Control of Two-Photon Absorption in Organic Compounds by Pulse Shaping: Spectral Dependence

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In this work, we investigate the control of the two-photon absorption process of a series of organic compounds via spectral phase modulation of the excitation pulse. We analyzed the effect of the pulse central wavelength on the control of the two-photon absorption process for each compound. Depending on the molecules' two-photon absorption position relative to the excitation pulse wavelength, different levels of coherent control were observed. By simulating the two-photon transition probability in molecular systems, taking into account the band structure and its positions, we could explain the experimental results trends. We observed that the intrapulse coherent interference plays an important role in the nonlinear process control besides just the pulse intensity modulation.

1. Introduction

Thanks to the broad spectral band of ultrashort femtosecond lasers[1] and to the pulse shaping techniques available,[2–4] one can manipulate femtosecond pulses to control optical processes.[5–8] This approach has been responsible for advances in the understanding and controlling of light-matter interaction, especially in nonlinear optical processes. Nowadays, pulse shaping techniques have been used to investigate and optimize two-photon absorption (2PA),[9–12] a nonlinear optical process that has found important technological applications such as microscopy,[13] optical power limiting,[14] microfabrication,[15] and photodynamic therapy.[16]

The sensitivity of 2PA processes to the pulse spectral phase configuration is a consequence of the multiphoton intrapulse interference (MII) process.[11,12] For ultrashort pulses, different spectral components of the pulse can interfere constructively favoring a particular transition. This interference can be controlled through phase modulation of the pulse spectral components (pulse shaping), and used to achieve control of the 2PA.[9–12] The understanding of the coherent control of a given nonlinear processes, using pulse shaping techniques, is a very complex subject. Several parameters, besides the phase, may affect the nonlinear signal during the pulse shaping process, for example, pulse intensity modulation.

In this work, we present the coherent control of the 2PA processes on several organic compounds with specific linear absorption bands and 2PA features. Using pulse shaping, we modulated the spectral phase configurations (cosine-like phase mask) and analyzed its effect on the two-photon induced fluorescence intensity. We employed ultrashort laser pulses centered at 760, 800, and 840 nm to investigate the influence of the excitation wavelength on the control of the 2PA. We show different trends on the 2PA modulation, achieved by coherent control, as a function of the excitation pulse wavelength. In order to support the interpretation of our experimental results a theoretical model based on the evaluation of the second-order electric field spectrum was used.

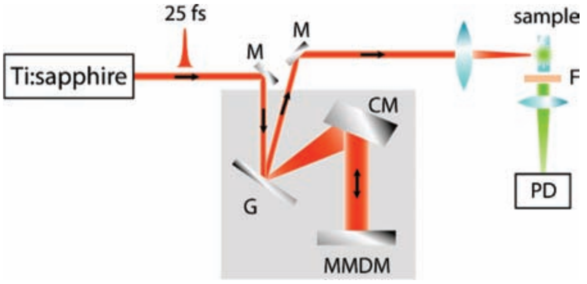

Figure 1. Experimental setup used for ultrashort pulse modulation two-photon excited fluorence 2PEF detection.

2. Experimental Section

The compounds investigated in our study were bis(benzimidazo) (AzoPTCD) and bis(benzylimido) (BePTCD) perylene tetracarboxylic derivatives (PTCDs),[17] fluorescein[18–20] and coumarin 522[19,20] dyes and a conjugated polymer known as MEH−PPV.[21] The PTCDs were diluted in 10% by volume trifluoroacetic acid /dichloromethane (0.5 mg/mL). Coumarin 522 and fluorescein were dissolved in methanol, and MEH−PPV was dissolved in chloroform, at a concentration of 0.5 mg/mL. The absorption spectra of all compounds in the UV−vis region were obtained with a Cary 17 spectrophotometer.

The experimental scheme used in this work is shown in Figure 1. The ultrashort laser pulse were produced by a Kerr-lens modelocked Ti:sapphire oscillator (~5 nJ and 80 MHz of repetition rate). The laser was adjusted to provide pulses with about 40 nm spectral bandwidth (~25 fs temporal duration) and centered at three different wavelengths; 760, 800, and 840 nm. A micromachined deformable mirror (MMDM)[4] was used to shape the phase of the pulse spectral components. The deformable mirror is a 600 nm gold-coated silicon nitride membrane (8 mm × 30 mm) suspended over an array of 19 electrode actuators. The MMDM was placed at the Fourier plane of a zero-dispersion stretcher consisting of a 600 groove/mm ruled grating (G) and a 25 cm focal-length curved mirror (CM). The deformation of the mirror was controlled by computer.

