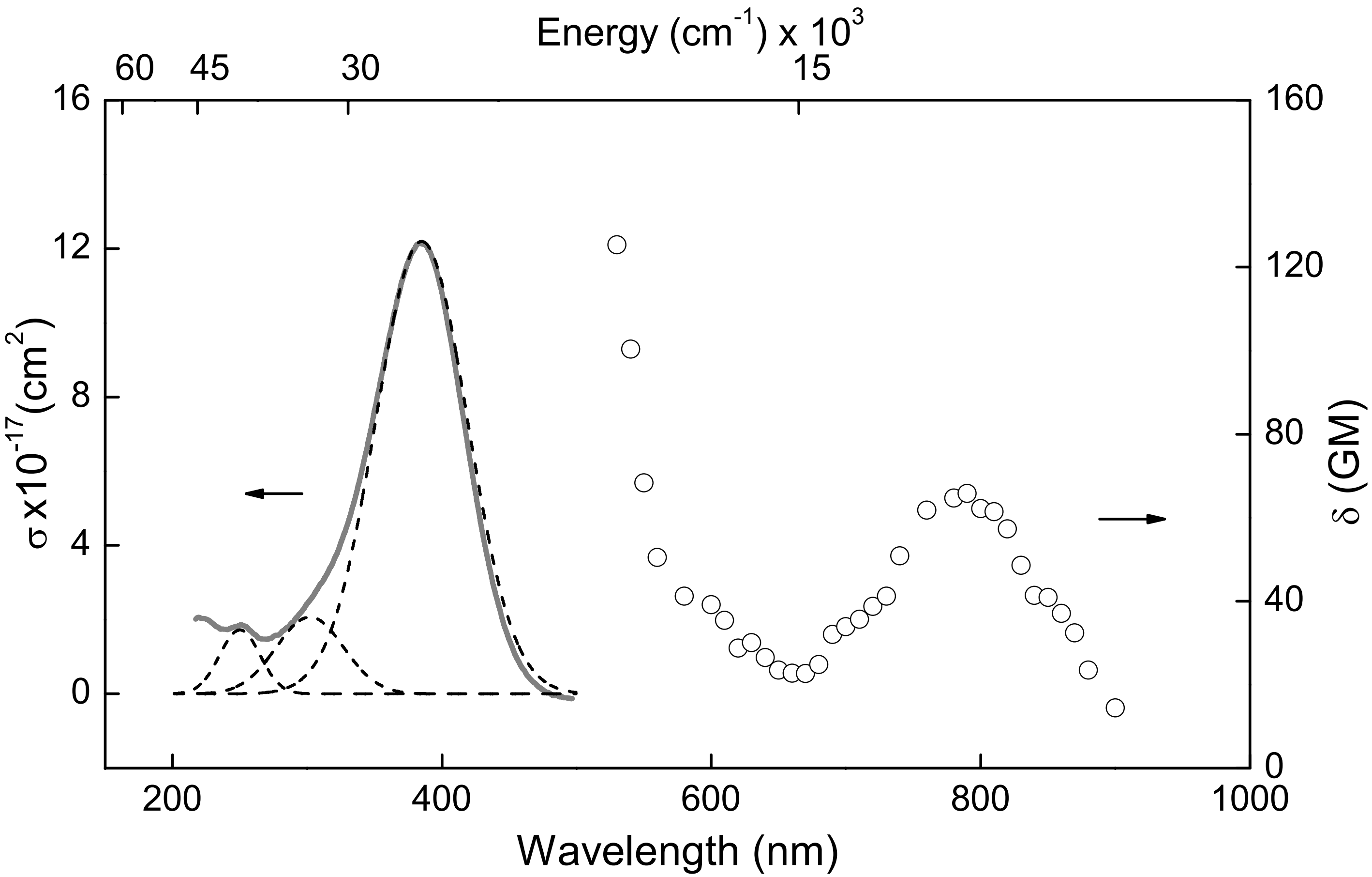
Quantum-chemical calculations

1PA and 2PA states of all trans retinal

DFT – response function formalism

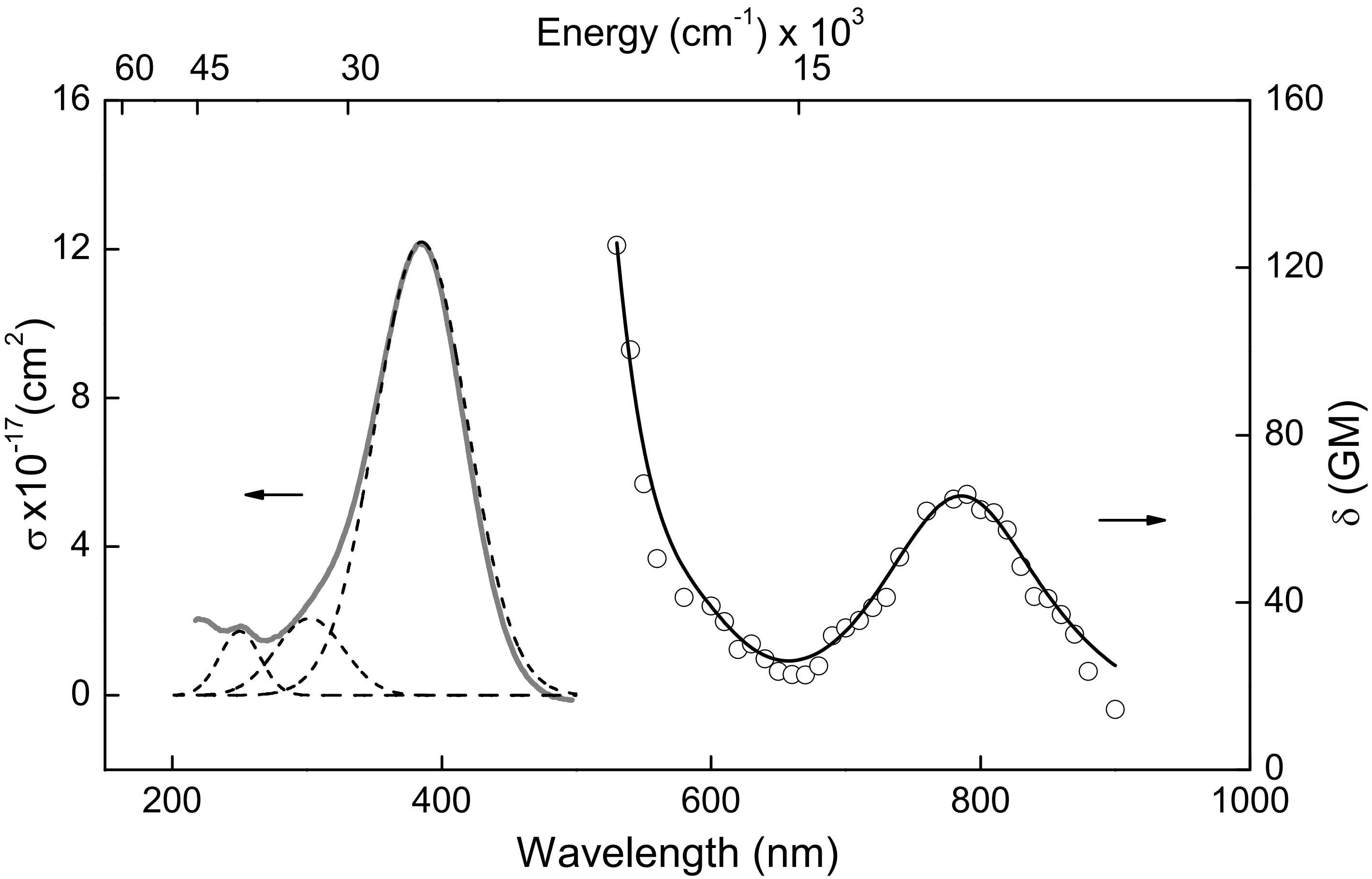
	1PA		2PA		
state	energy (eV)	oscillator strength	energy (eV)	transition probability (au)	2PA cross-section (GM)
S_2 ($\pi\pi^*$)	3.37	1.2244	3.37 (368 nm)	20000	22
S_3 ($\pi\pi^*$)	4.59	0.2033	4.59 (270 nm)	32800	51
S_4 ($\pi\pi^*$)	4.97	0.0855	4.97 (250 nm)	155000	391
S ($n\pi^*$)	3.54	0.0001	3.54 (350 nm)	0.475	

Two-photon absorption spectrum



$$\delta(\nu) = \frac{4}{5\pi}\frac{(2\pi)^4}{(hc)^2}\left\{\frac{|\mu_{01}|^2\Delta\mu_{01}{}^2\Gamma_{01}}{(\nu_{01}-2\nu)^2+\Gamma_{01}{}^2} + \frac{|\mu_{02}|^2\Delta\mu_{02}{}^2\Gamma_{02}}{(\nu_{02}-2\nu)^2+\Gamma_{02}{