Solvent-dependent ultrafast internal conversion dynamics of \(n'\)-apo-\(\beta\)-carotenoid-\(n'\)-acids (\(n = 8, 10, 12\))

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Received 2nd January 2008, Accepted 28th January 2008
First published as an Advance Article on the web 25th February 2008
DOI: 10.1039/b720037d

The ultrafast internal conversion dynamics of 12'apo-\(\beta\)-carotenoid-12'-acid (12'CA), 10'-apo-\(\beta\)-carotenoid-10'-acid (10'CA) and 8'-apo-\(\beta\)-carotenoid-8'-acid (8'CA) have been investigated by femtosecond pump–probe spectroscopy. The three apocarotenoid acids were excited to the S\(_2\) state with different excess energies. Time constants \(\tau_1\) for the IC process S\(_1\)/ICT \(\rightarrow\) S\(_0\) were measured by probing the dynamics at 390 nm (S\(_0\) \(\rightarrow\) S\(_2\)), 575 nm (S\(_1\)/ICT \(\rightarrow\) S\(_0\)), 850, 860 and 890 nm (S\(_2\) \(\rightarrow\) S\(_0\) and S\(_1\)/ICT \(\rightarrow\) S\(_0\)). In nonpolar solvents, the observed reduction of the \(\tau_1\) values with increasing conjugation length of the acids is consistent with a reduction of the energy gap between the S\(_1\)/ICT and S\(_0\) states. The values are in good agreement with those of the corresponding apocarotenals studied previously in our groups. In polar solvents, a pronounced reduction of \(\tau_1\) values was observed for 12'CA, however the behavior was different from that observed for the respective aldehyde 12'-apo-\(\beta\)-caroten-12'-al studied previously: First, the degree of \(\tau_1\) reduction in methanol was milder for 12'CA (218 \(\rightarrow\) 55 ps) than for 12'-apo-\(\beta\)-caroten-12'-al (220 \(\rightarrow\) 8 ps). Secondly, for 12'CA the plateau of solvent independent \(\tau_1\) values extended further into the mid-polar range (up to 0.5 on the \(\Delta f\) scale) than previously observed for the 12'-aldehyde. For 10'CA the polarity effect on the \(\tau_1\) values was weaker (~71 ps in n-hexane and 34 ps in methanol) and for 8'CA it disappeared completely (~24 ps averaged over all solvents). The polarity-induced reduction of \(\tau_1\) is likely due to the stabilization of an intramolecular charge transfer state in polar solvents. This S\(_1\)/ICT state is also responsible for the stimulated emission in the near IR, which has been observed in this specific class of carotenoids with a terminal carboxyl group for the first time. The occurrence of stimulated emission in the near IR region is also consistent with the steady-state fluorescence spectra which are reported along with the absorption spectra of these species. Possible reasons for the different behavior of the apocarotenoid acids compared to the respective aldehydes are discussed.

1. Introduction

The unique photophysics and time-resolved dynamics of carbonyl-substituted carotenoids have recently attracted considerable attention.\(^1\)\(^-\)\(^7\) In particularly, the intramolecular dynamics of peridinin after excitation to the second electronically excited state S\(_2\) has been in the focus of several ultrafast pump–supercontinuum probe spectroscopic studies, as this molecule is of central importance for the function of the peridinin–chlorophyll a-protein (PCP) complex. A unique feature of peridinin’s excited state absorption band in the 500–700 nm region has been observed behavior,\(^7\) and different interpretations have been suggested.\(^2\)\(^,\)\(^11\)\(^-\)\(^22\) Typically, the appearance of ICT character is signaled by the emergence of an additional transient stimulated emission feature in the near IR region, which decays with a time constant similar to that of the excited state absorption in the visible. Until very recently, evidence for ICT character without carbonyl substitution, like \(\beta\)-carotene. After extensive debates in the literature, which favored either a simple three-state (S\(_2\) \(\rightarrow\) S\(_1\) \(\rightarrow\) S\(_0\)) model\(^1\)\(^-\)\(^4\)\(^,\)\(^12\)\(^-\)\(^14\) or the involvement of additional excited states in the vicinity of S\(_2\) and S\(_1\),\(^15\)\(^,\)\(^16\) a simple three-state relaxation scheme is highly likely for \(\beta\)-caroten\(^17\) on the basis of pump–supercontinuum probe (PSCP) transient absorption spectroscopy\(^18\)\(^,\)\(^19\) covering a wide spectral window (330–1000 nm) at high temporal resolution (~10 fs), see ref. 17 and the accompanying extensive supporting information.

