



Two-photon absorption dependence on the periodic phase modulation of femtosecond pulses

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Investigated Compounds

The investigated organic compounds in this work were: MEH-PPV, coumarin, fluorescein and the perylenes tetracarboxylic derivatives (PTCD) AzoPTCD and BePTCD, Fig.1. The absorption spectra in the UV-Vis region, obtained with a Cary 17 spectrophotometer, are presented in Fig.2. The organic compounds present strong two-photon absorption (2PA) when excited above linear absorption wavelength, at nonresonant region, with strong laser pulse. All them present a subsequent light emission, two-photon excited fluorescence (2PEF), that was used to monitored the 2PA process.

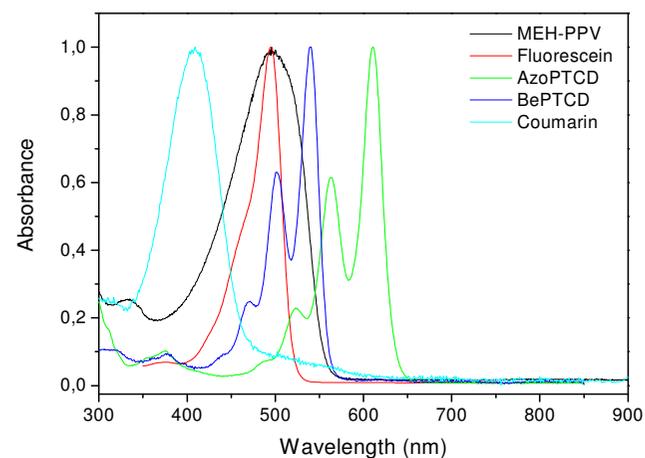
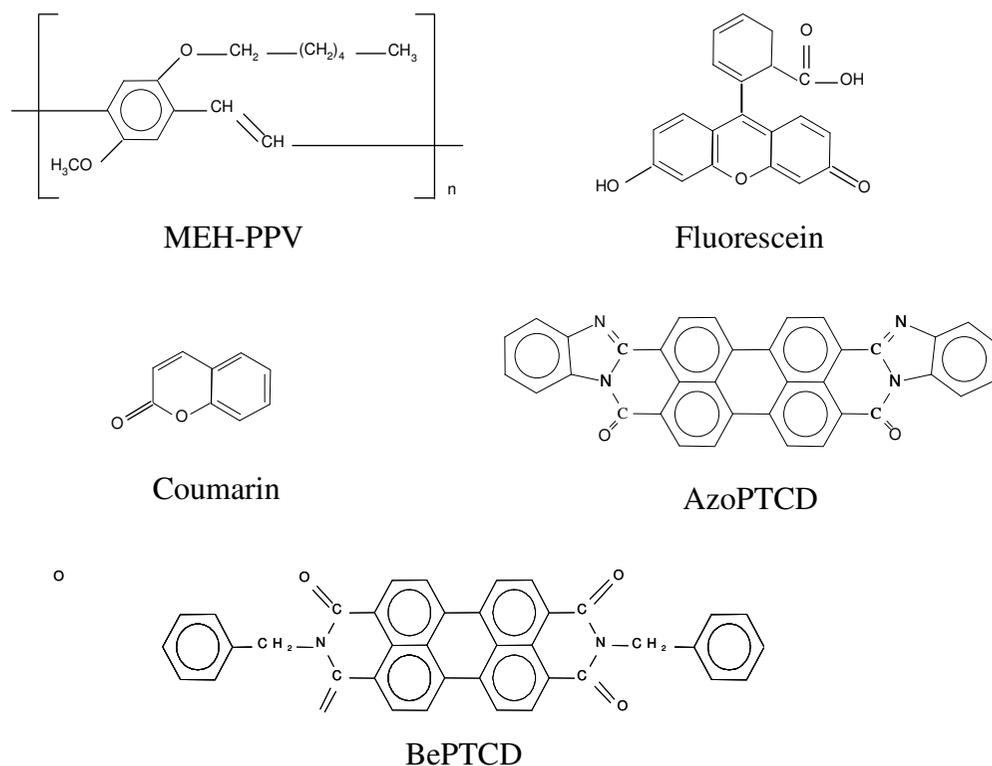


Figure 2: Absorbance spectra of the investigated compounds.