}^2} + \left[\frac{\nu^2}{(\nu_{02}-\nu)^2+\Gamma_{02}{}^2}\times\left(\frac{|\mu_{02}|^2|\mu_{23}|^2\Gamma_{03}}{(\nu_{03}-2\nu)^2+\Gamma_{03}{}^2} + \frac{|\mu_{02}|^2|\mu_{24}|^2\Gamma_{04}}{(\nu_{04}-2\nu)^2+\Gamma_{04}{}^2}\right)\right]\right\}$$

Two-photon absorption spectrum



$$\delta(\nu) = \frac{4}{5\pi}\frac{(2\pi)^4}{(hc)^2}\left\{\frac{|\mu_{01}|^2\Delta\mu_{01}{}^2\Gamma_{01}}{(\nu_{01}-2\nu)^2+\Gamma_{01}{}^2} + \frac{|\mu_{02}|^2\Delta\mu_{02}{}^2\Gamma_{02}}{(\nu_{02}-2\nu)^2+\Gamma_{02}{}^2} + \left[\frac{\nu^2}{(\nu_{02}-\nu)^2+\Gamma_{02}{}^2}\times\left(\frac{|\mu_{02}|^2|\mu_{23}|^2\Gamma_{03}}{(\nu_{03}-2\nu)^2+\Gamma_{03}{}^2} + \frac{|\mu_{02}|^2|\mu_{24}|^2\Gamma_{04}}{(\nu_{04}-2\nu)^2+\Gamma_{04}{}^2}\right)\right]\right\}$$