For carbonyl carotenoids the nature of the ICT contributions is still under debate. The transient dynamics of peridinin’s excited state absorption band in the 500–700 nm region have been interpreted in terms of the presence of two separate yet closely coupled states (S\(_1\) and ICT).\(^2\)\(^,\)\(^20\) It is however not clear, whether one or two states are responsible for the observed behavior,\(^7\) and different interpretations have been suggested.\(^2\)\(^,\)\(^11\)\(^,\)\(^20\)\(^-\)\(^22\) The appearance of ICT character is signaled by the emergence of an additional transient stimulated emission feature in the near IR region, which decays with a time constant similar to that of the excited state absorption in the visible. Until very recently, evidence for ICT character
in carbonyl carotenoids was found only in polar environments.\textsuperscript{10} However, in our time-resolved studies on 12'-apo-\(\beta\)-caroten-12'-al and 8'-apo-\(\beta\)-caroten-8'-al stimulated emission was also clearly detected in solvents like \(n\)-hexane or \(i\)-octane.\textsuperscript{7} Obviously, ICT character in carbonyl carotenoids can also be present in the excited state dynamics in nonpolar environments.

To fully understand the intramolecular dynamics of C==O substituted carotenoids, it is necessary to investigate a wide range of species with varying types of substituents (\(\text{C--O} \rightarrow \text{R}\)) at different positions of the conjugated chain and with varying conjugation length in nonpolar and polar environments. Among this line, we have studied the three aldehyde substituted apocarotenals 4'-apo-\(\beta\)-caroten-4'-al, 8'-apo-\(\beta\)-caroten-8'-al and 12'-apo-\(\beta\)-caroten-12'-al.\textsuperscript{5,7} The behavior of the 12'-species was particularly remarkable, as it showed a very strong reduction of the lifetime of the first electronically excited state with increasing solvent polarity (~220 ps in \(n\)-hexane, ~8 ps in methanol), due to the presence of ICT character, which results in a stronger relative stabilization of the excited state compared to the electronic ground state. An interpretation in the framework of an energy-gap-law type approach would then suggest a faster nonradiative transition back to \(S_0\).\textsuperscript{23,24}

In the present work, we extend our studies to the carboxyl substituted species 8'-apo-\(\beta\)-caroten-8'-acid (8'CA), 10'-apo-\(\beta\)-caroten-10'-acid (10'CA) and 12'-apo-\(\beta\)-caroten-12'-acid (12'CA). Fig. 1 illustrates their chemical structures. There are two previous experimental investigations available, which deal with the ultrafast dynamics of 8'CA in ethanol\textsuperscript{25} and 8'CA, 10'CA and 12'CA in an ethanol/tetrahydrofuran mixture.\textsuperscript{26} In the former study, a time constant of 26 ps was deduced from the absorption decay at 530 nm after photoexcitation at 480 nm and ascribed to the lifetime of the \(S_1\) state. In contrast to time-resolved experiments for apocarotenals,\textsuperscript{7} no stimulated emission and therefore no evidence of ICT character was found at probe wavelengths in the near IR (850 nm).\textsuperscript{25} In the latter study, time-resolved absorption spectra of 8'CA, 10'CA and 12'CA were recorded over the range 400–800 nm (for 8'CA also in the range 820–1020 nm).\textsuperscript{26} The transient \(S_1 \rightarrow S_0\) spectra of the three molecules in the visible range exhibited approximately a double band structure with features centered at 500/600 nm (12'CA), 520/620 nm (10'CA) and 540/640 nm (8'CA), where the amplitude of the higher wavelength band was always lower by a factor of 2–3. Both features decayed with the same time constant, and the dynamics for 12'CA and 10'CA were interpreted in terms of a simple three-state model \(S_0(1^1B_{\text{u}}) \rightarrow S_1(2^1A_{\text{g}}) \rightarrow S_0(1^1A_{\text{g}})\) (a possible involvement of an \(1^1B_{\text{u}}\)-type intermediate state has been claimed in the case of 8'CA). In that study, no stimulated emission in the near IR was reported for 12'CA, 10'CA and 8'CA. Interpretation of the measurements is somewhat difficult, because the solvent polarity is unclear due to the fact that the ethanol/tetrahydrofuran mixing ratio was not specified. Our lifetimes reported below suggest, that a large excess of ethanol was likely present in these measurements.

