Observation and control of all-*trans*-β-carotene wavepacket motion using pump-degenerate four-wave mixing

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Abstract. Wavepacket dynamics on the ground and optically dark, first electronic state of all-trans-β-carotene are studied with 16 fs time resolution using pump-degenerate four-wave mixing spectroscopy. Moreover control over the vibrational ground state modes is shown.

Carotenoids, being part of light-harvesting complexes (LH) play an important role in photosynthesis. They absorb light in blue-green and efficiently transfer energy to chlorophylls. The electronic states of interest to this study are the electronic ground $1^1A_g^-$ (S_0), the first optically allowed $1^1B_u^+$ (S_2) and the optically dark state $2^1A_g^-$ (S_1) [1]. The long time kinetics of β-carotene have been studied extensively [1,2] and only very recent work has been successful in monitoring the coherent dynamics of the very high frequency modes of S_0 using transient absorption [3]. To observe the wavepacket dynamics in S_1 poses an extra challenge besides the short pulse duration required, since this state is not directly optically accessible from the ground state, but only via the population transfer from S_2 to S_1. This pathway seems to be however incoherent [3], thus making simple pump probe measurements impossible. Recently it has been realized that by a pulse sequence that incorporates stimulated emission pumping (SEP) coherent motion in dark states can be observed [4]. FSRS is able to collect vibrational spectra of S_1 with high temporal and spectral resolution, but it is not sensitive to the relative phase between modes, thus a wavepacket motion cannot be reconstructed from this data.

In this work we apply degenerate four-wave mixing spectroscopy (DFWM) combined with narrowband detection (1nm spectral resolution) to probe and control the wavepacket dynamics in S_0. In combination with a pump pulse (pump-DFWM) we are able to monitor coherent dynamics of the dark S_1 state.
The vibrational spectrum of S_0 and S_1 has been observed in several picosecond resonance Raman studies and has been recently studied with <100 fs time resolution with femtosecond-stimulated Raman spectroscopy (FSRS) [5]. Compressed output pulses of 10 μJ from a NOPA are frequency tunable from 400-700nm and have a typical pulse duration of 16 fs. The output of one NOPA is split into the 3 DFWM beams. The pulses within two of the beams are passed

through an all-reflective pulse shaper to control their temporal profile. The second NOPA delivers the pump pulse for the pump – DFWM experiments used for probing S_1 dynamics. A 300μm sample holds all-trans-β-carotene dissolved in cyclohexane. The data obtained for resonant DFWM on the S_0-S_2 transition show pronounced wavepacket oscillations for red shifted small bandwidth detection at 546 nm (Fig. 1 (a)). Fourier transformation reveals that the wavepacket is due to coherent S_0 mode dynamics (Fig. 1 (b)). The low frequency peak at ~400cm-1 originates from beatings between the strongest β-carotene modes. No dynamics from S_2 can be observed, possibly due to its fast decay. The S_0 C=C stretch mode requires a more red shifted detection compared to the lower modes.
Non-resonant DFWM on the S_0-S_2 transition (center wavelength 555 nm) at higher pulse energies excites and probes a ground state wavepacket via Raman excitation (t_{12}=0). Again wavepacket motion is only observed for red shifted small bandwidth detection (see Fig. 1 (a)). Shaping the time coincident pump and Stokes into a pulse train allowed the selective excitation of the C-C stretch ground state mode (see Fig. 1 (a)).

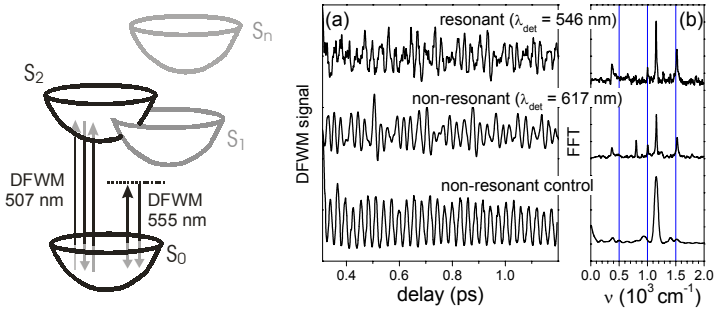
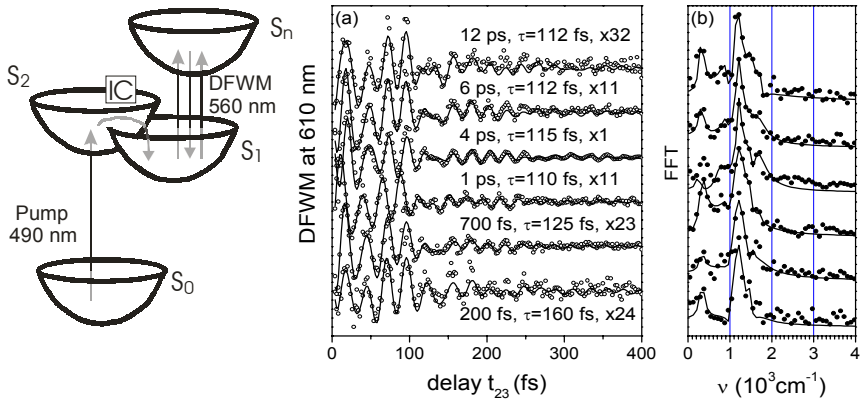


Fig. 1. Resonant and non-resonant DFWM data of the ground state S0. Also shown is the control of the S0 wavepacket using pulse train excitation.

We proceed with the first time observation of coherent motion in the S_1 / hot S_1 state of all-*trans*-β-carotene. The S_1 state can not be directly excited from S_0, and thus can only be populated via transfer through the conical intersection between S_2 and S_1. Since strong evidence exists that this population transfer occurs incoherently, it is necessary to create coherent motion in S_1 by a second optical excitation process in order to be able to probe the coherent time dynamics of S_1 modes. Therefore in our experiments we use a pump pulse at 490 nm previous to the DFWM sequence at 560 nm (the center wavelength of the S_1- S_n absorption band) to transfer population from S_0 to S_2 (see schematic in Fig. 3). This technique is known in literature as pump-DFWM [6]. The DFWM sequence at 560 nm is used to probe and excite the incoherent population originating from the population pumped into S_2 and transferred via conical intersection to S_1. In order to avoid non-resonant excitation of the ground state a much reduced pump and DFWM pulse energy were adjusted. A phase-locked chopper was used to periodically block the S_0-S_2 resonant pump. In all transients the DFWM pump and

Stokes were time coincident (t_{12}=0). No signal is observed when the pump is in its off state, while for "pump on" S_1 wavepacket dynamics could be observed when detecting at 610 nm (see Fig. 2 (a)). The oscillatory motion is located on top of an exponential decaying signal, with a decay constant of τ ~112-160 fs depending on the pump delay. Note that the wavepacket motion is strongest if the pump



precedes the DFWM sequence by 4 ps.

Fig. 2. Wavepacket dynamics of the optically dark S1 state of all-trans-β-carotene probed with pump-DFWM. (a) DFWM signal with "pump on" detected at 610nm, for different pump delays. Without pump no signal is observed. The oscillations are on top of a signal that decays exponentially with rate τ. Scaling factor x of the data, with respect to the transient recorded at a pump delay of 4 ps. (b) Fourier transform of the transients in (a).

Evidence for the S_1 nature of the observed modes is provided by a multimode fit model that fits all transients and spectra with good accuracy.
In summary we have shown that pump-DFWM in combination with spectral detection of 1nm resolution can be successfully applied to the study of complex molecular systems, where optically dark electronic states are common.

References

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