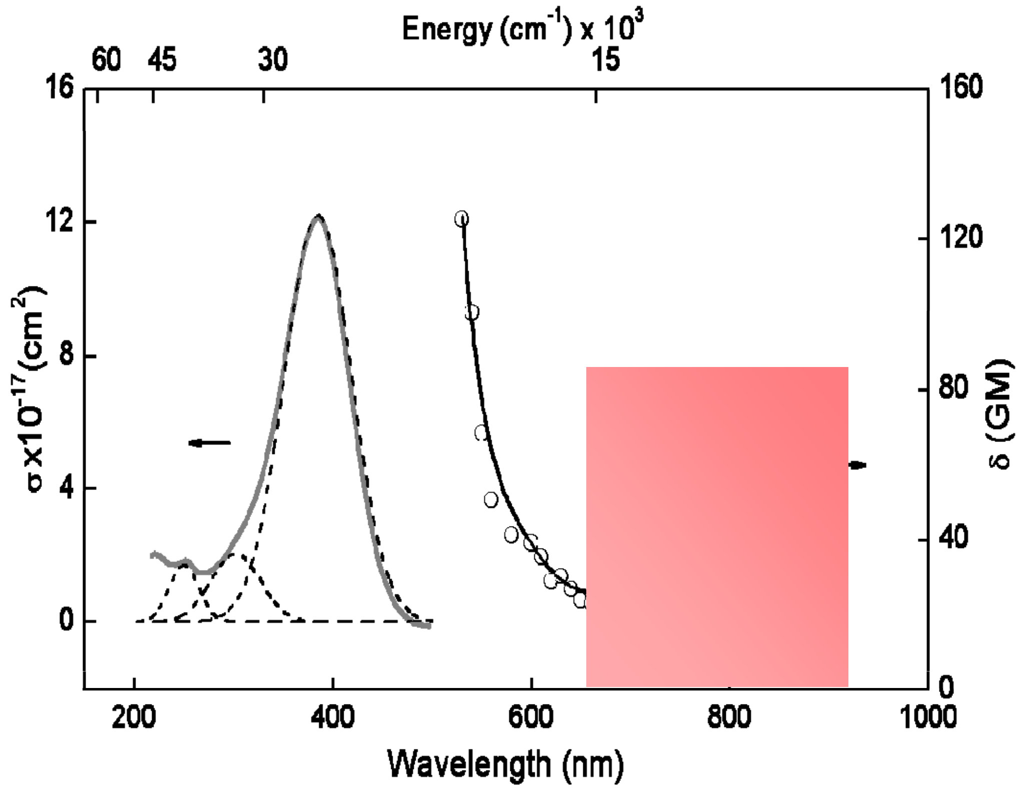
Two-photon absorption spectrum

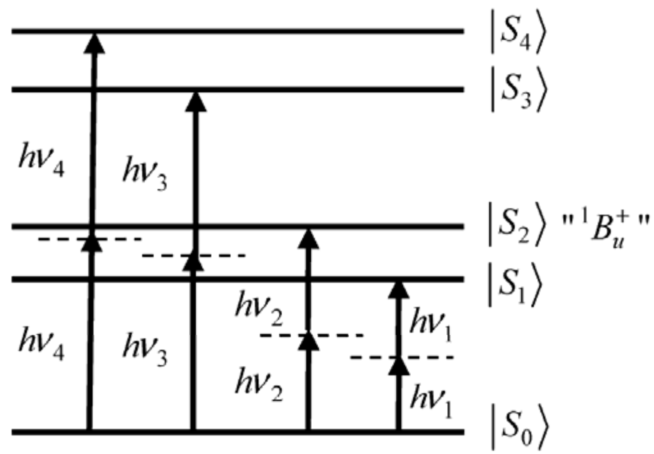
Spectroscopic parameters used/determined in the SOS

spectroscopic parameters	SOS model
ν_{01} (cm^{-1})	25290 (395 ± 5 nm)
ν_{02} (cm^{-1})	25940 (385 ± 2 nm)
ν_{03} (cm^{-1})	33350 (300 ± 2 nm)
ν_{04} (cm^{-1})	39960 (250 ± 2 nm)
Γ_{01} (cm^{-1})	4485 (70 ± 5 nm)
Γ_{02} (cm^{-1})	5530 (82 ± 2 nm)
Γ_{03} (cm^{-1})	6440 (58 ± 2 nm)
Γ_{04} (cm^{-1})	5760 (36 ± 2 nm)
μ_{01} (Debye)	3.5 ± 1 (f_{01} = 0.15 ± 0.08)
μ_{02} (Debye)	9.0 ± 0.5 (f_{02} = 1.0 ± 0.1)
μ_{23} (Debye)	2.6 ± 0.5
μ_{24} (Debye)	6.5 ± 0.5
$\Delta\mu_{01}$ (Debye)	12 ± 2
$\Delta\mu_{02}$ (Debye)	4 ± 1