Based on the experience from our earlier experiments on apocarotenoids we believe that ICT character is a fairly general property in the excited-state manifold of apocarotenoids with terminal carbonyl substitution. The motivation for our study was therefore twofold: First, we intended to find characteristic time-resolved stimulated emission features of 8'CA, 10'CA and 12'CA in the near IR range. These were indeed identified and assigned to the \(S_1/\text{ICT}\) state. Secondly, information on the solvent dependence of the \(S_1/\text{ICT}\) lifetime of carboxyl substituted apocarotenoids is obviously lacking, although such data are crucial for understanding the complex intramolecular dynamics in this class of molecules and related systems. Here, we present a first experimental investigation of these issues. The dynamics were monitored at several wavelengths covering the UV/Vis ground state bleaching (\(S_0 \rightarrow S_2\)), Vis excited state absorption (\(S_1/\text{ICT} \rightarrow S_0\)) and near IR excited state absorption/stimulated emission bands (\(S_1 \rightarrow S_0, S_1/\text{ICT} \rightarrow S_0\)) for a range of solvents covering a wide polarity range. In a future study we will provide time-resolved spectral data in the range 350–800 nm from PSCP spectroscopy, including a full global fitting of the ultrafast spectral dynamics.

2. Experimental

2.1 UV/Vis transient absorption experiments

The experimental setup was already described in our previous publications.\textsuperscript{5,6} Briefly, the output of a Ti:sapphire oscillator-regenerative amplifier system (780 nm, 1 kHz, 1 mJ pulse\textsuperscript{\textsuperscript{[1]}}) was split up into two beams. One beam was frequency-doubled in a BBO crystal (\(\lambda_{\text{pump}} = 390 \text{ nm, } S_0 \rightarrow S_2\)) and used for exciting the apocarotenonic acids into higher vibrational levels of the \(S_2\) state. The other beam was either frequency-doubled in a BBO crystal (\(\lambda_{\text{probe}} = 390 \text{ nm}\)) or directed into a home-built blue-pumped two-stage non-collinearly phase-matched optical parametric amplifier (NOPA) to generate the probe wavelength 575 nm (\(S_1/\text{ICT} \rightarrow S_0\)).\textsuperscript{27–29} The NOPA output was subsequently compressed by a pair of quartz prisms.

A computer-controlled stage served to delay the pump and probe pulses with respect to each other. Each beam was then attenuated and mildly focused into the sample cell under a small angle (diameter of the light spot approximately 250 \(\mu\)m). The relative polarization of the pump and probe beams was
adjusted to 54.7° (magic angle) to avoid any contribution from orientational relaxation. Probe energies were measured by two photodiodes, which were located in front of and behind the flow quartz cuvette (1 mm path length), which contained the sample solution. A chopper wheel was used to block every second pump pulse. The change in optical density (ΔOD) was obtained from the differences of the optical densities with and without the pump beam. Typically, 4000–16 000 laser shots were averaged for each delay time. The time resolution of the setup was between 100 and 150 fs. Pulse energies for the pump and probe beams were kept at 2 μJ or less to ensure that nonlinear effects had no influence on the extracted time constants. This was also independently verified using another pump–probe setup, where pulse energies ≤0.4 μJ were used. The apocarotenonic acid concentration was typically between 2.5 and 7.5 × 10⁻⁵ M.

