Assignment of carotene S* state features to the vibrationally hot ground electronic state†

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The so-called S* state has been suggested to play an important role in the photophysics of β -carotene and other carotenoids in solution and photosynthetic light-harvesting complexes, yet its origin has remained elusive. The present experiments employing temperature-dependent steady-state absorption spectroscopy and ultrafast pump-supercontinuum probe (PSCP) transient absorption measurements of β -carotene in solution demonstrate that the spectral features of S* are due to vibrationally excited molecules in the ground electronic state S₀. Characteristic spectral signatures, such as a highly structured bleach below 500 nm and absorption in the range 500–660 nm result from the superposition of hot S₀ absorption (“S₀’”) on top of the ground-state bleach of room-temperature molecules. Appearance and disappearance of the S₀* molecules can be completely described by a global kinetic analysis employing time-dependent species-associated spectra without the need to invoke the population of an intermediate electronically excited state.

1. Introduction

β -Carotene is the prototype of a diverse group of naturally occurring pigment molecules performing multiple functions, e.g. as light-harvesting pigments in the blue–green spectral region.¹ The strong absorption of β -carotene in the visible region is due to the S₀(1¹A_g[−]) → S₂(1¹B_u⁺) electronic transition. In *n*-hexane, the S₂ state prepared upon photoexcitation decays by ultrafast (*ca.* 160 fs) internal conversion (IC) to the S₁(2¹A_g[−]) state, which eventually internally converts back to S₀ in *ca.* 9 ps. Apart from these two excited states, additional electronic states have been suggested as important intermediates in the light-harvesting process, denoted as 1¹B_u[−] and S*. Their roles in the complex network of energy transfer processes are currently a matter of hot debate.²

The physical origin of the S* state absorption features of β -carotene and other carotenoids in solution and photosynthetic light-harvesting complexes has remained elusive despite of more than a decade of experimental research (for a comprehensive review see e.g. ref. 2). Transient spectra for β -carotene in solution demonstrate characteristic S* absorption as a pronounced extra feature on the blue side of the S₁ → S_n excited state absorption. Several competing models for S* exist, and none of them could be finally proved so far. Previous work suggested that S* is generated on a sub-100 fs timescale^{3,4} and is a *separate* electronically excited state populated from S₂ in parallel with S₁.^{3,5–7} However, other experiments in solution demonstrated that depletion of S₂ population by an ultrafast

laser pulse only affects the S₁ → S_n band.^{4,8} In such a case, S* cannot be formed from the S₂ state. Instead, it was hypothesized that S* is a highly *vibrationally excited* S₀ state generated by impulsive stimulated Raman scattering (ISRS) *via* S₂. Note that the assignment of S* features to hot ground state molecules (generated by IC from S₁) was already suggested in a seminal study by Gillbro and co-workers for two macrocarotenes.⁹ Papagiannakis *et al.* introduced an alternative model, where resonant two-photon excitation *via* S₂ as an intermediate state promotes a fraction of the β -carotene molecules into an energetically higher S_n state, from which they decay to form S* as an electronically excited state.¹⁰ In addition, van Grondelle and co-workers reported on a similar state, denoted as S[‡], which spectrally resembles S*, but has a longer lifetime.¹¹ Furthermore, structured S₀ bleach features have been observed by Andersson and Gillbro for macrocarotenes, and similarly by Motzkus and co-workers for macrocarotenes and β -carotene. These were sharper than in the steady-state absorption spectrum and emerged together with S* absorption.^{4,9} Very recently, Chabra *et al.* identified S* in four C₄₀ carotenoids and modeled their data in terms of an irreversible sequential kinetic scheme, yielding S* lifetimes in benzene of 5.6 and 9.1 ps for rhodoxanthin and canthaxanthin, respectively. No separate S* lifetime was identified for β -carotene and echinenone. They assigned the pronounced structure in the bleach region to electronic excitation of a specific S₀ sub-population.¹²

