ELECTRONIC SUPPLEMENTARY INFORMATION

Mapping Multidimensional Excited State Dynamics in Real Time Using Pump-Impulsive-Vibrational-Spectroscopy and Pump-Degenerate-Four-Wave-Mixing

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1. Detailed Experimental Methods

1a. Pump-IVS at 390 nm with Hyperspectral Detection

The following setup was used to record pump-IVS data with excitation wavelength at 390 nm (denoted IP(1) in the main text) and with hyperspectral detection. The experimental setup is the same as reported previously.¹ Briefly, Multipass amplified Ti;Sapph laser producing ~30 fs pulses centered at 790 nm with 0.7 mJ of energy was used at 370 Hz repetition rate to generate ~390 nm pulses by SHG in a 200 µm BBO crystal (IP(1)) and to seed a one-stage reconfigured commercial noncollinear optical parametric amplifier (NOPA). The latter produced a few µJ ultra-broadband pulses (~540-700 nm), whose typical spectrum is shown in Fig. 1 in the main text. These pulses were compressed to \sim 7.5-8.5 fs. which is within <10% from their transform limited value, by a BK7 prism pair followed by a 19-channel aluminium coated deformable mirror (OKO Flexible Optical) positioned in the Fourier plane of a 4-f shaper, as described in Ref 2. These pulses were sent to a degenerate push-probe setup, consisting of fused silica metallic beam splitters, which were compensated for in the appropriate beam paths. IP, push and probe pulses of typical intensities of 500 nJ, 50 nJ and 2 nJ were focused to a 1/e intensity diameter in the sample cell of \sim 300 µm, \sim 120 μ m, and ~120 μ m, respectively, as calculated by measuring their intensity through a circular aperture. Transmitted probe and reference (I_0) pulses, the latter of which was derived by an additional splitting of the NOPA output beams and bypassed the sample, were co-dispersed in a 1/8 meter imaging CCD spectrograph (Oriel/Andor Newton) using a multitrack fiber bundle and read shot-by-shot. For acquiring the vibrational data, the push pulse was chopped using an optical chopper (Thorlabs) operated at half the repetition rate of the system (185 Hz), and two consecutive readouts (push-on/push-off) were used to calculate optical density difference (Δ OD). Two-dimensional differential absorption spectra as a function of the probe

wavelength and delay $(\Delta OD(\lambda_{pr}, t))$ were acquired in the spectral range of ~540-700 nm. All beams had parallel polarizations.

1b. Pump-DFWM and Pump-IVS at 500 nm

The following setup was used to acquire homodyne and heterodyne-detected pump DFWM and pump-IVS data for excitation at 500 nm (denoted IP(2) in the main text).

For the pump-DFWM experiments a scheme with two NOPAs was used, both delivering sub-20 fs pulses, which were fed by a regenerative amplifier at 1 kHz repetition rate. Both NOPAs are tuneable to deliver spectra in sub-regions of 470 - 780 nm and were compressed with prism compressors to <20 fs. The output of the first NOPA served as an actinic-pump pulse (IP(2)), which excites the sample to an excited electronic state.³⁻⁷ It was tuned near the 0-0 transition of beta-carotene in THF (near ~ 500 nm). The system then evolves during a first period of relaxation (T). The evolution is probed at variable T-delays by a degenerate four-wave-mixing pulse sequence (DFWM). For this, the output of the second NOPA was split into three beams, whose spectra were tuned to cover the red wing of β -CAR's ESA-band from the S₁-state (see Fig. 1 in the main text), which were arranged in the folded BOXCARS geometry. The delay of a probe pulse (τ_{23}) is scanned relative to two pulses, (pump (pu) -and Stokes (St)). Excitation energies for IP-, pu/St- and pr- pulses were set to 100 nJ, 15 nJ and 10 nJ, respectively. The beam diameters were set to 100 µm and 70 µm for IP- and DFWM-pulses, respectively, as determined by a beam-analyzer CCDcamera. The delay between pu/St-pulses (τ_{12}) was set to zero in the present experiments. All beams had parallel polarizations. The signal in pump-DFWM was collected in the phasematching direction $+k_{IP}-k_{IP}+k_{pu}-k_{St}+k_{pr}$ using photomultipliers (pump-DFWM) and in direction of the probe-pulse (pump-IVS) using photodiodes equipped with interference filters of 10 nm bandwidth (FWHM).

2. Examples for Transient Absorption Spectra at different T-delays

Fig. 3(a) in the main text presents three representative transient absorption spectra at different IP delays, as color-coded contour maps (Δ OD(λ ,t)), acquired in IP(1) pump-IVS experiments. In all cases, the optical chopper was placed in the beam path of the *push* pulse, meaning that the Δ OD represents the relative contribution of the push-on vs. push-off to the transient absorption, with the IP always on. Here, in Fig. S1, we present additional examples, to present the full dynamics observed from short T-delays (S₂ and SEP to S₀), excited S₁, relaxed S₁, excited-S₀, and relaxed S₀.

