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# Early events of energy relaxation in all-*trans*-$\beta$-carotene following sub-10 fs optical-pulse excitation

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The rapid internal conversion to the lowest lying $2^1A_g^-$ state following photoexcitation is studied in all-*trans*-$\beta$-carotene with unprecedented time resolution. Visible optical pulses with time duration of 7 fs are used to resonantly excite and probe the optical dynamics of the molecule dissolved in solution. A picture for the relaxation dynamics during the first 100 fs following photoexcitation is proposed based on time-resolved transmission difference spectra and kinetics. Coherent nuclear motion is observed, assigned to impulsive stimulated resonant Raman scattering. Thermalization of the $2^1A_g^-$ state, evident from excited-state spectral evolution, is rather slow, indicating that the higher lying vibrational levels are populated during energy transfer within the photosynthetic systems.

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Carotenoids and their parent compounds, namely polyenes, are among the most extensively investigated molecules in organic physics and chemistry. The reason for that is twofold. They perform several vital functions in photosynthetic systems: Light harvesting, for instance, is accomplished by absorbing light in the blue-green region and transferring energy to chlorophylls, with efficiency close to one.[1,2] Additionally, polyenes are finite-size $\pi$-electron systems, which attracted a good deal of attention during the last 50 years as test banks for the development of molecular-orbital theory.[3] The most extensively investigated carotenoid is $\beta$-carotene, that is available with high purity by chemical synthesis in its more stable all-*trans* isomer. In addition to its role in biology and medicine (as antioxidant with anticarcinogenic properties), $\beta$-carotene is a model compound for degenerate ground-state conjugated polymers,[4] and it has also been considered as candidate for molecular macroelectronic applications.[5] The interest towards this molecule is thus quite extended, covering biology, chemistry, and physics.

Following the pioneering work of Hudson and Kohler in 1970,[6] much evidence has been obtained on the presence of a lower lying optically forbidden singlet state in linear $\pi$-conjugated chains, which is theoretically described by adopting configuration interaction as a covalent, spin-wave excitation.[3] Until very recently energy relaxation after photoexcitation in carotenoids was based on the three-level scheme:[7–9] $1^1A_g^- \rightarrow 1^1B_u^+ \rightarrow 2^1A_g^-$ (characters are given according to the approximate $C_{2h}$ symmetry). Here $1^1A_g^-(S_0)$ is the ground state, $2^1A_g^-(S_1)$ the dipole forbidden lowest lying state, and $1^1B_u^+(S_2)$ is the first optically allowed state responsible for the strong absorption band at wavelengths below 510 nm (about 20 000 cm$^{-1}$). Photoexcitation at the optical gap places energy into $S_2$; nonadiabatic coupling, promoted by vibrational motion of odd symmetry, leads to an ultrafast internal conversion to $S_1$ (about 6000 cm$^{-1}$ lower in energy), which subsequently decays to $S_0$ in about 40 ps. Measurements of photoluminescence quantum yield[10] and decay, about $10^{-4}$ and 170 fs in cyclohexane respectively, provide evidence for very short lifetime of the emitting state, $S_2$. Early pump-probe experiments with sub-ps time resolution showed that (i) $S_1$ gives rise to an induced absorption band centered around 560 nm (Ref. 11) and (ii) $S_1$ decays nonradiatively to $S_0$ with time constant of about 10 ps.[12] Theoretical work[13] and recent experimental results,[14–16] based on Raman and time-resolved spectroscopy, suggested reconsidering such a picture by including an intermediate, optically forbidden state $1^1B_u^-$, thus leading to the four-level scheme: $1^1A_g^- \rightarrow 1^1B_u^+ \rightarrow 1^1B_u^- \rightarrow 2^1A_g^-$. The role of the intermediate state $1^1B_u^-$ in the internal conversion process and thus in the energy transfer to chlorophyll remains obscure, because all these experiments could not reveal the early steps of the photoexcitation dynamics, due to the limited temporal resolution ($\approx$100 fs). So far the question of which relaxation path is the correct one is open.

