Coherent control of light-mater interaction

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Outline

Motivation for coherent control

Mechanism of coherent control

Pulse shaping

Controlling photo bleaching in MEH-PPV

Controlling emission in organic compounds

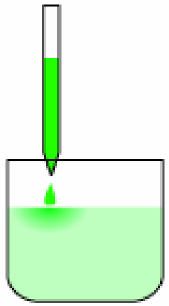
Control of Au nanoparticles formation

Conventional methods of chemical control

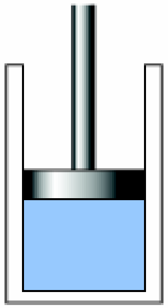
Macroscopically

temperature

concentration



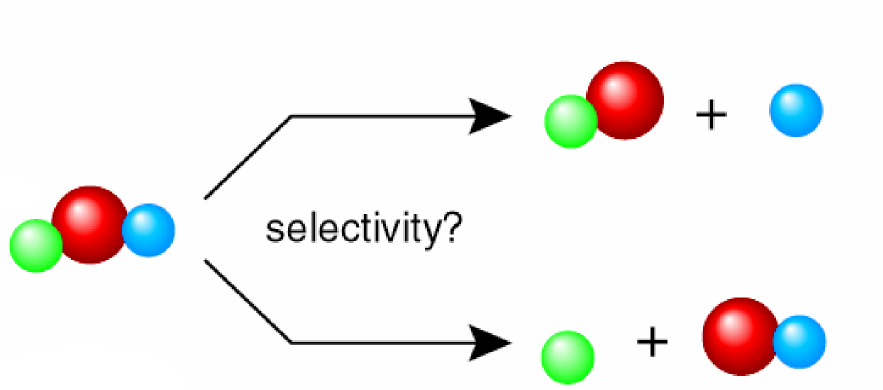
pressure



Microscopically

catalysis

Coherent Control

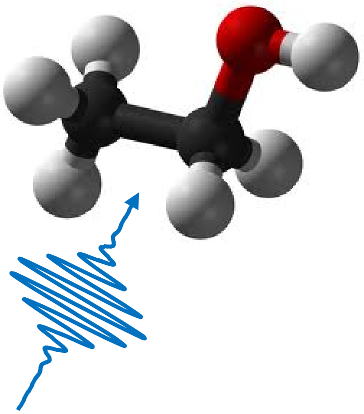


How to change a chemical reaction pathway and make different products?

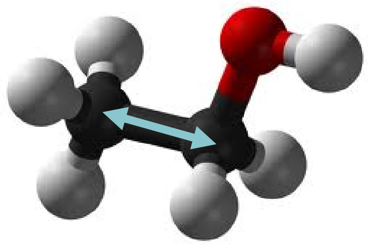
Use a light with a given frequency to excite the chemical bond we would like to break.

Intramolecular Vibrational Redistribution

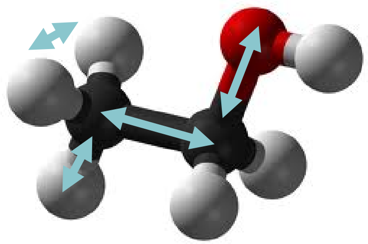
excite one bond



the bond vibrates



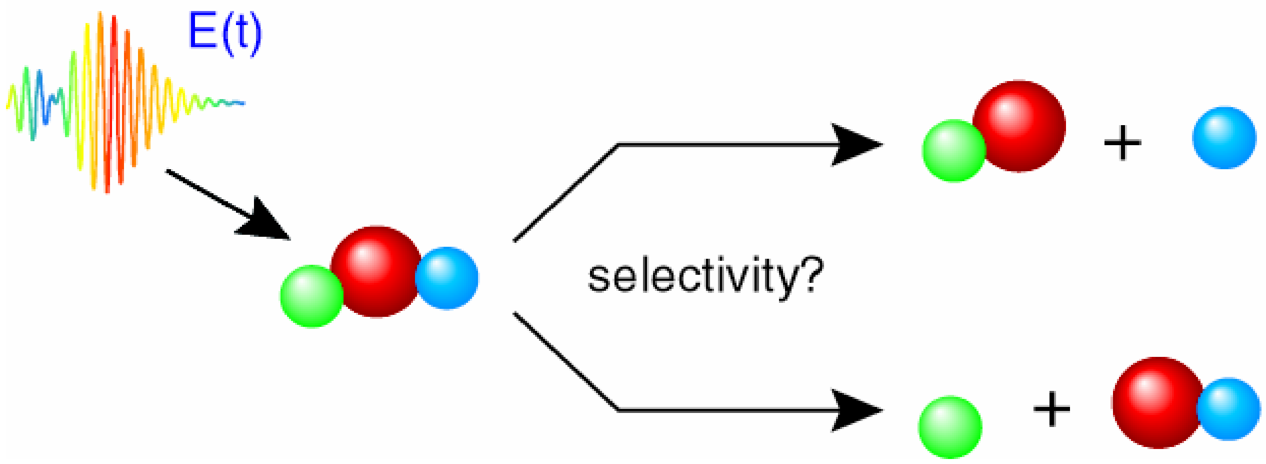
After a few fs the entire molecule is vibrating



IVR occurs on a few-fs , therefore long pulses excite the entire molecule, and the weakest bond breaks, no matter which bond was excited.

Coherent control: using shaped fs pulses

Can we used fs-pulses to cause a molecular vibration in such a way that a chosen bond is broken ?

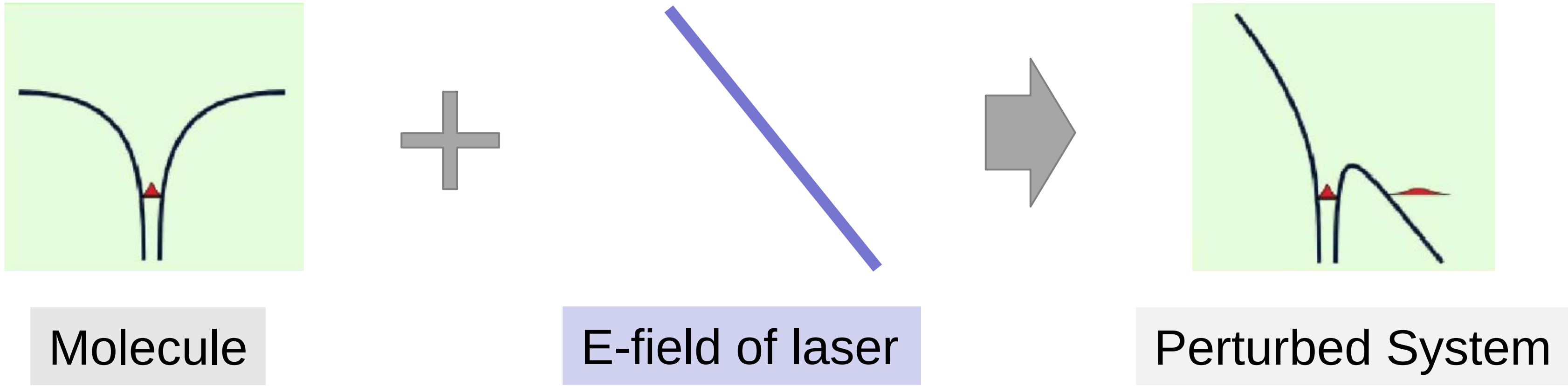


E(t) ?

The physics of coherent control

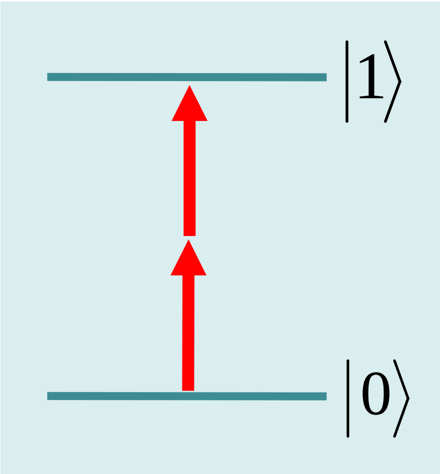
Nonperturbative nonlinear optics: strong field regime

The pulse electric field perturbs the molecule and can dissociates it

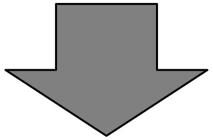


The required electric field of the pulse needs to be properly chosen

The physics of coherent control



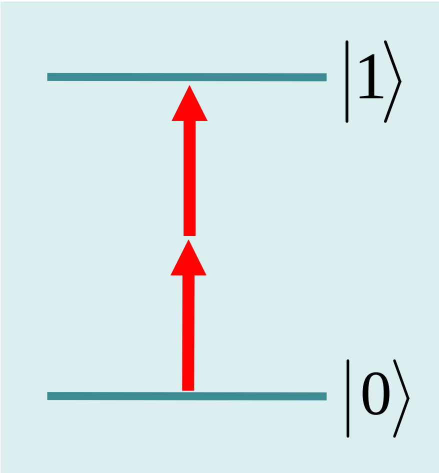
Using multi-photon absorption to excite a molecular system



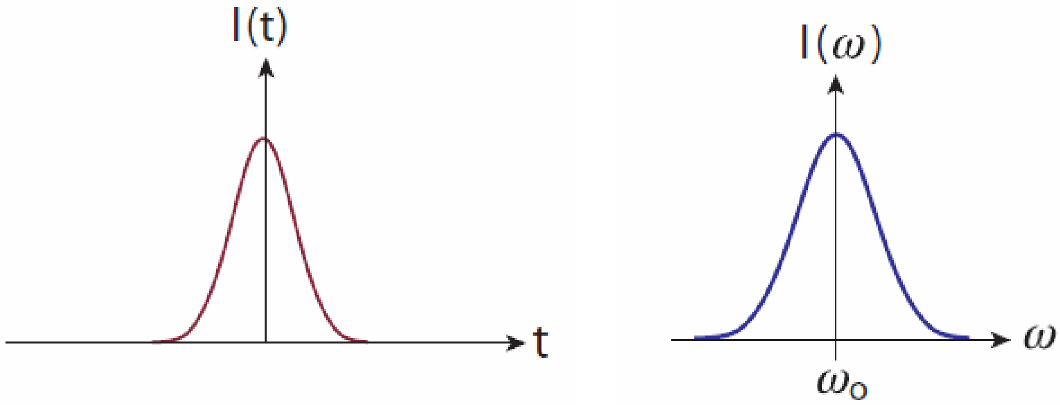
induce photoreaction

Perturbative nonlinear optics

The physics of coherent control



multi-photon absorption induced by ultrashort pulses

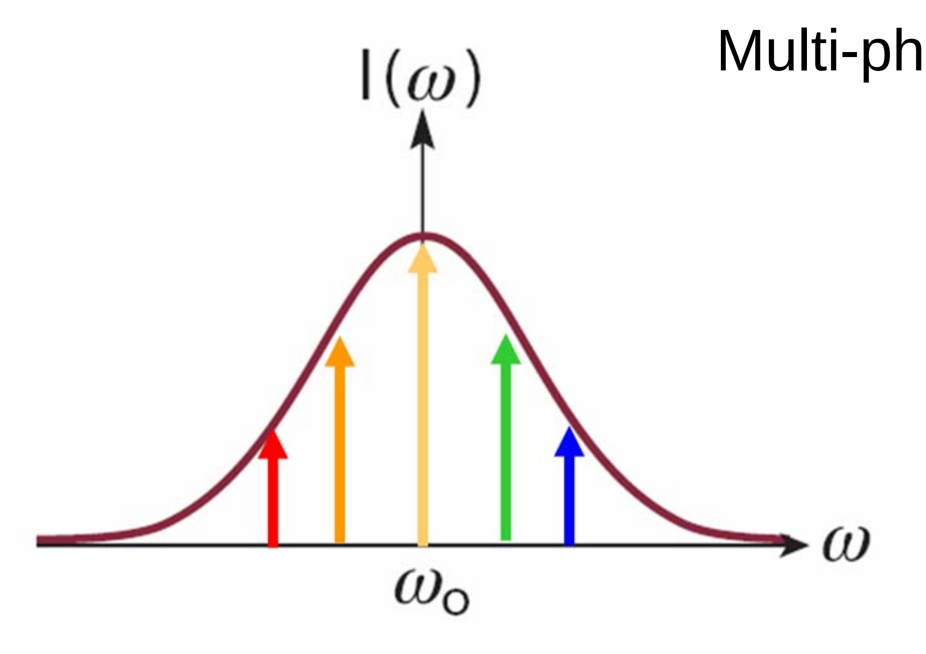


broad spectral band

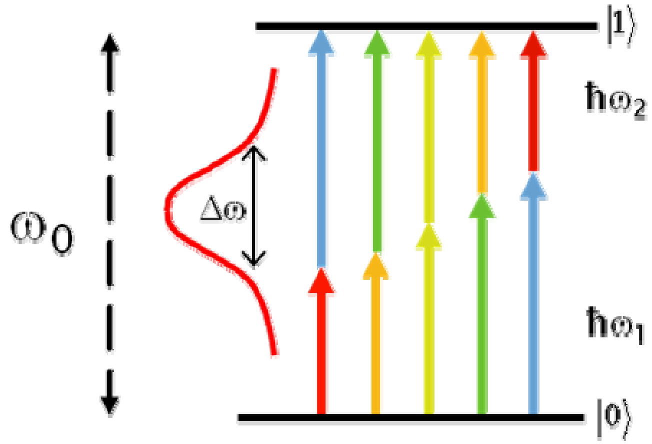
distinct photons of the pulse can promote two-photon absorption (**nondegenerate**)

multi-photon intrapulse interference

The physics of coherent control

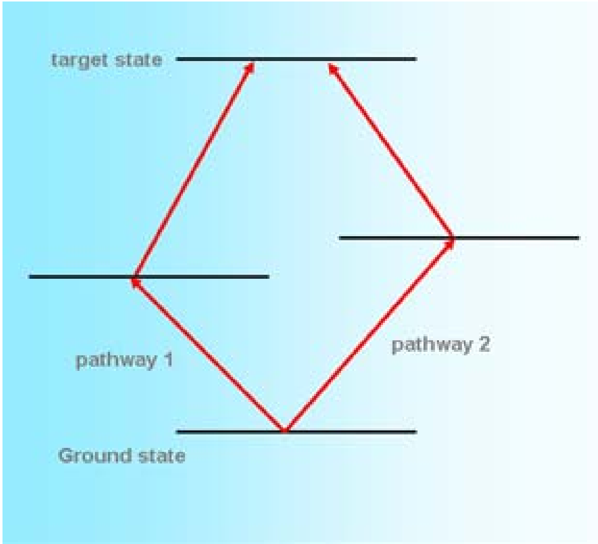


Multi-photon intrapulse interference



Distinct combinations of photons of the same pulse can lead the system to a final state through different pathways

