Singlet versus triplet dynamics of β-carotene studied by quantum control spectroscopy

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Abstract

Biomolecules very often present complex energy deactivation networks with overlapping electronic absorption bands, making their study a difficult task. This can be especially true in transient absorption spectroscopy when signals from bleach, excited state absorption and stimulated emission contribute to the signal. However, quantum control spectroscopy can be used to discriminate specific electronic states of interest by applying specifically designed laser pulses. Recently, we have shown the control of energy flow in bacterial light-harvesting using shaped pump pulses in the visible and the selective population of pathways in carotenoids using an additional depletion pulse in the transient absorption technique. Here, we apply a closed-loop optimization approach to β-carotene using a spatial light modulator to decipher the energy flow network after a multiphoton excitation with a shaped ultrashort pulse in the near-IR. After excitation, two overlapping bands were detected and identified as the S_1 state and the first triplet state T_1. Using the transient absorption signal at a specific probe delay as feedback, the triplet signal could be optimized over the singlet contribution.
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1. Introduction

Transient absorption spectroscopy is able to collect a great amount of information in time and frequency from biological systems [1]. However, depending on the complexity of the system, this technique may suffer from ambiguities in the analysis of the time-resolved spectral information, for example, due to overlapping excited state absorption (ESA), bleach and stimulated emission contributions. Often complex analyses, like those based on global fitting algorithms [2–4], require assumptions about the energy flow network to extract the dynamics of interest. Thus, there is a high demand for new approaches which are able to clarify these ambiguities, or even more, which are able to enhance determined molecular dynamics. One novel promising way, for example, is the recently proposed two-dimensional spectroscopy of electronic couplings in photosynthesis, which showed the dependence of the energy transport on the spatial properties of the excited-state wavefunctions [5]. Here we follow a different approach by quantum control spectroscopy, which combines coherent control and fs-spectroscopy [6].

Coherent control [7–9] techniques can be very rewarding in spectroscopy, where the selection of specific excitation pulses can enhance particular molecular dynamics of interest. Coherent selective spectroscopy in particular, is of great advantage for the study of complex biological systems, where the electronic states have overlapping absorption bands with a multitude of time constants. This has been implemented in our group in the study of several carotenoids by modifications of the pump–probe spectroscopy technique (Fig. 1). In general, transient absorption spectroscopy is performed with two pulses, a pump and a delayed broadband probe (Fig. 1A). The addition of a depletion pulse (Fig. 1B) allows to interfere during the evolution of the system at a point which is normally inaccessible with just one pump [10–13]. In the case of β-carotene, the depletion of the first allowed state S_2 influences the population of all subsequent electronic states. The so called pump–deplete–probe technique was able to identify the blue shoulder of the excited state absorption (ESA), the so called S^*, as the absorption of a vibrationally hot ground state, which is populated by impulsive Raman scattering enhanced by its electronic resonance [12]. This approach can be also interpreted as a manifestation of the well-known Tannor–Rice control mechanism [14].

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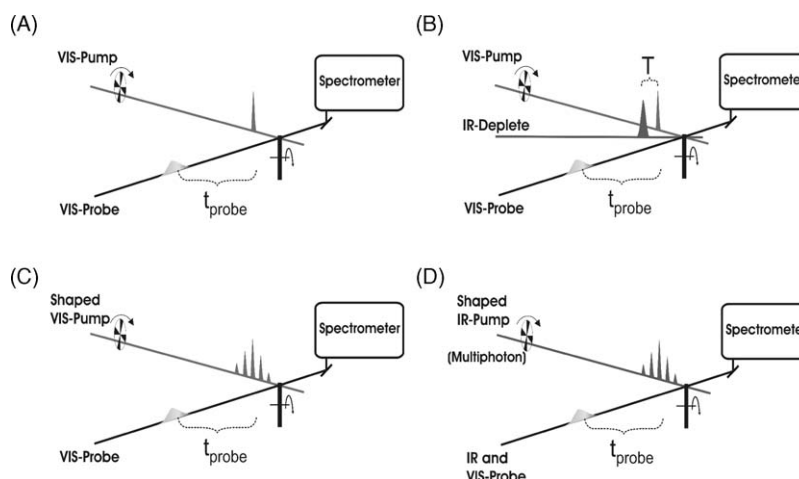
Fig. 1. Schematic approaches of transient absorption: (A) normal pump–probe, (B) pump–deplete–probe, (C) shaped VIS-pump and (D) shaped IR-pump for multiphoton spectroscopy.

