Supplementary Material to

Vibronic Dynamics Resolved by Global and Target Analysis of Ultrafast Transient Absorption Spectra

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Properties of the pulses used



Figure S 1. (A) Measured (solid red line) absorption spectrum of all-trans β-carotene in cyclohexane solution. Fit (dashed black line) of a typical pump/probe pulse spectrum (measured above 500 nm, solid black line) from Polli¹. The fit parameters of the Gaussian shape are 17785 cm⁻¹ and FWHM 3390 cm⁻¹. They correspond to a (10⁷/17785=)562 nm Gaussian shaped pulse of 7.4 fs FWHM (B).

A typical pump/probe pulse spectrum, measured above 500 nm, is depicted in Figure S 1A, solid black line. It was converted to wavenumber $\overline{v}(cm^{-1}) = 10^7 / \lambda(nm)$, and then fitted (Figure S 1A, dashed line) with a Gaussian shape $\exp(-\log(2)(2(\overline{v} - \overline{v}_{max}) / \Delta \overline{v})^2)$ from which we estimated the parameters $\overline{v}_{max} = 17785 / cm$ and $\Delta \overline{v} = 3390 / cm$. This spectral shape corresponds to the absolute value of the Fourier transform of a pulse $\exp(-\log(2)(2t / \Delta)^2)\sin(\omega t)$ with $\Delta = 7.4 fs$ and $\omega = 2\pi c \overline{v}_{max} = 3.35 rad / fs$ with $c = 3 \cdot 10^{-5}$ the speed of light in cm / fs, cf. Figure S 1B.



Figure S 2. Broad-band impulsive vibrational spectroscopy (BB-IVS) on β-carotene, Fig.1 from Liebel². (A) Energy level diagram for β-carotene, note that the hot S₁ state has been omitted. (B) Absorption spectra of the SO (black) and S1 (green) states in cyclohexane. (C) Typical spectra of the excitation pump (blue), impulsive pump (purple), and the probe pulse (green) used in BB-IVS. (D) Corresponding relative pulse durations and timing.



The coherent artefact in cyclohexane from Liebel²

Figure S 3. DOAS analysis of cyclohexane excited with a 12 fs pulse centered at \approx 570 nm and probed with a 5 fs pulse at 660 nm. The analysis at 759 nm is detailed in A,B,C,F. (A,B) Zoom from -0.1 ps to 0.5 ps (after the maximum of the IRF) of the data (in mOD, grey) and the fit (black). Note the different vertical scales: the CA is clearly visible in A, but clipped in B. (C,F) Same data on a timescale from 0.1 ps to 2 ps (after the maximum of the IRF) and residuals of the fit, with in the insets power spectra of the data (C) and the residuals (F). (D) CA IRF 0th, 1st and 2nd derivative (black, red and blue) (E) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (G,H,I) Overview of the estimated DOAS and phases. (G) Cosine oscillations with frequencies $\overline{V} n$ (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (H) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. (I) Estimated phase profiles of the DOAS. The grey vertical lines at 663 nm in panels H and I are discussed in the text.

Detailed DOAS analysis of Nile blue in methanol



Figure S 4. DOAS analysis of nile blue in methanol excited with a 10 fs pulse centered at 800 nm. (A) Population of the excited state. (B) Estimated SADS. The analysis at 630 nm is detailed in (C,F). Zoom from -0.1 ps to 0.5 ps (after the maximum of the IRF) of the data (in mOD, grey) and the fit (black), note the different vertical scales, the CA is clearly visible in F, but clipped in C. (D) CA IRF 0th, 1st and 2nd derivative (black, red and blue) (E) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (G,H,I) Overview of the estimated DOAS and phases with largest DOAS. (G) Cosine

oscillations with frequencies Vn (in cm⁻¹) (where *n* is the DOAS number) and damping rates γ (in ps⁻¹) written in the legend at the left, using the appropriate color. (H) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. Scaling of the DOAS is such that the product of the DOAS and the damped oscillation is the contribution to the fit. (I) Estimated phase profiles of the DOAS. (J,K,L) Comparison of DOAS #16 (black) to next seven DOAS. (M,N,O) Comparison of DOAS #16 (black, multiplied by 0.5) to smallest six DOAS. The shape of DOAS #15 (magenta) resembles that of DOAS #16, however its contribution to the fit is about four times smaller.

