Research Article

Optical control of excited state dynamics

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Abstract

In this article the author has reported on the field and one experimental result of optical control of ultrafast processes with the help of programmable pulse shaping technique by use of spatial light modulators. By modulating one or more laser pulse parameters, the shaped pulse is generated. Multiparameter control shaped pulse is iteratively obtained through the feedback mechanism and an automated optimization algorithm. I have presented an experimental result of obtaining a shaped pulse that decreases the absolute magnitude of transmittance change of a cyanine dye by controlling the decay pathway from $S_1$ state to an energy state below $S_1$ state.

Key Words: Optical control, Pulse shaping, Excited state dynamics

Introduction

The careful observation is the first step to understand nature. Advancement of ultrafast laser technology enables us to observe with high spatial and temporal resolution. The next should be the control of atoms and molecules involved in chemical reactions. The last two decades saw remarkable progress in the development of experimental methods for the optical control of chemical pathways and today, there is tremendous interest in the coherent control process among researchers.\textsuperscript{1-7} Several experimental techniques have been developed for various optical control concepts applicable to different quantum systems.\textsuperscript{1-3} Tsubouchi et al examined a technique of complex shaping of mid-infrared femtosecond laser pulses towards accurate and precise control of rovibrational wave packets of molecules in the ground electronic state by a Germanium acousto-optics modulator.\textsuperscript{4} F van Hulst and coworkers developed a universal method that allows full femtosecond pulse control in subdiffraction-limited areas by exploiting the intrinsic coherence of the second harmonic emission from a single nonlinear nanoparticle of deep subwavelength dimensions.\textsuperscript{5} Among the various methods, femtosecond pulse shaping, one of the most powerful tools for the quantum control
of photochemical reaction pathways, is now the most widely accepted tool by researchers. The recent growth of coherent control studies is based on pulse shaping technology.\(^2\) By phase/amplitude modulation, one may select the possible result of photoinduced physical or chemical processes as optical phase properties influence the excited state. The femtosecond pulse shaping is based on the use of spatial light modulator which is nothing but a spatially patterned amplitude and phase masks modulates phase and amplitude of ultra short pulse.\(^2\) A phase mask selectively delays colors and an amplitude mask shapes the spectrum. There are three types of spatial light modulators: Liquid crystal arrays, Acousto-optic modulators, Deformable mirrors. Among them, liquid crystal SLM is widely used due to its efficiency in both phase and amplitude modulation.

![Schematic diagram of pulse shaping technique using SLM](image)

**Figure 1:** Schematic diagram of pulse shaping technique using SLM

Generally, an optimization algorithm is used to form a shaped laser pulse obtained by automated search, via iteration loops, and then the phase-modulated laser pulse is utilized to achieve the desired outcome.\(^2-3\) By manipulating coherent light-matter interaction with the shaped pulse obtained by an appropriate program used with a feedback loop that optimizes the pulse, various chemical dynamics may be controlled to produce many interesting results.\(^3\) Genetic algorithm (GA) is suitable for this purpose.\(^9-11\)

Many groups are already succeeded to control different physical and chemical processes. Using GA, Assion et al. selectively controlled the photodissociation reactions of metal carbonyl complex in the gas phase.\(^9\) Taking practical importance into consideration, one may be interested in relevant work in the liquid phase.\(^10\) Numerous experiments and applications on a variety of condensed phase quantum systems have been realized using these
control methods. The control of two-photon excitation efficiency,\textsuperscript{12-14} photoisomerization (primary step of vision),\textsuperscript{14-16} bond activation,\textsuperscript{17} femtosecond photoassociation of thermally hot atoms in the gas phase,\textsuperscript{18} molecular switching processes,\textsuperscript{19} and different photoinduced processes\textsuperscript{9-10} has been demonstrated by many workers. Adaptive laser pulse shaping has enabled to control the photophysical processes in complex molecules. Kuroda et al. were able to enhance the emission quantum yield of a donor-acceptor macromolecule (a phenylene ethynylene dendrimer tethered to perylene) by 15\% through iterative phase modulation of the excitation pulse and isolated the dominant elements underlying the control mechanism.\textsuperscript{20} Scientists have also started to control biological system. Prokhorenko et al. succeeded to control the isomerisation of 13-cis retinal isomer of bacteriorhodopsin.\textsuperscript{21} Mayumi et al. succeeded to control of ultrafast cis-trans photoisomerization of retinal in rhodopsin via a conical intersection by optimally designed pulses, consist of shaping subpulses that prepare a wave packet, which is localized along a reaction coordinate and has little energy in the coupling mode, through multiple electronic transitions.\textsuperscript{22} Very recently, orbital and spin dynamics in a solid-state defect has been optically controlled by using picosecond resonant pulses of light.\textsuperscript{23} Not only in ground state, but also, people have examined a technique of complex shaping of mid-infrared femtosecond laser pulses towards accurate and precise control of wave packets of molecules in the ground electronic state.\textsuperscript{24} However, much more information of the energy levels and the excited state properties of the system is required to gain a thorough understanding of the detailed mechanism.