Another possible modification in the transient absorption technique is the tailoring of the pump pulse (Fig. 1C). The modulation of its phase and/or amplitude can be chosen to optimize a specific feedback parameter, called closed-loop approach, or without any feedback, called open-loop [15]. The shaping of the phase of the pump pulse using feedback-optimized coherent control allowed the steering of the flow of excitation energy in the light-harvesting process [16]. It was shown that complex matter waves in the internal degrees of freedom of the carotenoid can be controlled to increase the internal conversion in carotene [6].

Other examples of control experiments in biomolecules can be found in the work of Bardeen et al. [17] in the green fluorescent protein (GFP) using an open-loop approach with chirped excitation. Using a typical Tannor–Rice control method [14], stimulated emission was optimized through the adaptation of the linear chirp to the wavepacket. Very few studies using open-loop control followed this initial work, restricting themselves to multipulse excitation in rhodopsin or the use of chirped excitation in concanavalin A [11,18].

In this work we go one step further and interrogate electronically excited states of β-carotene, which cannot be excited by one-photon absorption, using tailored near-IR (NIR) pulses (Fig. 1D). We observe the contribution of different electronic states which are populated via a different number of photons and show that we can enhance one of these pathways. Transient absorption with two-photon excitation has already been implemented to study carotenoids in solution and as part of the light-harvesting complex [19,20].

2. Carotenoid electronic structure

Carotenoids are important pigments in nature which perform an important task in the light-harvesting process of bacteria and plants [21]. They are responsible for the absorption of light in the blue–green region of the visible spectrum and participate in the effective transfer of energy to the rest of the photosynthesis process. Although its role is crucial in these processes, several aspects of the energy deactivation network of carotenoids are still not fully understood. The main absorption of the carotenoids is due to the transition of the ground state to the second excited state (S_0–S_2). The first excited state (S_1) cannot absorb one single photon from the ground state. The S_2 state normally has a very short lifetime in the range of 100–200 fs which is determined by two major deactivation pathways: the energy transfer when incorporated in light-harvesting complexes and internal conversion. Fluorescence only plays a minor role for large carotenoids. S_1 decays on a slower timescale, ranging from some picoseconds up to several tens of picoseconds for carotenoids with a small number of conjugated double bonds ($N \sim 9$ double bonds). Besides these well known aspects, several ultrafast experiments [22–24], guided by some theoretical calculations [25,26], suggest the presence of additional electronic states in this three-level basic scheme. These states have received different names ($S^{\ddagger}$, S_x, S^*) and are often tentatively identified as one of the "dark" states ($3A_g^-$, $1B_u^-$). These states cannot be populated from the ground state via one-photon transition (Table 1). In the case of the $1B_u^-$, it is neither excitable with 1 nor 2 photons [27].

To make the congestion of spectral features even more complex, carotenoids show triplet absorption with overlapping bands with its singlet states. The triplet system is not as well characterized as the singlet due to the difficulty of populating these states. The triplet ground state T_1 has an energy of $7400 \, cm^{-1}$, about half of the S_1 energy [28]. Its lifetime is not well studied but is believed to be in microsecond regime. The T_1 state has a prominent band which absorbs to a T_n state in toluene at 525 nm [29,30]. Furthermore, there is an additional band in the near infrared at 900 nm, but it is 300 times weaker than the before

Table 1
Allowed (+) and prohibited (−) transitions from the ground state ($1A_g^-$)