The phase-modulated pulses were focused into the sample using a convergent $f = 10$ cm lens. The two-photon excited

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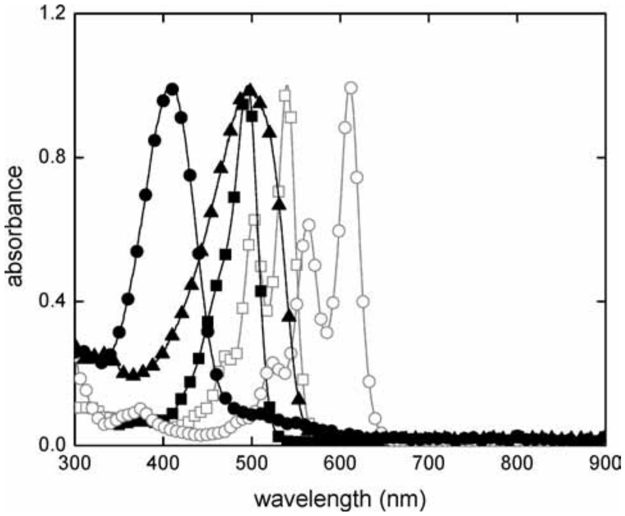

Figure 2. Absorption spectra in the UV−vis region of coumarin (●), MEH−PPV (▲), fluorescein (■), AzoPTCD (○), and BePTCD (□).

fluorescence (2PEF) was collected perpendicularly to the cuvette using a photo detector (PD) and a filter (F) to block the excitation laser light. As a reference signal, second-harmonic generation (SHG) from a KDP crystal (0.7 mm-thick) was measured as a function of the phase-mask.

We used a cosine-like spectral phase modulation with $\Phi(\omega) = \alpha \cos(\beta\omega + \delta)$, where α and β are the modulation depth and frequency of modulation, respectively, and δ is the phase. By scanning δ, we imposed sequentially symmetric and asymmetric phase modulations on the pulse spectral components and analyze the control on the 2PA process. The modulation observed on the SHG process of the KDP crystal was used as a reference signal (effective pulse intensity) for each spectral phase configuration introduced to the pulse. Linear chirp[1] (quadratic spectral phase) was introduced in the ultrashort pulse by changing the distance between the curved mirror (CM) and the MMDM, which was kept off (flat configuration) for this case.

The pulse characterization (phase, spectrum and temporal duration) for different phase configurations was performed with the FROG (frequency resolved optical gating) technique[22] (using the GRENOUILLE device).

3. Results

Figure 2 shows the absorption spectra in the UV−vis region of the compounds investigated. The samples are completely transparent around 800 nm, region where the two-photon excitation was carried out.

The results obtained in the study of the 2PA control using cosine-like spectral phase modulations are presented in the Figure 3a. The cosine-like phase modulation imposed to the micromachined deformable mirror used $\alpha = 0.5\pi$, $\beta = 2\pi/\Delta\omega_{\text{pulse}}$, where $\Delta\omega_{\text{pulse}}$ is the pulse frequency bandwidth (full-width at half-maximum − fwhm). This cosine-like phase modulation was scanned on the deformable mirror by varying δ from 0 to 4π. The data were normalized to enhance the contrast between the symmetric ($\delta = n\pi$) and asymmetric ($\delta = (2n + 1)\pi/2$) conditions.

It is worth mentioning that for all samples, the 2PEF intensity observed for a phase mask with $\delta = 0.5\pi$ is approximately 80% of the signal obtained for a Fourier transform limited (TL) pulse,[1] for each compound.

As one can observe in Figure 3a, the modulation observed on the 2PEF for the compounds are quite different, being ~20% for MEH−PPV, fluorescein and coumarin 522, and ~35% for BePTCD and AzoPTCD. The experimental parameters were kept the same for all samples to allow the comparison among the amplitudes of modulation. From Figure 3a, we also observe that the SHG process presents the higher amplitude of modulation.