Carbocyanine dyes are important for their use as saturable absorbers in mode-locked laser systems.\textsuperscript{25} Because they have strong absorption bands ascribed to the S\textsubscript{0} \rightarrow S\textsubscript{1} transition in the visible and IR regions. Recently, Misawa and Kobayashi studied the dependence of wave packet dynamics of a cyanine dye on the chirp rate of the excitation pulse because transient processes depend on the temporal form of the optical pulse,\textsuperscript{26} and found a dramatic difference in the temporal behaviour of the transmittance with negatively and positively chirped excitation pulse. Using chirped laser pulse, they investigated the mechanism for the control of wave packet dynamics. Very recently, Horikoshi et al. observed wave-packet dynamics, dependent on the pulse chirp by developing a sensitive wave packet spectrometer.\textsuperscript{27} As many excited state processes are closely related to vibrational wave packet dynamics, it may be used as a reference for coherent control.\textsuperscript{28} Pulse shaping techniques are more efficient for the control scheme than single-parameter control, such as the use of chirped excitation pulse. In this work, instead of chirped pulse, we studied the effect of phase-controlled shaped pulse on the transient
absorption of the cyanine dye, 3,3'-diethylthiatricarbocyanine iodide (DTTCI), in methanol solution as the femtosecond shaped pulse is more selective than linear chirping. The basic aim of this work was to observe the effect of shaped pulse used as the excitation pulse for \( S_0 \rightarrow S_1 \) transition of the DTTCI molecule on the transmittance change of an ordinary probe pulse. Our study may provide a crude idea of the control of the decay pathway from the \( S_1 \) state of DTTCI by adaptive pulse shaping. As already discussed above, spectral phase modulated laser pulse is capable of controlling the desired target, and the main goal of this study was to observe the effect of pulse shaping on the excited state dynamics of the DTTCI molecule. In this work, we were able to control the said decay pathway using the pulse shaping technique. The most important finding is that the absolute value of transmittance change is drastically decreased by the shaped pulse.

**Experimental**

The femtosecond laser system consisted of a mode-locked Ti:sapphire laser (Mira Seed, Coherent) pumped by an Nd:YVO\(_4\) laser (Verdi-6, Coherent). Center wavelength of the exciting laser beam was 795 nm, pulse width was approximately 50 fs, and repetition rate was 76 MHz (Fig. 2). A 4\(f\)-configuration zero-dispersion compressor setup (1200 grooves/mm grating) was used for spatial dispersion of the frequency spectrum and recollimation of the laser pulse. The spatially dispersed laser pulse was focused on a liquid-crystal display (LCD) in a spatial light modulator (SLM-256-NIR, CRI). Pulse shape control was achieved by applying a specific voltage to each pixel in the LCD and modulating the phase spectra of the input pulse in the frequency domain. Transmitted pulses were then reassembled to shaped pulse with a cylindrical output lens and a grating. The zero-order reflection beam from the input grating of the pulse shaper was used as the probe beam of the ordinary pump-probe experiment. The beam of the shaped pulse was modulated at 672 Hz by a mechanical chopper, and scattered light from the chopper was monitored by a photodiode and used to measure laser power. The shaped pulse and the probe pulse were focused on the same position of a sample cell after passing through optical delay lines. The intensity of the transmitted probe pulse was monitored by a photomultiplier after passing through a filter and a monochromator, and the modulated component corresponding to the transient absorption was subjected to phase-sensitive detection using a lock-in amplifier. The emission intensity from the sample was also monitored by another photomultiplier after passing through another monochromator and filter simultaneously.
During optimization, the blended crossover method and the minimal generation gap method were adopted as the evolution operators in GA. Pulse shape was modified to optimize the fitness, the ratio of laser power ($I_{LP}$) to the absolute value of transmittance change ($I_{Tr}$), i.e., $I_{LP}/I_{Tr}$, or the ratio of emission intensity at 850 nm ($I_{Em}$) to the absolute value of transmittance change ($I_{Tr}$), i.e., $I_{Em}/I_{Tr}$.