A few different behaviors are observed, differing even qualitatively from each other. First, for blocked-IP, the signal in general is much smaller, since the push pulse is only nearresonant with the S₀ absorption. This signal consists of an ultrashort (<50 fs) mixture of absorption and emission, consisting of the coherent artifact and electronic transitions from the ultra-short-lived S₂ state. Afterwards, the signal consists of the well-known excited state absorption centered at ~570 nm which blue-shifts and narrows with time.^{8,9} Second, for IP delays (T) of <200 fs, the transient absorption is dominated by a negative signal, spanning up to ~640 nm, which based on its much longer temporal decay reflects contributions of hot S₀, caused by the stimulated emission from S₂ or from a closely-lying excited state.^{4,8,10} For T>200 fs, the signal is dominated by a negative lobe at <600 nm, reflecting the bleaching of S₁ state, and a positive lobe at longer wavelengths which grows with a delay, reflecting the absorption of the created hot-S₁. The negative lobe decays on a few hundreds of femtoseconds due to sequential IC from S_n to S₁. The long T delays represent admixtures of Blocked-IP and medium delays presented above, with higher weight to the former as T is bigger, as expected.



Figure S1. Transient absorption of β -carotene in THF presented as color-coded contour map, representing: $\Delta OD(\lambda, \tau_{23})$. In all cases, push pulse was chopped, and is the one used as a reference for the differential absorption, after the IP excites the sample.

<u>3. Heterodyne-Detected Pump-DFWM signals of β-carotene</u>

The amplitude of vibrational coherence contributions in homodyne-detected pump-DFWM signals is influenced by the evolution of population contributions through nonlinear signal-polarization cross-terms. This artificial effect can, however, be removed by the introduction of an external local oscillator electric field such as an additional pulse which is phase-coherent to the excitation pulses, or alternatively through additionally generated stationary signals from an internal source such as an additional dye-molecule dissolved in the sample solution. As our current experimental setup for pump-DFWM does not allow for the generation of phase-stable local oscillator electric fields from external sources additional to the four excitation- and probing pulses, we employed the latter approach in this work to eliminate the effects from homodyne signal detection as shown in the following (Fig. S2(a)).

As a dye-molecule serving as an "internal local-oscillator" we chose the cyanine-dye HITCI for which the corresponding ground-state absorption spectrum only minimally overlaps with the ground-state absorption of β -carotene (Fig. S2(b)). Thus, the spectral position of the DFWM-sequence overlaps with the ground-state absorption of HITCI but not with the ground-state absorption of the carotenoid. This way, a third-order polarization is generated from the DFWM-sequence interacting with the ground-state absorption of HITCI if the IP-pulse (blue) arrives at the sample position at delays on which the DFWM-sequence has already passed the sample. For T-delays on which the IP-pulse precedes the DFWM-sequence, an additional fifth-order polarization is induced in the sample in addition to the third-order polarization are emitted from the sample in the same direction and are hence detected by the same detector (Fig. S2(a)). As the third-order polarization is much stronger in amplitude as the weak fifth-order signal, the third-order polarization acts an intrinsically phase-stable local oscillator to enhance the fifth-order signals. As the lifetime of the excited state in HITCI is on the order of nanoseconds (see below), the local-oscillator lives long

enough in τ_{23} -direction to compensate for the rapid signal decay in homodyne detected

pump-DFWM signals.



Figure S2. (a) Schematic representation of the experimental configuration of heterodynedetected pump-DFWM signals using a dye-molecule as an intrinsic local oscillator. From a mixture of the carotenoid and the dye a weak fifth-order signal stemming from the carotenoid is emitted on top of a strong third-order signal from the dye molecule alone. The third-order polarization acts as a local oscillator for the fifth-order polarization. (b) corresponding absorption spectra of β -carotene in THF without the dye (black), the dye absorption spectrum (cyan) and the absorption spectrum of the mixture (red) along with the applied DFWM-spectrum (orange) and the IP-spectrum (blue). The horizontal line indicates the value of $\Delta OD = 0$ mOD in a pump-probe experiment (dashed line, T = 1 ps).

Examples of homodyne and heterodyne detected pump-DFWM signals of β -carotene in THF are depicted in Figure S3(a) and S3(b), respectively. As discussed in Refs 3 and 5 extensively, the depicted dynamics for homodyne-detected pump-DFWM at early T-delays (T = 0.1 ps) and late T-delays (T ≥ 1ps) are due to signal contributions from a hot groundstate species induced via stimulated emission pumping (long-living signal at T = 0.1 ps) as well as depletion and subsequent repopulation of the S_1 state at later T-delays (short-living signal for $T \ge 1ps$), respectively (Fig. S3(a)).