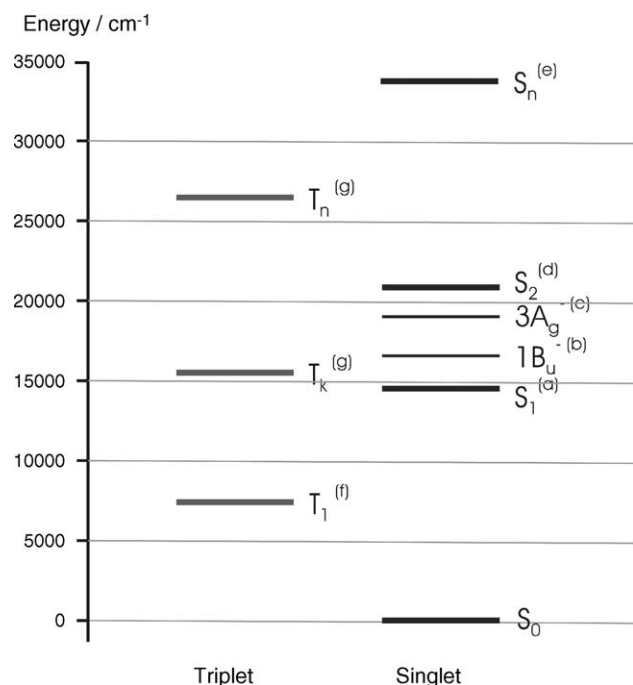| Excited state	$2A_g^-$ (S_1)	$3A_g^-$	$1B_u^-$	$1B_u^+$ (S_2)
1-Photon absorption	−	−	−	+
2-Photon absorption	+	+	−	−

Fig. 2. An overview of the discussed energy levels for β-carotene. Approximate values were obtained from the following references: (a) fluorescence measurement in *n*-hexane at 170 K [37], (b) resonant Raman measurement in crystal [38], (c) average value of the resonant Raman measurement of lycopene and sphaeroidene [22], (d) absorption spectrum, (e) maximum of the S_1–S_n absorption maximum, (f) phosphorescence measurement in benzene [28], and (g) measurement of the T_1 absorption spectrum in toluene [29].

mentioned band in the visible. The energy scheme of β-carotene is summarized in Fig. 2.

3. Experimental

The experimental setup can be seen in Fig. 3. The pump pulse was generated in a home-built two-stage non-collinear OPA (nc-OPA), which was pumped by a commercial Ti-Sapphire based femtosecond laser system. The idler pulse was centered at 1000 nm with a bandwidth of 70 nm and typical durations of 22 fs. This NIR pump pulse was characterized by a home-built second-harmonic FROG and also by using a commercial second-harmonic autocorrelator, always taking into account the first window of the sample cell (see below). Pump energies below 1.2 μJ were used in the multiphoton optimization experiments.

To generate the probe pulse, less than 1 μJ of the fundamental laser energy at 795 nm, was focused into a 1 mm sapphire window. The generated supercontinuum white-light (WL) cov-

ered a spectral range from 450 nm up to about 1100 nm. After attenuation and filtering of residual fundamental, less than 1 nJ was focused into the sample. To minimize dispersion and chromatic aberrations, all beams in the experiment were focused and overlapped in the sample with concave mirrors under an angle of 10°. β-carotene was obtained from Sigma–Aldrich (99%) and solvated in cyclohexane (HPLC grade) without further purification. Dense samples were prepared due to the low two-photon absorption cross-section. The solution was filtered through a 0.22 μm filter membrane. The measurements were performed in a rotating cell with 0.5 mm fused silica windows and an effective sample thickness of 200 μm.

The signal was detected by photodiodes with interference filters (FWHM = 10 nm) and digitalized with a BOXCAR and a 16 bit A/D converter. The coherent artifact of the transient absorption was fitted and subsequently deleted. The procedure will be explained elsewhere [31]. To modulate the phase of the pump pulse, a liquid-crystal mask (CRI, SLM 128 pixel) was used in a 4-*f* setup (*f* = 15 cm and grating with 600 g/mm). The transmission of the shaper setup was more than 50% and had a bandwidth about 140 nm.

4. Results and discussion

In the following we will first discuss the dynamics of the multiphoton excitation studied by traditional transient absorption with unshaped pulses. The results of the optimization experiment will be presented in Section 4.2. The experimental transient signals were fitted using an approach based on an evolutionary algorithm described in detail in Refs. [2,12]. The experimental trace was fitted with three different contributions, called here components. Each component had an individual amplitude and its rise and decay could be modeled with multi-exponentials as needed.