It is needed to “shape” the phase of the pulse



Theory for coherent control

The complete Hamiltonian for the system needs to be known

$$H_{system} = H_{molecule} + H_{radiation} + H_{interaction}$$

$H_{radiation}$ → known 

$H_{molecule}$ → small molecules: approximate

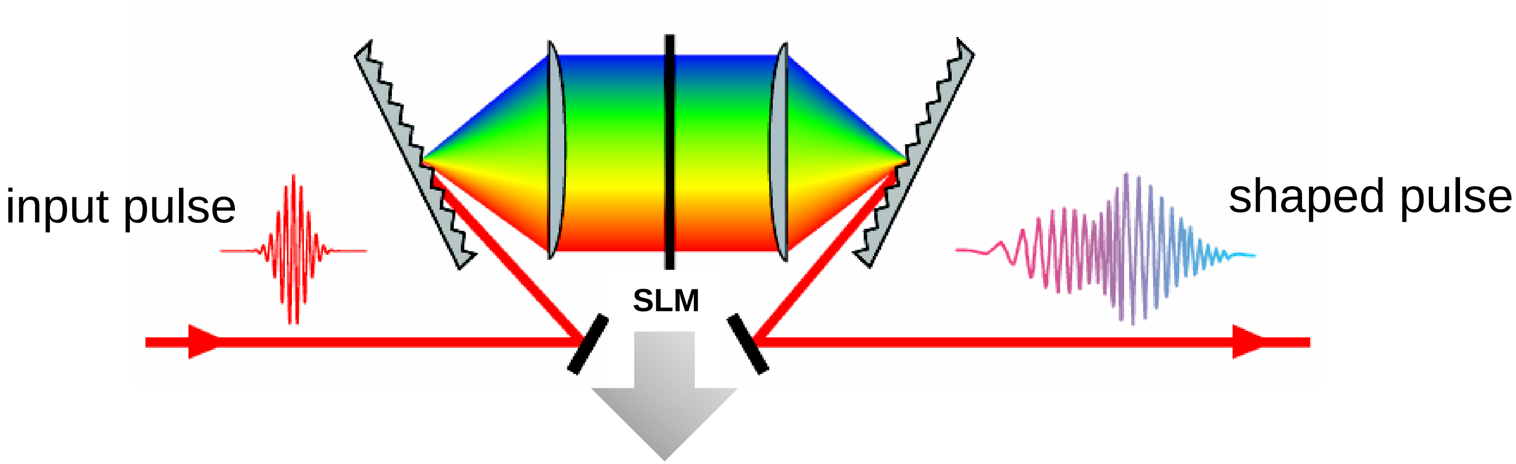
large molecules: unknown

$H_{interaction}$ → weak field: known $\langle \psi_f | \mu \cdot E | \psi_i \rangle$

strong field: unknown

It might be possible to solve the problems for **VERY** simple system/molecules

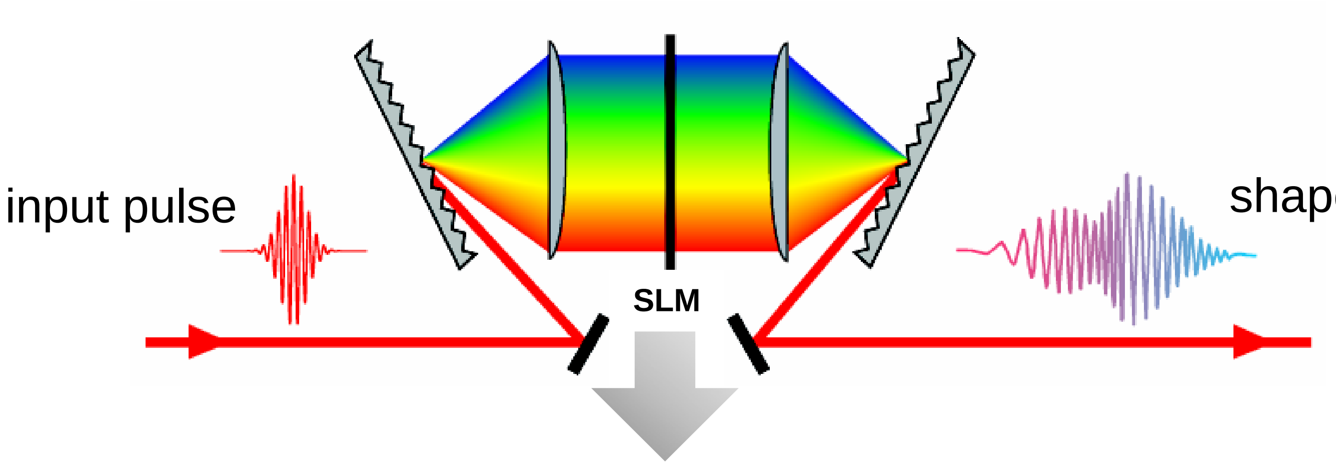
Pulse-shaping for coherent control



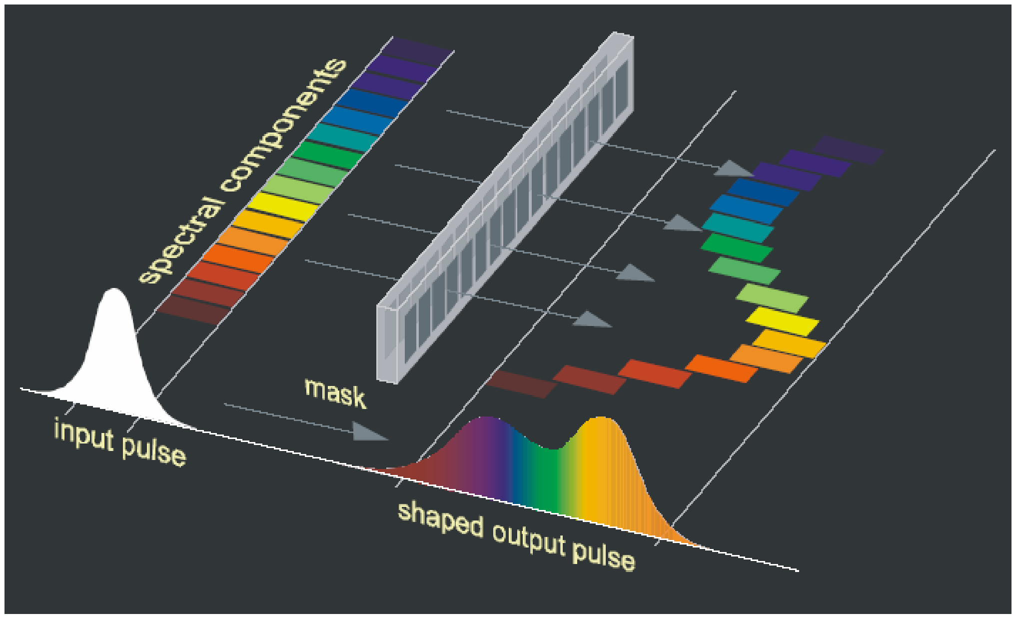
To generate pulses that are able to control optically-induced processes