2. Experimental

2.1 Steady-state absorption spectroscopy

Temperature-dependent S₀ → S₂ steady-state absorption spectra were recorded and internally background-corrected on a Varian Cary 5 E spectrometer with a wavelength step-size of 0.25 nm employing a temperature-controlled (±0.1 K) cell with 2 mm path length. In typical laser-excitation experiments,

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such as the pump–supercontinuum probe (PSCP) measurements reported below, β -carotene molecules are electronically excited, and after two consecutive IC steps the resulting vibrationally excited “hot” S_0^* molecules collisionally relax in a bath of *n*-hexane at 298.15 K. For best comparison of spectral features of “hot” molecules, one would therefore ideally like to measure temperature-dependent steady-state electronic absorption spectra of gas-phase β -carotene (*i.e.* without the influence of the solvent) and afterwards correct for solvent-induced shifts and broadening. This is, however, not possible, because of the non-volatility of β -carotene and its expected isomerization and thermal decomposition at high temperatures. We therefore used the following strategy: Steady-state absorption spectra were recorded in solution at the temperatures 298.15, 303.15, 313.15, 323.15 and 333.15 K and the amplitudes of the spectra were then corrected for the known density reduction of *n*-hexane with increasing temperature.¹³ A very small difference in oscillator strengths ($\ll 1\%$) of the spectra remained, and this was accounted for by appropriate scaling factors. The spectra also exhibited polarizability-related thermochromic shifts which will be dealt with in section 3.1.

2.2 PSCP experiments

The experimental setup for broadband transient absorption measurements has been described previously.¹⁴ Concepts and details of PSCP spectroscopy can be found in earlier publications.^{15,16} In the current experiments, β -carotene molecules were excited by a pump pulse centered at 487 nm (*n*-hexane) or 485 nm (acetone), which was generated in a noncollinearly phase-matched optical parametric amplifier (NOPA). The subsequent dynamics were probed by a supercontinuum over a particularly wide spectral range (350–770 nm). The supercontinuum was generated in a 1 mm thick CaF_2 plate using 540 nm pulses from another NOPA. Pump and probe pulses were time-delayed with respect to each other and overlapped in a flow-cell with 0.4 mm path length and 0.2 mm thick quartz windows, resulting in a pump–probe intensity cross-correlation time of *ca.* 55 fs. Measurements were performed at photon densities of *ca.* $5 \times 10^{14} \text{ cm}^{-2}$.

2.3 Chemicals and handling of solutions

High purity *all-trans*- β -carotene samples were employed. The absence of *cis*-isomers already became evident from the very low absorption in the 300–350 nm region (*ca.* 6% of the absorption maximum), which is characteristic for high-quality *all-trans*- β -carotene samples¹⁷ (solvents were of spectroscopic quality (Merck Uvasol)). Measurements under an argon atmosphere or ambient air showed no differences. Oxidation of β -carotene therefore played no role. Furthermore, there was no sample degradation, as clearly seen *e.g.* by identical spectral amplitudes in the *cis*-peak region after a heating–cooling cycle covering the range 333.15–298.15 K and the same room-temperature spectrum was recovered. Contamination of the spectra by *cis*-isomers or shorter-conjugated decomposition and oxidation products, which could lead to spectral distortion, can therefore be ruled out. This suggests that the spectral changes reported below are only due to temperature changes.

2.4 DFT calculations for the ground electronic state

To estimate the average thermal energy of β -carotene at different temperatures, we carried out complementary density functional calculations employing the B3LYP functional and a 6-311G(d,p) basis set using the Q-CHEM 3.0 package.¹⁸ The optimized structure has *s-cis* configurations of the two β -ionone rings with tilt angles of 46.6° . The calculated unscaled 282 harmonic frequencies (see ESI†) were used to determine the average energy of the molecules (above the zero point energy) at a given temperature *T* using the vibrational partition function:

$$\langle E \rangle = \sum_{i=1}^{282} \left[hc\tilde{\nu}_i / \left\{ \exp\left(\frac{hc\tilde{\nu}_i}{k_B T}\right) - 1 \right\} \right] \quad (1)$$

Anharmonicity effects were estimated by comparing the calculated harmonic C–H vibrational frequencies with typical experimental values,¹⁹ which leads to a scaling factor of *ca.* 0.96. When applying this scaling factor to the entire set of harmonic frequencies, the average energies determined by eqn (1) will not increase by more than 4%. This is negligible for the purpose of the current work.