4.1. Transients after multiphoton excitation of β-carotene

Transient absorption kinetics at an excitation wavelength of 1000 nm are shown in Fig. 4 for different probe wavelengths. The dynamics were fitted assuming three independent contributions. For longer wavelengths an exponential decay with a time constant of 9 ps (component I – dashes) was observed. This component has a risetime of about 0.3 ps. The other slow-decaying component (II – dots) had stronger amplitude for smaller wavelengths. The maximum of this band could not be measured for wavelengths smaller than 520 nm due to the strong absorption of the dense sample. This risetime of about 8 ps is much slower
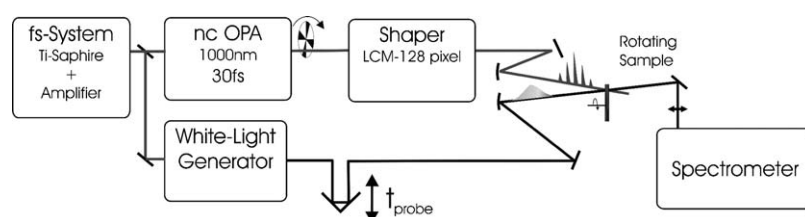
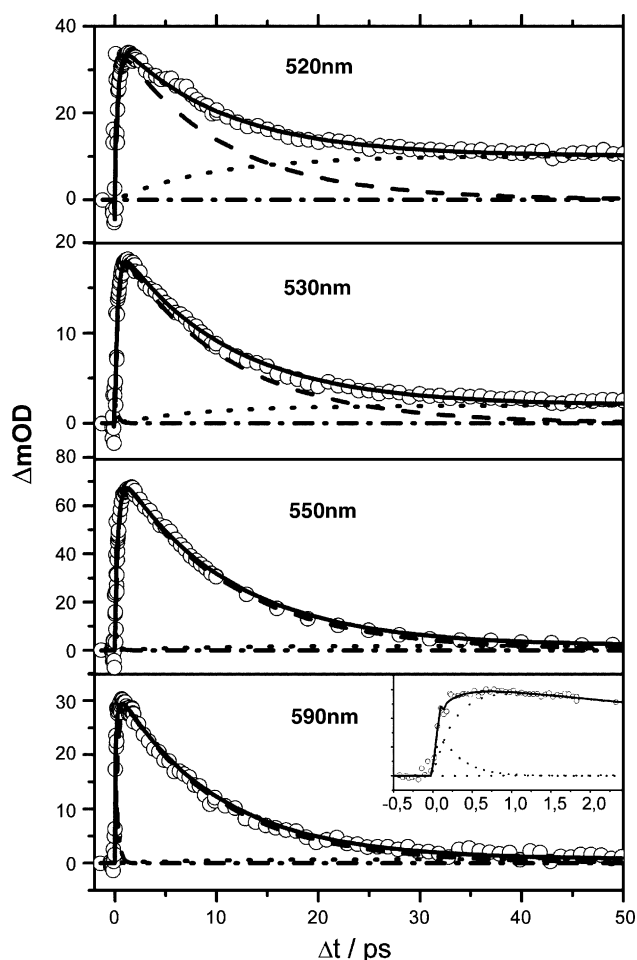

Fig. 3. Experimental setup.