Heterodyne-detected transients show a different temporal evolution in both T- and τ_{23} -direction. This is reasoned by interference contributions between population dynamics from third- and fifth-order signals as is discussed elsewhere. The signal of the sample solution interacting with the DFWM-sequence only (green line Fig. S3 (b)) show a nearly horizontal signal intensity despite the coherent artifact around time-zero. This is due to third-order DFWM signals from HITCI for which the DFWM-sequence is resonant with the ground-state absorption (Fig. S2 (b)). For T=0.1 ps the signal shows a fast decay followed by nearly invariant signal intensity on the timescale of our experiment in τ_{23} -direction (≤ 1 ps). For late T-delays (T ≥ 1 ps) the signal shows decay on the timescale of a few tens of femtoseconds followed by a rise in signal intensity and approximately constant signal intensity afterwards.



Figure S3. Experimental transients of homodyne-detected ((a) and (c)) and heterodyne-detected ((b) and)d)) pump-DFWM data of β -carotene in THF at 640nm. The signals at T = 0.1 ps and for HITCI + β -car for heterodyne-detection in (b) were scaled by a factor of 0.5 and 0.8, respectively. (c) and (d) show residuals of oscillatory signal contributions extracted from signals in (a) and (b) as discussed in the text.

As in all other datasets, the population dynamics were fit exponentially and the fit was subtracted to give the oscillatory residuals only (Fig. S3 (c) and (d)). For homodynedetected signals (Fig. S3(c)) long-lived oscillations are observed at early IP-delay (0.1 ps, black line) while the oscillations are only short-lived at late T-delays ($T \ge 1$ ps, red and blue lines). Contrasting to that, heterodyne-detection results in oscillations that live for several hundreds of femtoseconds and even exhibit considerable intensity at 1 ps τ_{23} -delay (Fig. S3 (d)). This observation is reasoned by the heterodyning-effect of the third-order polarization of the dye signal which interferes with the S₁ signal-polarization of the carotenoid and this is completely in line with results from pump-IVS experiments (see the main text). This hence proofs that the coherent oscillations that are observed in homodyne-detected pump-DFWM (Fig. S3 and the main text) live much longer as experimentally observed.

From the oscillatory residuals of heterodyne-detected pump-DFWM signals at different T-delays, FT-spectra were calculated which are shown in the main text (Fig. 8 (a) and (b)). The FT-spectra show the same sets of bands as already observed in homodyne detected pump-DFWM and pump-IVS experiments (Fig. 6 and 7 in the main text) for the carotenoid and an additional weak band that is attributable to HITCI vibrations (~1435 cm⁻¹). Figures S4 and S5 show the corresponding amplitude evolution in T-direction of the FT-bands at 1785 cm⁻¹ and 1250 cm⁻¹, respectively, at different detection wavelengths. The band at 1785 cm⁻¹ exhibits an initial rise in the FT-amplitudes which is best fit by a biphasic rise with time constants of $t_{rise1} \sim 300$ fs and $t_{rise2} \sim 1500$ fs and afterwards decay with a time constant of 9 - 12 ps. The band at 1250 cm⁻¹ exhibits a slightly different rise behavior compared to the 1785 cm⁻¹ amplitude evolution with only one dominant rise time-constant ($t_{rise1} \sim 500$ fs) and the maximum of the FT-amplitude between 1 - 2 ps, slightly dependent on the detection wavelength (Fig. S5). Most reliable data-points are observable around 620 nm detection because the amplitude of the 1250 cm⁻¹ mode decreases as the detection wavelength is tuned towards the red- and blue- edges of the applied DFWM-spectrum. As

observed for the 1785 cm⁻¹ mode, the decay of the 1250 cm⁻¹ band proceeds with a timeconstant of 9 - 12 ps.

Despite the observation of slightly different maxima (~1.7 ps and ~2 ps) for the two modes, the evolution of both band-amplitudes with T-delays is reasonably similar but it is different from the corresponding evolution of population dynamics in Pump-Probe dynamics which exhibits a maximum around 700 fs (see Fig. 9 in the main text). This shows that the mechanism that is responsible for the evolution of the FT-amplitudes is similar for both vibrational modes in S₁.



Figure S4. FT-amplitude evolution of heterodyne-detected pump-DFWM signals for the 1785 cm⁻¹ mode in β -carotene in dependence of the detection wavelength. Red lines indicate exponential fits with double exponential rise und mono-exponential decay.



Figure S5. FT-amplitude evolution of S_1 bands of β -carotene in THF at 1250 cm⁻¹ of heterodynedetected Pump-DFWM signals at 620 nm (blue), 630 nm (black), 640 nm (red). The amplitude of the 1250 cm⁻¹ at 650 nm is too low to result in reliable data points.