To compensate for distortions in the pulses

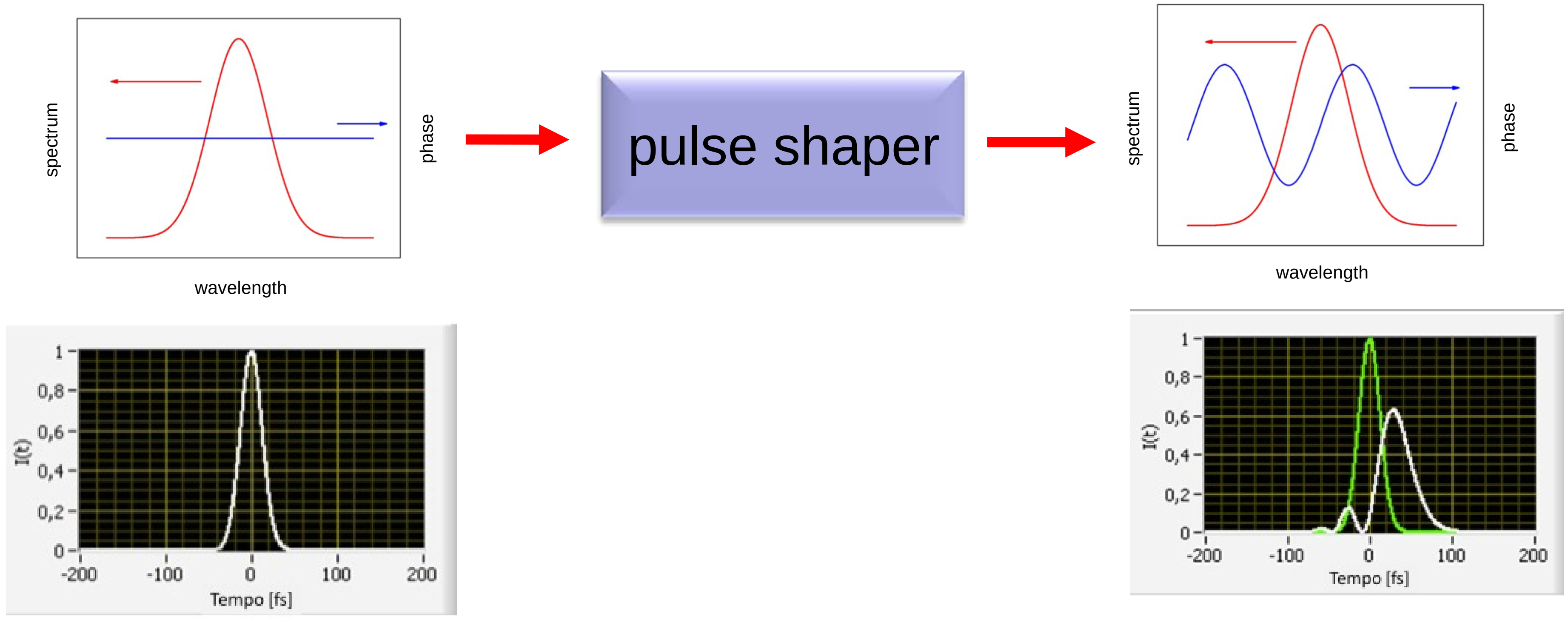
Pulse-shaping for coherent control



liquid crystal display



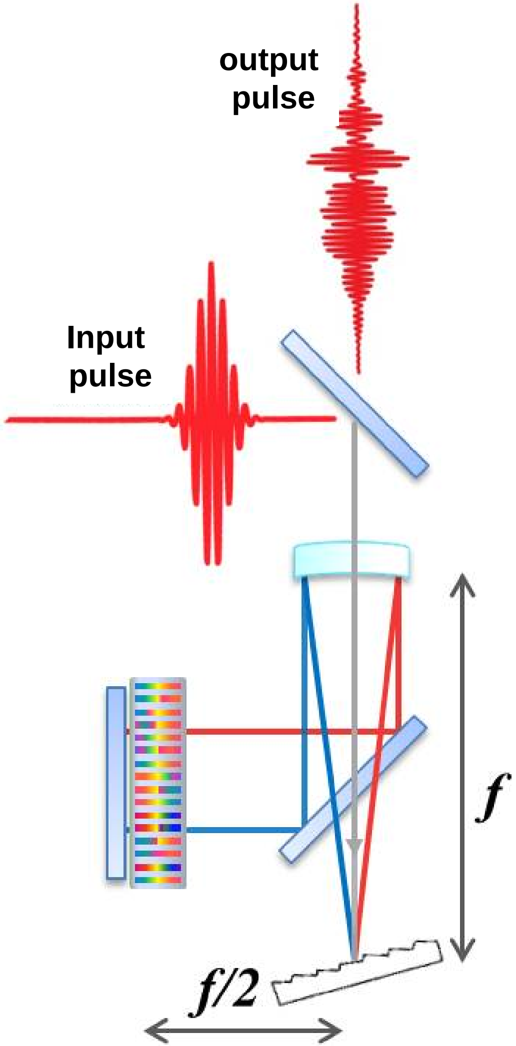
Pulse-shaping for coherent control

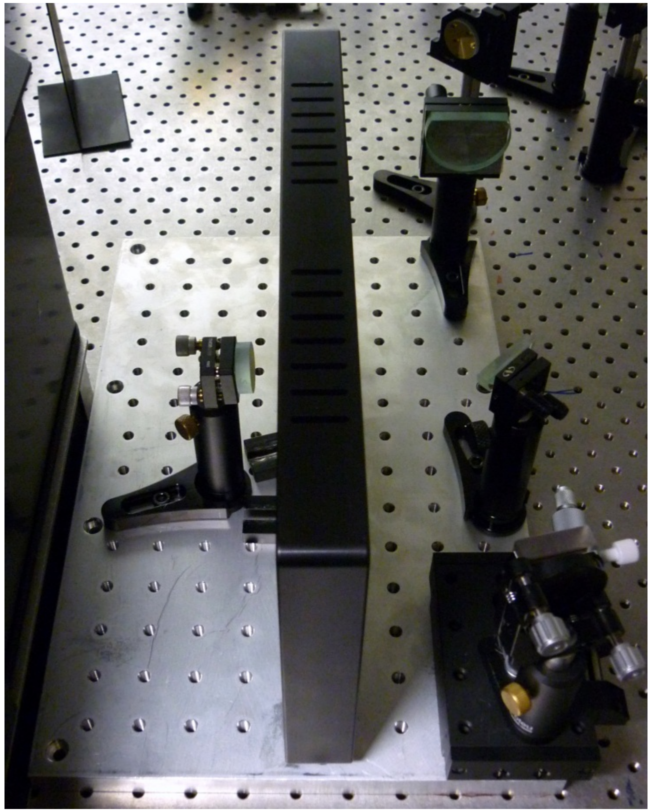


By changing the pulse shape we can alter the results of an experiment

Pulse-shaper

Reflection system





Shaping the pulse

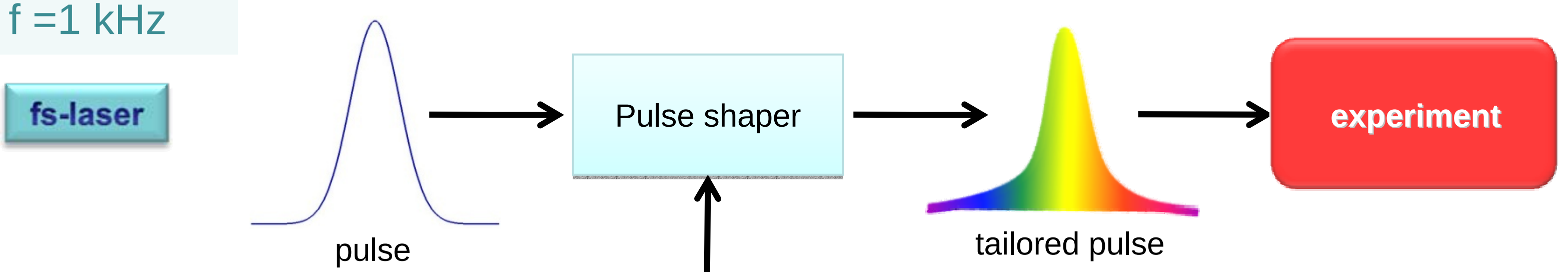
How to define which pulse shape to use ?

Learning algorithms

Defined phase masks

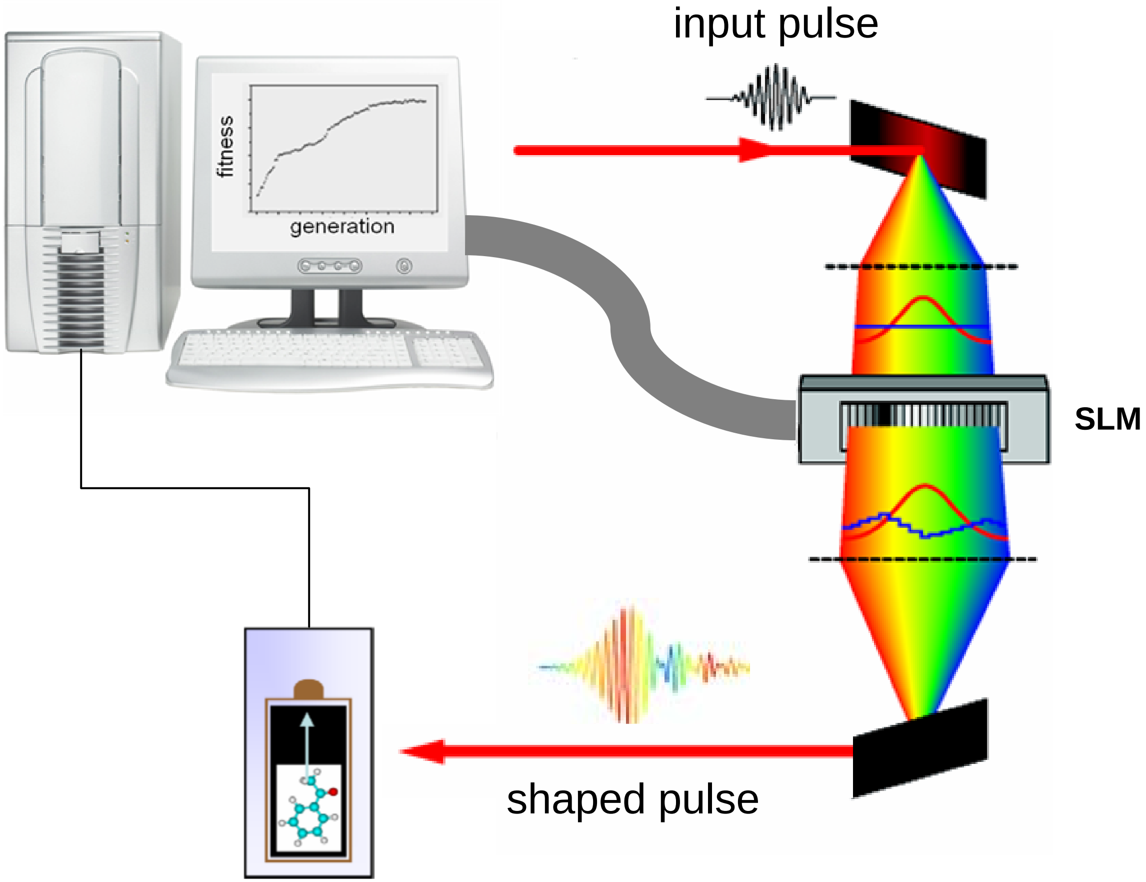
Coherent control: defined phase masks

τ = 30 fs
λ = 800 nm
f =1 kHz

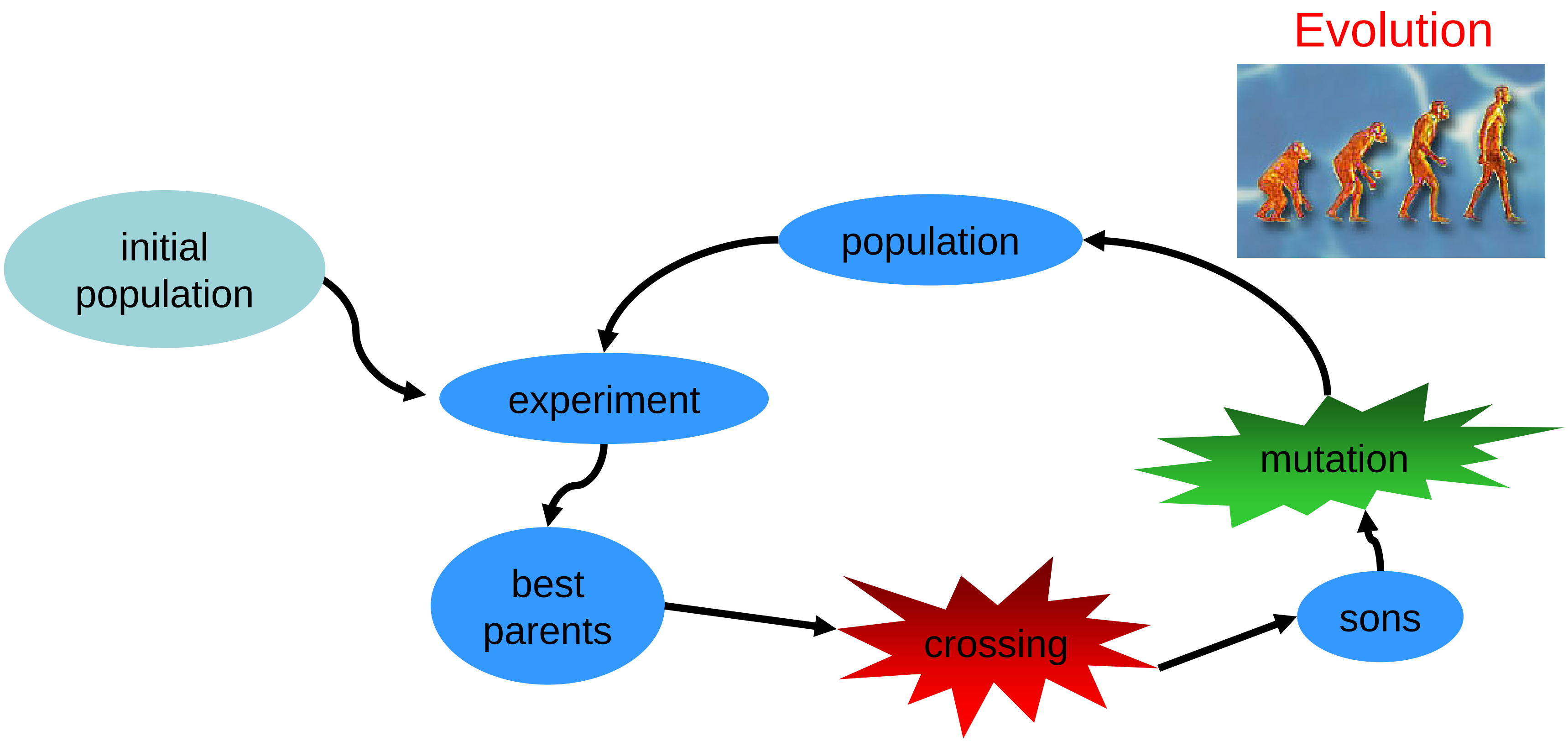


$$\Phi(\omega) = f\,(\omega)$$

Coherent control: learning algorithm



Genetic Algorithm



Results

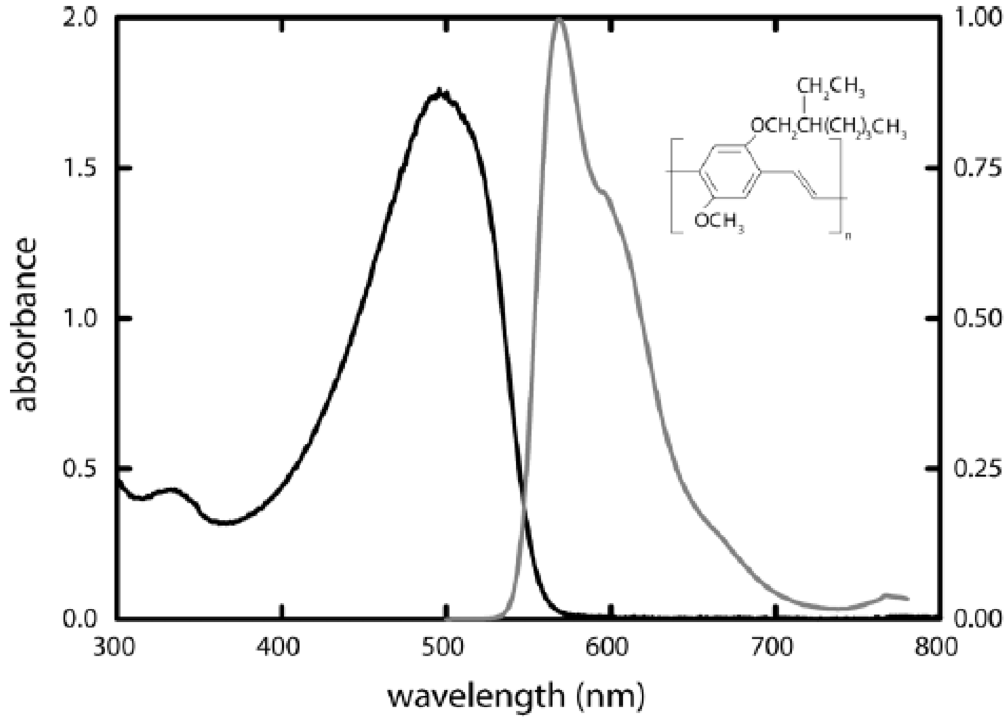
1 – Multi-photon intrapulse interference