3. Results and discussion

3.1 Temperature-dependent steady-state absorption spectra

Temperature-dependent $S_0 \rightarrow S_2$ steady-state absorption spectra for β -carotene in *n*-hexane in the range 298.15–333.15 K exhibited a well-known linear thermochromic blue-shift which is caused by the decrease of the polarizability $R(n)$ of *n*-hexane with increasing temperature (see inset in Fig. 1).^{20,21} Therefore, each spectrum was fitted to a sum of Gaussian functions, which provided the center position of the 0–0 transition at each temperature. Note that the characteristic spectral structure is mainly due to three vibrational modes, which are coupled to the $S_0 \rightarrow S_2$ electronic transition.^{22,23} The spectra were then overlaid at these center positions taking the 298.15 K spectrum as the reference. The resulting spectra are shown in Fig. 1. Evident is a broadening of the whole band with increasing temperature. The intensities of the absorption maxima decrease, intensities between absorption maxima increase, and there is a characteristic rise of the red band edge, indicating the population of higher S_0 vibrational levels.

In the context of the PSCP transient absorption spectra reported later on, we can also demonstrate how difference absorption spectra of vibrationally excited thermal β -carotene populations look. This can be done by subtracting the 298.15 K room temperature spectrum from the higher-temperature spectra, and applying the aforementioned correction for solvent effects. The results are shown in Fig. 2. Several characteristic features are notable. First, below $20\,500 \text{ cm}^{-1}$ absorption from hot ground state molecules is visible: a prominent broad hot band in the range $19\,000\text{--}20\,000 \text{ cm}^{-1}$ and also much weaker and more isolated hot band peaks at *ca.* $17\,900$, $16\,500$ and $15\,300 \text{ cm}^{-1}$. Actually, the latter two features are substantially separated from the main $S_0 \rightarrow S_2$ absorption band, so one might speculate that they could be due to extremely weak direct $S_0 \rightarrow S_1$ absorption. Such an

Fig. 1 Temperature-dependent steady-state absorption spectra of β -carotene in *n*-hexane corrected for the thermochromic shift. Arrows indicate the absorption change with increasing temperature. The inset illustrates the weak, linear thermochromic blue-shift of the absorption maximum in a plot vs. solvent polarizability (circles and solid fit line).

absorption has not been reported previously, but the additional thermal excitation might relax the strict selection rules, so that this formally not allowed transition could gain sufficient oscillator strength to produce such weak features. Increased absorption is also observed towards the blue, specifically at 21 500 cm^{-1} , and more weakly at 23 100 and 24 600 cm^{-1} .

Negative features arising from the subtracted 298.15 K spectrum are seen at 20 900, 22 300, 23 800 and 25 200 cm^{-1} . The strong modulation arising from the superposition of the hot positive-going and cold negative-going spectrum is striking. As expected, all features become more and more pronounced with increasing temperature difference. We already note at this point that these spectral characteristics are fully consistent with what has been previously observed in transient absorption experiments as features of the elusive “S* state” at longer delay times.^{4,9,12}

It is also enlightening to estimate the internal energies of the β -carotene molecules at the different temperatures. Based on eqn (1) we find average thermal energies $\langle E \rangle$ of 9320, 9613,

Fig. 2 Difference steady-state absorption spectra relative to 298.15 K of β -carotene in *n*-hexane at different temperatures. Weak absorption bands are magnified in the inset.