Taken together, the evolution of the amplitudes of the S₁-charateristic bands in heterodyne-detected pump-DFWM experiments exhibit a dependence on T-delays which is comparable to the dynamics of these modes that are observed in pump-IVS (see Fig. 7 and 9 in the main text). This is shown in Figure S6 below where the amplitude evolution of the 1785 cm⁻¹ mode in pump-IVS is compared with both homodyne- and heterodyne-detected pump-DFWM dynamics. Heterodyne detection in pump-DFWM results in a shift of the maximum of the mode-evolution from around 400 fs (red circles, homodyne detection) to around 2 ps (black circles, heterodyne detection), comparable to that of pump-IVS data (IP(2), blue circles, ~3 ps). However, slight differences are observed in the rise-dynamics of the FT-amplitudes, showing a slightly faster increase in FT-amplitudes for heterodyne-detected pump-DFWM compared to pump-IVS. Such subtle differences in dynamics

between pump-IVS and heterodyne-detected pump-DFWM with the method of an intrinsic local oscillator (here: HITCI) can be reasoned by alterations of the population dynamics by cross-terms between third- and fifth-order polarizations. In order to rigorously exclude such effects, heterodyne-detection needs to be performed with an externally generated phase-coherent local oscillator electric field which will be realized in future experiments.



Figure S6. Evolution of the FT-amplitude of the 1785 cm⁻¹ mode of β -carotene in THF in homodyne- (red), heterodyne detected pump-DFWM (black circles), and pump-IVS signals (blue circles) for signal detection at 640nm.

4. Two Vibrational Modes near 1800 cm⁻¹ – Additional Comments

As stated in the main text, current results suggest contributions from two modes between $1720 - 1800 \text{ cm}^{-1}$, the well-known location of S₁ terminal C=C stretching mode. Fig. 10 in the main text presents evidence from pump-IVS experiments, showing an additional band red-shifted to the main peak appearing around 1785 cm⁻¹ at short T-delays. Here, we show additional observations and analysis conducted on this and other datasets, as well as the complementary observation using pump-DFWM.

Fig. S7 presents an overlay of pump-IVS FT spectra acquired with IP(1), either using the same probing wavelength at different T-delays (panel (a)), or at the same initial time with different wavelengths (panel (b)).



Figure S7. Closer look on the ~1,800 cm⁻¹ S₁ C=C stretching mode, demonstrating the existence of two possible contributions, especially at short T delays, shown here for pump-IVS data. (a) presents the same dataset as in Fig. 7 in the main text with magnification on the relevant frequency area, demonstrating evolution of the mode and of the two contributions. (b) presents the wavelength-dependent lineshapes around the same frequencies in a single T=0.2 ps delay (such short delay was chosen since the two contributions are dominant then).

Panel (a) demonstrates in magnification the presence of two contributions to the band between 1700 - 1800 cm⁻¹: a main one around the known ~1785 cm⁻¹ frequency, and a smaller one centred around ~1740 cm⁻¹. The latter contributes mainly during the initial few picoseconds, and then disappears while leaving behind some asymmetry in the lineshape (shoulder towards lower frequencies). Panel (b) depicts the clear probing-wavelength (λ_{pr}) dependence, showing a general trend of stronger relative contribution for the lower-mode with increasing of detection wavelength (λ_{pr}).

The interpretation of these observations is discussed in the main text. Aware of the difficulties of fitting the data directly in the FT power spectra, due to interferences between real and imaginary parts in the spectra of adjacent modes, Figure S8 depicts a detailed analysis using fits with double-Gaussians since they help in demonstrating the multiple contributions. Two distinct bands are clearly depicted: a small band around ~1740 cm⁻¹ (blue line), which contributes during the initial few picoseconds of relaxation, together with a second band around 1785 cm⁻¹ (cyan line), which grows in intensity on a picosecond timescale.



Figure S8. Two-mode contributions to the 1,785 cm⁻¹ S1 C=C stretching mode. Fitting the experimentally observed band structure around 1700-1800 cm⁻¹ to a double Gaussian profile (open circles show experimental data, red line represents double Gaussian fit, blue and cyan lines indicate single Gaussian functions).

Similar observations and analysis are demonstrated next for pump-DFWM experiments as well. The data in Fig. S9 were acquired by heterodyning with the dye signal as described above. As explained in the main text, one can expect different relative

amplitudes of the two bands, depending on detection wavelengths. This is due to different maxima in the absorption spectra between vibrationally relaxed (570 nm) and vibrationally excited (red-shifted) molecules in S₁. Such a dependence on the detection wavelength is observed for the pump-DFWM data as well, manifested by an increase in the relative amplitude for the second band $(1730 - 1740 \text{ cm}^{-1})$ by going from 630 nm to longer wavelengths (640/650 nm).



