Transient Lens Spectroscopy of Ultrafast Internal Conversion Processes in Citranaxanthin†

Thomas Lenzer,*,‡,§,∥,⊥ Kawon Oum,*,‡,∥ Jaane Seehusen,∥ and Marco T. Seidel∥

Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany, and Max-Planck-Institut für biophysikalische Chemie, Abt. Spektroskopie und Photochemische Kinetik (10100), Am Fassberg 11, D-37077 Göttingen, Germany

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The ultrafast internal conversion (IC) dynamics of the apocarotenoid citranaxanthin have been studied for the first time by means of two-color transient lens (TL) pump−probe spectroscopy. After excitation into the high-energy edge of the S_2 band by a pump pulse at 400 nm, the subsequent intramolecular processes were probed at 800 nm. Experiments were performed in a variety of solvents at room temperature. Upper limits for the S_2 lifetime τ_2 on the order of 100−200 fs are estimated. The S_1 lifetime τ_1 varies only slightly between solvents (10−12 ps), and the only clear decrease is observed for methanol (8.5 ps). The findings are consistent with earlier results from transient absorption studies of other apocarotenoids and carotenoid ketones and transient lens experiments of C_{40} carbonyl carotenoids. Possible reasons for the observed weak solvent dependence of τ_1 for citranaxanthin are discussed.

1. Introduction

Carotenoids are of prime importance in photosynthetic organisms, where they actively participate in the light-harvesting process in the blue-green spectral region.[1] In addition, they protect against excessive light by quenching both singlet and triplet states of bacteriochlorophylls.[2] In the simplest model, carotenoid photophysics can be described by three electronic states. The strong absorption in the visible is due to the transition from the electronic ground state $S_0(1A_g^-)$ to the second excited singlet state $S_2(1B_u^+)$, with labels based on idealized C_{2h} symmetry. In contrast, the one-photon transition to the first excited singlet state $S_1(2A_g^-)$ is symmetry forbidden; however, this state can be studied spectroscopically employing two-photon spectroscopy.[3,4] There has been considerable interest in characterizing the excited-state dynamics of carotenoids on the femto- to picosecond time scale, to understand their role in the primary steps of photosynthesis.[1] Inter alia, transient absorption (TA)[5−8] and transient lens (TL) techniques[9,10] have been employed for studying internal conversion (IC) processes in the S_2 and S_1 excited states. In the course of the TA investigations, additional intermediate states have been proposed for the interpretation of the time-resolved dynamics.[1] Very recent femtosecond stimulated Raman studies on the prototypical β-carotene system after excitation at 497 nm, however, still favor the simple three-state model, because the temporal evolution of the Raman spectra is consistent with the presence of only two electronic states, S_2 and S_1.[11] A very recent TA study of zeaxanthin suggests that many of the observed features recently assigned to additional "states" between S_2 and S_1 can be understood in terms of vibrational or conformational relaxation processes within these two electronic states.[12]

Carbonyl-substituted carotenoids show a fascinating diversity in their intramolecular excited-state dynamics. One example is peridinin, which is the main light-harvesting pigment in the peridin-chlorophyll-a protein (PCP) complex of algae.[13] In nonpolar solvents, the lifetime of the peridinin S_1 state is about 160 ps, whereas in polar environments it is reduced to about 10 ps.[7,14,15] Currently, these findings are interpreted in terms of a combined S_1/ICT (intramolecular charge transfer) state, for which polar solvents stabilize a structure, where electron density is transferred from the polyene chain to the C═O group.[15,16] The presence of a S_1/ ICT state in polar media spectroscopically manifests itself by the appearance of excited-state absorption bands in the 600−700-nm region and a stimulated emission band around 950 nm. The magnitude of these phenomena correlates with the degree of CT character.[15] In another TA study for a series of apocarotenals and apocarotenoates a strong influence of the type of terminal carbonyl group on the IC dynamics was found.[17] Carbonyl carotenoids with long conjugation lengths showed no solvent dependence at all,[7,18] as for instance, demonstrated in a TL study of the C_{40} carbonyl carotenoids echinenone, canthaxanthin, and astaxanthin in a variety of polar and nonpolar solvents.[9] These results are consistent with TA measurements, where no spectral signatures of a S_1/ICT state have been observed for astaxanthin.[19] In addition, the orientation of the C═O group relative to the conjugated backbone has a great influence on the magnitude of solvent effects in carbonyl carotenoids.[15] As an example, in C_{40} carotenoids such as astaxanthin, canthaxanthin, and echinenone the keto groups are located on β-ionone rings, which are arranged out-of-plane with respect to the conjugated backbone. Therefore the C═C and C═O bonds in the rings are arranged in an *s-cis* orientation with respect to the polyene chain. This suggests that the extension of the conjugation to both terminal rings prevents polarity-induced changes in the internal conversion dynamics of the S_1 state.[9,19] A similar effect is observed for spheroidenone, which also features an *s-cis* orientation[20] resulting in a reduced conjugation, and thus a small polarity influence on the conjugated system.[15] In contrast, for the carbonyl carotenoid siphonaxanthin, where the orientation is known to be *s*-trans,[21] a considerable reduction of the S_1 lifetime by a factor of 3 is observed when changing from nonpolar to polar solvents. Clearly, the type and size of the substituent, which is attached