Figure 1: Molecular structures of the investigated compounds.

Two-Photon Absorption Modulation

As ready it is well-known, two-photon transition probability between atomic energy levels can be enhancement or totally canceled through pulse phase modulation Fig. 3, while at a molecular system the total two-photon transition probability, that in this case occur between energy levels (bands), can be enhancement being however possible to be only partially canceled, Fig. 4.

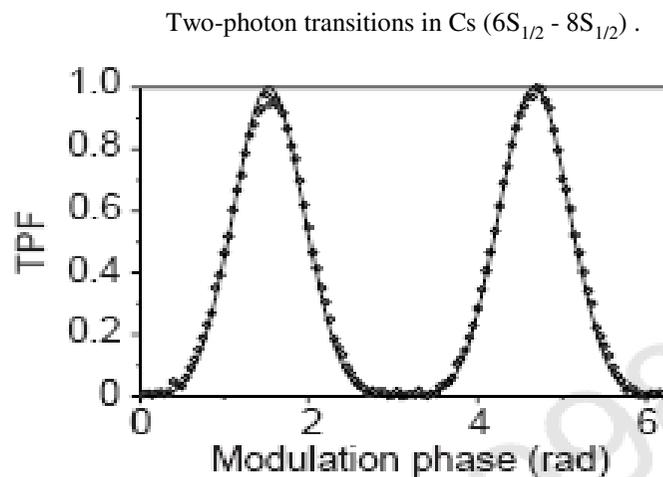


Figure 3: Coherent quantum control of two-photon transitions by a femtosecond laser pulse.
Doron Meshulach, Yaron Silberberg.
Nature, Vol.396, pg. 239 (1998).

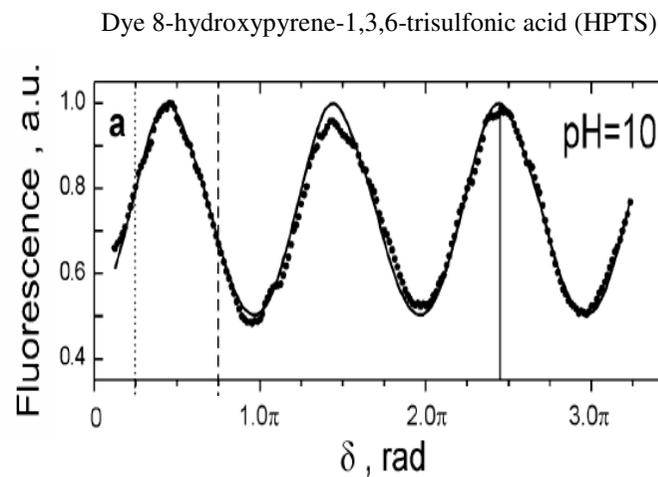


Figure 4: Multiphoton Intrapulse Interference 3: Probing Microscopic Chemical Environments
Johanna M. Dela Cruz, Igor Pastirk, Vadim V. Lozovoy, Katherine A. Walowicz, and Marcos Dantus
Journal of Physics Chemical, Vol. 108, pg 53 (2004).

It is presently unclear to what extent efficient laser control is possible via intrapulse interference on 2PA process in molecular systems. In this work, we investigate the efficiency differences observed in the coherent control over 2PA processes of some organic compounds achieved using well-defined phase modulation of the excitation pulse.

Theoretical Model

As already it was demonstrated in several works, in the two-photon interaction of an ultrashort pulse with a two-level atom, if the interaction is non-resonant (transition without intermediate states), the probability of inducing a transition to the excited state is proportional to:

$$S_2(\omega_0) \propto \left| \int_{-\infty}^{+\infty} A(\omega_0/2 - \Omega) A(\omega_0/2 + \Omega) \exp\{i[\Phi(\omega_0/2 - \Omega) + \Phi(\omega_0/2 + \Omega)]\} d\Omega \right|^2 \quad (1)$$

where $A(\omega)$ and $\Phi(\omega)$ are the spectral amplitude and the spectral phase of the spectral component ω of the ultrashort pulse.