Figure S9. Comparison of fitting of multiple mode contributions in heterodyne detected pump-DFWM signals at detection wavelengths of 630 nm (a), 640 nm (b) and 650 nm (c). Fitting with double Gaussian functions is only necessary for detection wavelengths in the red part of the ESA-band longer than 630 nm.

The last observation to be presented here is the attempt to follow the main frequency of the entire 1700-1850 cm⁻¹ spectral range directly in dependence of T-delays. If we determine the frequency-value of this mode as the frequency of the maximum amplitude for every T-delay as shown below in Fig. S10 the relative amplitudes of the two contributing bands change between T = 0.1 - 0.2 ps in a way that the band around 1785 cm⁻¹ becomes the dominant species for T > ~0.3 ps, but at previous delays causing a "jump" in frequencies at these delays from around 1740 cm⁻¹ to 1765 cm⁻¹. Since this effect makes the extraction of

lifetimes and comparison to previous data challenging, and due to its high sensitivity to both the acquired data and to the applied analysis, we opted to use a simple one-Gaussian analysis in the main text, as described there.

In any case, disregarding this ultrafast evolution in frequencies (T < 0.2 ps), we fit the frequency shift in the pump-IVS data for later delays by a single exponential with a time constant of 300 ± 50 fs and 550 ± 80 fs for IP(1) (open circles) and IP(2) (filled circles), respectively. This timescale of evolution is similar to that obtained with a simple one-Gaussian analysis (see main text), and both are in good agreement is similar with FSRS data (see text for details).



Figure S10. Evolution of the maximum frequency of the band in pump-IVS data (IP(1) open circles, IP(2) filled circles) together with exponential fits (black), when determined by the maximum amplitude for every T-delay. Clear "jumps" between the two adjacent lobes are apparent in the analysis, lending further support to the existence of two contributions (compare to Fig. 9(b) in the main text)

5. Application of Pump-IVS and Pump-DFWM on Lycopene/THF

To demonstrate strengths and robustness of both techniques that measure the FID of the vibrational response, we next present a set of results obtained for Lycopene, another carotenoid with similar vibrational signatures compared to β -carotene.

5a. Pump-IVS Experiments on Lycopene/THF

Fig. S11 presents time-resolved Raman-spectra acquired by pump-IVS after excitation at 500 nm (IP(2)).



Figure S11. Demonstration for pump-IVS on lycopene in THF. The data demonstrate the evolution of the Raman spectra of the sample, probed at λ_{pr} =640 nm, and are presented in a similar fashion to these of β -carotene found in Fig. 6-8 in the main text. The black line indicates the pure ground-state DFWM signal while grey lines report of pump-DFWM data after interaction with all four pulses. Data was collected using IP(2).

These again present observation of dynamics of vibrational modes on the groundand excited- electronic states, and in particular the observation of the build-up and decay of the S_1 characteristic C=C stretching mode which, after relaxation within the S_1 state, obtains values of ~1800 cm⁻¹. At very early delays of the IP-pulse (<0.2 ps, bottom spectrum), ground-state modes (e.g., 1520 cm⁻¹, 1160 cm⁻¹) are observed with fairly high intensity due to the induction of ground-state contributions, already observed with pump-DFWM previously.⁵ As the IP-pulse is delayed with respect to push and probe-pulses, we observe the growth of a vibrational mode at about 1800 cm⁻¹. As the photo-induced population of the S₁-state decays, this mode is also diminished in its intensity. The evolution dynamics of the S₁ characteristic modes agree well with the known different timescales for IC in both systems.

To demonstrate the amplitude wavelength-dependence of the vibrational modes in pump-IVS on Lycopene, Fig S12 presents two representative hyperspectral Raman spectra for blocked-IP (S_0 of lycopene and solvent only) and for T=2 ps with the presence of the IP, that were collected after excitation with IP(1). In the latter, the distinctive 1800 cm⁻¹ mode is observed, and as in β -Carotene has a bi-lobed intensity profile around the S_1 absorption of lycopene.



Figure S12. Hyperspectral Raman spectra of lycopene in THF, obtained in similar conditions to that of β -carotene. Two examples are shown for blocked-IP (push-probe only) and for T=2 ps delay of the IP, in the left and right panels, respectively. Lower panels demonstrate the full DFT-mapping of the data, while upper panels depict horizontal cuts of these at two representative probing wavelengths. Data was collected using IP(1).

5b. Pump-DFWM Experiments on Lycopene/THF

FT-spectra obtained from oscillatory residuals of pump-DFWM transients on lycopene in THF are presented in Figure S13(a) and (b) for detection wavelengths of 570 nm and 640 nm, respectively.