The grey vertical lines at 652 nm in panels H and I (and K, L, N, O) are discussed in the text.



Figure S 5. Decomposition of selected time traces of nile blue in methanol data (in mOD, grey, and the fit, maroon) from 0.1 to 2.2 ps after the maximum of the IRF. Key: lower black line, long lived excited state bleach and SE, upper black line is 0 mOD. Green is the superposition of the CA related signals (IRF and its derivatives, plus ultrafast damped oscillations). The sum of the contributions of DOAS #16 and #15 (592 and 595 cm⁻¹, damping rates γ 0.3 and 1.4 ps⁻¹) is depicted in red. The blue line is the sum of DOAS #1-14, and 17,18 (cf. Figure S 4G,J,M). Wavelength is indicated in the ordinate label.



Figure S 6. Conventional Fourier Transform analysis of the residuals at 20 selected wavelengths from 0.1 to 2.2 ps after the maximum of the IRF. Key: nile blue in methanol data (in mOD, grey, and the "fit" with an exponential decay, red). Insets depict the power spectra from 0-2000 cm⁻¹. Wavelength is indicated in the ordinate label.

DOAS simulations



Figure S 7. (A) Simulation (black) of estimated (grey) nile blue 592 cm⁻¹ DOAS (Figure 5A). (B) "DOAS contributions" of the electronically excited state (ES, red) and of the ground state (GS, black) computed from their cosine and sine contributions. (C) total cosine (black) and sine (red) contributions to the DOAS, compared to those from the data (grey, solid and dashed). (D) individual cosine (black) and sine (red) contributions of the GS (solid) and the ES (dotted), compared to those from the data (grey, solid and dashed).



Fit quality of the β -carotene in cyclohexane data from Polli¹

Figure S 8 Selected time traces of the all-trans β-carotene in cyclohexane data from Polli¹ (in mOD, grey) and fit (black). Wavelength is indicated in the ordinate label. Note that the time axis is linear until 0.3 ps (after the maximum of the IRF), and logarithmic thereafter.



Figure S 9. Residual properties after fitting the damped oscillations. First left (u res, A, zoom until 0.3 ps after the maximum of the IRF) and right (w res, B) singular vectors of the residual matrix. (C) screeplot of the singular values.



Detailed DOAS analysis of the β-carotene in cyclohexane data from Polli¹

Figure S 10. DOAS analysis of β -carotene in cyclohexane excited with a 10 fs pulse centered at 560 nm and probed with an attenuated pulse from the Polli¹ data. (A) Populations of the sequential kinetic scheme used. Estimated SADS (B) and DADS (C). Key A-C: 168 fs (S2, black), 0.38 ps (hot S1, red), and 9.0 ps (S1, blue). (D) CA IRF 0th, 1st and 2nd derivative (black, red and blue) (E) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (F) Zoom from -0.1 ps to 1.2 ps (after the maximum of the IRF) of the 580 nm data (in mOD, grey) and the fit (black).

Overview of the estimated DOAS and phases. (G,J,M) Cosine oscillations with frequencies V n (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (H,K,N) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. Scaling of the DOAS is such that the product of the DOAS and the damped oscillation is the contribution to the fit. (I,L,O) Estimated phase profiles of the DOAS. The grey vertical lines at 563 nm in panels H and I and at 523 nm in panels K and L are discussed in the text.



Fit quality of the β -carotene in cyclohexane data from Liebel ²

Figure S 11. Selected time traces of the all-trans β -carotene in cyclohexane data from Liebel² (in mOD, grey) and fit (black). Wavelength is indicated in the ordinate label. Note that the time axis is linear until 0.2 ps (after the maximum of the IRF), and logarithmic thereafter.