In this work, exploiting recent advances in ultrashort pulse generation, we present pump-probe experiments on all-*trans*-$\beta$-carotene ($\beta$-car) in solution with unprecedented time resolution; preliminary results of this study were reported in Ref. 17. 7 fs pulses in the visible energy region are used to excite and probe the photoexcitation dynamics, providing a picture of the wave-packet dynamics within the first 100 fs. We observe the optical signatures of the $S_2$ state and find that $S_1$ is generated in the hundred fs time scale, in a vibrationally hot configuration that is stabilized on the ps timescale. No direct evidence of the presence of an intermediate state is observed. The results provide a firm experimental base for further theoretical developments, which are now highly in demand.

$\beta$-car was purchased from Sigma and used without further purification. The laser system used for the experiment consists of a noncollinear optical parametric amplifier[18] pumped by the second harmonic of an amplified Ti: sapphire laser at 1 kHz. Broadband amplification of a white light seed is achieved in a $\beta$-barium borate (BBO) crystal, in a noncollinear phase matching geometry; the amplified pulses (500–650 nm bandwidth) are subsequently compressed to nearly transform-limited duration ($\approx$7 fs) by multiple reflections onto chirped dielectric mirrors. Pulses with fluence of about

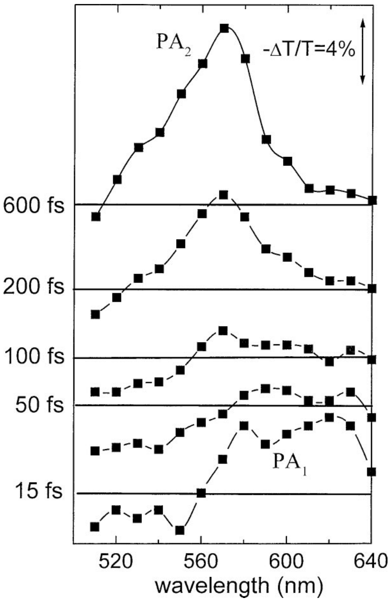

FIG. 1. Transmission difference spectra of $\beta$-carotene in cyclohexane, after excitation with a 7 fs pulse in the visible, at various time delays of the probe pulse. The spectra are reconstructed from single wavelength time traces.

0.1 mJ/cm$^2$ are used to excite and probe a solution of $\beta$-car in cyclohexane (about $10^{-4}$ M), kept into a 0.2 mm thick cuvette at room temperature. The average power is quite low, in the $\mu$W range, and no sample degradation was observed; nevertheless the sample was replaced at each experimental run. Transient changes in absorption ($-\Delta T/T$) are measured by two different techniques. Time-resolved measurements at specific wavelengths are obtained by spectrally filtering, with 10-nm bandwidth interference filters, the probe beam after passing through the sample and combining differential detection with lock-in amplification. $\Delta T/T$ spectra are then reconstructed plotting the signal amplitude at selected delays for each wavelength. To this purpose, a low-pass filter is applied to the data, to remove the high-frequency oscillatory component due to coherent vibrational motion and leave only the population contribution to the differential transmission signal. Transmission difference spectra over the entire bandwidth of the probe pulse are also obtained with a spectrometer coupled to a CCD detector, for time delays larger than 200 fs. In all measurements the maximum $\Delta T/T$ signal is less than 10%, assuring that saturation is not occurring.