control of MEH-PPV photodegradation
control of emission in Y-shaped molecules

2 – Strong field

control of Au nanoparticles formation in chitosan

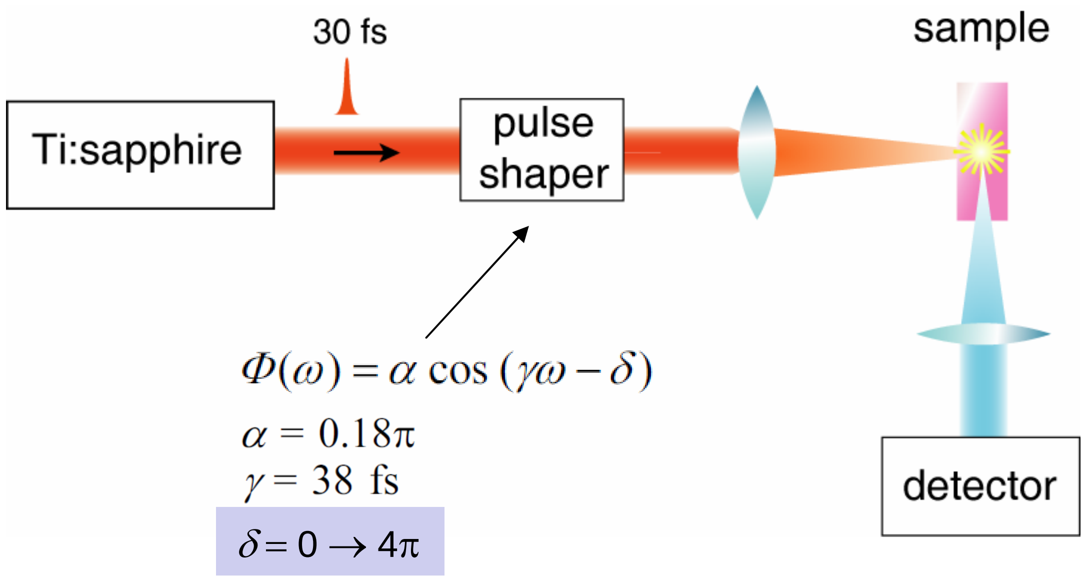
Control of MEH-PPV photodegradation



MEH-PPV: conductive and luminescent polymer with interesting properties for applications

However, MEH-PPV photo-bleaches due to a photoxidation reaction, causing a decrease in its emission

Control of MEH-PPV photodegradation

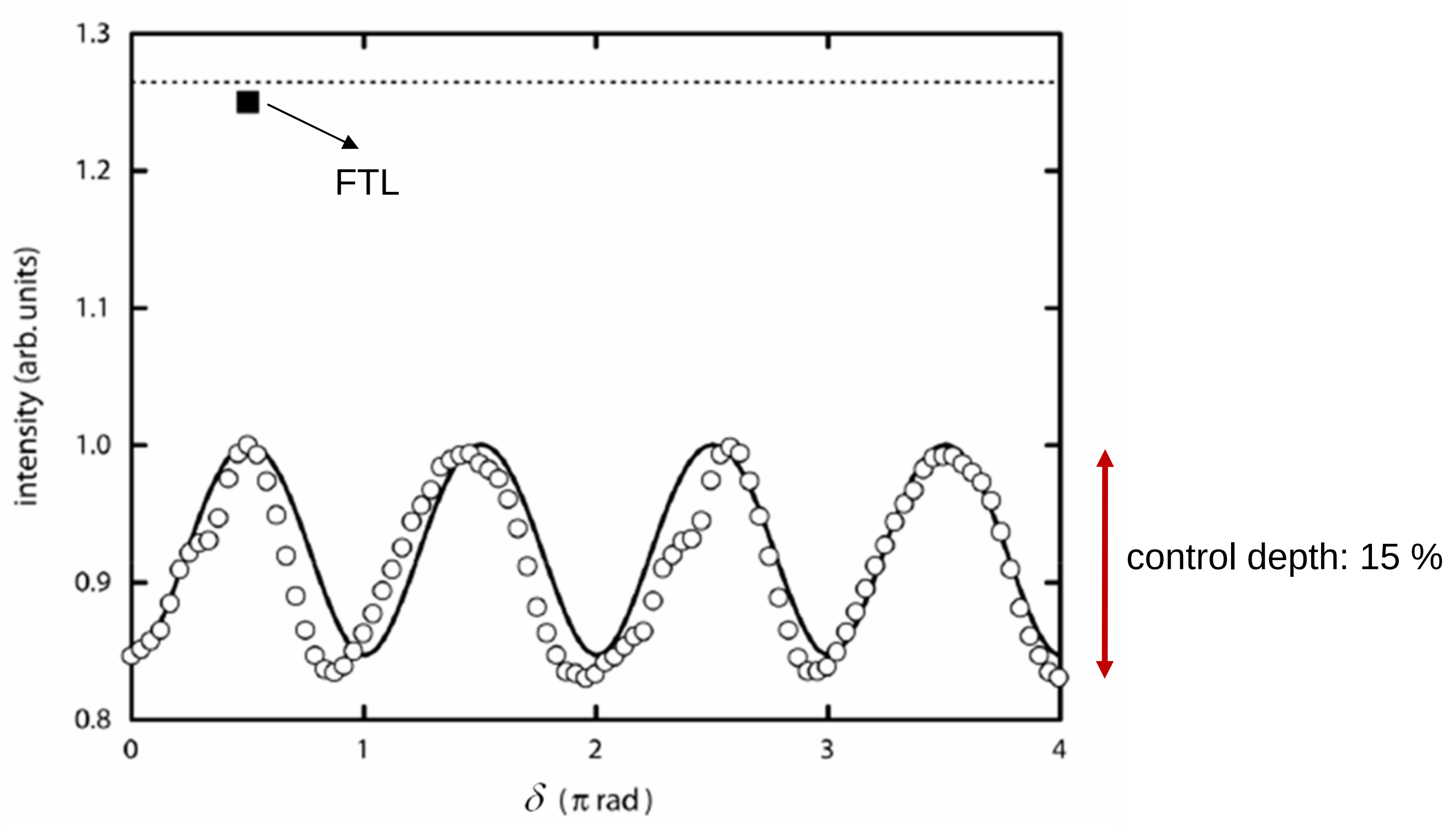


Measured

1 - two-photon excited emission as a function of the phase-mask

2 - photodegradation for distinct phase masks

Control of MEH-PPV photodegradation



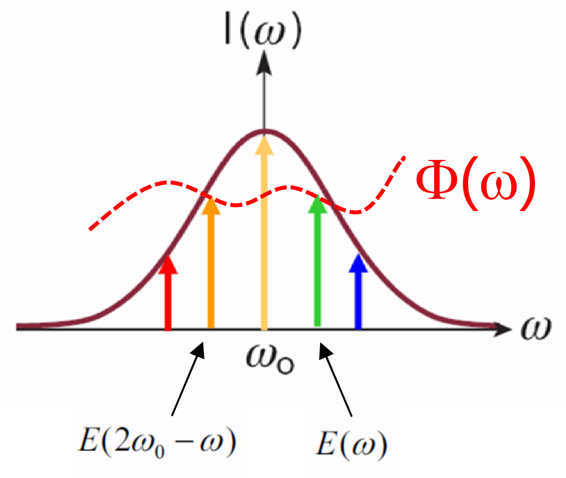
The emission with FTL pulses is ~ 25% higher than the one with the phase mask

Control of MEH-PPV photodegradation

Two-photon absorption transition probability for na atomic system

$$S^{(2)} \propto \left| \int_0^\infty E(\omega)\, E(2\omega_0 - \omega)\, \mathrm{d}\omega \right|^2 \mathrm{d}\omega_0$$

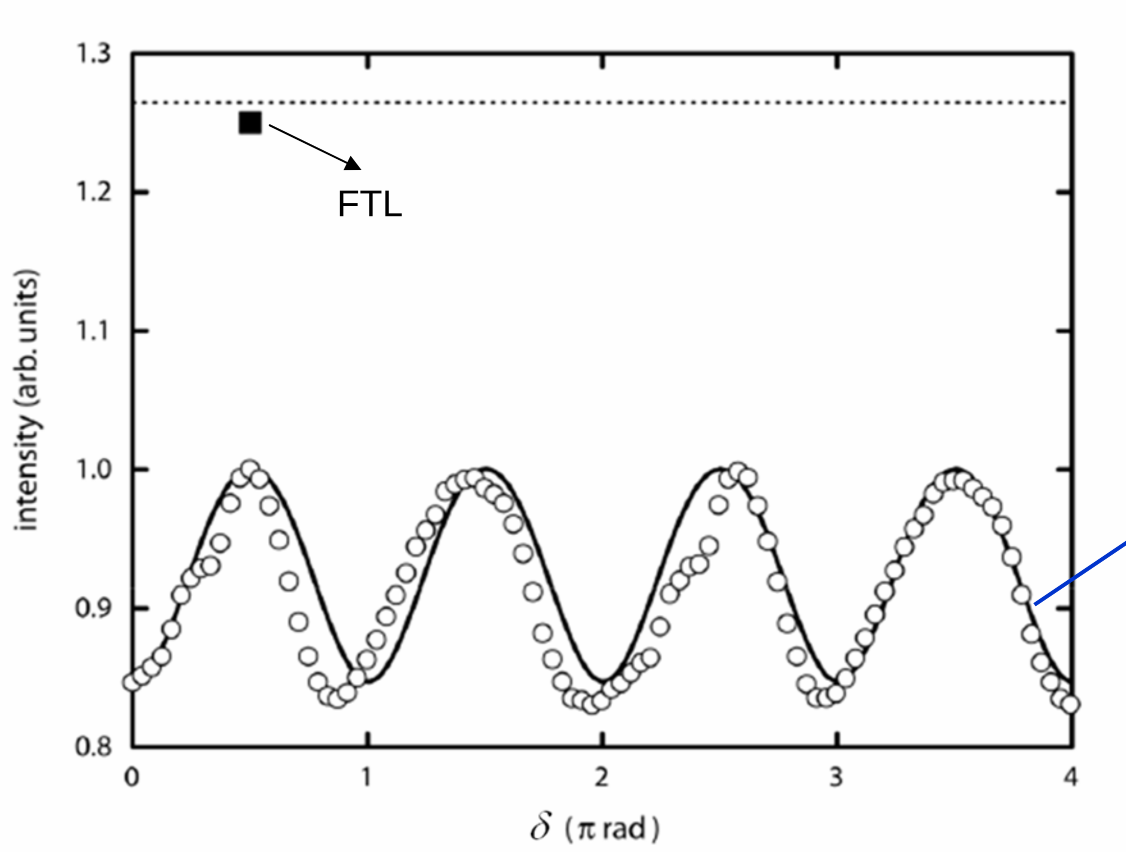
$$E(\omega) = A(\omega) \exp\left[\mathrm{i}\Phi(\omega)\right]$$



For a molecular system it is needed to include the integral on the 2PA spectrum $g(2\omega_0)$

$$S^{(2)} \propto \int g(2\omega_0) \left| \int_0^\infty E(\omega)\, E(2\omega_0 - \omega)\, \mathrm{d}\omega \right|^2 \mathrm{d}\omega_0$$

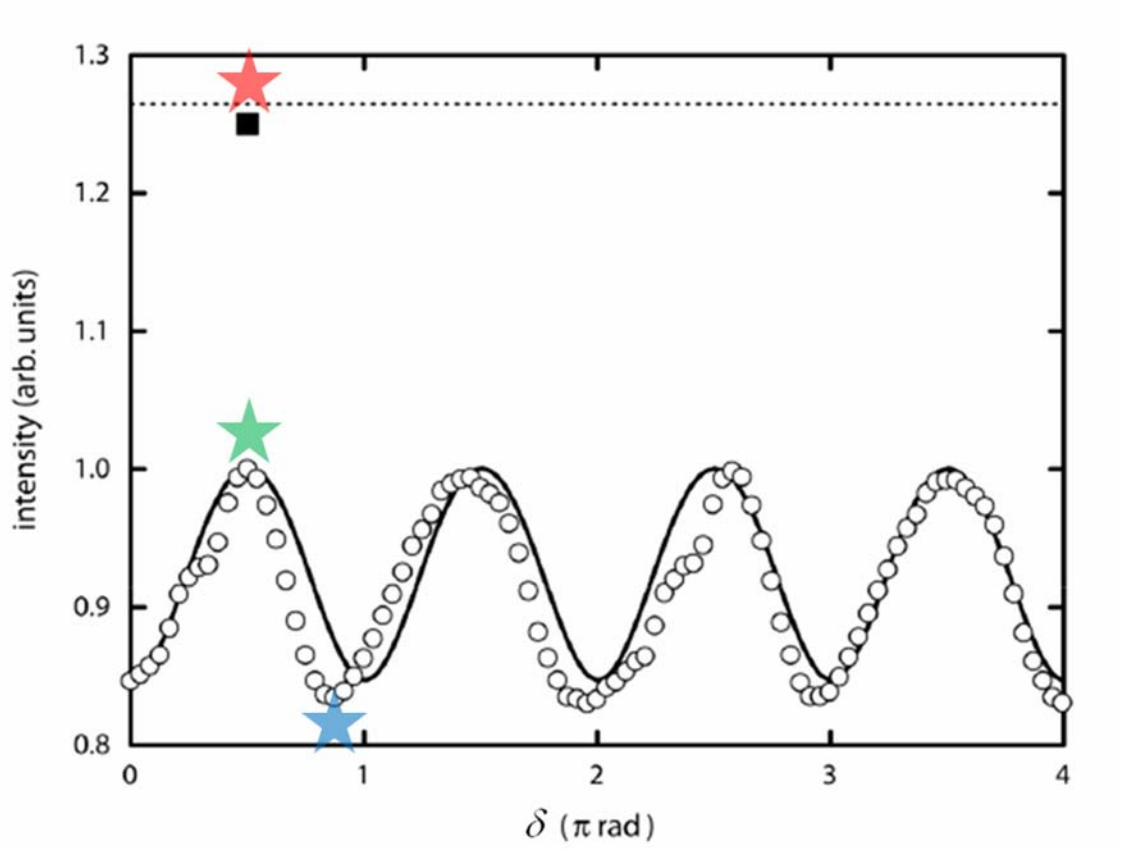
Control of MEH-PPV photodegradation



$$S^{(2)} \propto \int g(2\omega_0) \left| \int_0^{\infty} E(\omega)\, E(2\omega_0 - \omega)\, \mathrm{d}\omega \right|^2 \mathrm{d}\omega_0$$