Figure S13. FT-spectra of homodyne-detected Pump-DFWM experiments on Lycopene in THF detected at 570nm (a) and 640 nm (b). The build-up and subsequent decay of S_1 -specific modes is clearly observed as described in the text. Black lines indicate the pure ground-state DFWM signal while grey lines report of pump-DFWM data after interaction with all four pulses.

As characteristic for pump-DFWM experiments on carotenoids, the pump-DFWM data on lycopene report on the build-up and decay of vibrational bands in the FTs that are specific for different stages of relaxation. For instance, FTs for T-delays at very early IP-delays (e.g. 0.1 ps) exhibit bands that are indicative for ground-state modes induced by SEP-DFWM. Later stages (T>0.2 ps) report on generation of S₁-specific bands around 1800 cm⁻¹, 1555 cm⁻¹ as well as a broad feature comprising multiple closely spaced bands between1200 - 1350 cm⁻¹ that all exhibit continuous spectral evolution and decay traces indicative for vibrational relaxation in the S₁ state of lycopene and subsequent internal conversion to the S₀-

state. These characteristic dynamics are most clearly observed for detection wavelengths around 640 nm (Fig. S13(b)) since vibrationally excited molecules S_1 absorb strongly in this spectral region compared to 570 nm (Fig. S13(a)).

Following earlier lines of data-analysis the FT-amplitude of S₁-specific bands can be followed in time as is shown for 570 nm and 640 nm in Figure S14. As observed for βcarotene, a characteristic rise is observed for both detection wavelengths with time-constants of ~0.8 ps and ~0.25 ps for 570 nm and 640 nm, respectively. The FT-amplitudes peak at later IP-delays (T > 2 ps) for blue-detuned detection wavelengths (570 nm) compared to reddetuned detection wavelengths (640 nm, ~700 fs), in line with β-carotene data, followed by decay with a time-constant of 5 ± 1 ps, in reasonable agreement with the lifetime of lycopene's S₁ state.⁹



Figure S14. Comparison of FT-amplitude dynamics at red (640 nm) and blue (570 nm) detection wavelengths within the DFWM spectrum centered around 600 nm. Open circles are experimental data, solid lines are exponential fits to the data.

Clear dynamical shifts in the vibrational frequencies of especially C=C stretching modes are observed by going from the ground electronic state to the S₁ state in lycopene as well. This is demonstrated in Figure S15 where the dynamics of the two bands around 1500 cm⁻¹ (a)) an 1800 cm⁻¹ (b)) are compared. Starting from ground-state frequencies around 1520 cm⁻¹ the frequency of the first C=C stretching mode up-shifts \sim 35 cm⁻¹ on a timescale of a few hundred femtoseconds to reach a final and static value in the S₁ state of about 1555 cm⁻¹. Following electronic relaxation dynamics, the mode shifts back to its

relaxed ground-sate values (~1520 cm⁻¹) within a few picoseconds after excitation. Relaxation is approximately complete after 14 ps. Similar dynamics are observed for the 1800 cm⁻¹ mode which dynamically shifts from around 1740 cm⁻¹ to a final and static value of ~1810 cm⁻¹ in the S₁ state within the initial picosecond after excitation (Fig. S15 (b)) in line with the dynamics observed for β -carotene. The shaded region in Fig. S15(b) indicates values of less confidence since the amplitude of the S₁-specific modes is only very low at delays T> 10 ps.



Figure S15. Evolution of vibrational frequencies from the S_1 -state of lycopene in THF in Pump-DFWM data detected at 640 nm. (a) The double bond stretching mode around 1520 cm⁻¹ (ground state) shifts dynamically to around 1555 cm⁻¹ in the excited state and back to the ground-state value (~1520 cm⁻¹) after the decay of the excited-state population. (b) The double bond stretching mode exclusive to the S_1 state shifts dynamically from around 1740 cm⁻¹ (early initial pump-delays) to around 1800 cm⁻¹ in the relaxed S_1 state (T> 1 ps). The red-shaded area indicates values of less confidence due to low signal intensity.

Overall, the pump-IVS and pump-DFWM data on lycopene allow for a complete characterization of vibrational dynamics in the excited state. Taking into account the different electronic lifetimes of lycopene and β -carotene, the presented results are completely in line with the dynamics of β -carotene presented in the manuscript thus validating the approach to timely resolve vibrational relaxation dynamics in excited electronic states with time-domain spectroscopic techniques.