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* Corresponding authors.
‡ Tel: +49 551 39 12598. Fax: +49 551 39 3150. E-mail: tlenzer@gwdg.de, koum@gwdg.de.
§ Fax: +49 551 201 1501. Tel: +49 551 201 1344.
∥ Universität Göttingen.
⊥ Max-Planck-Institut für biophysikalische Chemie.

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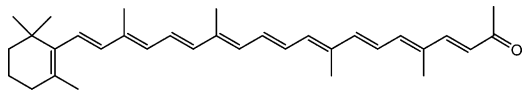

Figure 1. Chemical structure of citranaxanthin (conjugation 9O1β1).

to the C═O group, influences the relative orientation of this group with respect to the rest of the conjugated system. In addition, electronic effects due to the different type of substituent attached to the C═O function might also play a role. All these results show the rich and diverse photophysics and dynamics in carbonyl carotenoids and raise further questions about the nature of their electronic states. Therefore there is clearly a need for additional studies on the solvent-dependent dynamics of different carbonyl carotenoids.

In the current study we investigate for the first time the apocarotenoid citranaxanthin (6′-methyl-6′-apo-β-caroten-6′-one, for the structure see Figure 1).[22] Citranaxanthin is a constituent of citrus fruits.[22] It is also produced on an industrial scale, and, for example, used for egg yolk pigmentation in poultry farming.[23] To characterize its conjugated system, it is convenient to apply the nomenclature used by Polivka and Sundström,[1] where the conjugation of a carotenoid is characterized by the abbreviation *N*β*j*O*k*: The number of conjugated C═C bonds in the carotenoid backbone is given by *N*, an extension of this conjugation to *j* C═C bonds located at a terminal β-ionone ring is denoted βj, and the term O*k* means that the conjugation is extended to *k* carbonyl groups. This way, the conjugated system of citranaxanthin is characterized as "9β1O1".

Citranaxanthin is an interesting model system for studying the influence of carbonyl functional groups on the IC dynamics in carotenoid excited electronic states. In contrast to other apocarotenoids studied so far, citranaxanthin contains a terminal keto function. This allows us to compare our TL data with earlier TA studies on related apocarotenoids carrying a terminal aldehyde or ester group. The aldehyde systems typically show a pronounced decrease of the S_1 state lifetime with increasing solvent polarity, whereas for the esters almost no solvent dependence appears to be present.[17] As discussed above, this points toward a different degree of CT character in the S_1 ; however, the reasons for the observed variations in the solvent dependence with the type of C═O group are not yet clear. In addition to the different electronic structure of the carbonyl groups, it is also reasonable to assume that their orientation relative to the rest of the conjugated backbone is very important, as mentioned above. Clearly, systematic comparisons for a wide range of carbonyl carotenoids with different substituents attached to the C═O functional group are needed to understand the solvent-dependent nonradiative dynamics of these systems in detail, and our current study is regarded as one step in this direction.[7,9,15,17]

2. Application of the TL Technique

In the current investigation we apply TL spectroscopy[9,10,24] to investigate the IC dynamics of citranaxanthin. The principle of the technique has been discussed in detail in our very recent publication,[9] and only a brief summary is given here with the specific application to citranaxanthin. A simplified diagram together with a schematic TL signal is depicted in Figure 2. Pump-and-probe laser beams are focused by a lens into a cuvette