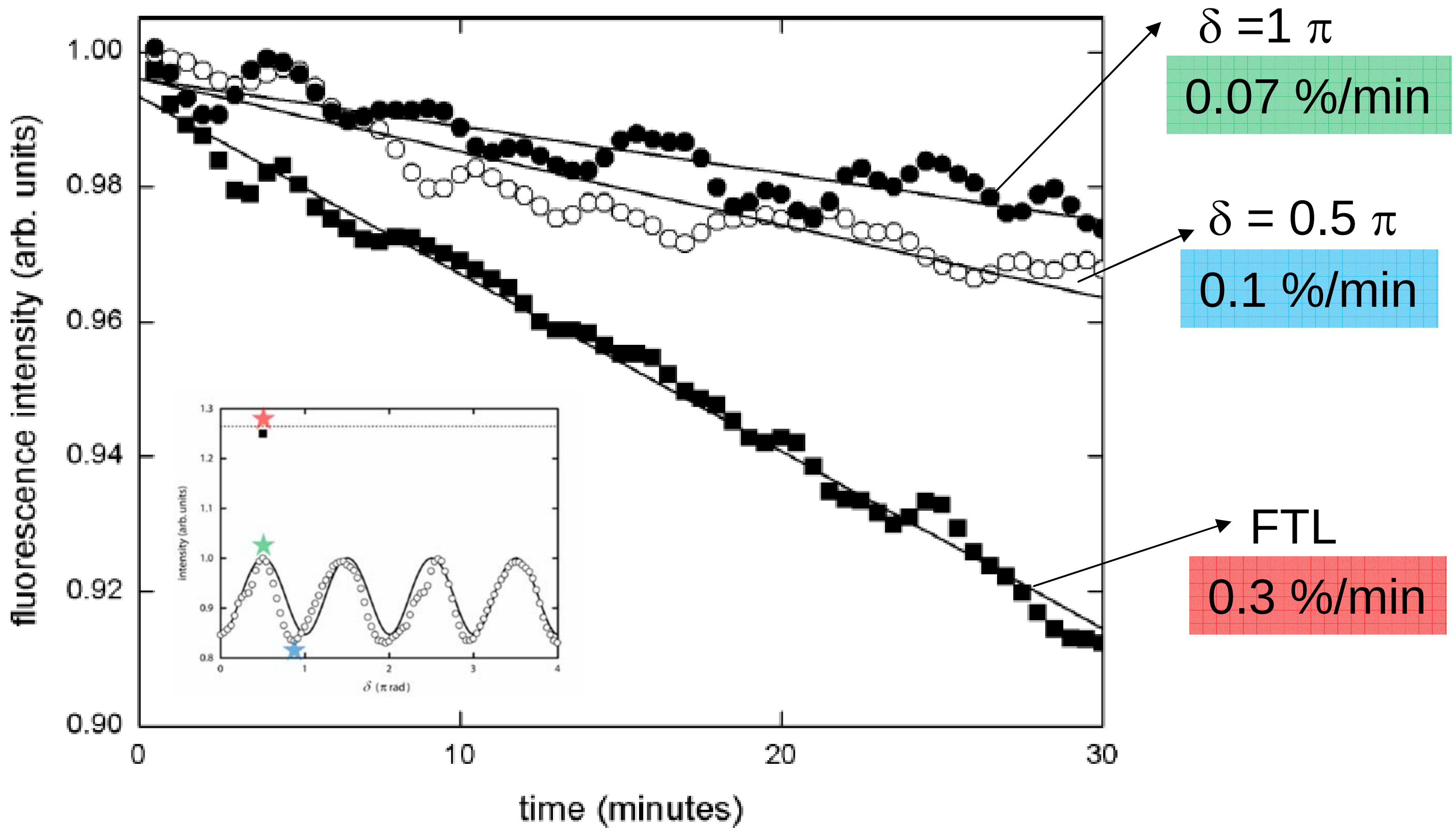
modeling of the coherent control

Control of MEH-PPV photodegradation



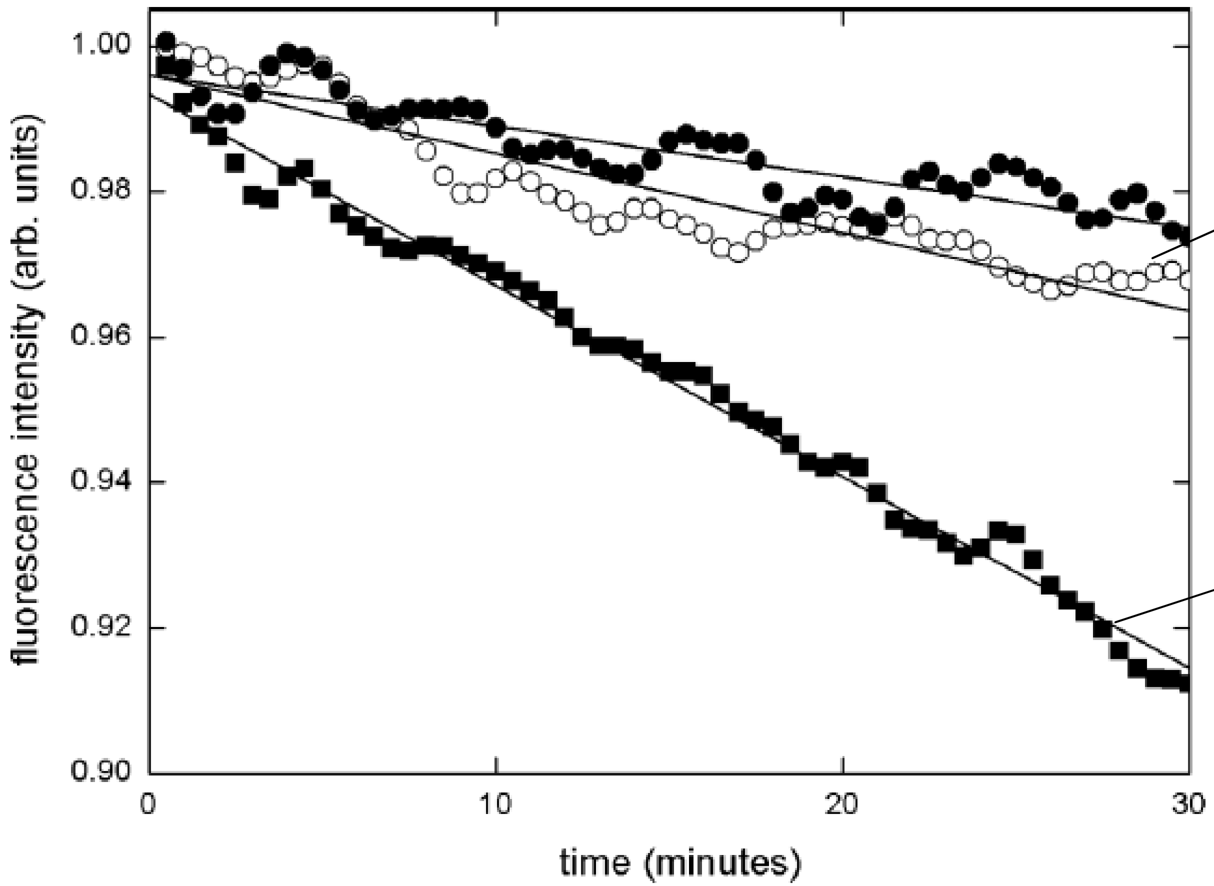
measuring the photobleaching rate with three diferent phase-masks

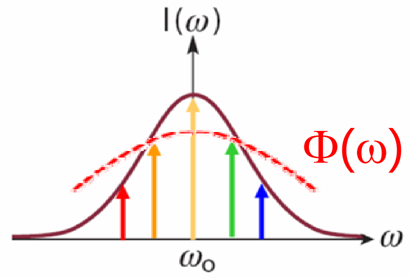
Control of MEH-PPV photodegradation



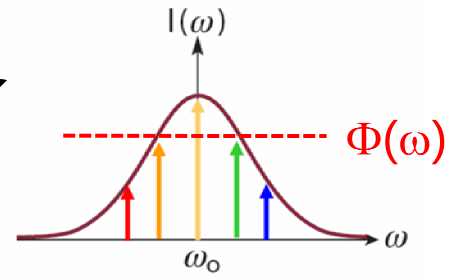
photobleaching rate <u>decreases 3 times</u> for the phase-masked pulses

Control of MEH-PPV photodegradation





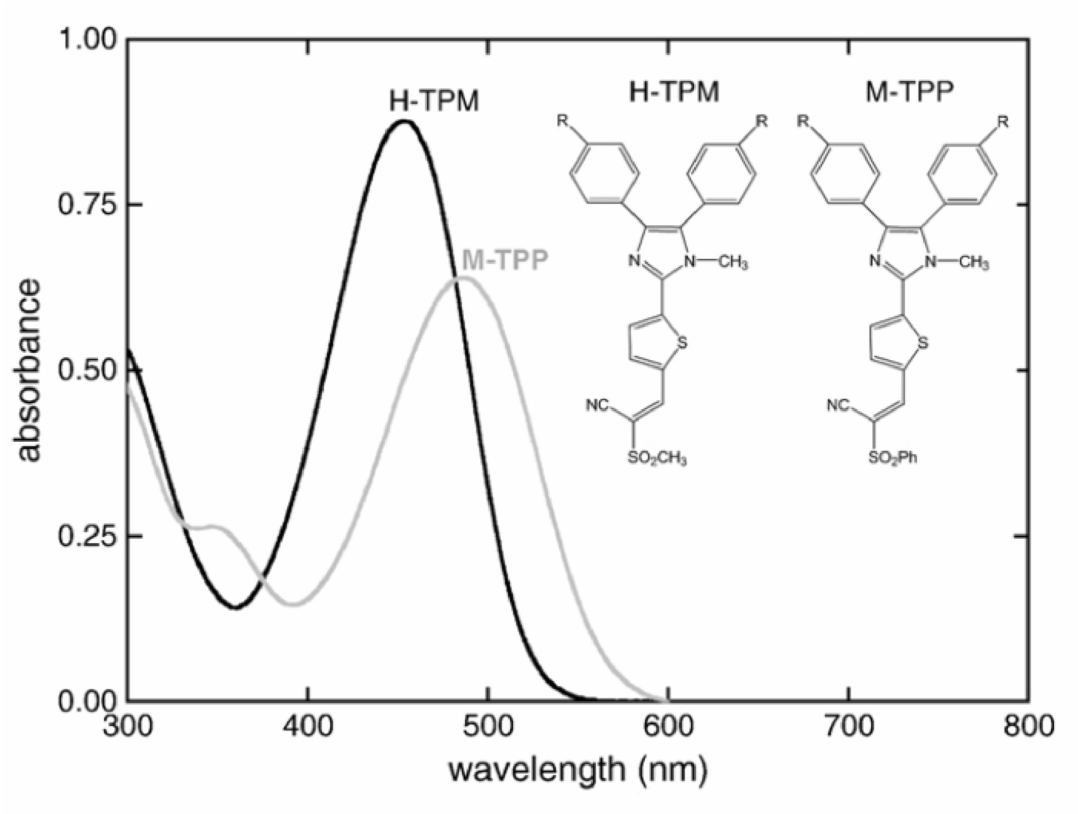
pairs in phase



all in phase

cosine-like mask: smaller amount of molecules is excited $\rightarrow$ less photobleaching