10 212, 10 829 and 11 464 cm^{-1} at 298.15, 303.15, 313.15, 323.15 and 333.15 K. We note that *e.g.* the 2144 cm^{-1} difference between the 333.15 and 298.15 K spectra is a realistic excess energy for excitation of β -carotene *via* impulsive stimulated Raman scattering (ISRS). This process was suggested by Motzkus and co-workers as one likely mechanism for the preparation of hot ground state β -carotene molecules in transient absorption experiments.^{4,8} Because it is well-known that the shape of “hot” absorption spectra only depends on the average vibrational excitation energy, but not on the detailed shape of the vibrational population distribution,^{24,25} the blue difference spectrum in Fig. 2 should be a realistic representation of any population of molecules with an excess energy of 2144 cm^{-1} relative to room temperature.

3.2 Transient PSCP spectra of β -carotene

The complete set of PSCP spectra for β -carotene in *n*-hexane is shown in Fig. 3. The short-time dynamics are depicted in the top panel. At early times, $S_0 \rightarrow S_2$ ground state bleach (GSB) as well as $S_2 \rightarrow S_0$ stimulated emission (SE) and $S_2 \rightarrow S_n$ excited-state absorption (ESA) appear, including superimposed Raman structure of β -carotene. The further spectral development is shown in the middle panel. The SE and ESA disappear with a time constant of 160 fs due to internal conversion (IC) and at the same time the $S_1 \rightarrow S_n$ ESA band appears, which peaks at *ca.* 550 nm. The ESA narrows with a time constant of 630 fs due to intramolecular vibrational redistribution (IVR) and possibly also collisional energy transfer to the solvent.^{8,26,27} In the bottom panel the decay of the S_1 and S* features is shown which is accompanied by the filling-up of the GSB. The S* shoulder around 510 nm is more pronounced at later times indicating a longer lifetime of S* compared to S_1 . The S_1 state internally converts with a time constant of 8.7 ps.

The dynamics will be subjected to a full global analysis in section 3.3, but at this point we would already like to highlight in more detail the spectral features related to S*. In the inset of Fig. 3 (bottom panel), we show an average of 21 PSCP spectra for the time range 65–75 ps in *n*-hexane, where the shorter-lived S_1 band has largely decayed. Transient absorption spectra at such late times have not been reported previously, but are essential to obtain useful estimates of the S* features because, as we will see later on in the global analysis, the time constant of S_0^* cooling is only *ca.* 3 ps larger than the S_1 lifetime. This averaged 65–75 ps spectrum, which has a bleach amplitude of *ca.* 1 mOD, shows striking similarities to the steady-state difference absorption spectra depicted in Fig. 2, specifically the highly structured bleach and the hot band at *ca.* 20 000 cm^{-1} . This already suggests that this signal arises from vibrationally hot S_0^* molecules superimposed on a bleach of cold room-temperature molecules. From a simple back-of-the-envelope calculation, we can directly correlate the ΔOD of this spectrum with the spectra in Fig. 1: Taking the initial bleach of *ca.* 100 mOD (Fig. 3) and full conversion of this population into S_0^* molecules with an average excess energy of 892 cm^{-1} ($T = 313.15$ K) relative to room temperature (298.15 K) one expects a transient absorption signal of this S_0^* population of *ca.* 1 mOD, which is consistent with the amplitude observed in Fig. 3 (inset).

Fig. 3 Transient PSCP absorption spectra of β -carotene in *n*-hexane for excitation at 487 nm (upper panel) from -0.2 to 0 ps at 20 fs steps; (middle panel) 0.05 to 0.5 ps and 0.50 to 1.50 ps at 50 fs and 500 fs steps, respectively; (lower panel) 2 to 20 ps and 25 to 50 ps at 2 ps and 5 ps steps, respectively. Some transient spectra are plotted as thick colored lines for guidance. The inverted steady-state absorption spectrum at 298.15 K is shown in the lower panel as a blue dashed line for comparison. The inset in the lower panel contains the average of 21 spectra in the range 65 – 75 ps (averaged bleach amplitude *ca.* 1 mOD).

Very similar S^* signatures must be also imprinted on the earlier transient spectra, because more vibrationally excited molecules with higher excess energy will be present at such times. Fig. 4 shows that this is indeed the case. We show three representative spectra at 2 , 12 and 24 ps. Evident is the well-known shoulder at about 510 nm and the increasingly prominent structure forming over the entire bleach region. We note that we obtain very similar results in other solvents and for a range of other C_{40} carotenoids.

