Transient grating spectroscopy of β-carotene pumped with spectrally chirped pulses

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Abstract. Nonlinear optical responses of β-carotene were investigated upon excitation using chirped pulses. We especially focus on spectrally resolved transient grating (TG) signals to discuss the influence of the spectral chirp over a wide spectral range. A significant change in the TG signal was observed when negatively chirped pulses were used. The experimental results were qualitatively reproduced by employing the Brownian oscillator model. The relationship between the wave packet motion in the excited state and spectral chirp is discussed. It is concluded that the third order nonlinear optical response reflects the competition between the spectral chirp and the energy separation of the potential curves.

1. Introduction
In the early events of photosynthesis, carotenoids absorb blue/green light, which matches the spectral maximum of solar radiation. The electronic excitation of carotenoids upon photoexcitation is then transferred to (bacterio)chlorophylls and forms excitonic states. In the early 2000s, it was demonstrated that the efficiency of the excitation energy transfer from carotenoids to bacteriochlorophylls in bacterial light-harvesting pigment-protein complexes can be manipulated using spectrally and temporally shaped pulses [1]. This fact indicates that exciton formation is controllable by designing the phase and amplitude of the spectral components of the excitation light. However, the underlying mechanism between the complicated shape of the optical pulses and the resulting efficiency of photosynthesis is still not clear. In the present study, we investigate how a simple spectral chirp influences the optical responses of carotenoid molecules. The experimental results are analyzed using the Brownian oscillator model. The temporal population change with the spectral chirp is discussed.

2. Experimental details
The setup for the nonlinear optical measurements has been reported before [2,3]. In the present study, a slightly modified configuration was employed for better operation. The excitation light source was a home-built non-collinear optical parametric amplifier (NOPA) pumped using a femtosecond Ti:sapphire regenerative amplifier (Coherent, Legend). The output pulses from the NOPA were passed through a prism compressor to compress or control the group velocity dispersion of the spectral components. The temporal width and phase of the excitation pulses were determined by means of the
so-called second harmonic (SH) frequency-resolved optical gating (FROG) technique, as shown in Fig. 1.

\(\beta\)-Carotene was purchased from Wako Pure Chemical Industries Ltd. and was purified by recrystallization from a benzene solution. For the optical measurements, \(\beta\)-carotene was dissolved in tetrahydrofuran (THF). The concentration of the sample was adjusted to an optical density of \(\sim 1\) at its absorption maximum. All optical measurements were performed at room temperature.

3. Results and discussion

Figure 2 shows the temporal change of the spectrally resolved transient grating (TG) signals from \(\beta\)-carotene measured under (a) positive, (b) zero, and (c) negative chirp conditions. Here, the first and second pump pulses were irradiated on the sample simultaneously, and the TG spectra were measured at various delay times \(\tau\) of the third pulse with respect to the second pulse. The strong signals at the origin of time are due to the coherent artifact, which are truncated in the figure and are not discussed in the present study. The TG signals following the coherent artifact are weak but increases with the evolution of the population time \(\tau\). The TG signals reach the maximum intensity at approximately 400 fs and then slowly begin to decay. The temporal profile shown in Fig. 2a under the positively chirped pulse excitation is very similar to that under the zero-chirp excitation in Fig. 2b. However, the TG

![Figure 1](image1.png)

**Figure 1.** (a) Temporal evolution of the sum-frequency spectra of pump pulses measured in the non-collinear configuration, i.e. the SH-FROG trace. (b) and (c) Temporal and spectral profiles through the maximum intensity of pump pulses. The phases retrieved from the FROG traces are also shown.

![Figure 2](image2.png)

**Figure 2.** Spectrally resolved TG signals from \(\beta\)-carotene measured with (a) positively, (b) zero, and (c) negatively chirped pulses. The ordinate indicates the temporal separation between the second and third pulses, i.e., the population time \(\tau\).
signal is approximately 30% weaker with the negatively chirped pulses, as shown in Fig. 2c.

As shown in Fig. 3, the TG spectrum changes its shape during the very early population times. Specifically, not only the increase in intensity but also the peak energy shift was observed. When the excitation energy is below the absorption edge, the TG signal monotonically decreases as time evolves [4]. However, reflecting the relaxation of the population from the S₂ to the S₁ state, the TG signal increases in intensity, especially on the higher energy side, up to approximately 400 fs. This is why the TG spectral shows a blueshift.

Nonlinear polarizability based on the Brownian oscillator model [5] was calculated as reported in our previous studies [2,4], but in the present study the spectral chirp of the excitation pulse was also taken into consideration. As the electronic state of β-carotene, the ground state S₀, the one-photon forbidden state S₁, the lowest optically allowed state S₂, intermediate state Sₓ, which is located between S₁ and S₂, and the more excited states accessible from S₁, Sₓ, and S₂ were considered when drawing the Feynman diagrams to calculate the response function of each optical process. The response function was calculated from the spectral density and the line-broadening function that indicates the time evolution of the transition frequency correlation. The material parameters used for the present calculation are listed in our previous paper [2].

Figure 3. TG spectra of β-carotene at T=130 fs (thick solid curve) and 170 fs (dotted curve) under the zero-chirp excitation. The spectral shape and peak energy changes with T. The stational absorption spectrum (thin solid curve) is also shown for comparison.

Figure 4. The calculated TG signals at T=50 fs and 150 fs. The spectral shape of the pump pulse and the absorption spectrum are also shown, which determine the spectral shape of the TG signal. Note that the TG signal at T=50 fs is magnified by 4.5 times for clarity.

Figure 5. The calculated temporal profiles of the TG signals excited with positively (red curve) and negatively (blue curve) chirped pulses.
The spectral shift observed in the experiment was qualitatively reproduced as shown in Fig. 4. However, in comparison with the experiment, the rise of the calculated TG spectrum is much faster, and significant spectral shift was seen on the slightly higher-energy side. The reason for the quantitative inconsistency between the experiment and the calculations is not clear at present. A possible interpretation is inappropriate evaluation of the decay rate from $S_2$ to $S_1$. It might be necessary to consider the involvement of another intermediate state to reach better agreement.

Figure 5 shows the calculated temporal profiles of the TG signals under the positively and negatively chirped pulse excitations. Again, the experiment and the calculation show qualitative agreement: the TG signal under negative chirp excitation is weak. This is because the wave-packet in the $S_2$ state is efficiently dumped into the $S_0$ state when a negatively chirped pulse is used, as schematically shown in Fig. 6: the constitution of the response function that reflects the population in the excited state becomes small, resulting in the weak signal.

4. Summary

We have observed significant changes in the spectral shape and intensity of the TG signals of $\beta$-carotene upon the excitation using zero and chirped pulses. The experimental results have been qualitatively reproduced by employing the Brownian oscillator model. We conclude that the reduction in intensity of the nonlinear optical response under the negatively chirped pulse excitation is most probably due to the efficient dumping of the population from $S_2$ to $S_0$. In future work, it will be necessary to determine the real shape of each potential curve to attain better quantitative agreement between the experiment and the calculations.

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