Control of emission in Y-sahped molecules

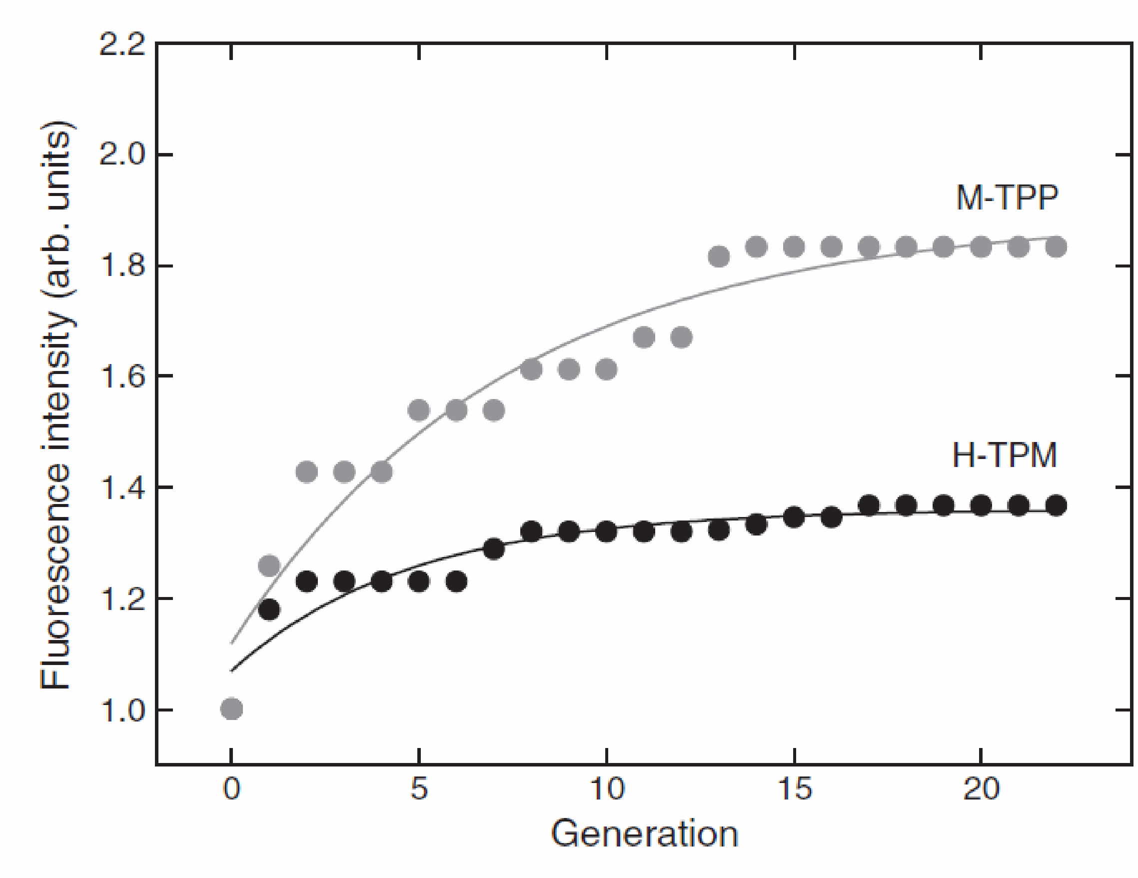


Optimize the two-photon excited emission of Y-shaped molecules using GA

Understanding the coherent control on the 2PA in molecular systems can lead to the development of new strategies to enhance ONL

Control of emission in Y-sahped molecules

Controlling the emission by Genetic Algorithm



$\bar{R} = 1.9 \pm 0.2$

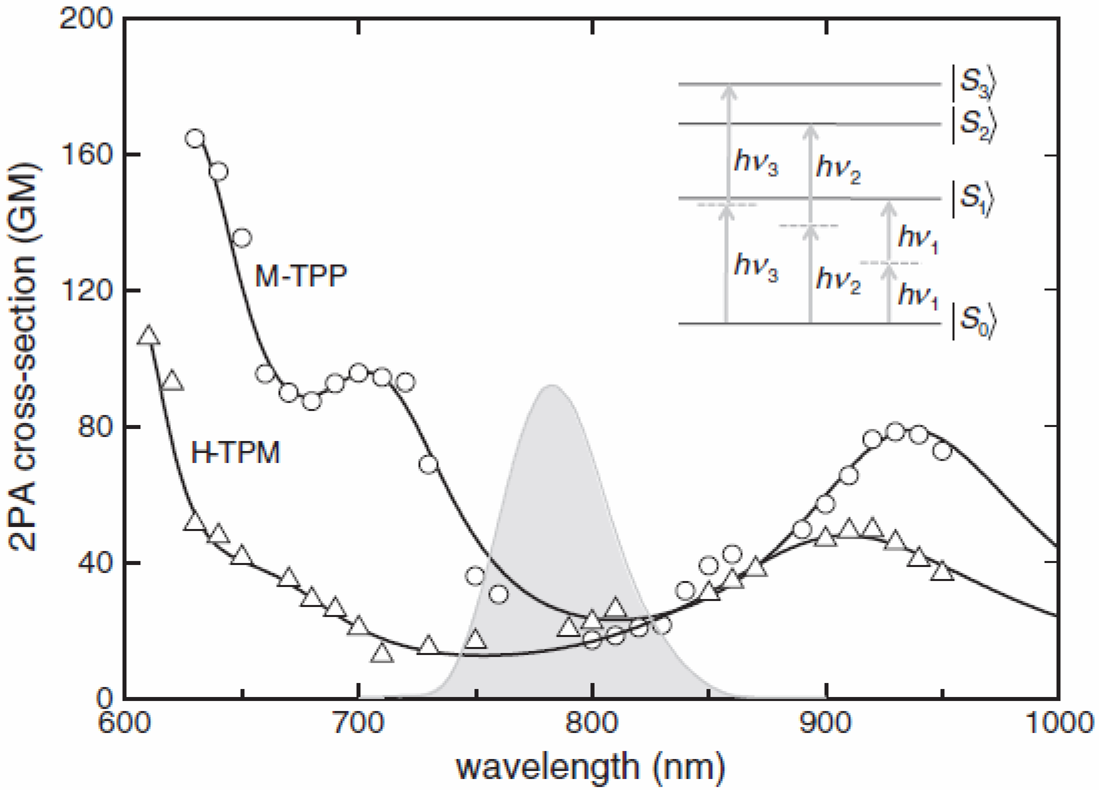
$\bar{R} = 1.4 \pm 0.1$

the final pulse is FTL for both molecules

specific molecular features affect the control over the 2PA process

Control of emission in Y-sahped molecules

Intra pulse multi-photon interference



$$S^{(2)} \propto \int_{-\infty}^{\infty} g^{(2)}(2\omega_0) \left| \int_{-\infty}^{\infty} E(2\omega_0 - \Omega) E(\Omega) d\Omega \right|^2 d\omega_0$$

distinct 2PA spectra

The detuning between the 2PA and the pulse spectrum is smaller for M-TPP

modeling the growth rate

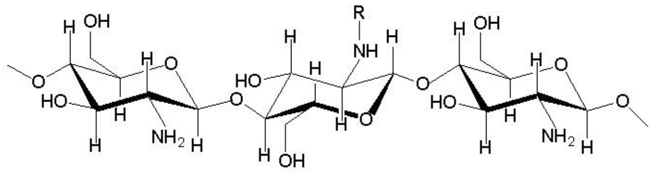
M-TPP $\bar{R}_{teo} = 1.8$

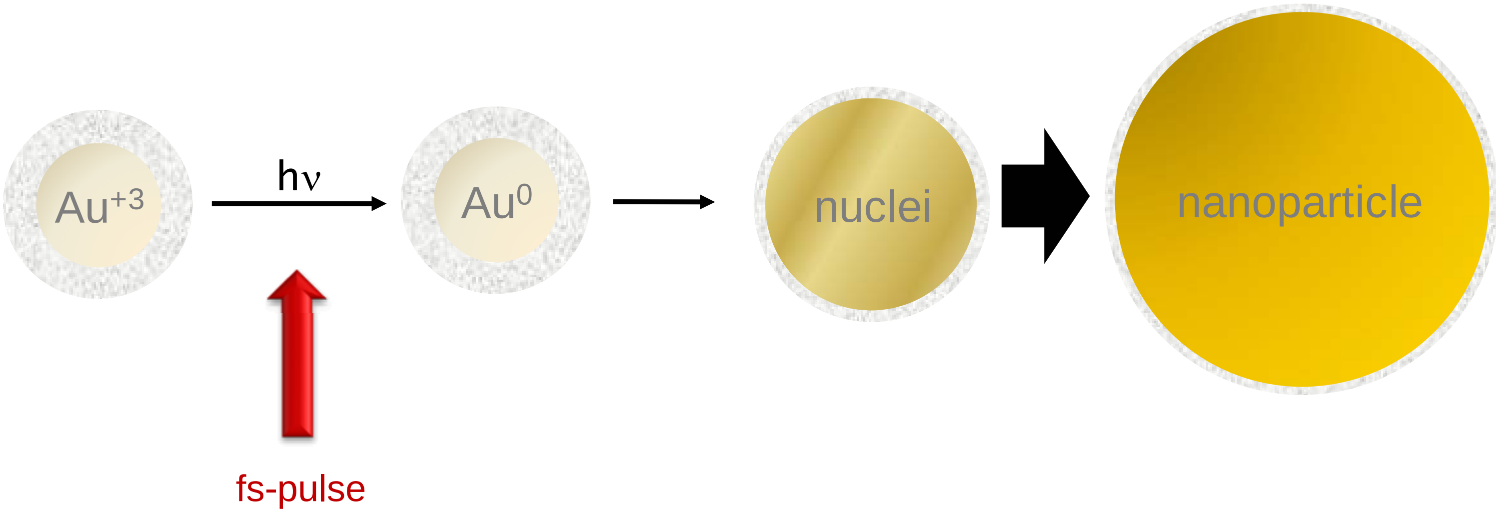
H-TPM $\bar{R}_{teo} = 1.5$

Photo-reduction

$HAuCl_4$ +

chitosan

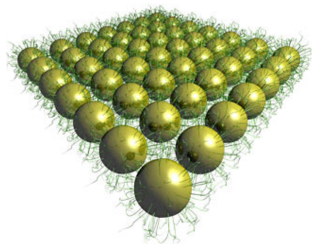




Control of Au nanoparticles formation

$$Ch + nh\nu \rightarrow Ch^{+} + e^{-}$$

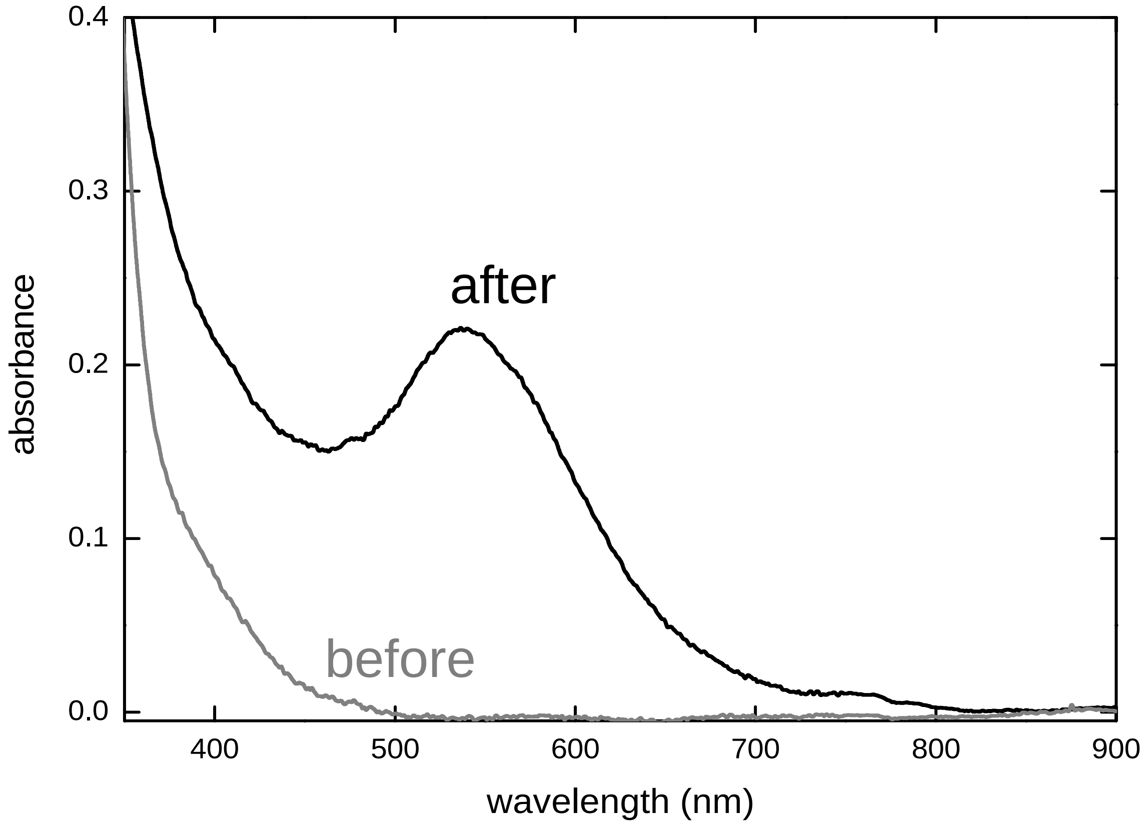
$$Au^{+} + e^{-} \rightarrow Au^{0}$$



excition laser used was a KMLabs – Dragon (multipass amplifier)