However, for molecular systems the probability of inducing a two-photon absorption transition to the excited state is proportional to:

$$S_2(\Delta\omega) \propto \left| \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} g(\omega) A(\omega/2 - \Omega) A(\omega/2 + \Omega) \exp\{i[\Phi(\omega/2 - \Omega) + \Phi(\omega/2 + \Omega)]\} d\Omega \cdot d\omega \right|^2 \quad (2)$$

which convolves the n th-order spectral amplitude of the laser pulse with the absorption spectrum of the system $g(\omega)$. $g(\omega)$ is the responsible for introduce the effect of the lost strict resonance condition on the total probability of inducing a transition to the excited state in molecules.

Periodic Phase Modulation

We limit our investigation to periodic spectral phase modulation with

$$\Theta(\Omega) = \alpha \cos(\beta\Omega + \delta),$$

where α and β are the modulation depth and frequency modulation, respectively, and δ is the phase modulation. For a given power spectrum $|A(\omega)|^2$, it is obvious that S_2 in atomic and molecular systems is maximized by the TL pulse, that is, a pulse having the minimum time duration with $\Theta(\omega) = 0$.

➤ *Antisymmetric Spectral Phase Distribution*

For a pulse with the same power spectrum, but having any antisymmetric spectral phase distribution around the atomic two-photon transition frequency $\omega_0/2$, that is $\Theta(\omega_0/2 + \Omega) = -\Theta(\omega_0/2 - \Omega)$, the transition probability ω_0 in a atomic system is independent of the spectral phase, and is identical to that of the TL pulse. However, for an ultrashort pulse exciting a molecular system, this condition (antisymmetric spectral phase distribution) can not be satisfied for all two-photon transition frequency possible ($\Delta\omega$).

➤ *Symmetric Spectral Phase Distribution*

Although antisymmetric phase distributions around the atomic two-photon transition frequency $\omega_0/2$ do not affect the two-photon transition probability, other phase distributions can be tailored to cancel it. Such pulses having, for example, any symmetric spectral phase distribution around the atomic two-photon transition frequency $\omega_0/2$, that is, can cancel the transition probability in a atomic system. However, again, for an ultrashort pulse exciting a molecular system, this condition (symmetric spectral phase distribution) can not be satisfied for all two-photon transition frequency possible ($\Delta\omega$), what make impossible to realize total 2PA cancellation in molecular systems.

Experimental Setup

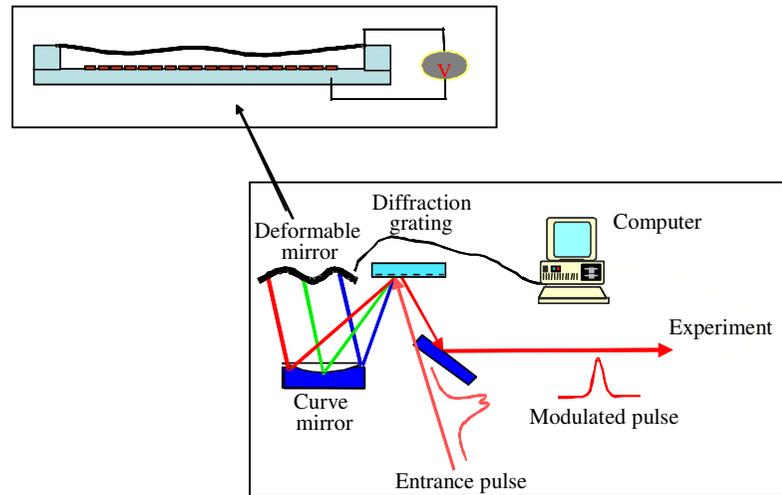


Figure 5: Experimental setup for ultrashort laser pulse shaping using periodic phase modulation.

In this investigation we used femtosecond pulses with around 40 nm of bandwidth and 25 fs of pulse duration, centered at 790 nm. The pulses were delivered by a commercial Ti:sapphire Kerr-lens modelocked (KLM) laser oscillator from K&M company, operating with a repetition rate of around 80 MHz. The typical used average power was 400 mW (~5 nJ per pulse). The 2PA efficiency was monitored by the intensity of the 2FEF, collected perpendicularly to the excitation beam direction using a silicon PIN photodetector coupled to a lock-in amplifier, Fig.6.

