

Optimal Control of Photoisomerization

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We report on optimal control of the photoisomerization of 3,3-diethyl-2,2-thiacyanine iodide dissolved in methanol. Enhancement and reduction of the relative yield of *cis* to *trans* isomers are achieved; i.e., the quantum efficiency of the photoisomerization is controlled with optimally phase and amplitude shaped 400 nm femtosecond laser pulses. Single-parameter control schemes, like chirp or intensity variation, fail to change the ratio of the photoproducts. The successful modification of the molecular structure can be regarded as a first step towards controlled stereoselectivity in photochemistry.

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Over the last decade remarkable theoretical and experimental progress was achieved in the field of optimal control of chemical reactions [1–5]. In this multiparameter control scenario, coherent electric fields best suited for solving the control task are found by the quantum system itself in an automated iteration loop. In this approach no *a priori* knowledge of the molecular Hamiltonian is required. The method is also applicable in the liquid phase, where interactions with the solvent molecules increase the complexity. None of the liquid-phase control experiments so far [3–6] have yet tried to control the modification of the molecular structure. In this context, *cis-trans* isomerization [7–10] has attracted much attention because of its importance in chemistry and biology (e.g., primary step of vision) [11,12]. Another example of rearrangement of the molecular structure is the conversion between enantiomers. The control of this stereochemical process with shaped laser fields has attracted great theoretical interest in recent years [13–16].

An intensely investigated class of molecules that exhibit *cis-trans* isomerization are symmetrical cyanines (see Ref. [17] for a summary). The molecule we have chosen to investigate in this Letter, the 3,3'-diethyl-2,2'-thiacyanine iodide (NK88), belongs to the group of cyanines with a short polymethine chain. The isomerization process of this type of cyanines is well investigated and understood [18,19], making them an ideal system for studying optimal control of *cis-trans* photoisomerization and thereby controlling the structural changes of molecules. The cyanine molecule NK88 exists in a *trans* and in a *cis* configuration [Fig. 1(a)]. Investigations of similar cyanines with NMR spectroscopy in solution [20,21] and x-ray analysis of the crystal structure [22,23] have shown that the thermodynamic stable isomer of these molecules has a *trans* geometry. Quantum-chemical calculations in our group of the absorption maxima for the two isomers in comparison to the experimentally observed ground-state spectrum show that this also applies to the NK88 isomers. Under room-temperature conditions the concentration of the unstable *cis* isomer is negligible. This can be seen by comparing our

measured ground-state absorption spectrum of the dissolved NK88 with the available literature spectra for both isomers [17]. Only the features of the *trans* spectrum can be seen in the measured spectrum. The observed time constant (≈ 0.5 ns) of the thermal back reaction of the unstable *cis* isomer also agrees with this finding.

The ground-state absorption spectra of the two isomers which are taken from Ref. [17] are shown in Fig. 1(c). While the *trans* isomer has a broad ground-state absorption around 420 nm, the absorption band of the *cis* isomer is redshifted with a maximum at 450 nm. As shown in Fig. 1(b), a simplified scheme for the photoisomerization process of the short-chain, symmetrical cyanines assumes only one reaction coordinate, namely, the twist about the C=C double bond. This simple model views the shape of the ground-state energy surface as a double-minimum potential. Calculations and experiments from the Sundström group indicate the first excited state to be barrierless for this type of cyanines [18]. A more detailed model of the potential energy surfaces includes as a second

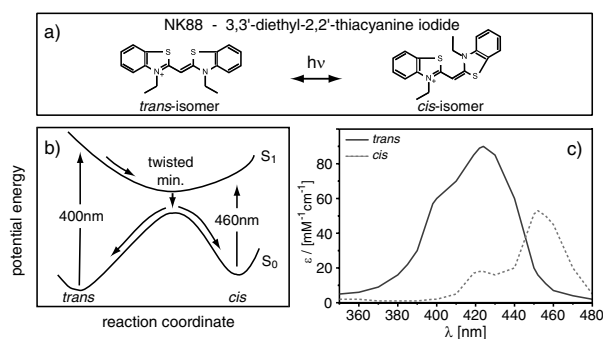


FIG. 1. (a) Molecular structure of the two isomer configurations of the cyanine dye NK88. Irradiated by light of the proper wavelength, this molecule can undergo *trans-cis* isomerization. (b) Simplified potential energy surface. The reaction coordinate is the twist angle about the C=C double bond. (c) The ground-state absorption spectra of the two isomers. While the *trans* isomer shows a broad ground-state absorption centered at 420 nm, the absorption band of the *cis* isomer is redshifted with a maximum around 450 nm.

reaction coordinate the skeletal stretching of the molecule [19]. The driving motion of the isomerization is the excitation of highest occupied molecular orbital into the lowest unoccupied molecular orbital, which has only a weak antibonding character [24]. Thus, the absorption of a 400 nm photon transfers the stable *trans* isomer from the ground state to the first excited state S_1 . From there, it reaches a twisted molecular configuration. Through a conical intersection it can relax back to either the *trans* or the *cis* ground state.