Transmission difference spectra of photoexcited $\beta$-car at different delays are shown in Fig. 1. At early times there are two distinct spectral signatures: First, between 500 and 550 nm a strong transmission increase (positive $\Delta T$), to be assigned to stimulated emission (SE), because ground state absorption is negligible at these wavelengths. Second, between 550 and 640 nm a photoinduced absorption band (PA$_1$), corresponding to negative $\Delta T$. Both features appear within the excitation pulsewidth, indicating that they share common origin, but evolve differently. The spectrum changes shape during the first 100 fs: PA$_1$ decays very rapidly and a new induced absorption band (PA$_2$), peaked at shorter wavelength, grows in reaching its maximum at 600 fs delay; the isobestic point initially shifts to the red, then back to the blue side of the spectrum. The PA$_2$ band peak matches the previously measured $S_1 \rightarrow S_n$ transition energy, suggesting its assignment. Kinetics at selected wavelengths are shown in Fig. 2. The fast decay of PA$_1$ and subsequent formation of PA$_2$ are clearly seen at 610 and 580 nm. At 520 and 540 nm, we observe an initial SE which turns into PA$_2$. We find a significant wavelength dependence in the build up kinetics of the PA$_2$ band, which is more rapid at longer wavelengths than at shorter ones (time constants, assuming single exponential kinetics, range between 140 and 190 fs). A strong periodic modulation is superimposed to the time traces, with a wavelength-dependent depth. Extended Fourier transform analysis of the time traces reveal a set of five frequencies, with dispersive amplitudes, as shown in Fig. 3, which can be associated with coherent motion of the nuclei.

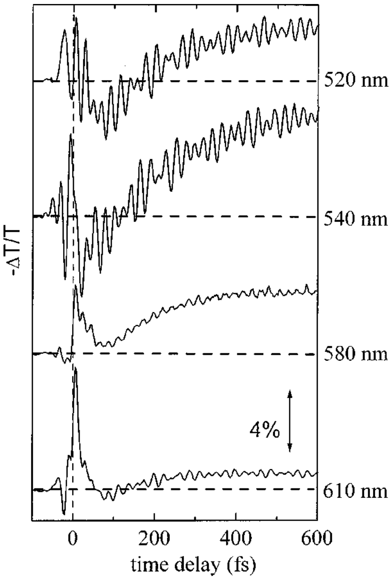

FIG. 2. Transient transmission measurements of $\beta$-carotene in cyclohexane at various probe wavelengths, following excitation with a 7 fs pulse in the visible.

The data in Figs. 1 and 2 present a picture of internal conversion in $\beta$-car following optical excitation with 7 fs pulses. Optical excitation creates a wave packet in the Franck-Condon region of the $1^1B_u^+$ potential energy surface, which gives rise to SE and induced absorption, assigned to $1^1B_u^+ \rightarrow 1^1A_g^-$ and $1^1B_u^+ \rightarrow m^1A_g^-$ transitions, respectively. Thus, our data provide the spectral signatures of the $1^1B_u^+$ state in $\beta$-car. Both appear immediately after photoexcitation, but the spectral evolution and the displacement of the isosbestic point indicate that they have different decay paths. We interpret this as caused by wave-packet motion onto the potential energy surface. The wave-packet leaves the Frank-Condon region of excited state absorption while approaching the conical intersection between the $1^1B_u^+$ and $2^1A_g^-$ potential energy surfaces, from which internal conversion will take place. This occurs along a configuration coordinate that apparently does not involve the emitting transition, thus leaving essentially unchanged its amplitude, while it gives rise to a decay of the PA$_1$ band. At pump-probe delays longer than

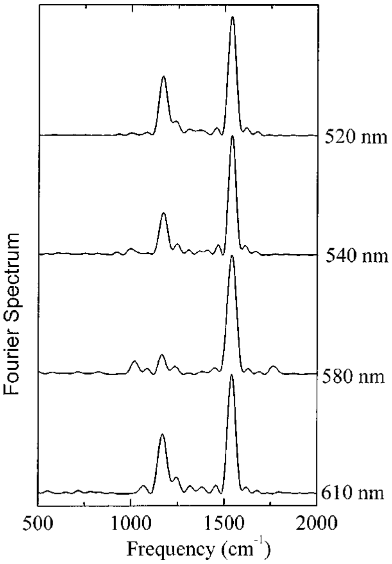

FIG. 3. Fourier power spectra of the transient transmission measurements reported in Fig. 2.