To obtain a first rough impression of how the features connected to S^* look like at that time, spectra were normalized at $18\,500\text{ cm}^{-1}$ (where, as we will show later on in the global analysis, S_1 absorption dominates) and then the 2 ps spectrum was subtracted from the 24 ps spectrum. Results of such a procedure for the solvents *n*-hexane and acetone are shown in Fig. 5. Overall, the appearance is very similar to the spectrum at long times in the inset of Fig. 3. Again, there is a highly structured bleach region, and also additional absorption below $19\,000\text{ cm}^{-1}$, which appears to have larger amplitude towards

Fig. 4 Normalized transient PSCP spectra at 2 , 12 and 24 ps demonstrating S^* features for β -carotene in *n*-hexane. Vertical lines indicate the center wavelength of the pump pulse and its spectral FWHM.

the red than the spectrum in Fig. 3 (inset). This is reasonable considering the fact that at this point of collisional deactivation the β -carotene molecules must be considerably hotter. The interpretation of the amplitudes is of course dependent on the relative scaling of the two transient spectra and should be taken with some caution, yet it will become apparent from the global analysis reported below, that this qualitative procedure is well justified. We also note that in the two solvents the shift of the bleach and absorption peaks follows the shift in the position of the respective steady-state absorption spectra over the complete spectral range, which is easily understandable, because both the hot S_0^* spectrum and the S_0 GSB show the same spectral shift which is mainly determined by solvent polarizability. Also, as expected, a more structured steady-state absorption spectrum (*n*-hexane) results in a deeper modulated S^* spectrum.

3.3 Global analysis

We now present a complete modeling of the β -carotene dynamics based on a global kinetic analysis. We use a kinetic scheme considering three electronic states and intermediately formed vibrationally hot ground electronic state molecules: $S_2 \rightarrow S_1 \rightarrow S_0^* \rightarrow S_0$. We also include time-dependence of the species-associated spectra of S_1 and S_0^* . Time constants and spectra are globally optimized in a fully automatic fashion.²⁸ Fig. 6 shows the resulting best fit for the species-associated spectra and Fig. 7 the corresponding kinetics at four selected wavelengths for β -carotene in *n*-hexane. This procedure provides four different time constants, and in the following we identify and discuss the corresponding processes:

(a) τ_2 for the IC process $S_2 \rightarrow S_1$: We obtain a value of 160 fs for the decay of the initially prepared S_2 state, in very good agreement with previous studies.^{4,29,30} In each kinetic trace of Fig. 7 the time-dependent S_2 contribution is shown as a red line, which on the chosen time scale appears as a spike: either as a quickly disappearing stimulated emission (481 , 517 and 579 nm) or as a quickly decaying weak absorption (405 nm). The presence of absorption features in the UV and also towards the red is notable. It is therefore very likely that some

Fig. 5 Approximate S^* difference spectra (solid lines) obtained from subtracting scaled PSCP spectra at 2 and 24 ps for β -carotene in n -hexane (black) and acetone (red). Corresponding inverted steady-state absorption spectra are shown as dashed lines.

Fig. 6 Species-associated spectra from global kinetic analysis for β -carotene in n -hexane. (Solid lines, right side): time-dependent S_1 spectra at 0.06 (black line), 0.2, 0.4 (green line), 0.8 and 2.0 ps (magenta line). (Red line): S_0^* spectrum at 10 ps. (Blue dashed line): steady-state S_0 absorption spectrum (298.15 K). (Dotted black line): transient spectrum of S_2 .

weak $S_2 \rightarrow S_n$ excited state absorption is also superimposed on the $S_2 \rightarrow S_0$ stimulated emission.