parameters obtained from the linear absorption

Two-photon absorption spectrum





The 2PA band is described by the S_1 (70 %) and S_2 (30 %) states

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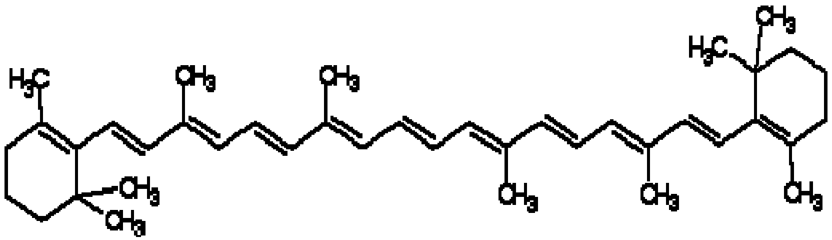
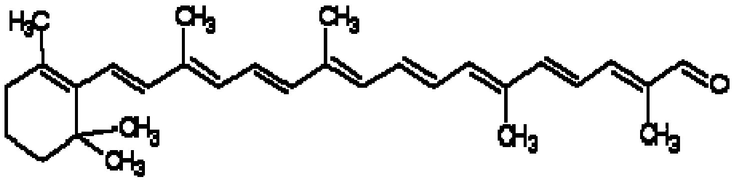
carotenoids derivatives



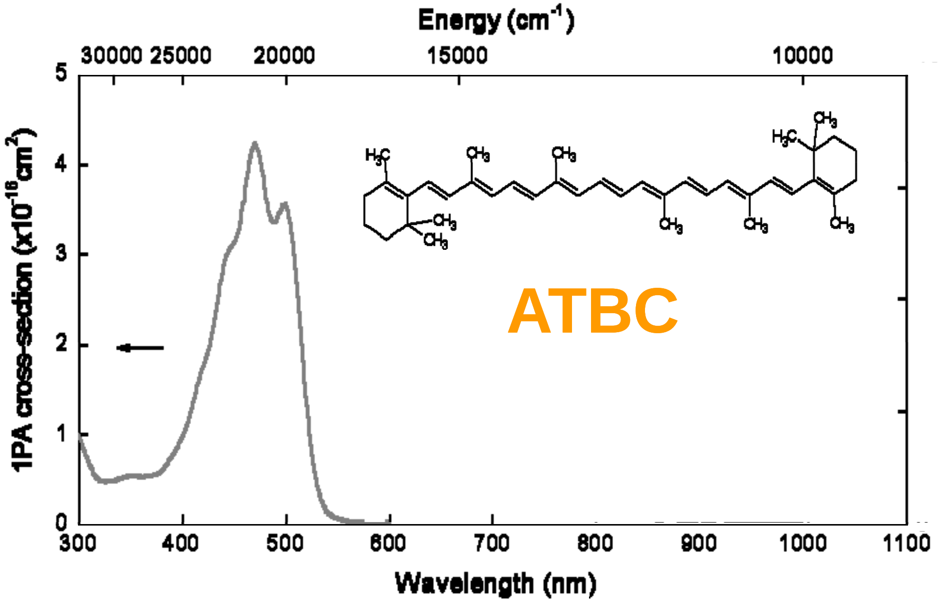
all-trans β-carotene



trans β-apo-8´carotenal

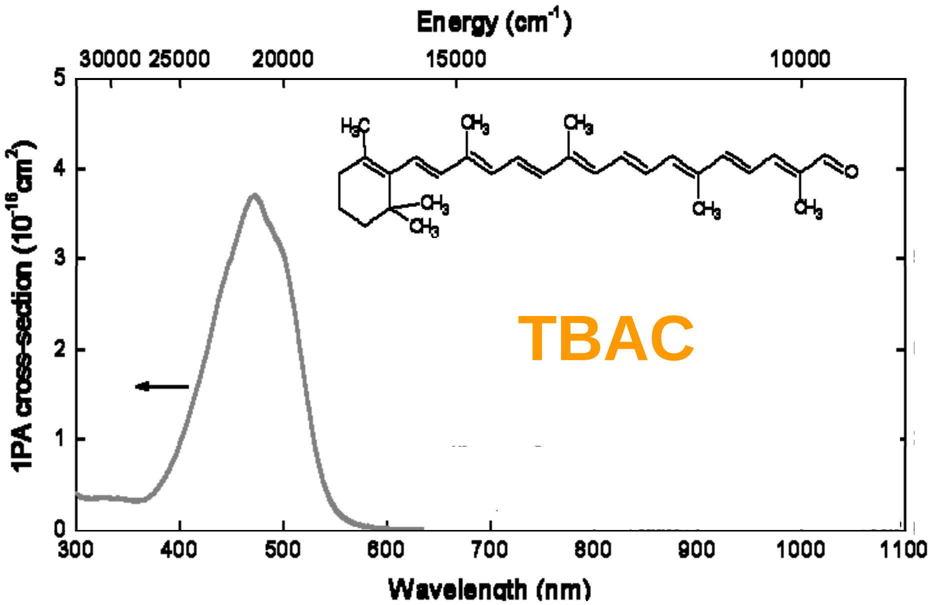
- π-conjugated molecule with high electronic delocalization
- ultrafast dynamics
- similar to all-trans retinal