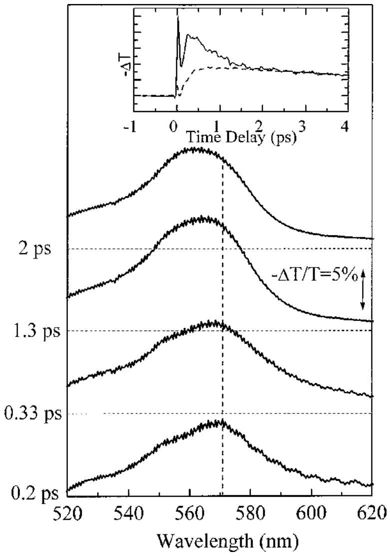

FIG. 4. Transmission difference spectra of $\beta$-carotene in cyclohexane, after excitation with a 7 fs pump pulse in the visible, at various time delays of the probe pulse. The long-time scale is shown. The inset shows transient transmission dynamics at 540 nm (dashed line) and 610 nm (solid line).

100 fs, the growth of PA$_2$ around 570 nm indicates the build up of $S_1(2^1A_g^-)$ state population, which occurs *simultaneously* with the decay of SE. We note that the buildup kinetics of $S_1$ measured by us matches very well that of the photoluminescence decay,[10] consistently with the conjecture of $1^1B_u^+ \rightarrow 2^1A_g^-$ internal conversion. This argues in favor of the three-level model for internal conversion. On the contrary population of an intermediate state, which is optically forbidden, would dramatically affect the emission process. If alternancy symmetry selection rules break down the $1^1B_u^-$ state becomes optically allowed. In this case PA$_1$ could be assigned to transitions from this state. As far as we know however, ground-state absorption spectroscopy does not provide any evidence of a second allowed state absorbing in the visible region. Furthermore, its existence is unlikely on the basis of the reasonable agreement between the experimental lifetimes and those calculated with the fluorescence yields and radiative rates.[11] Symmetry breaking could be the consequence of geometrical relaxation in the excited state. In this case however we should detect a population buildup kinetics in the lower lying $1^1B_u^-$ state. An additional possibility would be that the $1^1B_u^-$ state is very short-lived, with the $1^1B_u^- \rightarrow 2^1A_g^-$ conversion rate much greater than the $1^1B_u^+ \rightarrow 1^1B_u^-$ conversion rate. In this case, the differential transmission dynamics would be the same as in the three-level scheme. However, our experimental data do not present any evidence in favor of this hypothesis. For this reason we consider it more likely that the simpler direct $1^1B_u^+ \rightarrow 2^1A_g^-$ energy transfer is involved.

We now discuss the oscillating pattern superimposed on the transmission signal. The Fourier power spectrum, calculated on the 20–2000 fs time interval (Fig. 3) shows several coupled modes, the two strongest being at 1170 and 1539 cm$^{-1}$. The observed frequencies match the typical values of nuclear vibration, and are assigned to collective vibrational coherence initiated in the ensemble of photoexcited molecules by the ultrashort pump pulse.[19] The oscillation amplitude is slowly damped in time and lasts longer than 1 ps. Thus most likely these are due to coherent nuclear motion in $S_1$ or $S_0$, because $S_2$ is short lived. The observed frequencies correspond well to those observed in resonant Raman spectra,[20] are negligible in the wavelength range probing $S_1 \rightarrow S_n$ transitions and seem to be present since the very beginning. Based on these observations we propose their assignment to wave-packet propagation onto the ground-state potential energy surface $S_0$, generated by impulsive stimulated resonant Raman scattering.[21] In principle, internal conversion $S_2 - S_1$ could take place *coherently*, i.e., preserving the phase of the collective nuclear motion in the final state ($S_1$). The apparent loss of coherence during $S_2 - S_1$ internal conversion is most likely due to dephasing as the system evolves onto an anharmonic potential energy surface. As a consequence it is the ground-state contribution that dominates the oscillatory response.