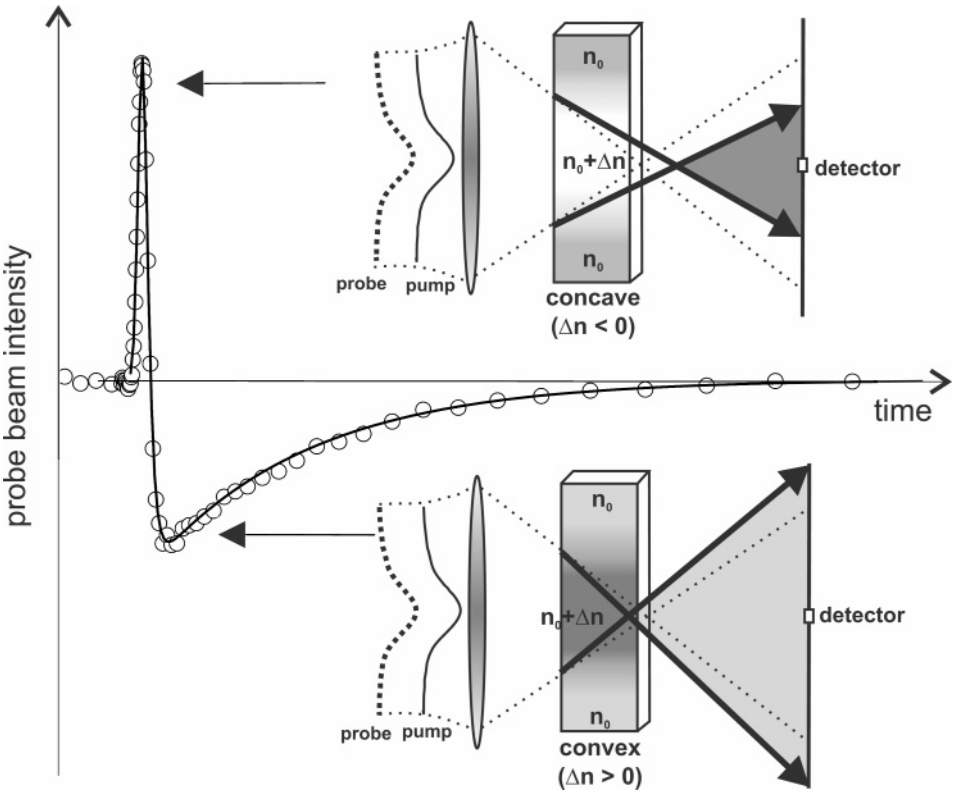

Figure 2. Generation of a transient population lens. A pump beam with Gaussian intensity profile is focused into the carotenoid solution contained in a cuvette located in a prefocal position. The type of transient lens (TL) depends on the difference in refractive index Δn between the molecules in the excited (S_2) and ground electronic state (S_0). For citranaxanthin, the initially prepared S_2 state has a smaller n than S_0 (so $\Delta n < 0$), which leads to the formation of a "concave" TL (upper scheme). At very short delay times the probe beam therefore detects an increased signal, as recorded on a small-area photodiode in the far field, because it is less diverging (thick arrows) than without the presence of the TL (thin dotted line). This corresponds to the positive peak in the TL signal (open circles and fit line). Ultrafast internal conversion from S_2 leads to formation of the S_1 state which has a larger refractive index than S_0 ($\Delta n > 0$). The S_1 state population therefore generates a convex TL, leading to an increased probe beam divergence and therefore a reduced signal (lower scheme and negative part of the TL signal). Finally, the molecules decay to S_0, so the TL vanishes, and the negative TL signal goes back to zero.