Fig. 4. Kinetic traces at selected probe wavelengths with excitation at 1000 nm. Three components can be seen in each fitting: (I) dashes, (II) dots and (III) dot-dash. The solid line is the best fit with these three components. The inset in the graph for probe wavelength at 590 nm shows the fast component III, which has mainly a non-neglectable contribution at this wavelength.
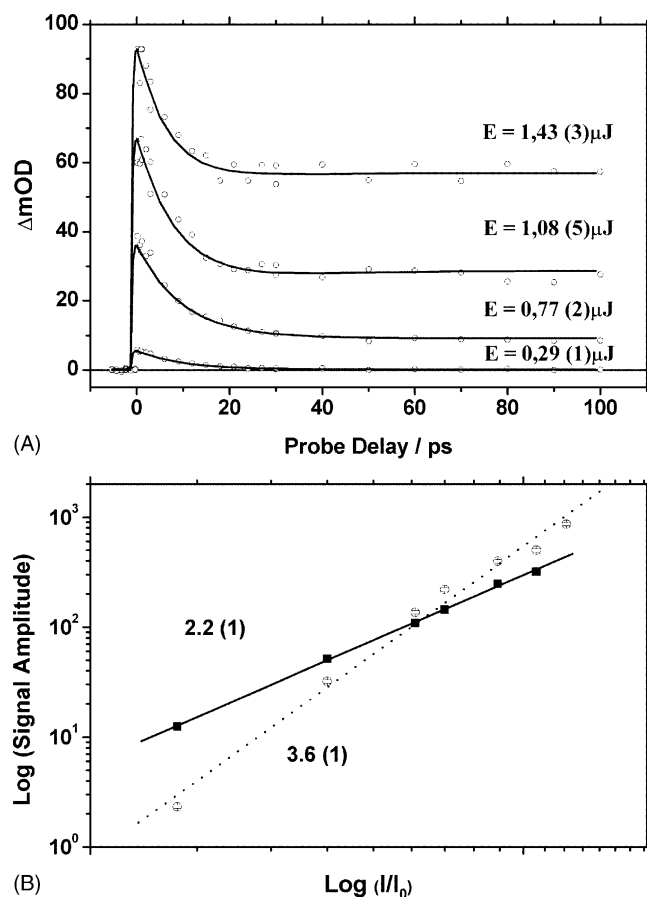

Fig. 5. (A) Selected transients measured at different pump intensities. (B) Pump intensity dependence for two components. Component I is displayed with filled squares and component II with open circles.

and the decay is much longer than 1 ns. Besides these two main contributions, it was necessary to introduce a third component which exhibits an instantaneous rise within the experimental temporal resolution and a decay around 0.3 ps (III – dot-dash). This component is more pronounced for longer wavelengths. Note that the component II can also be fitted with an instantaneous risetime but with the same long decay time. Whether the component II is directly populated or whether it has a finite lifetime cannot be affirmed by the fitting procedure.

The transients were measured for different pump energies (Fig. 5A) and were fitted with the same procedure mentioned above. The pump intensity dependence of the two slower components (I and II) are shown in Fig. 5B. No changes of the time constants could be observed. However, the intensity dependence of the amplitudes exhibits very different behaviors: the component I shows a dependence of about 2.1 [1] photons of the pump intensity, while the intensity dependence of component II scales with a factor between 3 and 4 photons.

The 2 photon dependence on the pump intensity of component II corresponds to an excitation energy of 20,000 cm^{-1} for

the excitation wavelength used here (1000 nm). Since the S_2 state is not absorbing two photons from the ground state, it must be absorption of either a hot-S_1 or maybe absorption of one of the predicted dark states ($3A_g^-$). The $1B_u^-$ would be excitable by this photon energy, however, it can neither be populated from the ground state by 1 nor 2 photons [27]. The risetime of this signal gives new evidences for a tentative identification of a hot-S_1. Its time constant matches perfectly the decay time of component III, which can be identified with the cooling process of the vibrationally hot-S_1 state due to its red shifted absorption. This spectral signature agrees well with findings of experiments using one-photon excitation [12,32] and with the recently performed two-photon transient absorption experiments [20,31].

The very long decay (>1 ns) of component II and its maximum intensity in the blue region of the ESA match also very well the experimental observations of other groups, which were identified as the absorption of T_1–T_n (Fig. 1) [29]. The observed 3–4 photon pump intensity dependence places the excitation between 30,000 and 40,000 cm^{-1}. It is highly above the supposed energy level of the triplet state T_1 (7400 cm^{-1}). The question now is, how is this triplet state populated? A direct excitation of the triplet system from the singlet ground state does not seem to be very physical, since no direct light absorption can lead to a spin flip independently of the number of the photons involved.

A more probable pathway requires the fragmentation of the four photon excitation in two sequential two-photon steps. In this case the first step excites the S_1 state by two-photon absorption followed by a second two-photon step to a highly excited S_n state, from where the intersystem crossing to the triplet system could happen. In the first case, the time constant of 8–9 ps can be identified as the relaxation time inside the triplet system while in the second case it could be the intersystem crossing itself from the S_n to T_1. Such fast intersystem crossings were already observed in several carotenoids with similar conjugation lengths when the carotenoid was part of the light-harvesting complex [2,33,34].