Linear absorption

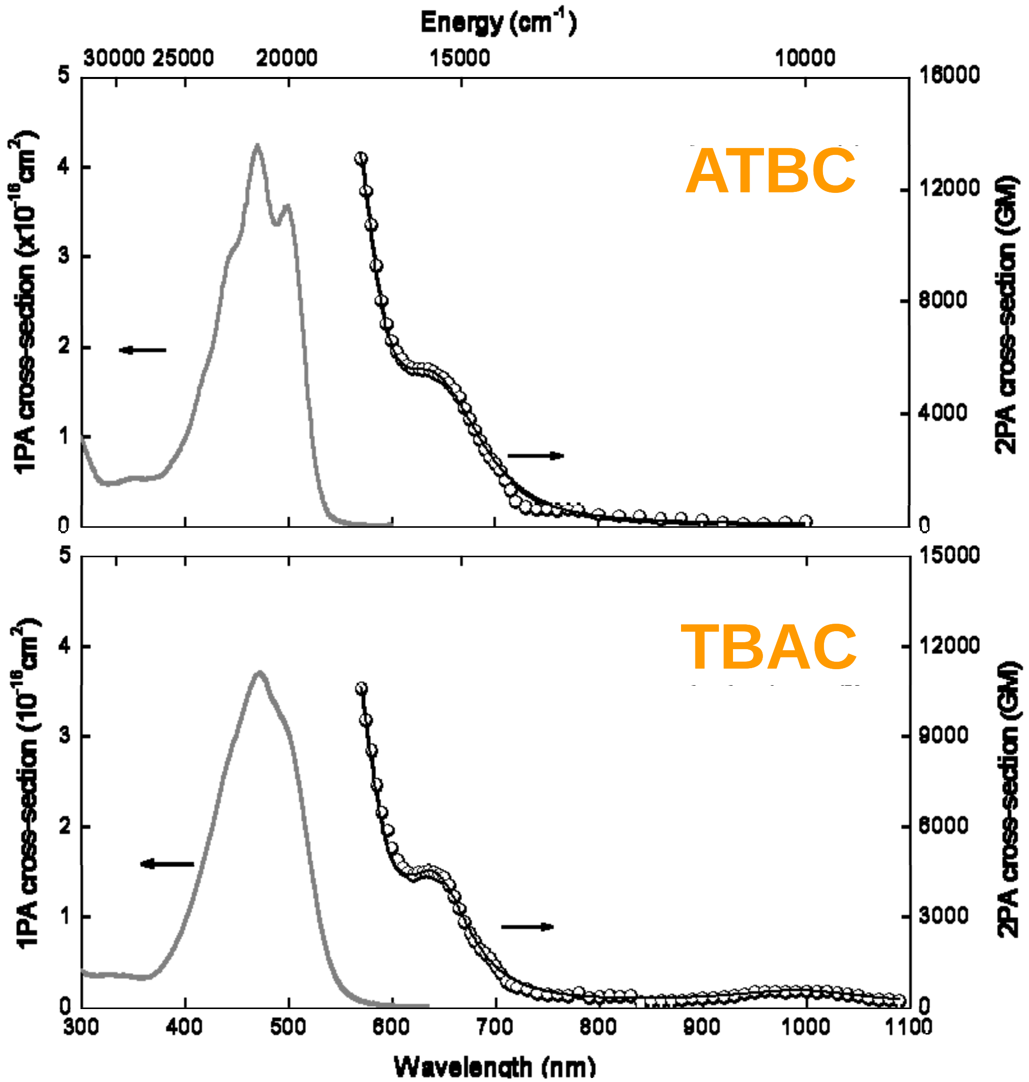


vibrational progression

155 meV



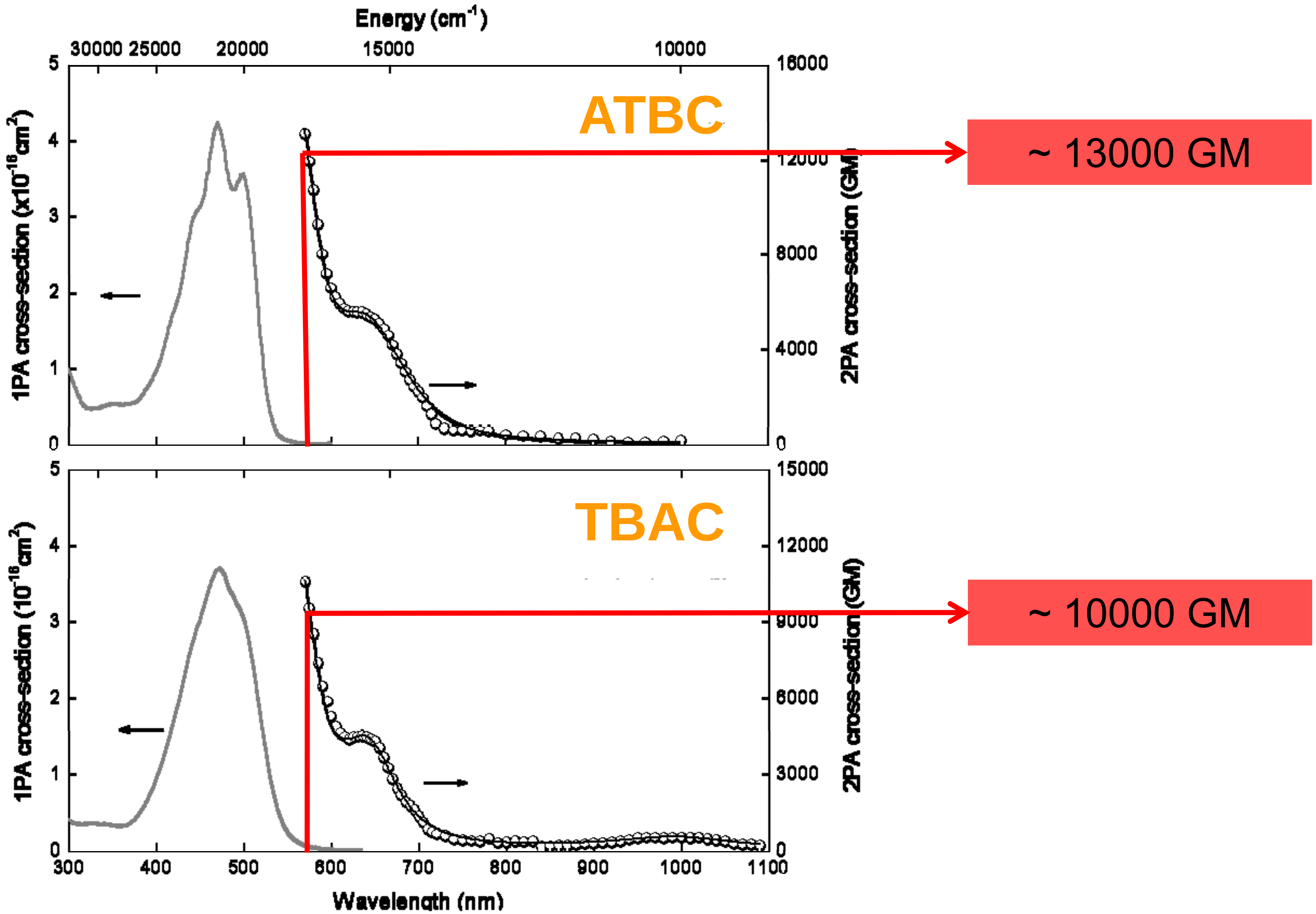
Two-photon absorption spectrum



- peak at 635 nm

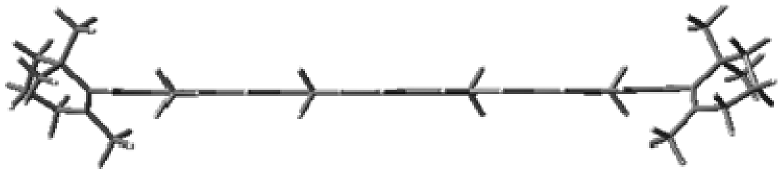
- peaks at 635 nm and 1000 nm

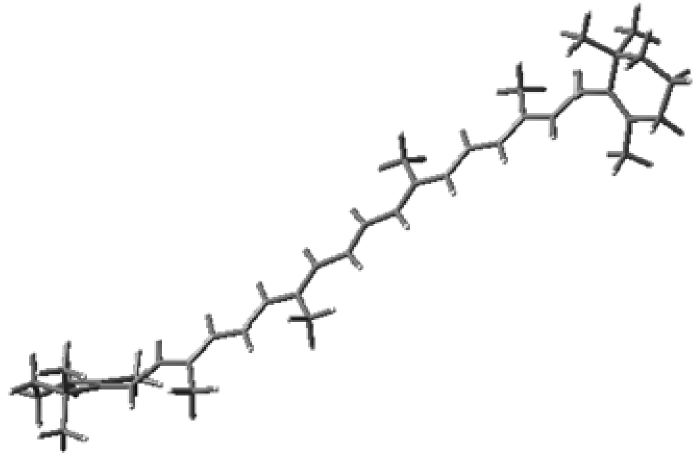
Two-photon absorption spectrum



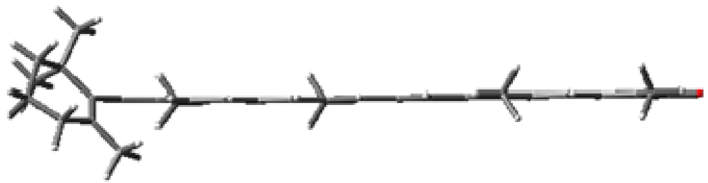
Equilibrium molecular geometry

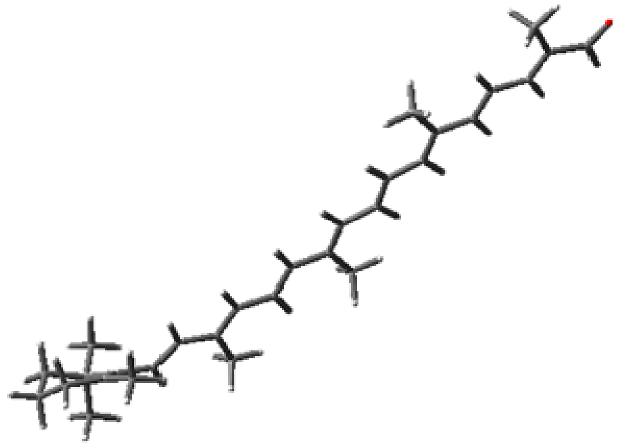
ATBC





TBAC





High 2PA cross-section related to the planar configuration of both molecules

Quantum-chemical calculations

all-trans-β-carotene

States	Transition Nature	1PA Energy (cm^{-1})	1PA Oscillator Strength	2PA Energy (cm^{-1})	2PA Transition probability (A.U.)	2PA cross-section (GM)