containing the citranaxanthin solution, as shown in the upper right part of the figure. The cuvette is positioned in front of the lens focus. A small-area photodiode detector, shown as a white square, is located in the far field. The pump laser beam has a Gaussian intensity distribution and excites citranaxanthin molecules (with the index of refraction n_0 in the ground electronic state S_0) to the second excited electronic state S_2. Molecules in this state have a smaller index of refraction $n_0 + \Delta n$ ($\Delta n < 0$) than in S_0. Due to the Gaussian intensity distribution of the pump beam, $n_0 + \Delta n$ will be smaller in the center than at the edges (shown by the brighter shading in the middle of the cuvette), which leads to the formation of a transient "concave" lens. After a short time delay, the second (= probe) beam is focused into the cuvette. Without the pump laser, the probe beam would diverge to a diameter given by the dotted lines in the upper right scheme of Figure 2. However, because of the additional transient concave lens the beam diameter is reduced (solid arrows), and an increased intensity is detected on the photodiode. This produces the positive peak in the schematic transient lens signal on the left side of Figure 2. Subsequently, IC from the S_2 to the S_1 state occurs. The S_1 state has a larger index of refraction than the S_0 state, that is, $n_0 + \Delta n$ with $\Delta n > 0$, see the scheme on the lower right of Figure 2. In this case a transient "convex" lens is formed inside the cuvette (shown by the darker shading in the middle of the cuvette). Correspondingly, an intensity minimum is observed at the detector, when the probe beam samples the TL at a delay time, when the excited-state population consists of S_1 state molecules. This produces the negative portion of the time trace shown in Figure 2. The negative signal finally decays to zero, indicating the transition of the citranaxanthin molecules by IC from S_1 to S_0. The sign of the TL effect depends on the position of the cuvette. Placing the cuvette behind the lens focus would result in a TL signal where positive and negative signs will change exactly around.

The TL experiment therefore monitors a citranaxanthin "population lens",[24] because the change in the electronic state of the carotenoid is accompanied by a change of its refractive index. As shown above, this technique is able to track the population transfer of citranaxanthin molecules due to IC from S_2 via S_1 to S_0. Note, that the TL method is therefore purely sensitive to electronic population transfer, that is, the IC time constants in the case of the carotenoids. Superimposed vibrational energy transfer or conformational relaxation processes within one electronic state[12] are unlikely to influence the TL signal. A more detailed discussion with respect to advantages and disadvantages of the TL approach compared to traditional TA detection methods can be found in our earlier publication.[9]

3. Experiment

A detailed description of our TL setup has already been given previously.[9] Briefly, the output from a mode-locked Ti:sapphire oscillator (800 nm, 82 MHz, average laser power 1.5 W) was split up into two beams; 90% were doubled in a LBO crystal to generate the pump beam at 400 nm (<0.1 nJ/pulse). The remaining 10% were directly used as the probe beam (<1 nJ/pulse) and time-delayed using a computer-controlled delay stage. Note that the pulse energies are very weak compared to standard setups employing transient absorption detection.[1] No change in the signal shape was observed when the pump energy was varied by up to a factor of 10. The time resolution of this setup was about 130 fs. The beams, which both had an approximately Gaussian intensity profile, were recombined and focused into a quartz flow cuvette (path length 1 mm) using a 50-mm quartz lens. The position of the cuvette was optimized by performing "Z-scans",[25−27] to obtain the largest TL signal, as described in detail earlier.[9] The time-dependent divergence of the probe beam was detected by a small-area avalanche photodiode (APD) in the far field, which monitored only a very small center area (with the pump beam cut off by appropriate color filters). A good signal-to-noise ratio was achieved by a lock-in-detection scheme, where a pulse generator drove an acousto-optic modulator (AOM) for modulating the pump beam intensity and at the same time served as the 2 MHz reference for the lock-in amplifier, which recorded the modulated output of the APD. Highly purified *all-trans* (*all-E*) citranaxanthin samples were generously provided by BASF AG with a purity > 97%. All solvents had a purity ≥ 99%. Absorption spectra of citranaxanthin in all solvents were recorded using a Varian Cary 5E spectrometer. No sample degradation was observed. This was controlled by comparing the absorption of the carotenoid solution before and after the measurements. In the TL experiments a typical citranaxanthin concentration of about 2×10^{-4} M was used. The pure TL signal was obtained from the experimental raw signal by subtracting small contributions originating from the Kerr response of the solvent and transient absorption of citranaxanthin, which mainly occurred around $t = 0$, using the procedure described in detail in our earlier publication.[9] At this moment, we cannot precisely quantify how large the Kerr contribution of the carotenoid is in our signals. However, our experimental observations clearly indicate that they have to be much smaller than the solvent contribution, as also seen in our previous study on a series of C_{40} carotenoids: The fast electronic Kerr component in the experimental raw signal of the carotenoid solution had the same amplitude as the electronic Kerr signal for the pure solvent.[9] We believe that this is due to the low carotenoid concentration. Possible enhancement effects of the Kerr signal for the carotenoid due to resonant amplification apparently are not large enough to show a visible influence on the carotenoid TL signals.[28−30]