Although transient absorption spectroscopy is not able to unambiguously clarify how the triplet is populated, the experimental results of the transient absorption motivate the question: if the components I and II are indeed different target states as the pump intensity dependence suggests, is it possible to enhance one of these pathways?

4.2. Coherent control of triplet/singlet states

In order to optimize the triplet contribution, the transient absorption signal at a large probe delay of, for example, 15 ps was optimized using polynomial Taylor functions in a closed-loop evolutionary algorithm approach [35]. At this delay, as discussed in the previous section, the triplet contribution dominates the transient signal. Thus, an optimization of the total transient absorption signal would preferably enhance the triplet amplitude. A typical convergence of the algorithm is shown in Fig. 6A. An optimized transient and its unshaped reference are shown in Fig. 6B. The ratio of triplet over singlet signal amplitude was calculated from the fitting of the transient, once an optimal shaped pulse had been found.

Since the decay time of the S_1 and the risetime of the triplet have almost the same magnitude, one expects that the later the transient is probed, the more signal of the triplet will be contributing to the transient absorption signal. For a delay of 20 ps, for example, the triplet is already formed and the S_1 has almost fully decayed back to the ground state (if a finite risetime of the triplet is supposed). Optimizations were then performed for three different delays (10, 15 and 20 ps) in order to study the dependence of the optimization result on the transient absorption delay. The results presented in Fig. 7 shows that the evolutionary algorithm does not produce substantially different solutions at different probe delays. The "error" bars in Fig. 7 were calculated for each delay and mirror the scattering of the optimization results

The optimization results showed the same tendency as the optimization presented in Fig. 6B: although the ratio T_1/S_1 was optimized, no shaping solution could be found that could optimize just the triplet. In all cases, the singlet was also improved by a certain amount, but much less than the triplet contribution, as can be seen in Fig. 6. A more sophisticated feedback signal, which probes the singlet and the triplet separately, would possibly overcome this problem.

Before we discuss the possible mechanism behind the successful optimization of the ratio T_1/S_1 with shaped pulses, we should address possible artifacts in our measurements. The fact
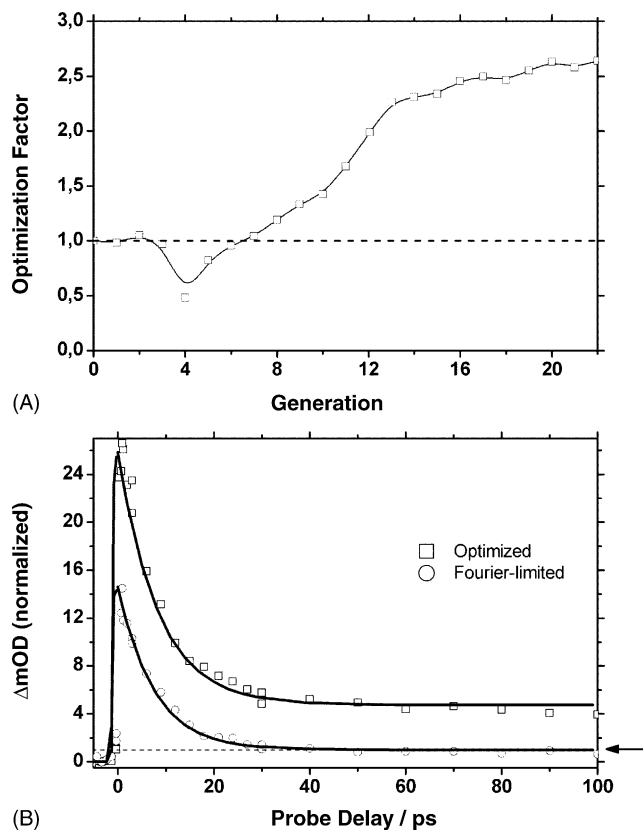

Fig. 6. (A) Convergence curve for a run of the evolutionary algorithm optimizing at 15 ps delay, normalized by the signal of the unshaped transient at the same delay. (B) Typical transient after optimization (squares) using shaped pulses and transient measured with unshaped pump (circles) normalized by the signal of the unshaped transient at delays >60 ps.