DTTCI (Exciton) and methanol (Wako) were used as received. Methanol solution of 1 mM DTTCI was circulated in a 0.2 mm thick quartz flow cell.

**Results and discussion**

The temporal behaviour of the transmittance of the probe pulse was measured as a function of delay time between pump pulse and probe pulse. The transmittance change at the negative delay time corresponding to approximately 13.7 ns delay from the previous pump pulse shows a negative value (Fig. 3a) that indicates the increase of absorbance by the pump pulse irradiation.
In the case of the pump-probe experiment that is related to only two level systems, $S_0$ and $S_1$, the transmittance change should be positive and converge to zero. In our experiment, however, the transmittance change has a negative value and its magnitude at the positive delay time is comparatively smaller than that at the negative delay time, -10 ps (Fig. 3a). This would be ascribed to the presence of pump-induced absorption from an energy state that lies just below the $S_1$ state of the DTTCI molecule (Fig. 4) and has a lifetime much longer than 14 ns (time interval between the two successive pump pulses). Hereafter, the long-lifetime energy state is abbreviated as transit state.

From the temporal profile of the transmittance change, it is clear that after excitation to the $S_1$ state, transmittance is relatively increased as a result of ground state bleaching or
stimulated emission, and then the molecules start to decay to the transit state. However, the magnitude of the transmittance change is small up to 10 ps (Fig. 2). This would be attributed to the fact that the time constant for the decay pathway from the \( S_1 \) state to the transit state is much larger than 10 ps. The large negative value of the transmittance change at negative delay time is due to the absorption of long-lifetime DTTCI molecules in the transit state and the absolute value of the transmittance change is found to be directly proportional to the laser power. In this context, it should be mentioned that the lifetime of DTTCI molecules in the \( S_1 \) state is about 1.3 ns.\(^{29}\)

In our optimization experiment, we succeeded in decreasing (approximately 0.64 times in comparison with an ordinary single pulse) the absolute value of the transmittance change by using the optimized shaped pulse (Table 1). We used the evaluation function to optimize the excitation pulse shape is \( I_{LP} / I_{Tr} \) at two different delay times (-10 ps and 1 ps) as our aim is to change the contribution of long-lifetime components in the transit state. One significant finding of our optimization experiment is that the maximum value of the evaluation function is obtained within the range of 1.3-1.4.

**Table 1:** Magnitude of transmittance change, laser power, and emission intensity with single pulse and shaped pulse optimized using the evolution function of \( I_{LP} / I_{Tr} \)

<table>
<thead>
<tr>
<th>Nature of Pulse</th>
<th>Laser Power at 850 nm (arb. unit) ((I_{LP})^a)</th>
<th>Emission Intensity at 850 nm (arb. unit) ((I_{Em})^a)</th>
<th>Absolute Value of Transmittance Change (arb. unit) ((I_{Tr})^a)</th>
<th>( I_{Em} / I_{Tr} )</th>
<th>( I_{Em} / I_{LP} )</th>
<th>( I_{Tr} / I_{LP} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Pulse</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Shaped Pulse (optimized at -10 ps)</td>
<td>0.85</td>
<td>0.84</td>
<td>0.64</td>
<td>1.32</td>
<td>0.99</td>
<td>0.75</td>
</tr>
<tr>
<td>Shaped Pulse (optimized at 1 ps)</td>
<td>0.85</td>
<td>0.83</td>
<td>0.63</td>
<td>1.35</td>
<td>0.98</td>
<td>0.74</td>
</tr>
</tbody>
</table>

\(^a\) Normalized to data corresponding to the single pulse

From Table 1, it is clear that the excitation pulse energy (laser power) is decreased to approximately 0.85 times (compared to the single pulse) with the optimized pulse. This decrease in laser power results in 0.84 times decrease in the emission intensity at 850 nm with the shaped pulse (Table 1). In this context, it is noted that the value of \( I_{Em} / I_{LP} \) is 0.99, which
means that the excitation efficiency of the optimized shaped pulse is the same as that of the unshaped single pulse.