4. Results and Discussion

4.1. Ground-State Absorption Spectra of Citranaxanthin in Different Solvents. Figure 3 contains an overview of the $S_0 \rightarrow S_2$ steady-state absorption spectra of citranaxanthin in all solvents. The corresponding absorption maxima can be found in Table 1. There is an approximate correlation of the spectral shift with the polarizability factor $R(n) = (n^2 - 1)/(n^2 + 2)$ of the solvents.[31,32] On average, for solvents with larger $R(n)$ a larger red-shift of the absorption band is found. Nonpolar solvents such as *n*-hexane, *n*-heptane, and *i*-octane show a typical three-peak structure (spacing around 1350 cm^{-1}), which is also observed for other carotenoids. It originates from the combination of two symmetric vibrational stretching modes, C−C (1150 cm^{-1}) and C=C (1600 cm^{-1}).[1] In more polar solvents, the structure is less well-resolved, but still visible, whereas the spectra in strongly polar hydrogen-bonding solvents such as methanol are virtually structureless. A similar loss of structure has also been observed for other apocarotenoids. For instance, He et al. reported absorption spectra for ethyl-6′-apo-β-caroten-6′-oate and ethyl-4′-apo-β-caroten-4′-oate in 3-methylpentane and acetonitrile, which look very similar to our *n*-hexane and acetonitrile spectra.[17] The disappearance of structure in the static $S_0 \rightarrow S_2$ absorption spectra in polar hydrogen-bonding media might be due to an enhancement of a dipolar ground-state structure of citranaxanthin, a broader distribution of conformers in the electronic ground state (each having a slightly differently absorption spectrum), and possibly an increased mixing of the S_2 state with other excited electronic states.[1,16]

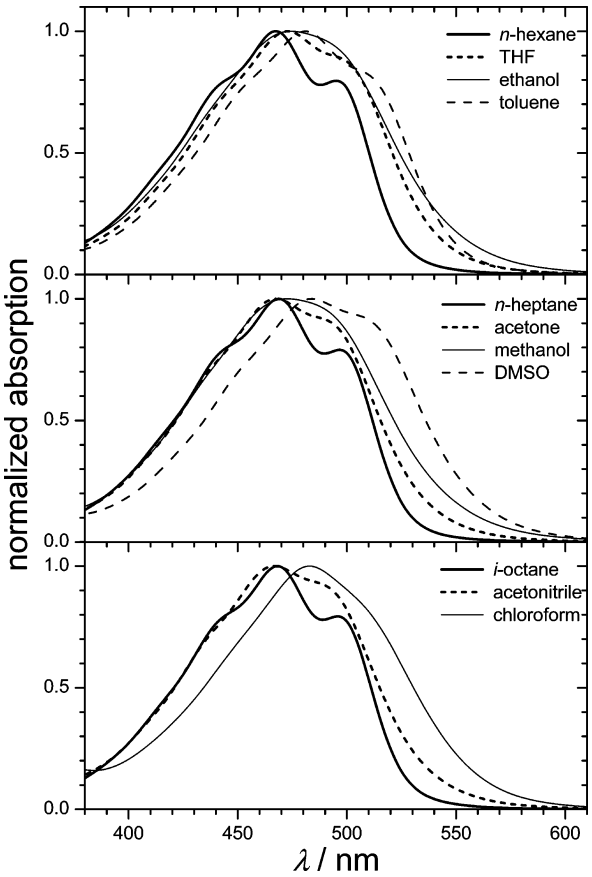

Figure 3. $S_0 \rightarrow S_2$ steady-state absorption spectra of citranaxanthin in different solvents.