(b) $\tau_1(S_1 \rightarrow S_0^*)$: The internal conversion from S_1 to S_0^* proceeds with a time constant of 8.7 ps. This is in good agreement with previous transient absorption studies, which typically found values of 9 ps or above.³¹ Our slightly smaller value is a direct consequence of the more detailed kinetic treatment of the transient absorption features which can separate the S_1 population decay from contributions due to slower cooling of vibrationally hot molecules in the ground electronic state S_0^* described in (d).

Fig. 7 Selected kinetic traces for β -carotene in n -hexane at four representative probe wavelengths (405, 481, 517 and 579 nm): (○) Experimental PSCP data from Fig. 3. (Black lines) Simulation results from global kinetic analysis with individual contributions from S_2 (red line), S_1 (blue line), S_0^* (magenta line) and S_0 (green line).

(c) $\tau_{\text{relax}}(S_1)$ -relaxation within the S_1 state (630 fs): While the S_1 state decays by IC to S_0^* , a superimposed relaxation process takes place in S_1 , which manifests itself as a transient change in shape of the $S_1 \rightarrow S_n$ absorption. Therefore, in the global analysis procedure we describe this process in terms of a time-dependent S_1 spectrum. The best fit is illustrated in Fig. 6 and characterized by a narrowing and amplitude rise of the $S_1 \rightarrow S_n$ ESA band. The time constant of 630 fs is consistent with fits of earlier transient absorption experiments, which however used an approximate sequential kinetic scheme with an intermediately formed “hot S_1 ” species.^{8,32} The type of spectral evolution we observe in Fig. 6 can be assigned to IVR processes within S_1 after IC from S_2 ,³³ possibly with some minor contributions of slower collisional energy transfer from vibrationally excited S_1 molecules to the solvent.⁹

The kinetic traces for S_1 in Fig. 7 (blue lines) clearly demonstrate the presence of the two processes described in (b) and (c): For instance, at 579 nm the decay looks clearly biexponential. The first fast component is $\tau_{\text{relax}}(S_1)$ (the band narrowing on the red edge of the S_1 band), and the slower component is $\tau_1(S_1 \rightarrow S_0^*)$. At 517 nm, $\tau_{\text{relax}}(S_1)$ correspondingly appears as a 630 fs rise component (compare the time-dependent S_1 spectra in Fig. 6), whereas the 8.7 ps decay is again due to IC from S_1 to S_0^* .

(d) $\tau_{\text{cooling}}(S_0^* \rightarrow S_0)$: Most relevant to the current study are the dynamics of S_0^* β -carotenes, *i.e.* their formation by IC from S_1 and subsequent vibrational cooling by collisions with the solvent. This is shown by the magenta lines in Fig. 7. The

S_0^* population is formed with the $S_1 \rightarrow S_0^*$ IC time constant of 8.7 ps and cools with a time constant of 11.9 ps, as obtained from our global analysis procedure. This is best seen in the profiles at 405 and 481 nm. The curved recovery of the bleach of the “cold” S_0 population (green lines in Fig. 7) is also easily explained by the formation of S_0 via the sequential steps $S_1 \rightarrow S_0^*$ and $S_0^* \rightarrow S_0$.

The S_0^* cooling time constant of 11.9 ps is in very good agreement with results for the collisional relaxation of other highly vibrationally excited organic molecules in *n*-alkanes, such as azulene.³⁴ A slightly faster value (10.2 ps) was reported by Motzkus and co-workers which is based on biexponential fits to the kinetics in the region spanning the red-edge of the $S_0 \rightarrow S_2$ GSB to the blue-edge of the $S_1 \rightarrow S_n$ ESA. In that case, the underlying model assumed an ISRS process for generation of S_0^* (see below).⁴ The influence of S_0^* formation and cooling on the kinetic profiles is of course most pronounced in the spectral region below 520 nm (Fig. 7). One representative example, in which way the individual species S_1 , S_0^* and S_0 contribute to the transient spectrum, can be found in Fig. 8 for a delay time of 27 ps. It clearly demonstrates how the superposition of the “hot” S_0^* absorption on a “cold” S_0 GSB produces the pronounced structure in the experimental PSCP spectrum.