Detailed DOAS analysis of the β -carotene in cyclohexane data from Liebel²



Figure S 12. DOAS analysis of β -carotene in cyclohexane excited with a 12 fs pulse centered at \approx 570 nm and probed with a 5 fs pulse at 660 nm from the Liebel² data. (A) Populations of the sequential kinetic scheme used. Estimated SADS (B) and DADS (C). Key A-C: 199 (S2, black), 337 fs (hot S1, red), and 8.9 ps (S1, blue). (D) CA IRF 0th, 1st and 2nd derivative (black, red and blue) (E) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (F) Zoom from 0.1 ps to 1.1 ps (after the maximum of the IRF) of the 579 nm data (in mOD, grey) and the fit (black).

Overview of the estimated DOAS and phases. (G,J,M) Cosine oscillations with frequencies V n (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (H,K,N) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. Scaling of the DOAS is such that the product of the DOAS and the damped oscillation is the contribution to the fit. (I,L,O) Estimated phase profiles of the DOAS. The grey vertical lines at 630 nm in panels H and I and at 606 nm in panels K and L are discussed in the text.

Reproducibility with β-carotene in cyclohexane data from Liebel²

A second experiment with slightly different pulse properties of β -carotene in cyclohexane demonstrates the reproducibility of the results. The oscillations from 0.1-2.1 ps after the maximum of the IRF are depicted in Figure S 13. They can be well fitted with rms errors of 54 and 41 μ OD, respectively.



Figure S 13. Selected time traces of the all-trans β -carotene in cyclohexane data from Figure 5 (in mOD, grey) and fit (black). The data from a second experiment are in orange and their fit is in red. Wavelength is indicated in the ordinate label. Note that the time axis is linear from 0.1-2.1 ps (after the maximum of the IRF),

The slightly different pulse properties cause slightly different SADS (demonstrated in Figure 8A) resulting in apparent offsets of many of the black and red traces in Figure S 13. The summary of the fit results for the second experiment is shown in Figure S 14.



Figure S 14. Reproducibility of the results for a second experiment of the DOAS analysis of β -carotene in cyclohexane excited with a 12 fs pulse centered at \approx 570 nm and probed with a 5 fs pulse at 660 nm from the Liebel² data. (A) Populations of the sequential kinetic scheme used. Estimated SADS (B) and DADS (C). Key A-C: 199 (S2, black), 337 fs (hot S1, red), and 8.9 ps (S1, blue). (D) CA IRF 0th, 1st and 2nd derivative (black, red and blue) (E) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (F) Zoom from 0.1 ps to 1.1 ps (after the maximum of the IRF) of the 579 nm data (in mOD, grey) and the fit (black).

Overview of the estimated DOAS and phases. (G,J,M) Cosine oscillations with frequencies V n (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (H,K,N) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. Scaling of the DOAS is such that the product of the DOAS and the damped oscillation is the contribution to the fit. (I,L,O) Estimated phase profiles of the DOAS. The grey vertical lines at 630 nm in panels H and I and at 606 nm in panels K and L are discussed in the text.

When comparing Figure 5/Figure S 12 and Figure S 14 the qualitative similarities are striking. The second experiment was analysed with exactly the same nonlinear parameters as the first experiment, and the SADS, IRFAS, DOAS and phases are free parameters. One major difference is the scale of the data, the SADS amplitudes are \approx 65% as large. This is attributed to the slightly different pulse properties. Some of the phase unwrapped curves in panels L show different unwrappings with 2π differences. Overall, the agreement between Figure 5/Figure S 12 and Figure S 14 is considered excellent, which comes as no surprise in view of the close correspondence observed in the raw data, cf. Figure S 13.

The slightly different pulse properties provide additional information. In the second experiment the S2 ESA is smaller above 600 nm, indicating that the S2 state has less vibrational excitation, cf. the grey and black SADS in Figure S 15F. Consequently, also the hot S1 ESA is smaller above 550 nm, cf. the orange and red SADS in Figure S 15F. Smaller amplitudes in the 2nd experiment are present from \approx 580-700 nm in the CA 0th and 1st IRFAS, cf. the grey vs. black and the orange vs. red SADS in Figure S 15E. Figure S 15A-C demonstrate that in a subset of the DOAS smaller amplitudes from \approx 580-700 nm can be attributed to the S2 excited state. Of course, one has to take into account that these frequencies are also present with the solvent only, but the DOAS are quite distinct from those in Figure S 3G-I.