$S_1(\pi\pi^*)$	(HOMO -1 → LUMO +1) 3% (HOMO → LUMO) 47%	20919 (478 nm)	4.126	20970 (477nm)	79	0.3
$S_2(\pi\pi^*)$	(HOMO -2 → LUMO +1) 3% (HOMO -1 → LUMO) 45%	29239 (342 nm)	0.000	29278 (341nm)	1.58E6	1465
$S_3(\pi\pi^*)$	(HOMO -1 → LUMO +2) 3% (HOMO → LUMO +1) 44%	31381 (319 nm)	0.000	31456 (318nm)	2.93E6	3403
$S_4(\pi\pi^*)$	(HOMO -3 → LUMO) 2% (HOMO → LUMO+4) 1% (HOMO → LUMO +6) 11% (HOMO → LUMO +7) 25% (HOMO → LUMO +14) 3%	38758 (258 nm)	0.000	38876 (257nm)	3.22E6	6599

2PA at 635 nm

Three two-photon states that are forbidden by one-photon

centrosymmetric molecules

Quantum-chemical calculations

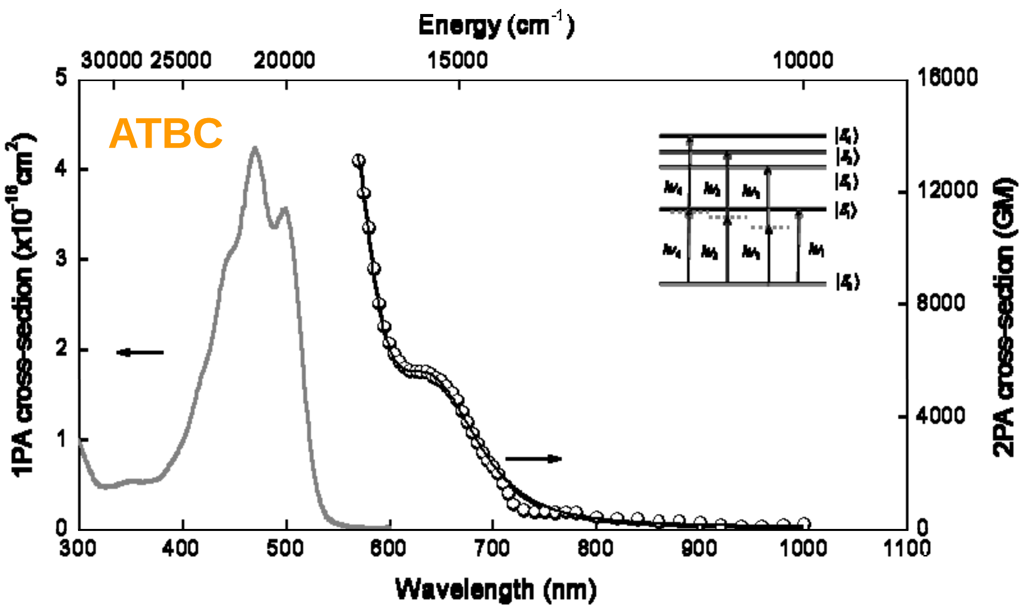
trans-β-apo-8’-carotenal

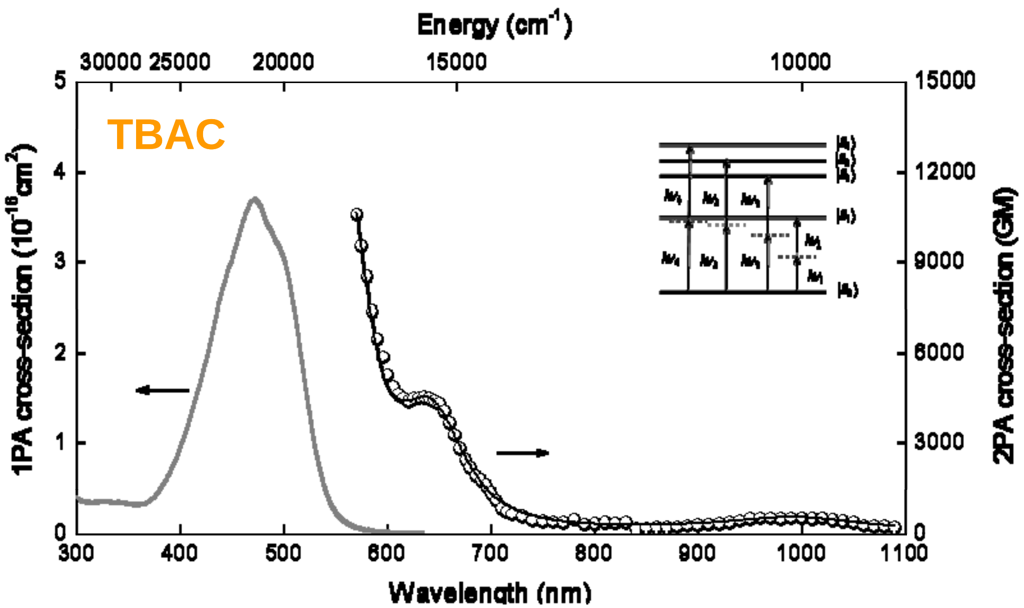