We also note, that the best global fit was achieved by employing a time-dependent hot S_0^* spectrum, which evolves with the same 11.9 ps time constant as the $S_0^* \rightarrow S_0$ decay: At earlier times, the main band is broader and less structured, and the spectrum has an additional 560 nm hot band. This spectrum progressively narrows at later times, and the hot band disappears. This evolution is clearly seen in Fig. 6 when comparing the S_0^* spectrum at 10 ps (red line) with the S_0

steady-state absorption spectrum (blue dashed line). It is exactly this time dependence which is required to describe the finer details of the changes in the spectral region above 400 nm, which are seen in the normalized representation of Fig. 4. Such a time-dependent spectral development is also consistent with the spectra in Fig. 2 and well-known for other vibrationally “hot” molecules relaxing from higher to lower vibrational excess energies.^{34,35}

3.4 Mechanism of S_0^* formation

We finally discuss the photoinduced processes for S_0^* formation considering previous interpretations available in the literature.² It appears to be clear from our time-resolved data and the global kinetic analysis that absorption of vibrationally hot β -carotene initially formed via IC from S_1 make the decisive contribution to the S_0^* features. The excess energy provided by the pump laser is $E_{hv} = 20\,530\text{ cm}^{-1}$, and if all this energy would end up as vibrational excess energy in S_0^* then this would correspond to a total excitation energy of $\langle E \rangle = E_{hv} + \langle E \rangle_{298.15\text{ K}} = (20\,530 + 9320)\text{ cm}^{-1} = 29\,850\text{ cm}^{-1}$, corresponding to a temperature of 555 K (eqn (1)). Yet, some fraction of this excess energy is lost already by vibrational relaxation in S_1 during the lifetime of this state (the S_2 – S_1 energy gap is *ca.* 6000 cm^{-1} and part of the narrowing in the S_1 spectrum in Fig. 3, is likely due to this process). The 555 K should therefore be better taken as an upper limit for the achievable S_0^* energy. S_1 is located *ca.* $14\,500\text{ cm}^{-1}$ above S_0 ,³¹ so we can also determine a lower limit of vibrational excitation for molecules entering S_0 : Assuming that the S_1 vibrational frequencies are not largely different from S_0 we can estimate $\langle E \rangle = (14\,500 + 9320)\text{ cm}^{-1} = 23\,820\text{ cm}^{-1}$ (492 K) for molecules internally converting from a thermal distribution in S_1 . Regardless which limit is taken for further consideration, upon entering the ground electronic state such a population will definitely produce a hot difference spectrum with a larger amplitude than that seen in the spectra depicted in Fig. 2. These hot S_0^* molecules are formed with the S_1 lifetime (8.7 ps) and relax by intermolecular vibrational energy transfer to the solvent with a characteristic cooling time constant of 11.9 ps in *n*-hexane. Our signal-to-noise ratio is obviously sufficiently high to follow this cooling process up to very long times where deactivation is still not completely finished (Fig. 3, inset). We note that S_0^* formation according to this route was already suggested in the seminal paper of Andersson and Gillbro on the relaxation of two macrocarotenes.⁹

As a second process we consider ISRS, such as proposed by Motzkus and co-workers,^{4,8} which can certainly produce hot S_0^* molecules when ultrafast pulses of sufficient bandwidth are employed. The bandwidth of the pump pulse used in the current experiment is *ca.* 1000 cm^{-1} (Fig. 4). ISRS will therefore instantaneously produce S_0^* molecules with a rather low excess energy and spectral characteristics similar to that in Fig. 1. However, with respect to the current results, it is difficult to imagine how this pathway, starting with molecules which are already “almost cold”, could contribute to the signal of hot molecules up to the 70 ps range we observe. Molecules forming S_0^* by IC from S_1 will start at a much higher excess energy and overwhelm any ISRS contribution.

Fig. 8 Result of the global kinetic analysis for the transient PSCP spectrum (black line) at 27 ps. (Red line) Simulation result with individual contributions from S_1 (blue line), S_0^* (magenta line) and S_0 (green line).