6. Sliding-Window Analysis of the Vibrational Free Induction Decay

In order to obtain the lifetime of the coherent high-frequency oscillations from the S₁ state of the carotenoids, a spectrogram-analysis was performed on the residual oscillations after subtraction of an exponential fit to the experimental data. Such a spectrogram-analysis can reveal frequency- and amplitude-evolution of the oscillations during relaxation.¹¹⁻¹⁴ Results are shown in Figure S16 during the initial 500 fs of window-delays of experimental pump-IVS data (a), heterodyne-detected pump-DFWM data (b) from ß-carotene in THF (T = 3 ps) together with a comparison with simulated data from a set of exponentially decaying oscillations (c)) is shown. The simulation comprise three independent, uncoupled vibrational modes (915 cm⁻¹, 1540 cm⁻¹, 1785 cm⁻¹) that decay exponentially in amplitude with time constants of 950 fs, 550 fs and 350 fs, respectively. These time-constants were set to match the experimentally determined time constants from fits to the amplitude-decay of the main bands. The spectrograms from the experimental data exhibit very similar amplitude and frequency evolution of the two high-frequency modes in the S_1 state (~1544 cm⁻¹ and 1785 cm⁻¹). Both carotenoid-modes decay on a much faster timescale compared to the solvent mode (915 cm⁻¹) which decays with a time-constant of 950 fs. The contribution of artificial frequency- and amplitude evolution of vibrational frequencies of closely spaced modes in a time-resolved spectrogram analysis has been discussed in reference 14 extensively. These effects are seen here as oscillatory amplitude and frequency-modulations with a period of about 130 fs (~ 250 cm^{-1} , corresponding approximately to the differencefrequency of the 1540 cm-1 and 1785 cm⁻¹ mode) in the high-frequency modes (1540 cm⁻¹ and 1800 cm⁻¹) which are present in both experimental (a) and b)) and simulated data (c)). Such effects in a sliding window-FFT analysis of closely-spaced high-frequency modes do not bear any physical-interpretable information of vibrational coupling of the modes in the excited states due to the limited bandwidth of the applied window function (500 fs here).

Figure S16 d) shows a comparison between experimental (het. Pump-DFWM, b)) and simulated FFT-spectra calculated from the full-length transient (transient-length ~1.6 ps). The line widths (~27 cm⁻¹ and 35 cm⁻¹) of the peaks of the high-frequency modes (1540 cm⁻¹ and 1800 cm⁻¹) can be seen from the inset and reveal a close matching between experimental and simulated data. Also shown is a FFT-spectrum of the pure ground-state DFWM dynamics for comparison (blue line, inset). These data reveal that vibrational dephasing in the S₁ state of carotenoids is mode-specific as discussed in the main text.



Figure S16. Spectrogram-Analysis of the vibrational FID of experimental and simulated high-frequency oscillations from the S₁ state of carotenoids obtained by pump-IVS (IP(2)) (a), heterodyne-detected pump-DFWM experiments from β -carotene in THF (b) along with simulated data. (d) comparison between FFT-spectra of β -carotene in the S₁ excited state (black), ground-state (blue) and simulated data (red) calculated from the full-length transients. For the sliding window calculations a super-Gaussian window width of 500 fs (FWHM) was employed and a stepwidth of $\Delta T = 10$ fs in window-delay direction. Dephasing time-constants (1785 cm⁻¹ (350 fs), 1540 cm⁻¹ (550 fs), 915 cm⁻¹ (950 fs)) were obtained by fitting exponential functions to the decay-profiles of the modes. For details please see the text.

7. Additional Traits of Hyperspectral Probing

As mentioned and demonstrated in the main text, one of the main advantages of the time-domain pump-IVS and pump-DFWM methods is the wealth of information recorded by hyperspectral probing. As previously pointed, this is an additional spectral "axis" to the signal, missing in frequency-domain techniques like FSRS, in which such information can be obtained only by a set of distinct experiments with different Raman pulses, which of course leads to additional experimental changes.¹⁵ Simultaneous recording of structural information within the same experiment in different detection wavelengths gives further insights on vibrational and electronic population dynamics.

In the current work, this strength is demonstrated in numerous aspects. First, the recording of multispectral population and vibrational kinetics helps in interpreting the resulting data and Raman spectra. Second, the amplitude and phase profiles of different vibrational modes might help in their assignment to different electronic states, as pointed up in the main text and in Fig. 12 there. As suggested, it can also help in differentiating contribution of normal modes from beating (differences or sums) of a number of modes. Third, in the case of possible multimode contributions to a seemingly broad peak, λ_{pr} -dependence of Raman spectra can help in their interpretation and assignment. This is not really a strength (compared to, e.g., FSRS), but rather a way to overcome difficulties in time-domain vibrational spectroscopy. It is demonstrated for the distinctive S₁ C=C stretching mode near ~1800 cm⁻¹ (Fig. 10 in the main text).