States	Transition Nature	1PA Energy (cm^{-1})	1PA Oscillator Strength	2PA Energy (cm^{-1})	2PA Transition probability (A.U.)	2PA cross-section (GM)
$S_1(\pi\pi^*)$	(HOMO -1→ LUMO +1) 2% (HOMO → LUMO) 46%	21212 (472 nm)	3.560	21293 (470 nm)	9.74E4	56
$S_2(\pi\pi^*)$	(HOMO -2 → LUMO) 1% (HOMO -2 → LUMO +1) 1% (HOMO -1 → LUMO) 44% (HOMO -4 → LUMO) 22% (HOMO -4 → LUMO+1) 15% (HOMO -4 → LUMO+2) 7%	30407 (329 nm)	0.081	30408 (329 nm)	9.21E5	945
$S_3(\pi\pi^*)$	(HOMO -1 → LUMO +2) 2% (HOMO → LUMO +1) 44%	31553 (317 nm)	0.091	31617 (316 nm)	1.68E6	2066
$S_4(\pi\pi^*)$	(HOMO -3 → LUMO) 3% (HOMO -3 → LUMO +1) 1% (HOMO -2 → LUMO) 36% (HOMO -2 → LUMO +1) 1% (HOMO -1 → LUMO +1) 4%	36620 (273 nm)	0.070	36620 (273 nm)	4.04E5	721