TABLE 1: Lifetimes of Citranaxanthin in Various Solvents: $\tau_1(S_1 \rightarrow S_0)$ and $\tau_2(S_2 \rightarrow S_1)$ (TL pump wavelength: 400 nm; probe wavelength: 800 nm)

solvent	λ_{max}[a]/nm	$R(n)$[b,c]	Δf[b]	τ_1/ps	τ_2/fs[d]
n-hexane	467	0.23	0.00	11.0	130
n-heptane	469	0.23	0.00	10.3	140
i-octane	468	0.24	0.00	10.0	140
toluene	481	0.29	0.01	10.9	190
chloroform	483	0.27	0.15	12.0	190
tetrahydrofuran	473	0.25	0.21	12.0	160
dimethyl sulfoxide	484	0.28	0.26	10.6	190
acetone	467	0.22	0.28	11.5	140
ethanol	475	0.22	0.29	10.6	130
acetonitrile	467	0.21	0.31	10.3	110
methanol	473	0.20	0.31	8.5	120

[a] λ_{max} values correspond to the position of the maximum of the $S_0 \rightarrow S_2$ steady-state absorption spectrum in each solvent. [b] Solvent indices of refraction n and dielectric constants ϵ for the calculation of Δf (eq 1) were taken from ref 32. [c] $R(n) = (n^2 - 1)/(n^2 + 2)$ is the polarizability factor of the solvent. [d] Upper limit.

4.2. TL Signals for Citranaxanthin. A typical experimental TL signal for citranaxanthin in acetonitrile can be found in Figure 4, and a magnification of its early part is depicted in the inset. The shape of the signal is characteristic for all the citranaxanthin solvent pairs investigated in this work and is also very similar to those observed in our earlier TL study of the C_{40} carotenoids canthaxanthin, astaxanthin, echinenone, lycopene, β-carotene, (3*R*,3′*R*)-zeaxanthin, and (3*R*,3′*R*,6′*R*)-lutein.[9] Initially, a fast rise is observed, which occurs within the time-resolution of our experimental setup. It is due to the initial preparation of the S_2 state by the pump beam. Afterward, the signal decays very quickly to negative values. It is reasonable to assume that this process is due to ultrafast IC from the S_2 to the S_1 state.[1,9] Finally the negative signal decays to zero on a much slower time scale, and this part is due to IC from S_1 to S_0. This allows us to determine well-defined time constants for the $S_1 \rightarrow S_0$ transition. The IC time constants were extracted from the TL curves by performing Levenberg−Marquardt least-squares fits of a sum of two exponentials to the experimental traces, applying a convolution with the cross-correlation of the laser pulses. An example is included in Figure 4. The sign changes in the TL signal also allow us to determine the relative order of the indices of refraction of the three electronic states involved. Because a negative signal with prefocal position of the cuvette corresponds to a convex transient lens, the relative order must be $n(S_1) > n(S_0) > n(S_2)$, see also section 2.

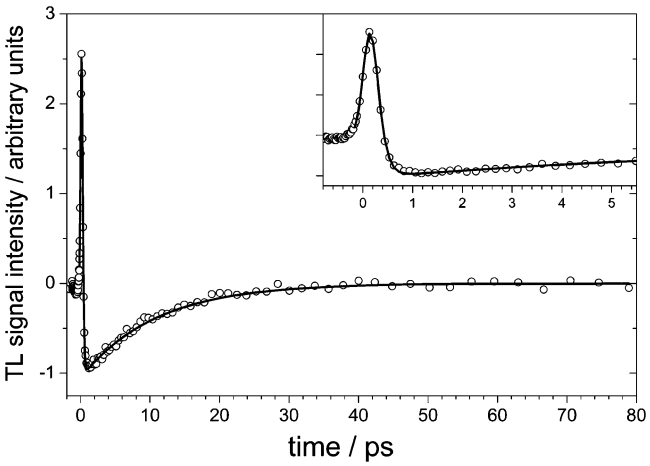

Figure 4. TL signal of citranaxanthin in acetonitrile. The inset shows a magnification of the signal at early times. The line represents the result of a Levenberg−Marquardt least-squares fit of a sum of two exponentials to the experimental traces, applying a convolution with the cross-correlation of the laser pulses.