From the optimization experiment with the evaluation function $I_{Em}/I_{Tr}$ at the negative delay time (-10 ps), we observed that the emission intensity at 850 nm is decreased to approximately 0.9 times with the optimized excitation pulse as a result of the small decrease in laser power, as we have already mentioned that the excitation efficiency remains unchanged with the shaped pulse. However, the magnitude of change in the transmittance intensity is decreased to approximately 0.65 times of that obtained by the single pulse and the maximum value of the evaluation function is approximately 1.4. The change of $I_{Em}/I_{Tr}$ (also $I_{LP}/I_{Tr}$) is not due to the intensity decrease of the pump pulse because the magnitude of transient absorption is proportional to the pump intensity, as described above. This indicates that the genetically evolved optimized laser pulse is capable of controlling the magnitude of transmittance change at negative delay time. The decrease in the magnitude of transmittance change obtained by the shaped pulse can be attributed to the presence of a relatively small number of DTTCI molecules in the transit state. This may be due to the fact that the decay rate from the $S_1$ state to the transit state is decreased by the shaped pulse as the absorption of DTTCI molecules lying in the transit state.

On the assignment of the transit state, DTTCI molecule is known to undergo the trans-cis photoisomerization following the $S_1 \leftarrow S_0$ transition. Namely, the DTTCI molecules excited to the $S_1$ state by the optimized laser pulse would have two different fates. One is the return to the $S_0$ state by radiative or non-radiative pathway, and another is the non-radiative decay from $S_1$ to the ground state of photoisomer. In a previous work, Fouassier et al. observed the photoisomerization process in DTTCI molecules and reported the absorption maximum at 800 nm. Sahyun and Serpone reported the photoisomerization involving some radiationless deactivation of photoexcited cyanine dyes. However, according to Kovalenko et al, photoisomerization is usually observed when the molecules are excited at the blue end of the absorption band with very high pulse energy. We excited DTTCI molecules at the red end (795 nm) and the pulse energy of our setup is much lower (approximately 1 nJ) than the required amount. It should be noted that Lee et al. did not observe the photoisomerization process even with the pulse energy of approximately 40 nJ. In order to assign the nature of the transit state, therefore, the further investigation using time-resolved spectroscopy is needed and, we are unable to assign the nature of the transit state in this study.

If the decay rate from $S_1$ to the transit state is decreased without affecting the radiative/non-radiative pathway to the ground state, the population in the transit state will be
decreased. This leads to the decrease in the absolute value of the transmittance change at negative delay time. In this context, one may think about the increase in emission intensity as the rate of non-radiative decay pathway to the transit state is decreased with the shaped pulse. However, if the shaped pulse opens some other relaxation pathway that competes with the non-radiative decay pathway to the transit state, the population in that unknown state will be decreased without hampering the radiative pathway, i.e., emission from S\textsubscript{1}. Thus, it may be concluded that the shaped pulse obtained by GA and the feedback mechanism is capable of decreasing the rate of decay from S\textsubscript{1} to the transit state. However, we were unable to accelerate this decay process by using I\textsubscript{T}/I\textsubscript{LP} as the evaluation function.

The shape of the optimized pulse was derived by cross correlation with the ordinary probe pulse (single pulse) using a second harmonic BBO crystal. Figure 5 shows the cross correlation trace of the shaped pulse.