Our shaping technique uses a micromachined deformable mirror (MMDM) from OKO technologies to pulse shaping in the phase domain. The mirror in the MMDM is a 600 nm gold-coated silicon nitride membrane (8 mm x 30 mm) suspended over an array of 19 actuator electrodes on a printed circuit board. Potential applied to the actuator creates an electrostatic attraction between the membrane and the electrode, deforming the mirror surface. The MMDM is placed at the Fourier plane of a zero dispersion stretcher consisting of a 600 groove/mm ruled grating and a 25 cm focal-length mirror, Fig.5. In order to control the deformation of the MMDM we have used a program implemented in LabVIEW.

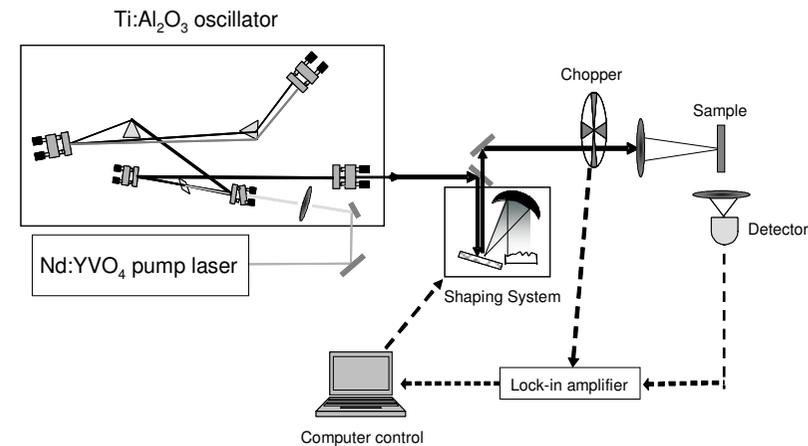


Figure 6: Experimental setup for 2PEF intensity measurement.

Experimental Results

The results obtained in the investigation of the organic compounds' 2PA dependence on the periodic phase modulation of femtosecond pulses are present in the Fig. 7. The data were normalized such that the maximum intensity observed was equals to unity.

Through our investigation scanning periodic spectral phase modulation on the deformable mirror we impose symmetric and asymmetric phase distributions on the pulse spectral components and we were able to understand better the importance of the intrapulse interference for the control of the 2PA processes and its dependence on the material absorption band (resonance enhancement of the two-photon absorption).

Deformation parameters

$$\Theta(\Omega) = \alpha \cos(\beta\Omega + \delta),$$

Deformation Scan: 4π ($\delta: 0 \rightarrow 4\pi$)

$$\alpha = 2\mu\text{m}$$

$$\beta = 3\pi/\Delta\omega_{\text{pulse}} = 3,1 \cdot 10^{-14} \text{ rad}^{-1}$$

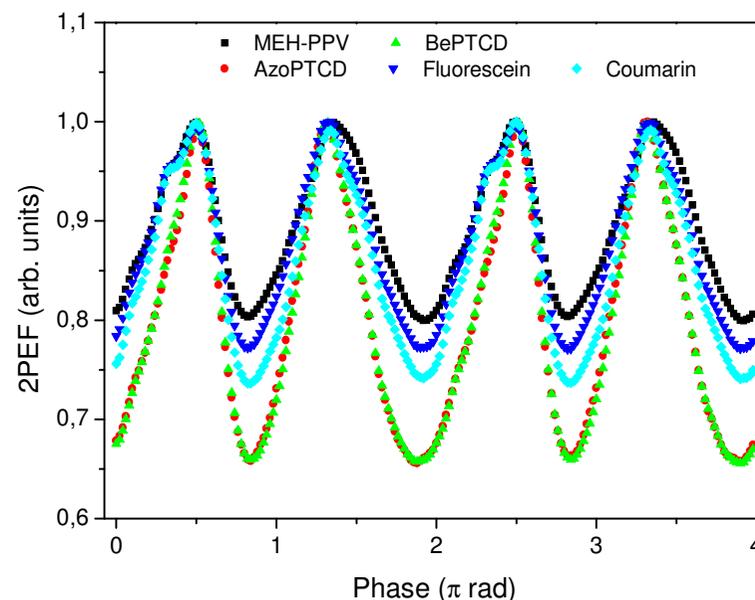


Figure 7: 2PA modulation of each one of the investigated organic compounds obtained scanning periodic spectral phase modulation on the deformable mirror.