Figure S 15. Overlay of selected fit results from the 1st and 2nd experiment of β -carotene in cyclohexane indicated with dark and light colors, respectively. Estimated SADS (F), key: 199 (S2, black/grey), 337 fs (hot S1, red/orange), and 8.9 ps (S1, blue/cyan). (D) CA IRF 0th, 1st and 2nd derivative (black/grey, red/orange and blue/cyan) (E) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (A-C) Selected estimated DOAS and phases. (A) Cosine oscillations with frequencies $\overline{V} n$ (in /cm) (where *n* is the DOAS number) and damping rates γ' (in 1/ps) written in the legend at the left, using the appropriate color. (B) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. Scaling of the DOAS is such that the product of the DOAS and the damped oscillation is the contribution to the fit. (C) Estimated phase profiles of the DOAS.

DOAS analysis of β -carotene in cyclohexane measured with 3 fs time resolution over a 12 ps time scale



Figure S 16. DOAS analysis of β -carotene in cyclohexane excited with a 10 fs pulse centered at 606 nm *measured with 3 fs time resolution over a 12 ps time scale*. (A) Populations of the sequential kinetic scheme used. Estimated SADS (B) and DADS (C). Key A-C: 168 (S2, black), 356 fs (hot S1, red), and 9.0 ps (S1, blue). (D) CA IRF 0th, 1st and 2nd derivative (black, red and blue) (E) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (F) Zoom from -0.2 ps to 1.2 ps (after the maximum of the IRF) of the 580 nm data (in mOD, grey) and the fit (black).

Overview of the estimated DOAS and phases. (G,J) Cosine oscillations with frequencies \overline{Vn} (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (H,K) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. Scaling of the DOAS is such that the product of the DOAS and the damped oscillation is the contribution to the fit. (I,L) Estimated phase profiles of the DOAS. The grey vertical lines at 606 nm in panels H and I and at 685 nm in panels K and L are discussed in the text.





The 802/cm damped oscillation has been observed with 3 fs time resolution over a 12 ps time scale. The plot of the 539 nm trace demonstrates that it is damped with 0.18/ps. In this experiment the pulse power was maximal at 606 nm, as deduced from the node in the DOAS accompanied by a phase jump (Figure S 16H,I). The CA in Figure S 16F is about twice as large as in Figure 5F, whereas the S1 SADS is 10% smaller, cf. Figure S 15B and Figure 5B. The SADS and the DOAS both show wavy patterns in the wavelength dimension. Most probably the SNR is too low, the rmse is 0.29 mOD, which is five times higher than with Figure 5. The similar SADS amplitudes suggest that the overlap of the pump pulse with the red edge of the β -carotene absorption is comparable. The nodes in the DOAS accompanied by phase jumps (Figure S 16K,L) near 685 nm, i.e. in the ESA region, could perhaps be interpreted as a wavepacket.



Decomposition of the β -carotene in cyclohexane data

Figure S 18. Decomposition of selected time traces of the all-trans β-carotene in cyclohexane data from Figure 7 (in mOD, grey) and fit (maroon). Wavelength is indicated in the ordinate label. Note that the time axis is linear from 0.1-1.1 ps (after the maximum of the IRF). Key excited state contributions: S2, black; hot S1, red; S1, blue. Key damped oscillations: green is the 803/cm cyclohexane ISRS, cyan is the sum of the CA damped oscillations (decay rates 18-26/ps), magenta is the sum of all the β-carotene damped oscillations (i.e., without any cyclohexane contribution).