2.2 Near IR transient absorption/stimulated emission measurements

This setup has been used previously in our transient lens (TL) and transient absorption (TA) experiments. Briefly, a mode-locked Ti:sapphire oscillator pumped by a Nd:YVO₄ laser was used to generate pulses at 850, 860 or 890 nm with a repetition rate of 82 MHz and an average laser power of about 1.0–1.5 W. A dichroic mirror was used to split the laser beam into two parts. One part passed through an acousto-optic modulator (AOM, operating at a frequency of 2 MHz provided by a pulse generator) and was subsequently frequency-doubled in a LBO crystal to generate an intensity-modulated pump beam (425, 430 or 445 nm) with pulse energies 0.1 nJ. The other part was used as probe beam, which had a typical energy <1 nJ pulse⁻¹ and was time-delayed with respect to the pump beam by means of a motorized delay line. The time resolution was typically about 120 fs. The pump and probe pulses were recombined in a collinear beam-in-beam arrangement, with the relative polarization set to magic angle to avoid any contributions from orientational relaxation. The pulses were mildly focused into a quartz flow-through cuvette containing the apocarotenonic acid solution and directed onto an avalanche photodiode. The time-dependent absorption/stimulated emission signal of the sample detected by the probe beam was fed into a lock-in amplifier which used the 2 MHz modulation of the pulse generator as its reference signal. The lock-in-signal was then transferred to a PC for further processing.

2.3 Chemicals

All-trans (all-E) samples of 8'-apo-β-carotenonic-8'-acid (8'CA), 10'-apo-β-carotenonic-10'-acid (10'CA), 12'-apo-β-carotenonic-12'-acid (12'CA), 8'-apo-β-caroten-8'-al, 12'-apo-β-caroten-12'-al and ethyl-8'-apo-β-caroten-8'-oate (–COOEt) were generously provided by BASF AG. All substances were used as received or purified by HPLC with final purities ≥97%. All solvents had a purity ≥99%. Steady-state absorption spectra were recorded on a Varian Cary 5E, fluorescence spectra on a Jobin-Yvon FluoroLog-3 spectrometer.

3. Results and discussion

3.1 Steady-state absorption and fluorescence spectra of n'-apo-β-carotenonic-n'-acids

Fig. 2 compares S₀ → S₂ steady-state absorption spectra of apocarotenoids with different terminal carbonyl groups in n-hexane (A) and methanol (B): 12'-apo-β-caroten-12'-al (12'C), 12'-apo-β-caroten-12'-acid (12'CA), 8'-apo-β-caroten-8'-al (8'C), 8'-apo-β-caroten-8'-acid (8'CA), and ethyl-8'-apo-β-caroten-8'-oate (8'COE). In Fig. 3, we present the absorption and fluorescence spectra of the three carboxylic acids 8'CA, 10'CA and 12'CA in i-octane and methanol, respectively. In the case of nonpolar solvents (Fig. 2(A)), changing from an aldehyde group to a carboxyl group results in a spectral shift to higher energy, both for 12'C/12'CA and 8'C/8'CA. Among the 8'-species, the aldehyde shows the strongest red-shift, i.e. the –CHO group exhibits the most efficient conjugation with the rest of the polyene chain. This is likely due to the following effects: (1) Larger residues, which are present in the other two species (8'CA and 8'CE) might favor structures where the carbonyl function is rotating out of the plane of the polyene system, minimizing steric congestion. (2) Differences in electronic structure induced by the different
and 12-apo-β-caroten-12'-al. The crossover from $S_1 \rightarrow S_0$ to $S_0 \rightarrow S_2$ transition energies.

In addition, we recorded steady-state fluorescence spectra of the three apocarotenoid acids in i-octane (nonpolar) and methanol (polar). These are also included in Fig. 3. Beside the location of different emission bands they provide a comparison of the relative fluorescence amplitudes. The most prominent feature of the spectra in i-octane is the change from weak $S_2 \rightarrow S_0$ fluorescence around 530 nm (with possibly even weaker $S_1 \rightarrow S_0$ fluorescence around 800 nm) observed for 8'-apo-β-caroten-8'-acid to $S_1 \rightarrow S_0$ emission for 12'-apo-β-caroten-12'-acid peaking around 720 nm. For the 12'-species the $S_2 \rightarrow S_0$ fluorescence is probably buried under the blue edge of the $S_1 \rightarrow S_0$ main band, whereas the left part of the fluorescence spectrum of the 8'-species almost resembles the mirror image of the $S_0 \rightarrow S_2$ absorption spectrum. This behavior is consistent with that observed for other carotenoid series 34–39 where a relatively abrupt change in emission behavior occurs upon extension of the conjugated system. From comparison with other carotenoids the position of the $S_0 \rightarrow S_1(0\rightarrow 0)$ transition can be assigned to the shoulder appearing around 18 000 cm$^{-1}$. This is consistent with the value of 17 750 cm$^{-1}$ previously deduced by us for the corresponding aldehyde 12'-apo-β-caroten-12'-al. The crossover from $S_1 \rightarrow S_0$ to
S2 → S0 fluorescence with increasing conjugation length in nonpolar solvents can be explained by the decrease of the time constant τ1 (i.e., increase of the rate constant k1) of S1 → S0 internal conversion with decreasing S1–S0 energy gap (see below), which results in a lower quantum yield for S1 fluorescence in the latter solvent. 10