Finally, Fig. 4 shows the evolution of the differential spectra on the picosecond timescale, providing insight in the subsequent relaxation process of $S_1$. There is a loss of intensity on the red edge of the absorption band and the maximum of the band shifts from ≈570 nm to ≈555 nm within 2 ps. The isosbestic point of the $S_1 \rightarrow S_n$ transition band keeps on shifting to the blue, falling out of the experimental range for delays longer than 200 fs. The $S_1$ band changes shape, becoming narrower at longer delays. In the long-wavelength region an additional fast decay of absorption intensity, not present at shorter wavelength, becomes evident, with a time constant of $(623 \pm 50)$ fs (see inset of Fig. 4). Intramolecular vibrational energy redistribution, thermalization, and conformational relaxation are possible causes of the observed phenomenon. From studies on polyenes it is known that the structure of the lower lying excited state,[3] of $A_g$ symmetry, differs from that of the next excited state, of $B_u$ symmetry, in the dimerization pattern. The vibrational modes that can drive a change in bond order have typical energy of 1500 $\mathrm{cm}^{-1}$, and should thus lead to a very fast geometrical rearrangement. This argues against the assignment to conformational relaxation because the observed time scale is ps, we consider more likely the possibility of intraband vibrational cooling associated to dissipation of the excess energy initially deposited in $S_1$, which is approximately 6000 $\mathrm{cm}^{-1}$. This conjecture, based on the notion that excited state intraband relaxation in large organic molecules usually takes less than 0.5 ps, suggests that there is a sort of bottleneck effect in the excess energy dissipation of $S_1$, with important implications for the light harvesting process.

Thanks to a detailed determination of the structure of a light-harvesting complex, Damjanovic *et al.*[8] have been able to calculate the energy transfer rate between carotenoid and the surrounding bacteriocholorophylls, based on Coulomb coupling and Dexter exchange mechanisms. Their calculations suggest that by Coulomb coupling 40% of the initially absorbed energy can be transferred from the bottom of the $S_2$ vibronic manifold, i.e., after vibrational relaxation. The calculations further indicate that the residual ~50% of the energy cannot be transferred from the bottom of $S_1$ with similar mechanism, neither it can by Dexter coupling. The prolonged existence of a vibrationally hot $S_1$ state following $\beta$-car photoexcitation, as indicated by our results, is thus supporting the conjecture that energy transfer to chlorophyll could take place from a nonequilibrium configuration of $S_1$.

In conclusion, in this work we present sub-10 fs pump-probe measurements on $\beta$-car in solution, providing a picture of the early events of energy relaxation. Spectral features of the optically active state $1^1B_u^+$ are assigned and the whole process of relaxation and internal conversion investigated. No direct evidence of the presence of an intermediate state $1^1B_u^-$ is observed and the results are consistent with a direct three-level energy transfer scheme $1^1A_g^- \rightarrow 1^1B_u^+ \rightarrow 2^1A_g^-$. Vibrational coherence in the ground state allows estimating a rather long time of dephasing of the optically active phonons, in the ps time scale. The kinetics of population transfer to a hot $2^1A_g^-$ state and its thermalization are observed by following the transmission difference spectra evolution and the characteristic time scale of the processes, 0.5 and 2 ps, respectively, are evaluated from the transient data at specific wavelengths. The comprehensive picture of $\beta$-car optical dynamics here reported should help elucidating the light harvesting function of carotenoids and the relevant energy transfer mechanism to chlorophyll, in particular supporting the conjecture that hot vibrational levels in the $2^1A_g^-$ state may play a fundamental role.

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