that in all optimizations triplet as well as singlet was optimized, leads to the assumption that the coherent control results could also be explained by a pure intensity effect. Since the triplet and the S_1 components have different intensity dependences, one should expect that for increasing pump intensities the ratio
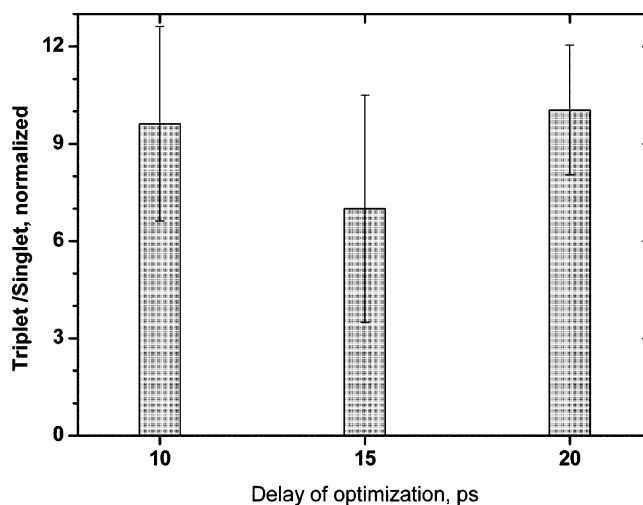

Fig. 7. Optimization of the triplet/singlet ratio for optimization runs performed at different probe delays. The results were normalized by the corresponding triplet/singlet ratio obtained for unshaped pulses.
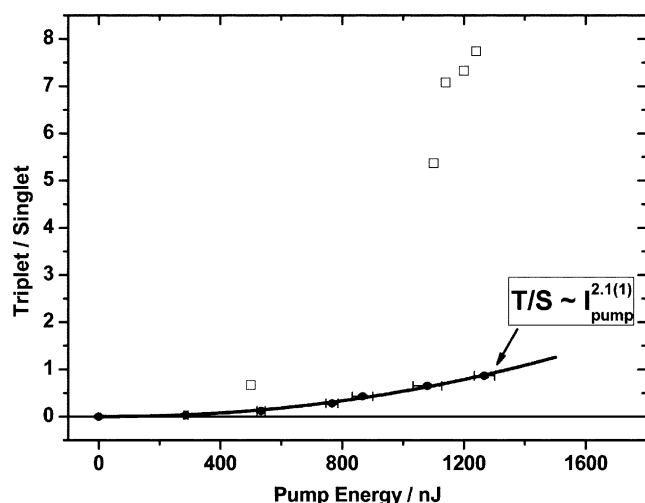
Fig. 8. The dependence of the ratio of triplet over singlet for different pump intensities using transform-limited pulses (closed circles) and using optimized pulses (open squares).

T_1/S_1 should increase with I^2 because of the I^4/I^2 dependence. In order to test this influence the dependence on the pump intensity was first measured for unshaped pulses and is presented in Fig. 8 (closed circles). The expected behavior of this quadratic dependence is nicely reproduced. Also shown in Fig. 8 (open squares) are the results obtained for optimized pulses in several algorithm runs. Care was taken that the energies of shaped and unshaped pulses were equal. An improvement of the ratio up to one order of magnitude could be observed. Since all optimizations of T_1/S_1 ratios are clearly higher than its unshaped counterparts, a pure intensity effect can be excluded.

The autocorrelation traces for the optimized pulses provide additional insight that the intensity of the pump pulse is not responsible for the obtained results. In all optimization runs shaped pulses were obtained which were slightly stretched in time (Fig. 9) compared to their unshaped counterparts making the intensity of each pulse even smaller.
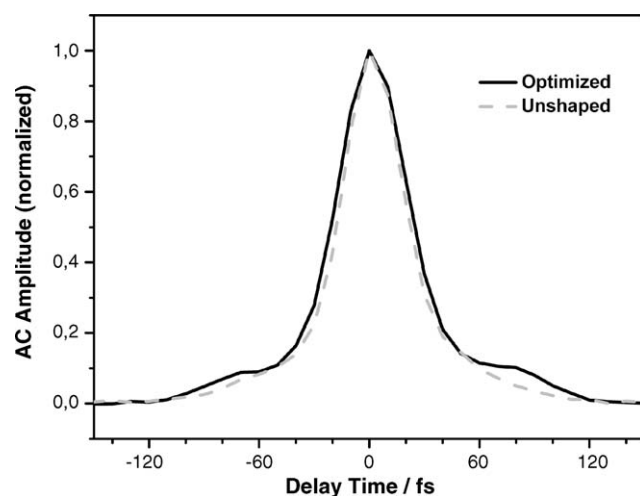