ISRS also cannot explain the hot band at 560 nm, because the molecules are simply not hot enough to produce such a clear feature.

However, because of the instantaneous formation process, it should be possible to trace any absorption contribution due to the ISRS process at very early times, where population of S_0^* via IC from S_1 is negligible. If such a process would be present, we should be able to observe an instantaneous formation of S_0^* features within the cross-correlation time of 55 fs. However, such a component is absent and we only see formation of S_1 absorption with a time constant corresponding to the IC process $S_2 \rightarrow S_1$ (160 fs). This finding is in excellent agreement with the earlier study of Motzkus and co-workers, where only a single exponential rise was observed for β -carotene in the S^* region.⁴ Therefore if ISRS is present in our current experiments, it must be a small channel. However, ISRS can certainly gain a more appreciable contribution when a pump pulse with very large bandwidth and high energy is applied.

In previous studies, a different intensity dependence of S^* and S_1 absorption has been reported, suggesting that the S^* state absorption features become more prominent at increasing excitation intensities.^{10,36} Papagiannakis *et al.* suggested either an “inhomogeneous model”, where excitation of two different ground state conformers is involved, or a “two-photon model”, where an electronically excited state S^* is populated from a higher electronic state after two-photon excitation (with S_1 being generated from S_2). They favored the latter model based on simulation results.¹⁰ Alternatively, Savolainen *et al.* were able to explain the intensity dependence by assuming formation of S^* by two channels: a coherent ISRS process and noncoherent decay from S_1 .

In any case, the current study is at variance with a conformer-related “inhomogeneity” in S_0 and unambiguously assigns the highly structured spectral features to a superposition of absorption of vibrationally hot molecules on a bleach of room-temperature molecules (Fig. 8). It also supports the conclusion of Motzkus and co-workers that S^* is the vibrationally hot ground electronic state S_0^* ,^{4,8,36} yet the formation mechanism of the hot molecules from S_1 suggested here is in line with the very early study of Gillbro and co-workers.⁹ Absorption features on the red side of the GSB, the transient spectral characteristics and the observed time constants are fully consistent with a vibrationally hot ground electronic state (Fig. 2 and 3 (inset)). With respect to the intensity dependence, it can certainly be the case that in experiments such as those by Motzkus and co-workers, the employment of very short pulses and high pump pulse energies can lead to a formation of S_0^* via ISRS, which in combination with the IC channel from S_1 would result in the nonlinear intensity dependence reported earlier. One might also speculate on two-photon excitation as another source for a small fraction of very hot molecules, e.g. a small channel of fast $S_n(\rightarrow S_2 \rightarrow S_1) \rightarrow S_0$ internal conversion populating S_0^* with $\leq 41\,000\text{ cm}^{-1}$ excess energy could be available. Our current global modeling certainly suggests the presence of some $S_2 \rightarrow S_n$ absorption superimposed on the $S_2 \rightarrow S_0$ SE, as seen in the S_2 spectrum in Fig. 6, which shows ESA features to the blue and the red of the SE. The feasibility of such a process is also supported by findings for other organic molecules, such as

benzene derivatives.³⁷ With respect to naturally occurring light-harvesting under continuous-wave illumination conditions such a process, as well as the ISRS channel, will however not be relevant.

4. Conclusions

Our investigations provide strong experimental evidence that the S^* state of carotenes is the vibrationally hot ground electronic state S_0^* . Spectral signatures in the transient femtosecond pump–probe absorption spectra of β -carotene in solution are very similar to difference spectra obtained from steady-state absorption spectroscopy at different temperatures. The data can be fully modeled by a global kinetic analysis using a scheme involving three electronic states and immediately formed vibrationally hot molecules in the ground electronic state ($S_2 \rightarrow S_1 \rightarrow S_0^* \rightarrow S_0$). It is likely that similar features observed in carotenoid-containing light-harvesting complexes arise from the same process, because the spectral signatures are virtually identical. Collisional relaxation however might proceed on a slightly different timescale in these protein environments.

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