Here, we demonstrate the third point also for the ~1510-1540 cm⁻¹ C=C stretching mode, which is more challening to interpret due to known adjacent contributions from S_1 , hot- S_0 and relaxed- S_0 . Similar considerations apply also to the ~1150-1160 cm⁻¹ C-C mode. In both peaks, existence of blue- and red- shifted components – manifested either by shifting of the peak position or by two-contributions ("shoulders") on the same peak – are apparent. These are likely to reflect additional contributions from hot- S_0 (at 1145 and 1515 cm⁻¹, respectively), which were shown to relax with time constant of \sim 5 ps after creation. While this is hard to quantify in our current data, due to overlap of contributions from different states, the general timescale is consistent with that number.

The weight of different contributions is expected to be time- and wavelengthdependent. This is demonstrated in Fig. S17 by a series of Fourier spectra taken at different T-delays and different λ_{pr} for the 1530 cm⁻¹ C=C mode.



Figure S17. Traits of hyperspectral probing of pump-IVS experiments. Time-dependence and wavelength-dependence of the ~1530 cm⁻¹ C=C mode, which is build of contributions of relaxed- S_0 (1525 cm⁻¹), hot- S_0 (1515 cm⁻¹), and S_1 (1544 cm⁻¹), as marked by the vertical lines portrayed on the curves. The absolute amplitude between different T's is arbitrary.

The full quantitative modeling of these curves and of the λ_{pr} -dependence will require further work, especially for taking into account the phase-dependent interference structures of closely-lying modes. This leads to challenges in the interpretation of different observations, due to slight changes in the relative phase of oscillations (leading to different pattern due to above mentioned interferences), in the characteristics of the FT and the apodization-window used, etc. Nonetheless, even at the current level, a few clear trends are observed (and were checked for reliability by conducting the analysis using a variety of parameters): (a) In all probing wavelengths, a gradual shift of the weight of contributions from $S_1 \rightarrow$ hot- $S_0 \rightarrow$ relaxed- S_0 is apparent, corresponding in time scales to the relevant processes ($S_1 \rightarrow S_0$ IC, S_0 cooling). (b) The different contributions are highly λ_{pr} -dependent, and this relation is time-dependent, as expected from changes in the transient spectrum, leading to changes in resonance conditions with time. At the longest delays shown (30-50 ps), the Fourier spectra closely resembles that of the ground state, obtained with the AP blocked (see Figures 2b and 4a), as expected after full $S_1 \rightarrow S_0$ IC and S_0 vibrational relaxation.

In any case, this analysis demonstrates a big advantage of both time-domain methods, employing hyperspectral detection, and that is the ability to discriminate for and against different contributions based on the probing wavelength within the same experiment.. Nonetheless, since different contributions are summed up not coherently in the latter, the analysis is far more simple since simple subtractions can aid in differentiating contributions to the vibrational data.

8. Examples of Signal Contributing Energy-Level Diagrams

In order to explain arrow-coding and signal generation in pump-DFWM and pump-IVS in more detail (see Fig. 1 in the main text), Figure S18 shows examples of three contributing response pathways in terms of energy level diagrams of carotenoids, relevant for interpretation of observations described in the main text. Following general conventions for these energy level diagrams, solid and dashed arrows represent light matter interaction on the |ket>- and <bra|-side of the density matrix, respectively. Wavy arrows indicate signal generation. Figure S18(a) shows the induction of ground state dynamics in carotenoids via stimulated emission pumping (SEP) from the one-photon transition allowed S₂ state. Figure S18(b) shows induction of vibrational coherence in the S₁ state of carotenoids after relaxation between S₂ and S₁ states. This diagram can be associated with the representation of the arrows in the pulse sequence in the manuscript (Figure 1). Figure S18(c) shows the induction of an excited state population in the S_n state (and correspondingly a "hole" in the S₁ state) which quickly relaxed back to the S₁ state (re-filling of the "hole").



Figure S18. Examples of energy-level diagrams for relevant signal dynamics in pump-DFWM experiments on carotenoids. S_0 is the electronic ground state and S_1 , S_2 and S_n are excited electronic singlet states. Solid and dashed blue and red arrows represent action on the |ket>- and
bra|-side of the density matrix. The black arrows indicate a population relaxation between excited states. (a) Example of a stimulated emission pumping (SEP) pathway inducing ground state dynamics in the pump-DFWM signal for positive T-delays. (b) Example of an ESA-DFWM (ESA – excited state absorption) pathway inducing excited electronic state coherence dynamics in the pump-DFWM signal for positive T-delays via a transition of excited state absorption between S_1 and S_n . (c) Example of an ESA-DFWM pathway involving excited state repopulation dynamics of the S_1 state in the pump-DFWM signal induced via population of the S_n state by electronic ESA transition. For clarity, SEP- and ESA-DFWM pathway signal contributions consist of relaxation dynamics in S_0 and S_1 and S_1 and S_n states, respectively, from which only one representative example is shown. Similar diagrams can be easily drawn for pump-IVS as well, with the pump/St pulses interactions replaced by two interactions of the push pulse.

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