In order to measure and control the isomerization reaction, we employed a femtosecond laser system which delivers pulses with a duration of 80 fs, a pulse energy of up to 1 mJ at a center wavelength of 800 nm and at a repetition rate of 1 kHz. For the pump pulse 50 μJ are split off and shaped using frequency-domain pulse shaping. Our pulse shaper is described elsewhere in detail [25]. Briefly, it consists of a 128-pixel liquid-crystal phase modulator in a $4f$ -geometry zero-dispersion compressor setup. By applying different voltages to the pixels a frequency-dependent phase is acquired across the laser spectrum. The phase-shaped 800 nm femtosecond laser pulse is then frequency doubled in a 400 μm thick lithium barium borate crystal. The resulting laser pulse at 400 nm is therefore shaped in spectral phase and amplitude [26,27]. The maximum pulse energy of the second harmonic at 400 nm is 1.5 μJ with a pulse duration of 100 fs for a bandwidth-limited 800 nm fundamental laser pulse. The shaped 400 nm pump pulse is then focused into a 200 μm flow cell where the sample ($OD = 0.3$), dissolved in methanol, is constantly exchanged. For the probe-laser pulse we take about 50 μJ of the unshaped 800 nm laser pulse and frequency double it in a 300 μm beta barium borate crystal. The resulting 400 nm laser pulse is employed to generate a chirped supercontinuum by focusing into a sapphire disk. The generated white-light laser pulse is delayed in a computer-controlled delay stage and focused into the sample under an angle of about 10° with respect to the pump-laser beam. The polarization between pump and probe-laser beams is set at the magic angle (54.7°). The white-light probe-laser beam is split into two light beams after passing through the flow cell and sent to separate monochromators. This allows the simultaneous acquisition of transient absorption spectra at two distinct wavelengths.

The overall spectrally resolved dynamics are plotted in Fig. 2(a) as a function of the probe wavelengths and the time delay between the 400 nm pump and the probe-laser pulses. There the z axis ($\Delta T/T$) of the contour plot describes the change in transmitted probe light normalized to the transmission without the 400 nm pump laser. While red (black) denotes a high transmission through the sample, blue (gray) marks the absorption of the probe beam. The region between 400 and 430 nm probe wavelengths corresponds to pump depletion and reflects the decrease of concentration of the *trans* isomer in the ground state. On the other hand, the transient absorption of the probe in the region around 460 nm, after a pump-probe delay time of a

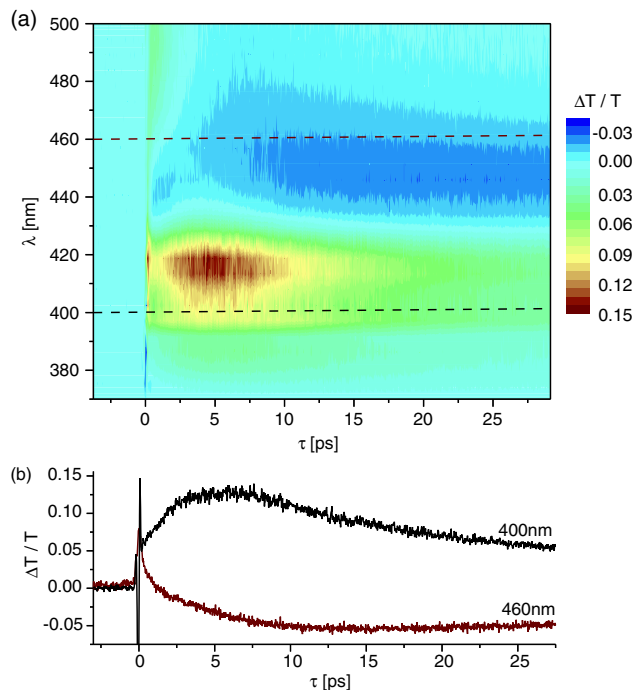


FIG. 2 (color online). (a) Spectrally resolved pump-probe transients. The z axis ($\Delta T/T$) of the contour plot describes the change in transmitted probe light normalized to the transmission without the pump laser. While red (black) denotes a high transmission through the sample, blue (gray) marks the absorption of the probe beam. (b) Pump-probe absorption transients recorded with a 400 nm pump and 460 nm as well as 400 nm probe wavelengths.

few picoseconds, originates from the absorption of the *cis* isomer ground state.