Fig. 9. Autocorrelation traces obtained for a typical optimized pulse (continuous line) and an unshaped pulse (traced line).
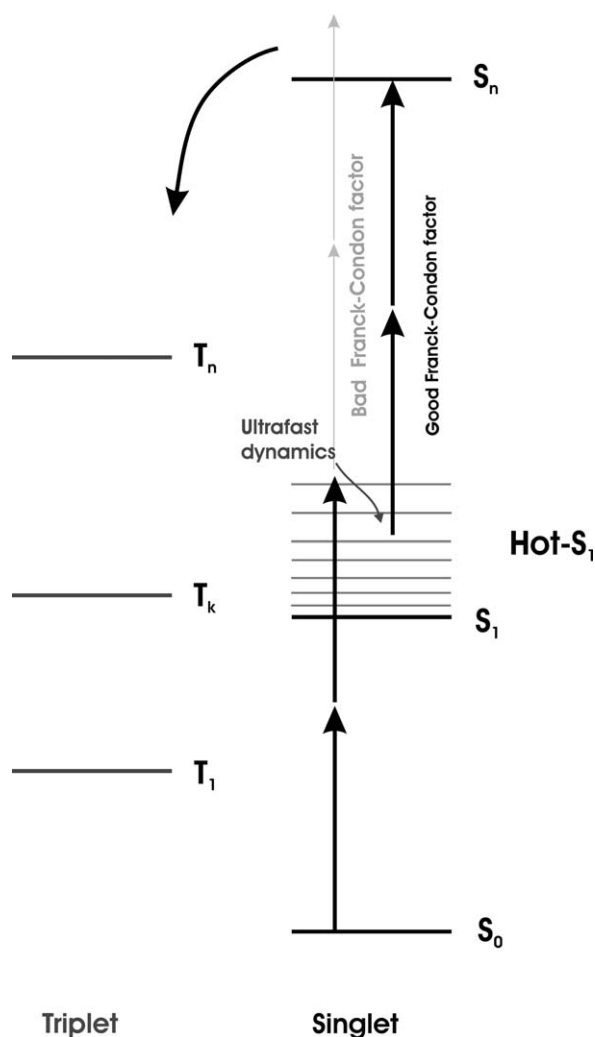

Fig. 10. A possible mechanism for the optimization of a sequential multiphoton transition.

However, although shaped pulses could be found which improve the T_1/S_1 ratio by a factor up to 10, the coherent control results cannot distinguish at this moment if the triplet system is populated via a pathway that needs the hot-S_1 as an intermediate state. In this case the shaped pulse would have temporal characteristics that match the cooling dynamics of the hot-S_1 state. The optimized multiphoton excitation is split into several subsequent steps, which could be adapted to better Franck–Condon factors between the potential surface of the S_1 and a S_n state (Fig. 10). This would require ultrafast dynamics in the 10 fs range in the energetic region between S_2 and hot-S_1. Such ultrafast relaxations were already observed in β-carotene after excitation by one-photon interaction [36]. In order to elucidate more clearly the proposed mechanism and to understand the role of such small phase modulations in sequential multiphoton transitions, quantum control spectroscopy offers another strategy: the pulse shape obtained in the present work can be compared with its orthogonal pulse shape, i.e. the pulse shape obtained when the triplet state is suppressed, and the differences will provide additional information about the mechanism.

5. Conclusion

In this article we have applied coherent control in conjunction with transient absorption to the complex energy relaxation network of β-carotene after ultrafast multiphoton excitation. We have shown that we are able to excite a vibrationally hot-S_1 state by absorption of 2 photons and a triplet state T_1 via 3–4 photons. Using a closed-loop approach with an evolutionary algorithm, we managed to increase the amount of the triplet signal in comparison to the singlet signal. Although further work is needed to explain the specific triplet formation, the possibility to specifically manipulate the population of the triplet versus singlet states provides a new spectroscopic tool to help to understand the underlying mechanism.

Acknowledgements

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