Theoretical Calculation

Theoretical calculations of the convolution of the n th-order spectral amplitude of the laser pulse with the theoretical absorption spectrum of each one of the organic compounds ($g_{th}(\omega)$) were realized and the results obtained are present in the Fig. 8.

$$S_2(\Delta\omega) \propto \left| \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} g(\omega) A(\omega/2 - \Omega) A(\omega/2 + \Omega) \exp\{i[\Phi(\omega/2 - \Omega) + \Phi(\omega/2 + \Omega)]\} d\Omega \cdot d\omega \right|^2$$

$g(\omega) = \text{Lorentzian Function}$

<i>Compounds</i>	Lorentzian Function	
	$\lambda_c(\text{nm})$	$\Delta\lambda(\text{nm})$
MEH-PPV	490	90
Fluorescein	490	50
Coumarin	410	70
BePTCD	540	70
AzoPTCD	610	70

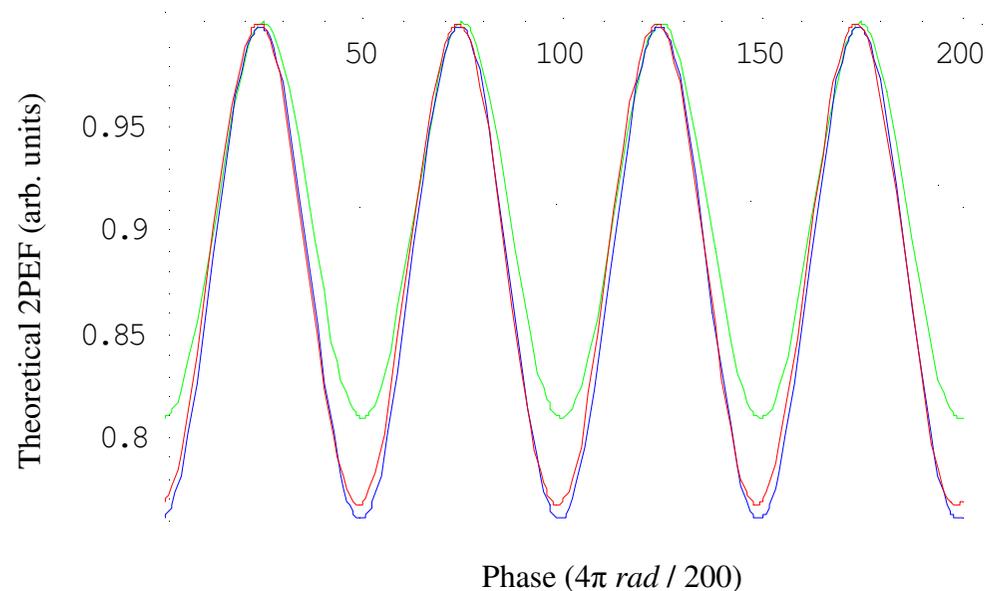


Figure 8: Theoretical calculations of the 2PA modulation of each one of the investigated organic compounds. The black, yellow, green, red and blue lines correspond to 2PA modulation of the MEH-PPV, fluorescein, coumarin, BePTCD and AzoPTCD respectively.

Conclusion

- We observed distinct amplitude modulation on the 2PA for each investigated organic compounds, which we believe are related to the detuning between the pulse spectrum and the material absorption band (for the compounds MEH-PPV, fluorescein and coumarin) and the effect of the resonance enhancement of the two-photon absorption (for the compounds BePTCD and AzoPTCD);
- Theoretical calculations of the convolution of the n th-order spectral amplitude of the laser pulse with the theoretical absorption spectrum of each one of the organic compounds ($g_{th}(\omega)$) were realized and the obtained results confirm the observed behavior;

Work Continuation: Analyzing the effect of the detuning of the laser pulse spectral band on the control of the two-photon absorption process of these organic compounds to confirm our interpretations.