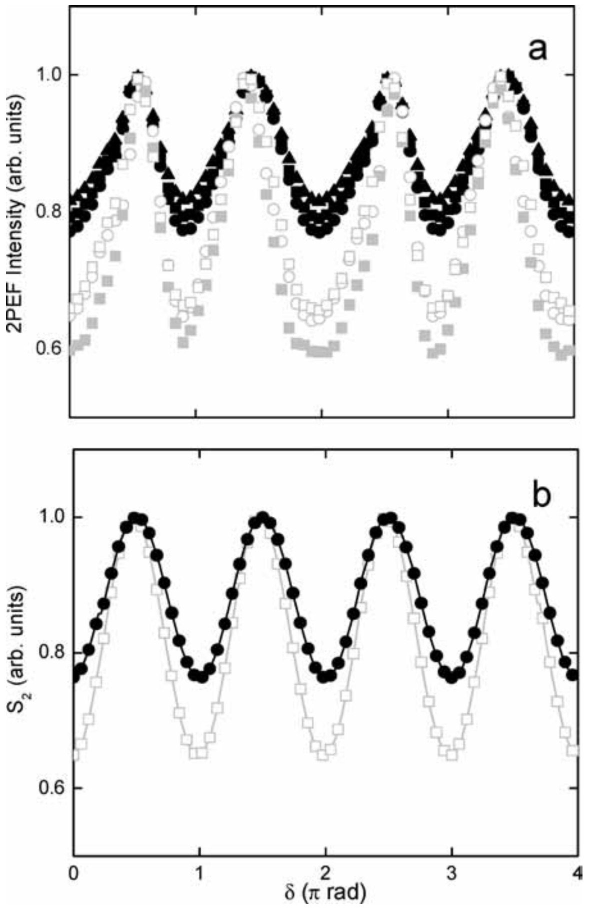

Figure 3. Normalized 2PEF (and SHG) modulation of the compounds obtained scanning the cosine-like phase mask, with pulse centered at 800 nm. (a) Experimental results for MEH−PPV (▲), fluorescein (■), coumarin 522 (●), BePTCD (□), AzoPTCD (○), and SHG (gray box). (b) Simulation obtained for the normalized modulation for two distinct 2PA bands interactions: (●) coumarin's group and (□) PTCDs' group.

To extend our investigation on the 2PA control of these compounds, we repeated the experiment of Figure 3a using fs-pulses centered at 760 and 840 nm. The results obtained (amplitude of modulation as a function of excitation wavelength) were gathered and are presented in the Figure 4a.

As one can observe in the Figure 4a, the control of 2PA process of each organic compound is affected by the central wavelength of the phase-modulated pulse. For SHG, similar modulations were obtained for the three excitation wavelengths, which mean that the pulse intensity modulation was similar in the three conditions. It is interesting to observe that while for BePTCD and AzoPTCD the modulation of the 2PEF increases when the laser spectral band was shifted to the red, for coumarin 522, fluorescein and MEH−PPV the opposite behavior was observed.

4. Discussion

Two types of experiments were made with cosine-like phase modulation. In the first one (Figure 3a) we kept the excitation pulse wavelength fixed and observed different modulations on