2PA at 635 nm

Four two-photon states allowed by one-photon too

Two-photon absorption spectrum





Sum-over-states calculation using the energy diagram based on the experimental results and theoretical calculations

solid line: fitting with the SOS model

$$\delta(\nu) = \frac{4}{5\pi}\frac{(2\pi)^4}{(hc)^2}\left\{\frac{|\mu_{01}|^2\Delta\mu_{01}^2\Gamma_{01}}{(\nu_{01}-2\nu)^2+\Gamma_{01}^2} + \left[\frac{\nu^2}{(\nu_{01}-\nu)^2+\Gamma_{01}^2} \text{ x } \left(\frac{|\mu_{01}|^2|\mu_{12}|^2\Gamma_{02}}{(\nu_{02}-2\nu)^2+\Gamma_{02}^2}+\frac{|\mu_{01}|^2|\mu_{13}|^2\Gamma_{03}}{(\nu_{03}-2\nu)^2+\Gamma_{03}^2}+\frac{|\mu_{01}|^2|\mu_{14}|^2\Gamma_{04}}{(\nu_{04}-2\nu)^2+\Gamma_{04}^2}\right)\right]\right\}$$

Two-photon absorption spectrum

Spectroscopic Parameters	All-trans β-carotene	trans-β-apo-8’-carotenal
ν_{01} (cm^{-1})	21280 (470 ± 2 nm)	20000 (500 ± 2 nm)
ν_{02} (cm^{-1})	29687 (337 ± 2 nm)	30020 (333 ± 2 nm)
ν_{03} (cm^{-1})	31020 (322 ± 2 nm)	31020 (322 ± 2 nm)
ν_{04} (cm^{-1})	35714 (280 ± 2 nm)	35700 (280 ± 2 nm)
Γ_{01} (cm^{-1})	4000 (88 ± 3 nm)	3335 (83 ± 3 nm)
Γ_{02} (cm^{-1})	4200 (48 ± 5 nm)	4000 (45 ± 5 nm)
Γ_{03} (cm^{-1})	3870 (40 ± 5 nm)	3670 (38 ± 5 nm)
Γ_{04} (cm^{-1})	3335 (26 ± 1 nm)	3335 (26 ± 1 nm)
μ_{01} (Debye)	14.8 ± 1	14.0 ± 1
μ_{12} (Debye)	12.5 ± 1	9.0 ± 1
μ_{13} (Debye)	13.0 ± 1	11.0 ± 1
μ_{14} (Debye)	16.0 ± 1	14.0 ± 1
$\Delta\mu_{01}$ (Debye)	--	13.0 ± 1

(shaded) parameters entered in the fitting

Conclusions

cytochrome c

We determined the nonlinear absorption spectrum;

reverse saturable absorption $\lambda < 520$ nm

saturable absorption 520 nm $< \lambda <$ 570 nm

saturable absorption + two-photon absorption $\lambda >$ 570 nm

all-trans retinal

The 2PA peak at 790 nm is attributed to two distinct electronics states; a transition to S_2 (one-photon allowed) and to a S_1 only allowed by two-photon absorption

carotenoids derivatives

all-trans-β-carotene and trans-beta-apo-8'carotenal present high two-photon absorption cross-sections (10000 GM) around 570 nm. The noncentrosymmetry of trans-beta-apo-8'carotenal lead to an extra 2PA band around 1000 nm.

using our experimental techniques we are able to characterize and understand the nonlinear optical properties of interesting biomaterials

Outline

- Introduction and Motivation
- Experimental
- Results
  - Resonant optical nonlinearities in ***cytochrome c***
  - Two-photon absorption spectrum in ***all-trans retinal***
  - Two-photon absorption of ***carotenoids derivatives***
- Final remarks

Final Remarks

Besides the results presented here, we have been working in

- resonant nonlinearities in porphyrins and phthalocyanine
- two-photon spectroscopy in other materials (organic/inorganic)
- multi-photon absorption in ZnO
- ultrafast laser micromachining of polymeric surfaces
- microfabrication of 3D doped microstructures (2PP)

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Chemical Physicsl Letters (in preparation)

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Thank you !

for a copy of this presentation

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Presentations