Repumping the S1 state of β-carotene in cyclohexane from Liebel²

In Liebel² an experiment is described (Figure S 2.C) where a 460 nm prepulse is administered 2 ps before the ISRS pulse. The data could be well described using a sequential kinetic scheme with four lifetimes (Figure S 19A): 71 fs (black), 176 fs (red), 520 fs (blue) and long lived (green). At 2 ps after the prepulse most of the relaxation is over, and the still excited molecules are in the S1 state. Then the ESA of the ISRS pulse excites these S1 states to higher excited states Sy, thus the S1 ESA disappears, resulting in a bleach of the S1 ESA (black SADS in Figure S 19B). Note that the IRFAS (Figure S 19E) also show clear features, indicating near-immediate disappearance of part of this bleach. The relaxation of the Sy states (blue). These hot S1 states relax in 520 fs to the final S1 state. Unexpectedly, the final S1 SADS (green) is not zero. It shows excess ESA at 580 nm (albeit less) in combination with bleach at \approx 560 nm (Figure S 19B). Since the vibrational relaxation is assumed to be over after 2 ps, it appears that we are dealing with a mixture of S1 and S? excited states, probably attributable to different conformations. The ISRS pulse appears to differently excite the different excited states, which after relaxation are redistributed, resulting in this excess ESA at 580 nm in combination with a bleach at \approx 560 nm. It is striking that in this experiment there was no detectable excitation of the β-carotene S0.

The estimated DOAS (Figure S 19H,K,N,Q) show complex patterns. The clearest indication of a possible wavepacket in S2 and (hot) S1 is the node near 565 nm which is with 401/cm (#11, Figure S 19M-O, black, damping rate 0.7/ps). At 665 nm the by now well-known cyclohexane 802/cm ISRS mode is present (#10, Figure S 19J-L, magenta, damping rate 0.2/ps).



Figure S 19. DOAS analysis of the β-carotene S1 state (initiated by a 460 nm prepulse at -2 ps) in cyclohexane with a 12 fs pulse centered at ≈570 nm and probed with a 5 fs pulse at 660 nm from the Liebel² data. (A) Populations of the sequential kinetic scheme used. Estimated SADS (B) and DADS (C). Key A-C: 71 (black), 176 fs (red), 520 fs (blue) and long lived (green). (D) CA IRF 0th, 1st and 2nd derivative (black, red and blue) (E) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (F) Zoom from 0.1 ps to 1.1 ps (after the maximum of the IRF) of the 580 nm data (in mOD, grey) and the fit (black).

Overview of the estimated DOAS and phases. (G,J,M,P) Cosine oscillations with frequencies $\overline{V}n$ (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left, using the appropriate color. (H,K,N,Q) Estimated DOAS (with number indicated in the legend at the far left), scaled for comparison. Scaling of the DOAS is such that the product of the DOAS and the damped oscillation is the contribution to the fit. (I,L,O,R) Estimated phase profiles of the DOAS. The grey vertical lines at 665 nm in panels K and L and at 565 nm in panels N and O are discussed in the text.

Global target analysis of FSRS measurements of all-trans β-carotene



Figure S 20. Target analysis for FSRS experiments performed on β -carotene in cyclohexane after 495 nm excitation. Transient Raman difference absorption (in units of μ OD) at selected wavenumbers (every 10 cm⁻¹, indicated in the ordinate label). Key: data (grey), target analysis fit (black). Note that the time axis is linear until 1 ps and logarithmic after that. Note also that each panel is scaled to its maximum.



Figure S 21. Selection of DOAS analysis of the β -carotene in cyclohexane after 495 nm excitation (A) 950 cm⁻¹ data (in mOD, grey) and the fit (black). (B) IRFAS. Scaling of the IRFAS is such that the product of the IRFAS and the IRF derivative is the contribution to the fit. (C) CA IRF 0th, 1st and 2nd derivative (black, red and blue)

Overview of the estimated 94 cm⁻¹ DOAS and phases. (D) Cosine oscillation with frequency $\overline{\nu}2$ 94 cm⁻¹ and damping rate γ 2.5/ps. (E) Estimated DOAS. (F) Estimated phase profile of the DOAS.



Figure S 22. Decomposition of selected time traces of the all-trans β-carotene in cyclohexane FSRS data from Figure S 20 (in mOD, grey) and fit (maroon). Wavenumber is indicated in the ordinate label. Note that the time axis is linear from -1 till 1 ps (after the maximum of the IRF). Key excited state contributions: S2, black; hot S1, red; S1', blue; S1, green. Key damped oscillations: magenta is the 94/cm damped oscillation (cf. Figure S 21D-F), cyan is the sum of the CA IRF and other damped oscillations.

References

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