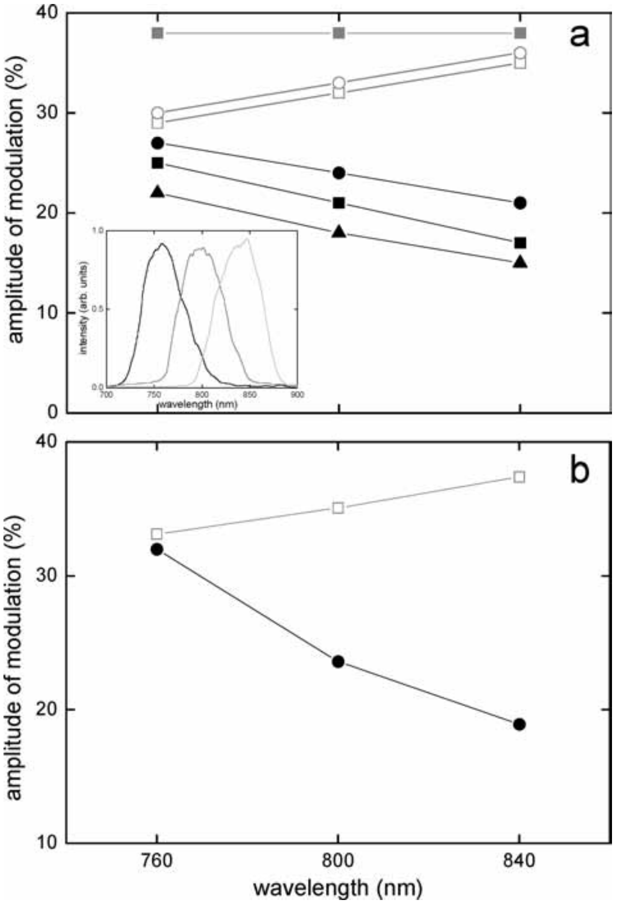

Figure 4. Nonlinear signal modulation of the compounds using ultrashort pulses centered at three different wavelengths, 760, 800, and 840 nm (shown in the inset). (a) Experimental results for MEH−PPV (▲), fluorescein (■), Coumarin 522 (●), BePTCD (□), AzoPTCD (○) and SHG (gray box). (b) Simulation for the two groups using the appropriate 2PA bands.

the 2PEF signal for each sample. In the second one (Figure 4a), we changed the excitation wavelength and observed two distinct trends in the modulation for two distinct groups of compounds. Our results show that asymmetric phase configuration ($\delta = (2n + 1)\pi/2$) influence the 2PEF in the same way. In this case, the 2PEF intensity is approximately 80% of the one obtained with the TL pulse, for each compound investigated. On the other hand, when a symmetric phase mask is used ($\delta = n\pi$), a higher amplitude of modulation is observed for PTCDs than for the other compounds (coumarin 522, fluorescein and MEH−PPV), as can be seen in Figure 3a. This result indicates that 2PA is more efficiently diminished in PTCDs, by the introduction of a symmetric phase mask, than in coumarin 522, fluorescein and MEH−PPV. To verify that such different amplitudes of modulation, for these two groups of materials, are related to distinct intrapulse quantum interference processes and not to the pulse intensity (SHG signal in Figure 3a), we performed the experiments tuning the laser wavelength (Figure 4a). From the results in Figure 4a, we see that the detuning between the pulse spectrum and the materials' absorption bands affects the action of the pulse spectral phase configuration on the intrapulse quantum interference taking place in each compound.

Because the pulse intensity modulation is the same for these three excitation wavelengths (Figure 4a, SHG), the increase observed on the modulation amplitude for PTCDs (Figure 4a, open symbols) to the red should be related to the fact that the intrapulse quantum interference is stronger affected by the symmetric phase configuration imposed to the pulse in this condition. For coumarin 522, fluorescein, and MEH−PPV, in contrast, the intrapulse quantum interference is stronger affected by the phase configuration imposed to the excitation pulse in the bluer excitation condition. These distinct behaviors seem to indicate that the detuning between the second-order pulse spectrum and the two-photon absorption band of the materials investigated affect the control over the 2PA process. Such assumption was verified by modeling the experimental results assuming that the two-photon transition probability to an excited-state in molecular systems is describes by[11,12]

$$S_2 \propto \int_{-\infty}^{+\infty} g(\omega)\left|\int_{-\infty}^{+\infty} E(\omega/2 - \Omega)E(\omega/2 + \Omega)\, \mathrm{d}\Omega\right|^2 \mathrm{d}\omega \qquad (1)$$

where $E(\omega) = A(\omega) \exp[i\Phi(\omega)]$ refers to the electric field of the ultrashort pulse with $A(\omega)$ and $\Phi(\omega)$ being its amplitude and spectral phase, respectively. Ω is the spectral detuning between the pulse frequency and half of the electronic transition frequency ($\omega/2$) considered. Equation 1 reflects the fact that two-photon transition occurs for all pairs of photons of the excitation pulse, whose frequencies are complementary to induce a given electronic transition at ω. For this reason, every spectral component of the ultrashort pulse contributes to the effective two-photon absorption transition induced in the system, and the transition probability can be controlled by modulating the phase of the pulse spectral components. For a pulse centered at the two-photon transition frequency $\omega_0/2$, having an asymmetric spectral phase configuration ($\Phi(\omega_0/2 + \Omega) = -\Phi(\omega_0/2 - \Omega)$), the two-photon absorption probability is maximized. However, symmetric spectral phase configuration ($\Phi(\omega_0/2 + \Omega) = \Phi(\omega_0/2 - \Omega)$) decreases the 2PA probability. In order to describe the two-photon process of molecular systems, eq 1 convolutes the second-order spectrum amplitude of the excitation pulse with the function $g(\omega)$, responsible for introducing the broad spectral band of two-photon allowed states.[11,12]