τ = 30 fs
λ = 800 nm
f =1 kHz
E = 2 mJ

Control of Au nanoparticles formation



FTL pulse

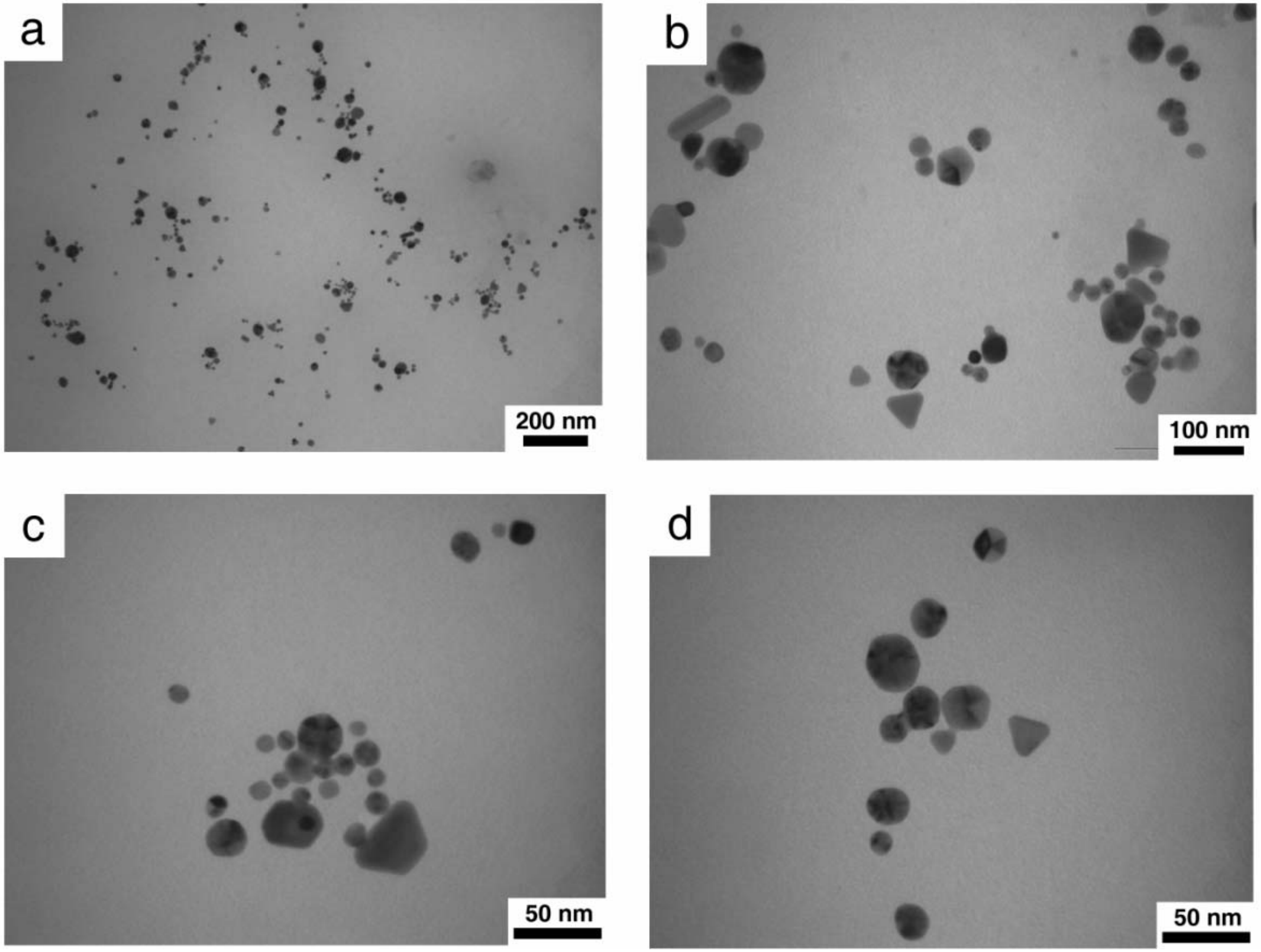
E = 185 μJ
I = 5 x 10^{11} W/cm^2

λ= 800 nm

sample absorption spectrum before and after irradiation

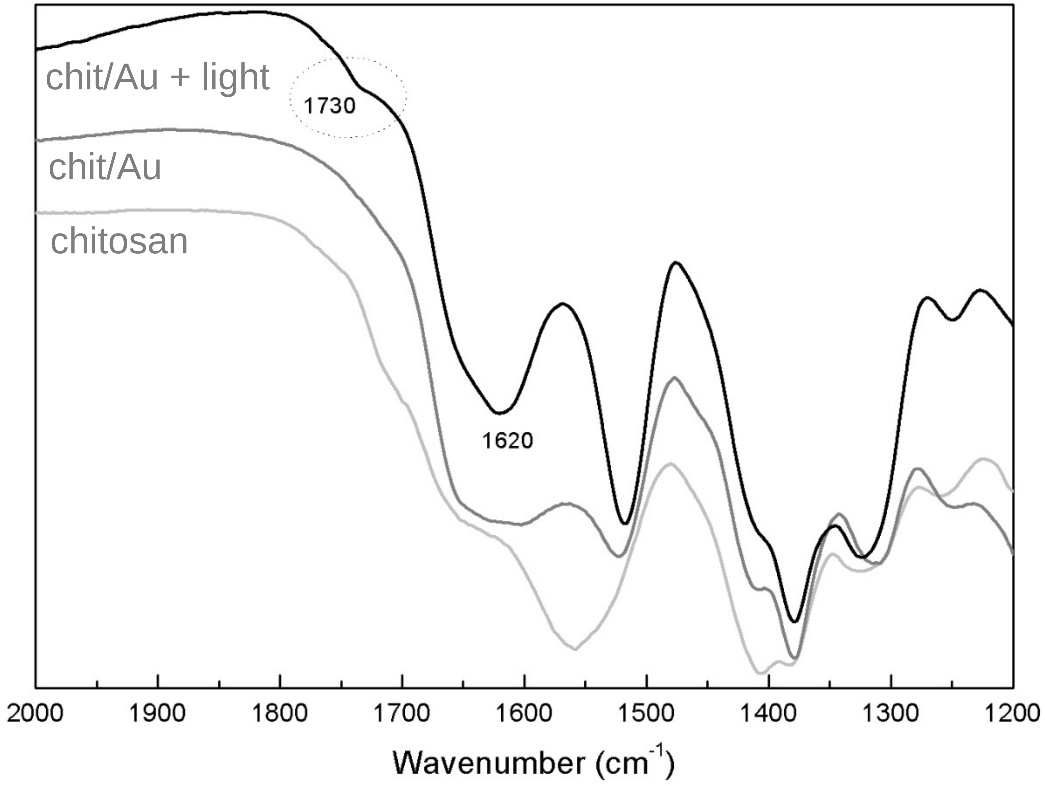
Results

Gold nanoparticles – TEM images



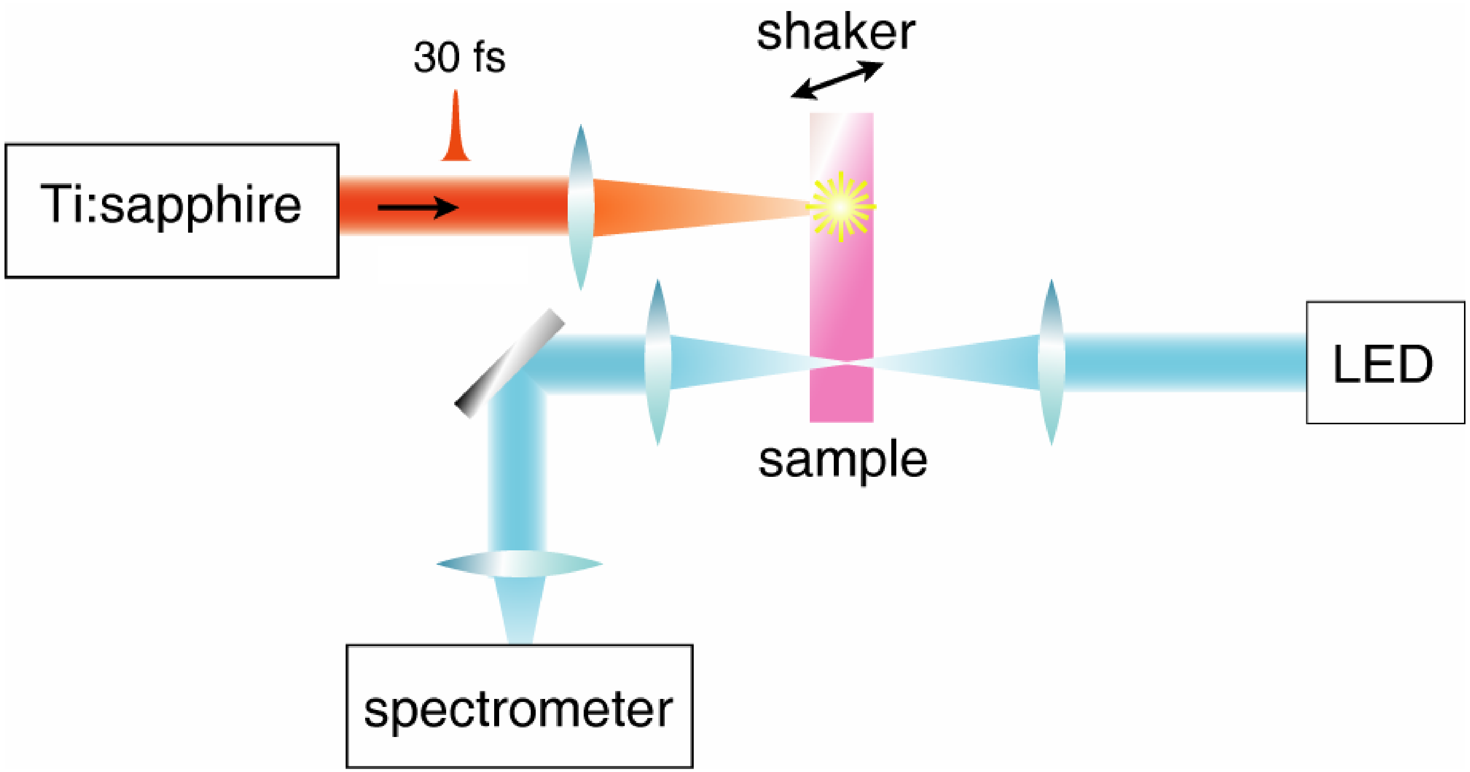
Control of Au nanoparticles formation

FTIR spectra of the samples



indicates that the reduction of the gold ions for the formation of the gold nanoparticles is related to the oxidation of hydroxyl groups in chitosan to carbonyl groups

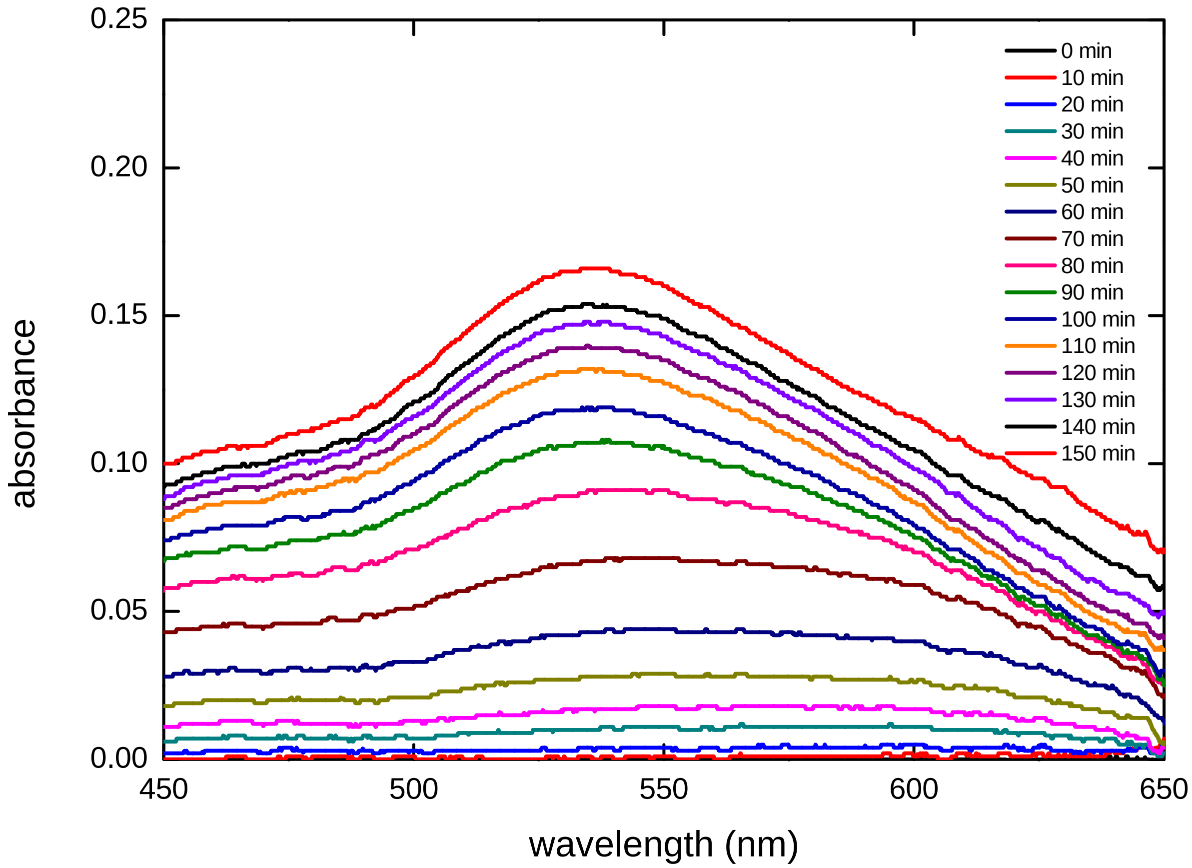
Control of Au nanoparticles formation



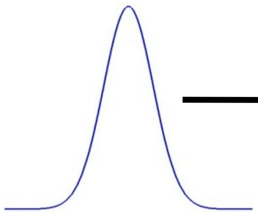
to determine the the dynamics of nanoparticles formation