The pump-probe transients recorded at probe wavelengths of 400 and 460 nm [shown in Fig. 2(b)] are for large delay times mainly affected by one of the two isomers, respectively. The pump-probe signal at 400 nm for larger delay times is proportional to the amount of *trans* molecules that were initially excited, while the curve at 460 nm measures the fraction of molecules that actually undergo *trans-cis* isomerization. The ratio of the probe signals $\Delta T(460 \text{ nm})/\Delta T(400 \text{ nm})$ therefore reflects directly the isomerization efficiency (i.e., quantum yield). The more complicated dynamics at early pump-probe delay times originate from stimulated emission and absorption of the probe-laser pulse to higher-lying electronic states. A more detailed discussion of this will be given in a future publication [24].

The goal of our experiment was to demonstrate that adaptive femtosecond pulse shaping is able to control the *cis-trans* isomerization of a complex molecule in the liquid phase. As already discussed above, the pump pulse is sent through a femtosecond pulse shaper capable of producing complex laser pulse shapes by spectral phase modulation. An automated “learning loop” is then employed, wherein an experimental feedback signal from the physical control object itself guides the evolutionary algo-

rithm to find laser fields optimized for the control task. In our case, we have chosen as the feedback signal the ratio of *cis* isomers in its ground state after the photoisomerization process to the amount of initially excited *trans* isomers (i.e., the relative reaction yield). To determine these quantities, we recorded the transient absorption signal at the two wavelengths of 400 and 460 nm at a given specific pump-probe delay time. The pump-probe delay time during the optimization experiment was set to 20 ps, because both transients show only small changes at this large delay time. The ratio between the two signals can only negligibly be changed by the time shift of the tailored pump pulse. Additionally, an appreciable influence of stimulated emission or absorption to higher-lying states is limited to very early pump-probe delay times and therefore is negligible at a pump-probe delay time of 20 ps.

By employing the automated learning loop, we find laser pulse shapes, which enhance or reduce the isomerization reaction. The evolution of the *cis/trans* ratio as a function of the generation number is shown in Fig. 3 for the two cases of enhancement and reduction of isomerization.

In the case of maximization of the *cis/trans* ratio, i.e., the enhancement of the isomerization, the evolution of the optimization is shown in Fig. 3(a). Each data point is the average of the ten best laser pulse shapes of the generation. In order to monitor the stability of the experimental conditions, we applied an unshaped laser pulse after each generation of the evolutionary algorithm. The statistics of this reference measurement is 10 times smaller than in the case of the shaped laser pulses. The *cis/trans* ratio for unshaped laser pulses is essentially constant over the time of the optimization (open circles). In contrast, the *cis/trans* ratio measured with modulated and optimized laser pulses clearly rises above that level as a function of the generation number and converges finally to an optimum (solid circles). This shows the ability to increase the ratio between the amount of *cis* to *trans* molecules using adaptively shaped femtosecond laser pulses. On the other hand, the algorithm is able to minimize that ratio

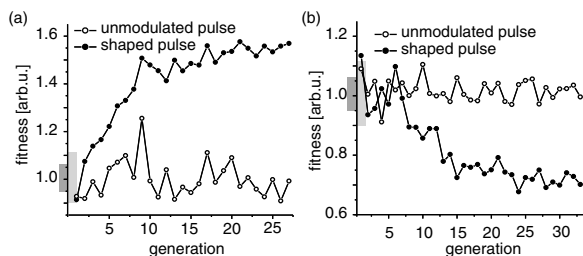


FIG. 3. (a) Maximization and (b) minimization of the *cis/trans* ratio as a function of iterations using an evolutionary algorithm. The filled dots represent results obtained with shaped laser pulses, and the open dots show the reference signal obtained with an unshaped laser pulse. On the y axis of both graphs the achievable ratio changes for the single-parameter control schemes of intensity (dark gray, 2σ width) and quadratic spectral phase (light gray) variation are also shown.

[Fig. 3(b)] as well. In this case a laser pulse shape is found that reduces the isomerization efficiency.