4.3. Solvent Dependence of the IC Time Constants τ_1 and τ_2. Table 1 contains a list of lifetimes $\tau_1(S_1 \rightarrow S_0)$ and $\tau_2(S_2 \rightarrow S_1)$ for the IC processes of citranaxanthin in different solvents obtained from this work. For easier comparison, we arranged the solvents by their polarity quantified by the orientation polarizability Δf given as[33−35]

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (1)$$

with values for the indices of refraction n and the dielectric constants ϵ taken from the literature.[32] There are no previous lifetime data available for citranaxanthin from other experimental sources. From *n*-hexane up to acetonitrile we find values for τ_1 in the range 12.0 to 10.0 ps (Table 1). Only in the polar solvent methanol is a shorter lifetime of 8.5 ps observed.

Although we have a limited time resolution and uncertainties mainly at early pump−probe times related to the subtraction of a transient absorption feature in the raw signal, we can nevertheless give upper limits for the lifetime τ_2 of the $S_2 \rightarrow S_1$ IC process. Typical estimates are in the range 110−190 fs, and no clear solvent dependence is found. This is also in good agreement with previously published data on other carotenoids.[1,9]

It is instructive to compare the lifetimes τ_1 of this work with data of earlier TA and TL measurements for related carbonyl compounds. He et al. reported time-resolved measurements for the decay of the $S_1 \rightarrow S_n$ transient excited-state absorption of a series of apocarotenoates and apocarotenals in 3-methylpentane and acetonitrile.[17] Their results for ethyl-6′-apo-β-caroten-6′-

TABLE 2: Comparison of the Lifetimes $\tau_1(S_1 \rightarrow S_0)$ for Ethyl-6′-apo-β-caroten-6′-oate, Citranaxanthin, and 6′-Apo-β-caroten-6′-al in Unpolar and Polar Solvents[a]

apocarotenoid	terminal carbonyl function	τ_1/ps (nonpolar)	τ_1/ps (polar)	refs
ethyl-6-apo-β-caroten-6-oate	ester	12.4[b]	11.4[d]	17
citranaxanthin	ketone	11.0[c]	10.3[d]	this work
6-apo-β-caroten-6-al	aldehyde	12.0[b]	6.3[d]	17

[a] Note that all carotenoids have the same conjugation length (9O1β1) and differ only by the type of terminal carbonyl function −CO−R, where R = H (aldehyde), CH_3 (ketone), or $O-C_2H_5$ (ester). [b] In 3-methylpentane. [c] In *n*-hexane. [d] In acetonitrile.

oate and 6′-apo-β-caroten-6′-al are of particular relevance to the present study. These carotenoids have the same type of conjugation (9O1β1) as citranaxanthin; however, all three differ by the type of terminal carbonyl function −CO−R (R = H, CH_3, or $O-C_2H_5$). A comparison of the lifetimes from their measurements in 3-methylpentane and acetonitrile with our data for citranaxanthin in *n*-hexane and acetonitrile is shown in Table 2.

Ethyl-6′-apo-β-caroten-6′-oate shows only a weak τ_1 reduction by 1 ps (within the error limits of the experiments) when going from the nonpolar to the polar environment. In contrast, 6′-apo-β-caroten-6′-al exhibits a marked solvent dependence, and the lifetime reduction reaches almost a factor of 2. Essentially no clear change with solvent polarity (except for the reduction of τ_1 in methanol) is observed for citranaxanthin, and its behavior is therefore very similar to that of ethyl-6′-apo-β-caroten-6′-oate. It is interesting that the slight change from H to CH_3 in the carbonyl functional group has such a pronounced influence on the solvent dependence.

A marked solvent dependence of τ_1 in carbonyl-substituted carotenoids is typically explained by the appearance of considerable charge-transfer character[1,17] through formation of a combined "S_1/ICT" state in polar media.[15] In nonpolar solvents, the stepwise relaxation would then be $S_2 \rightarrow S_1 \rightarrow S_0$, whereas in polar solvents one would have $S_2 \rightarrow$ "S_1/ICT" $\rightarrow S_0$. In both cases, a three-state relaxation scheme is present, and therefore the observed relaxation dynamics should be similar, showing signals with two components (time constants τ_2 and τ_1) characterizing the first and second steps in the relaxation scheme.

Obviously, carotenoids with an aldehyde function tend to form such an "S_1/ICT" state already at smaller solvent polarities than those with ester and keto groups. Besides a change in the electronic properties of the carbonyl group, another tentative explanation for the different behavior would be that a small substituent attached to the C═O functional group (like hydrogen in the aldehyde) could favor carotenoid geometries in which an *s*-trans arrangement is possible, leading to an optimum conjugation and a marked influence of the solvent polarity.[36] More voluminous substituents could then lead to reduced conjugation, resulting in a smaller susceptibility to polarity effects.