![Cross correlation traces](image)

**Figure 5:** (a) Cross correlation trace of shaped pulse optimized at –10 ps delay with ordinary probe pulse (single pulse) (b) Cross correlation trace of shaped pulse optimized at 1 ps delay with ordinary probe pulse (single pulse)

Cross correlation traces of the shaped pulses optimized at –10 ps and 1 ps delay times are almost the same in shape (Fig. 5a and 5b). Clearly, the optimized pulse is very complex in shape. Actually, the pulse envelope consists of four different groups of pulses, each of which consists of 2–4 pulses. The interval between the small pulses is approximately 0.22 ps, whereas that between two groups of pulses is approximately 0.67 ps.
Fourier transform of the temporal profile of the cross correlation trace obtained by the shaped pulse that controls the decay pathway from the \( S_1 \) state, gave two intense peaks along with few other weak peaks in the power spectrum in the frequency domain (Fig. 6).

![Fourier transform of temporal profile of the cross correlation trace](image)

**Figure 6:** (a) Fourier transform of temporal profile of the cross correlation trace obtained by the shaped pulse optimized at -10 ps delay (b) Fourier transform of temporal profile of the cross correlation trace obtained by the shaped pulse optimized at 1 ps delay

The peak frequency around 150 cm\(^{-1}\) is similar to the wave-packet oscillation of the DTTCI molecule. Misawa and Kobayashi reported this type of vibration around 160 cm\(^{-1}\).\(^{26}\) According to them, this vibration is due to torsional motion of the bond connecting the two rings and this type of vibrational motion may be coupled strongly with the electronic transition of DTTCI molecules. In a very recent work, Misawa and co-workers reported a vibrational wave packet having 4.5 THz frequency, i.e., 150 cm\(^{-1}\), in the excited state of the DTTCI molecule.\(^{27}\)

Another peak appearing around 50 cm\(^{-1}\) may be obtained by the Fourier transform of some other oscillatory motions. We have already mentioned that the time interval between the two groups of pulses is approximately 600-800 fs and this periodical motion can be attributed to the second peak (at approximately 50 cm\(^{-1}\)) in the frequency domain. There are two candidates for the origin of the low frequency peak: one is the intermolecular librational motion
between solute and solvent molecules,\textsuperscript{34-36} and the other is low frequency intramolecular vibrational motion, such as large amplitude motion.\textsuperscript{37-38} Regarding librational motion, optical heterodyne detected Raman-induced Kerr effect spectroscopy (OHD-RIKES),\textsuperscript{34} dielectric relaxation study,\textsuperscript{35} and terahertz time domain spectroscopy\textsuperscript{36} have demonstrated that the spectrum in the frequency region lower than 100 cm\textsuperscript{-1} is the characteristic region of librational motion as a result of solute-solvent interaction. Regarding the large amplitude intramolecular vibrational motion, the phenyl groups at both ends of the stilbene molecule show vibrational motion at frequencies lower than 100 cm\textsuperscript{-1}.\textsuperscript{38} It is, therefore, natural to consider that the vibrational motion involving benzothiazole groups at both ends of the DTTCI molecule has frequencies lower than 100 cm\textsuperscript{-1}. Thus, the peak at approximately 50 cm\textsuperscript{-1} can be interpreted as a special kind of intermolecular vibration or a large amplitude intramolecular vibration that decreases the rate of the decay pathway to the transit state. Since the Fourier spectrum of the cross correlation trace of the complex shaped pulse gives a qualitative indication of different types of vibrational dynamics of DTTCI molecules, we conclude that the different types of oscillations may have some linkage to the decay pathway from $S_1$ to the transit state.

**Conclusions**

Control of the molecules as well as of the chemical processes in nature may be the next possible scientific goal and using programmable ultrafast Pulse Shaping technique many physical as well as chemical processes have already been controlled.

We have obtained completely different transient absorption of DTTCI molecules by using an optimized shaped pulse. The excited state dynamics of DTTCI is dependent on the nature of the excitation pulse. The phase modulated pulse obtained from the optimization experiment is capable of controlling the decay pathway from the $S_1$ state to the transit state of DTTCI, thereby decreasing the population in that energy state below the $S_1$ state. In consequence, the absolute value of the transmittance change is decreased by the GA optimized pulse. The temporal behaviour of the optimized pulse is very complex in nature and different periodical motions of that shaped pulse may be coupled with some intra and intermolecular vibrational modes of DTTCI molecules and these vibrational modes control the decay pathway from $S_1$ state.

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