Using eq 1 and employing appropriated values for the parameters that describe the laser pulse spectrum, the cosine-like spectral phase and the 2PA absorption band of the compounds, we carried out simulations to support the results obtained and their interpretations (Figure 3b and Figure 4b). The laser pulse bandwidth ($\Delta\lambda \sim 40$ nm) at 760, 800, and 840 nm was experimentally obtained (fwhm). The spectral phase mask parameters were also directly obtained from the experiment.

For the two-photon absorption parameters of the studied compounds, which are related to their molecular structures, we used the information available in the literature. MEH−PPV is known to present a two-photon absorption band around 337 nm (3.68 eV).[21] Although the 2PA spectrum of coumarin 522 have not been reported, coumarin 307 and coumarin 485 present a 2PA peak at 400 and 390 nm in methanol, respectively.[19,20] As for fluorescein, this compound is shown to exhibit a 2PA peak at approximately 385 nm in water.[19,20] In general, it seems reasonable to say that, for the compounds studied here, the 2PA band is located in the UV-region. This way, to model MEH−PPV, coumarin 522 and fluorescein (first group of experimental results) we have assumed that the 2PA band is centered at approximately 340 nm with a bandwidth of 80 nm. PTCDs, however, present two-photon absorption peaks around the minima of the one photon absorption bands.[17] For the PTCDs investigated here, the center of the two-photon absorption band, available with excitation around 800 nm, is located around 420 nm. Such a value was used to simulate the experimental results obtained for PTCDs (second group of experimental results).

Figure 3b shows the simulation results obtained using the parameters described previously for the two groups of compounds, considering laser excitation at 800 nm. As it can be seen, the simulations describe very well the two behaviors observed experimentally. In addition, in Figure 4b we gathered the simulation results obtained for the pulse spectrum centered at 760, 800, and 840 nm. As one can see, the simulations describe correctly the experimental trends (Figure 3a and Figure 4a). For MEH−PPV, coumarin 522 and fluorescein the model predicts a decrease in the amplitude of modulation as the excitation pulse moves to the red while the opposite behavior is predicted for the PTCDs. Such behavior is due to the relative position between the second-order pulse central frequency and the two-photon absorption band of each group of material. For PTCDs, for instance, the two-photon state (420 nm) is centered at lower energy than the second-order pulse central frequency. Of course, for the other compounds, the reverse argument is valid.

Therefore, the simulation results clearly allow one to state that the different spectral shift (positive or negative) between the second-order pulse spectrum and the two-photon absorption band is the main reason to the two distinct trends observed as the excitation pulse spectrum is changed. However, as the second-order pulse spectrum approaches the molecule's 2PA band, a higher modulation is achieved by the coherent control method in both cases.

To further confirm that the differences observed in the control of the 2PA are in fact related to the intrapulse quantum interference process for each compound, we investigated the 2PEF dependence with the quadratic phase configuration. The insertion of quadratic phase (linear chirp) in the ultrashort pulse produces its temporal stretching and therefore the reduction of its peak intensity.[1] We observed that the linear chirp (positive or negative) reduces the 2PEF intensity in all compounds in the same manner as for the SHG intensity. Therefore, this result supports that the intrapulse quantum interference process is very effective to control the nonlinear process beyond the simple intensity variation.

5. Conclusions

By applying cosine-like phase masks to a fs-laser pulse we studied the control of the 2PA in different organic compounds. Our results show that the coherent control of the 2PA process depends on the detuning between the 2PA band of compounds and the second-order pulse spectrum. Such results were verified by simulations based on the evaluation of the two-photon transition probability in molecular systems, taking into account the spectroscopic features of the studied molecules. This study brings new insights on the understanding of the coherent interaction of molecules and laser, with potential applications in nonlinear spectroscopy.

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