It is also interesting to compare our results for citranaxanthin (9O1β1) with earlier data on other carotenoid ketones with different conjugation lengths. This is done in Table 3 for siphonaxanthin (8O1), spheroidenone (10O1), and canthaxanthin (9β2O2).[7,9,15] First of all, one observes a reduction of τ_1 with increasing conjugation length, as was found in earlier studies.[1,9] This observation can be well described by an energy-gap-law approach. With increasing conjugation length the energy gap between the S_1 (or S_1/ICT) state and the S_0 state decreases, which accelerates the internal conversion processes.[37−39] Note also, that—for the same conjugation length—double bonds located in β-ionone rings are not as efficiently conjugated as in the conjugated backbone, as seen in the comparison between citranaxanthin and spheroidenone, where the lifetime τ_1 of the latter one is clearly smaller.

TABLE 3: Comparison of the Lifetimes $\tau_1(S_1 \rightarrow S_0)$ for Carotenoid Ketones with Different Conjugation Lengths

carotenoid ketones	conjugation	τ_1/ps (unpolar)	τ_1/ps (polar)	refs
siphonaxanthin	8O1	60[a]	20[c]	15
citranaxanthin	9O1β1	11.0[a]	10.3[c]	this work
spheroidenone	10O1	6[a]	6[c]	15,7
canthaxanthin	9β2O2	4.9[b]	5.1[c]	9

[a] In *n*-hexane. [b] In toluene. [c] In acetonitrile.

Interesting effects are seen for the solvent dependence. Only siphonaxanthin shows a considerable reduction (by a factor of 3) when switching from nonpolar to polar solvents. This can again be explained by the orientation of the carbonyl group with respect to the conjugated backbone.[15] In siphonaxanthin this orientation is known to be *s*-trans,[21] leading to an optimum conjugation and a strong polarity effect. Deviations from this configuration (in the extreme case *s*-cis as in spheroidenone)[20] result in a reduced conjugation and thus a smaller polarity influence on the conjugated system. This appears also to be the case for citranaxanthin. In addition, carbonyl carotenoids with a particularly long conjugation length, such as spheroidenone and canthaxanthin, presumably have a smaller energy gap betweeen S_0 and S_1 (or S_1/ICT), facilitating coupling even in nonpolar solvents.[15] Specifically for the C_{40} carbonyl carotenoid canthaxanthin (and related compounds such as astaxanthin and echinenone), earlier studies using transient absorption[19,40] and transient lens detection[9] have found no solvent dependence of τ_1. In these cases, one (echinenone) or two keto groups R−CO−R′ (canthaxanthin and astaxanthin) are located on the β-ionone rings. Because the rings are forced out of the plane of the carotenoid backbone the conjugation is again less favorable, and the influence of the CO groups is diminished. Therefore the insensitivity of these carotenoids to solvent polarity is not unexpected.

5. Conclusions

We have reported the first time-resolved study of internal conversion processes in the apocarotenoid citranaxanthin. Its ultrafast dynamics was investigated in eleven solvents of varying polarity using TL spectroscopy. Only upper limits can be given for the time constant τ_2 for IC from the S_2 to the S_1 state, and values between 100 and 200 fs are found. Typical time constants τ_1 for the IC process $S_1 \rightarrow S_0$ are much larger and lie between 10 and 12 ps. They are largely independent of solvent polarity, except for methanol, where a moderate decrease of τ_1 to 8.5 ps was observed. Comparison with earlier TA and TL results for other carbonyl carotenoids suggests that only for the polar solvent methanol might increased charge transfer occur. In future TL studies, it will also be interesting to see if a change in the refractive index occurs when the S_1 state acquires considerable ICT character. The current data for citranaxanthin show slight changes in the ratio of the maximum and minimum TL amplitudes as a function of solvent polarity, which might be indicative of such an effect. In this respect, it would be particularly interesting to look at a system with extremely large solvent dependence of τ_1, for instance, peridinin. We are also currently studying a variety of other apocarotenoids to understand the interesting dynamics of carbonyl-substituted systems in more detail.

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