Control of Au nanoparticles formation

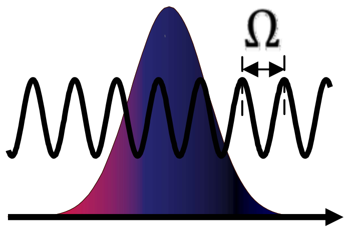
I= 12 x 10 ^{11} W/cm^2

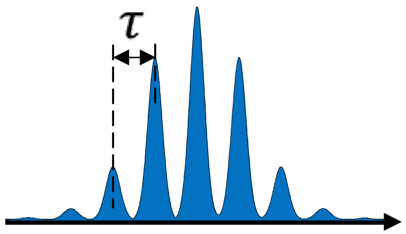


creating a pulse train



Pulse shaper



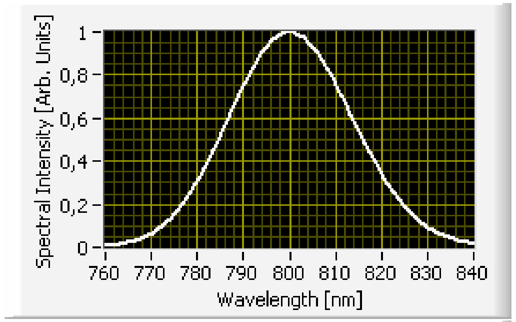


experiment

$$\varphi(\omega) = \alpha \sin(\tau\omega + \delta)$$

$$\Omega_R = {}^{2\pi}\!/_{\tau}$$

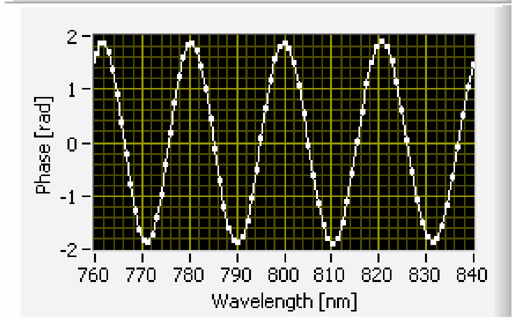
Control of Au nanoparticles formation

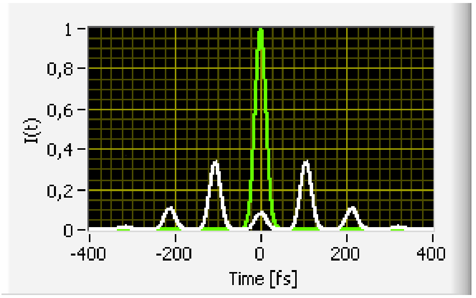


varying the period of the sinusoidal phase mask

$$\emptyset(\omega) = \alpha \, sin(\gamma\omega + \delta)$$

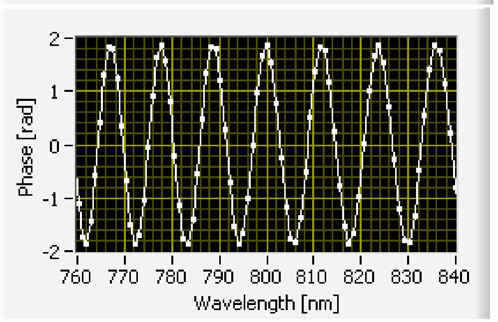
generate pulse trains with distinct separation time

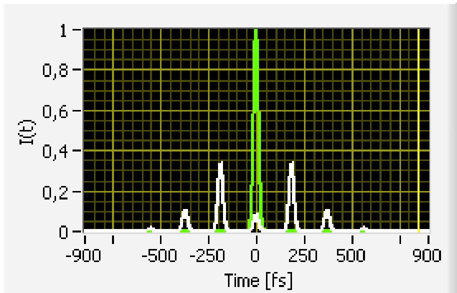




$N_{periods} = 4$

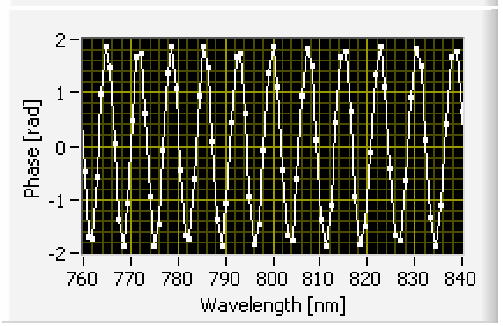
$t_{sep} = 106$ fs

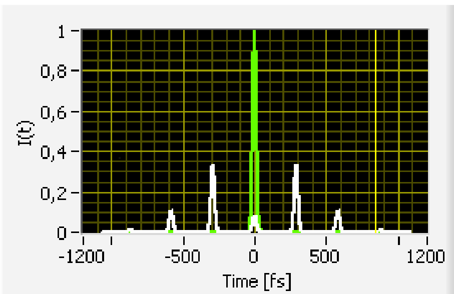




$N_{periods} = 7$

$t_{sep} = 186$ fs

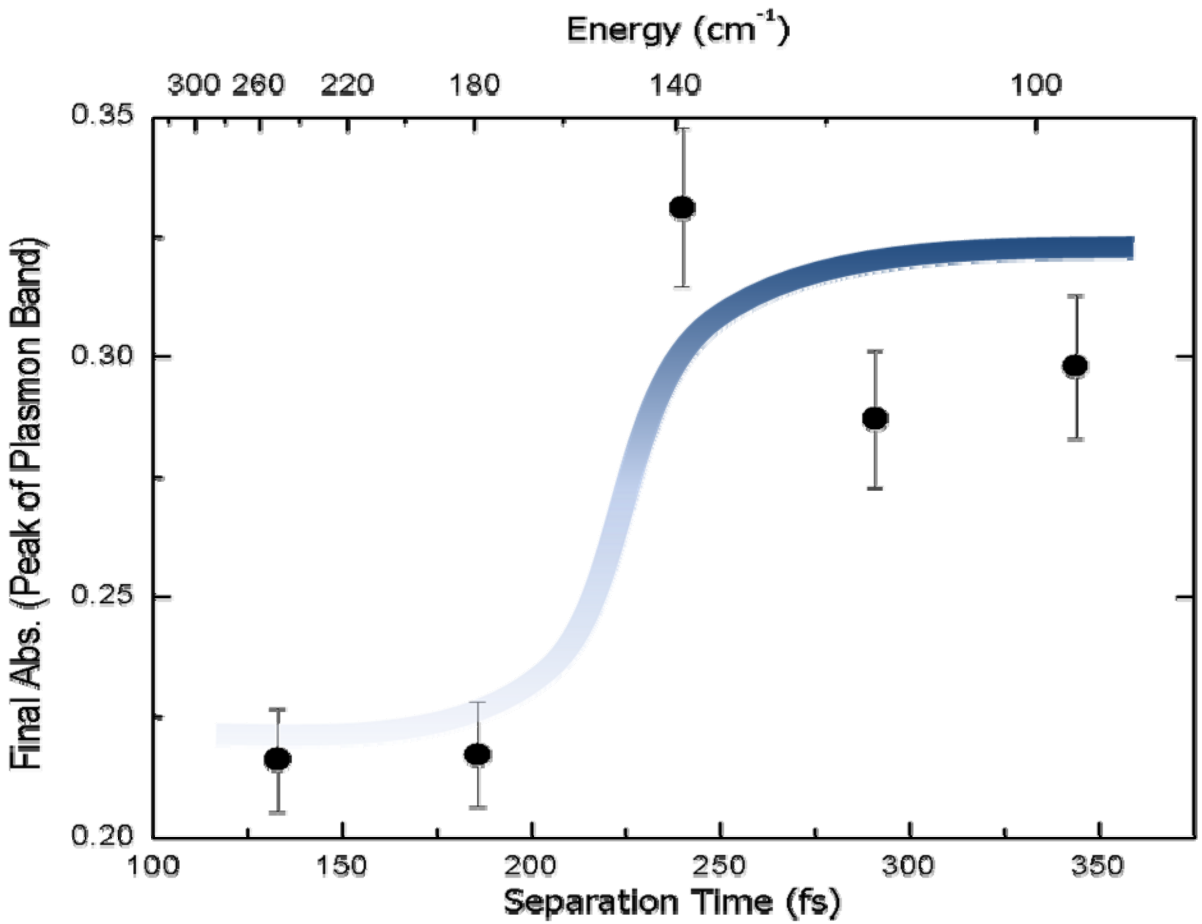




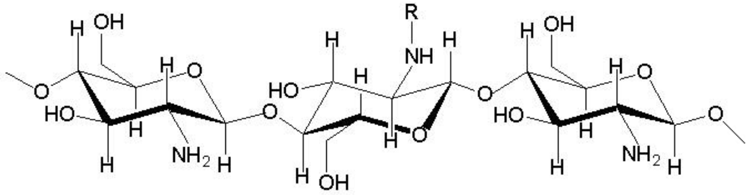
$N_{periods} = 11$

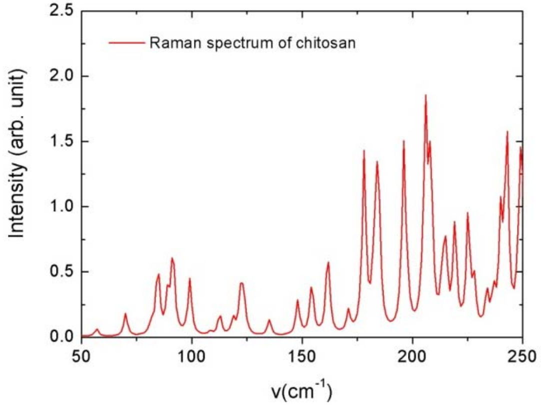
$t_{sep} = 291$ fs

Control of Au nanoparticles formation

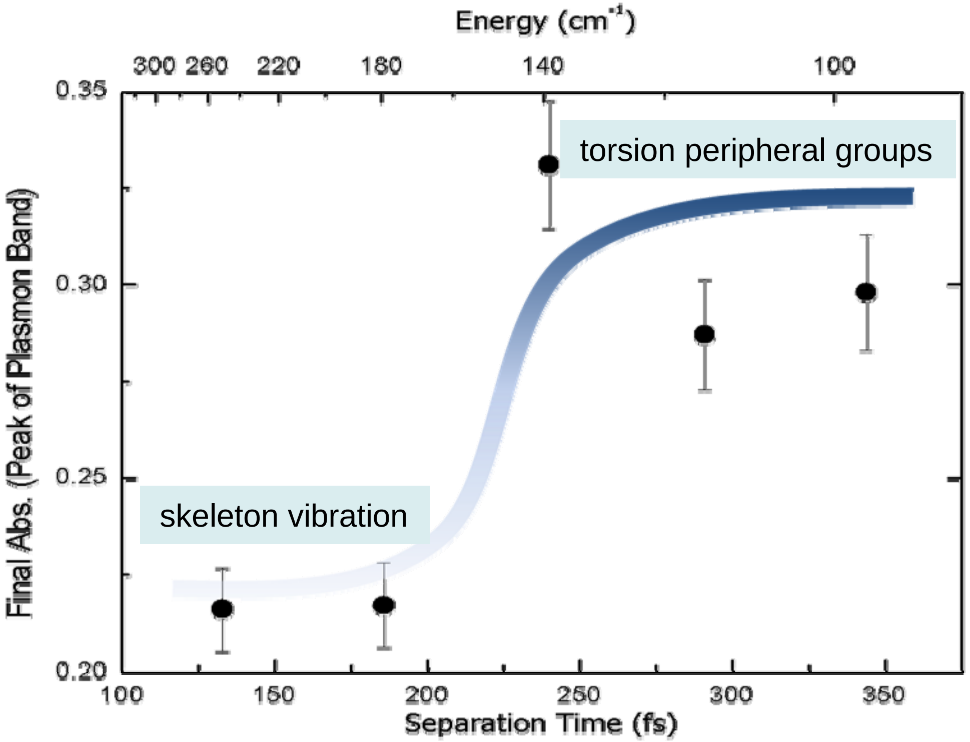


Control of Au nanoparticles formation





lower frequencies are related to peripheral groups (OH and NH_2), which are propably related to the gold photoreduction



Conclusions

Pulse shaping methods + coherent control of the nonlinear interaction seems to be an interesting method to further control nonlinear optical processes.

Acknowledgments

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