The optimized laser fields were characterized by the cross-correlation frequency-resolved optical gating (XFROG) technique. This pulse characterization scheme is based on spectrally resolved cross correlation of the modulated 400 nm pulse and an unmodulated 800 nm reference pulse [28]. The XFROG traces of the optimized pulse shapes are shown in Fig. 4(a) for the maximization and in Fig. 4(c) for the minimization, respectively. It is well known that the potential energy surface S_1 of the excited state is barrierless. In this context, one possibility for control might be the creation of different coherent vibrational wave packets on the S_1 surface by the differently shaped laser pulses. Subsequently, the nature of the wave packet controls the passage through the conical intersection [29] and thereby the isomerization efficiency. However, already the pump-probe measurements in Fig. 2 indicate that higher-lying electronic states are involved. One can see from Fig. 4(a) that, in the case of maximization, an only slightly modified laser pulse compared to the unshaped one is needed to increase this efficiency even more. The almost unshaped laser pulse for the maximization means that a strong laser pulse is necessary for nonlinear transitions. It may well be the case that upper potential energy surfaces S_n are reached in a nonlinear multiphoton excitation, which allows a direct motion through the conical intersection to reach the *cis* electronic ground state without any vibrational wave packet dynamics. In contrast to maximiz-

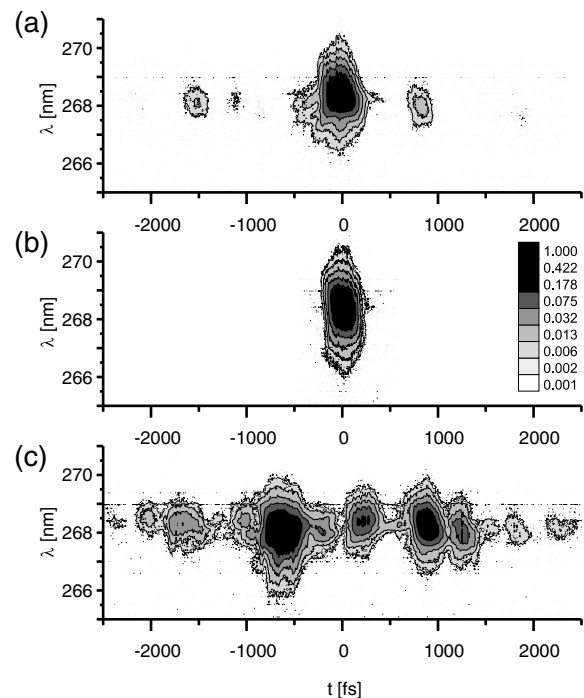


FIG. 4. XFROG traces of the optimal pulse shapes for (a) maximizing and (c) minimizing the ratio between the *cis* and *trans* isomers. For comparison the XFROG trace of the unmodulated pulse is shown in (b).

ing photoisomerization, the suppression of this process obviously needs a train of laser pulses with reduced intensity for each of them. One possible interpretation is that here vibrational wave packet dynamics in upper (S_n) potential energy surfaces are necessary to open an exit to the *trans* ground state via the conical intersection. The laser pulse train probably induces electronic transitions between these different excited potential energy surfaces. Each of the (differently) shaped individual laser pulses, which are still coherent to each other, changes the vibrational wave packet dynamics accordingly. Explanations of the XFROG traces from a theoretical approach are currently under investigation [30]. In summary, without the result of theoretical work it seems impossible to accurately assign the involved dynamics on the upper potential energy surfaces. However, the optimal laser pulses still give an indication what sort of dynamics is required for maximizing and for minimizing photoisomerization.

In order to check that these results cannot be obtained by employing “trivial” single-parameter control schemes, the effect of the variation of different pulse parameters on the isomerization reaction was studied. First, the influence of the varying pulse energies of the pump pulse was investigated. We find that the ratio between the generated ground-state *cis* isomers and the excited *trans* isomers does not change for pump-pulse energy variations of a factor of 5. Another single-parameter variable frequently used in coherent control schemes is chirp. Under the given experimental conditions we find no change of the ratio between the generated ground-state *cis* isomers and the excited *trans* isomers within the statistical uncertainty of 10% for varying the second order spectral phase from -7500 fs^2 to $+7500 \text{ fs}^2$. Both results of the single-parameter variations are shown as bars in Figs. 3(a) and 3(b). The bars in both cases show the 2σ width of the standard deviation of the two measurements, i.e., 95% of all data points lie within this range. Furthermore, in order to avoid having a very small *trans* excitation signal with a low signal-to-noise ratio enter into the fitness function and thereby cause physically meaningless high values of the *cis/trans* ratio, a suitable discriminator is used as a lower threshold [26]. This discriminator is given by the lowest measurable denominator for our signal-to-noise ratio. Hence our experimental results clearly demonstrate that optimally shaped fs-laser pulses open up a new level of quantum control in complex molecular systems.

In summary, we have demonstrated that adaptive femto-second pulse shaping is able to control isomerization reactions of a complex molecule in the liquid phase. By optimizing the ratios of the *trans* and *cis* isomers in a multiparameter optimal-control experiment, we demonstrate that isomerization efficiencies can be either enhanced or reduced. This can be regarded as a first step towards controlled stereoselectivity in photochemistry. The obtained optimization results show that adaptive femto-second pulse shaping can be applied to many challenges

in physical, chemical, and biological research where isomerization reactions are of vital importance.

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