The measurements of time-resolved pump–probe signals for the three n'-apo-β-carotenoic-n'-acids (n = 8, 10, 12) were carried out in liquids at room temperature. Various solvents were chosen to cover a wide polarity range. Time constants τ1 of the S1/ICT → S0 internal conversion process for all acids are comparable). 10

3.2 Transient absorption signals

The measurements of time-resolved pump–probe signals for the three n'-apo-β-carotenoic-n'-acids (n = 8, 10, 12) were carried out in liquids at room temperature. Various solvents were chosen to cover a wide polarity range. Time constants τ1 of the S1/ICT → S0 internal conversion process for all measurements are summarized in Table 1 in a systematic listing of conjugation length, solvent polarity and pump/probe wavelengths.

### Table 1

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<th>R(e)b</th>
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* Δε = R(e)–R(n), where R(e) = (ε – 1)/(ε + 2) and R(n) = (n2 – 1)/(n2 + 2) with the dielectric constant ε and the index of refraction n of the solvent (ref. 42). a Position of the maximum of the S0 → S2 absorption band. All values from ref. 26: Steady-state absorption spectra in ethanol; time-resolved measurements were carried out in an ethanol/THF mixture with an unspecified excess of ethanol using a white-light continuum for probing. From ref. 25: Additional measurements at λprobe = 850 nm did not detect S1/ICT → S0 stimulated emission.
12'-CA was excited to the $S_2$ state at 390 nm which is located to the blue of the absorption maximum of the $S_0 \rightarrow S_2$ transition. The subsequent dynamics were probed at the wavelengths 390 nm (ground state recovery, GSR) and 575 nm (excited state absorption, ESA). For 12'-apo-β-carotenoic-12'-acid, the GSR signals at the probe wavelength 390 nm show an immediate drop at $t = 0$. Subsequently, the negative signal decays back to zero on a slower timescale. The fast initial drop is due to up-pumping of 12'-apo-β-carotenoic-12'-acid to the $S_2$ state. After a very fast IC step $S_2 \rightarrow S_1$/ICT, which typically occurs with a time constant $\tau_2 = 100–200$ fs for most carotenoids,1 the second IC step $S_1$/ICT $\rightarrow S_0$ takes place resulting in a slower final recovery of the absorption signal. The signal can be analyzed in the framework of a simple kinetic model assuming two consecutive IC processes $S_2 \rightarrow S_1$/ICT $\rightarrow S_0$ with characteristic time constants $\tau_2$ and $\tau_1$ ($= k_1^{-1}$) for the $S_2 \rightarrow S_1$/ICT and $S_1$/ICT $\rightarrow S_0$ steps (where $k_2$ and $k_1$ are the corresponding rate constants).5 Using this model, one determines $\tau_1$ to be 233 ps in $n$-hexane and 56 ps in methanol (Table 1), with estimated uncertainties of the time constants $\tau_1$ of less than ten percent. All $S_0 \rightarrow S_2$ and $S_1$/ICT $\rightarrow S_0$ absorption-time profiles in this work were well-reproduced by this kinetic model with a typical regression coefficient of 0.9998. A Levenberg–Marquardt least squares fitting procedure was used to extract the best fit parameters for the time constants $\tau_1$

The probe wavelength 575 nm is located in the region of the ESA band $S_1$/ICT $\rightarrow S_0$ of 12'-apo-β-carotenoic-12'-acid.26 Therefore, the fast initial rise of the signal within the experimental time resolution is due to formation of $S_1$/ICT state population by excitation of the molecules to the $S_2$ state and subsequent ultrafast IC. On the basis of the current data we can only give a rough estimate for this step of $\tau_2 \leq 300$ fs. The ESA profiles decay with the time constants $\tau_1(S_1$/ICT $\rightarrow S_0) = 203$ and 60 ps for $n$-hexane and methanol, respectively. These values are in good agreement with those extracted from the GSR profiles recorded at 390 nm. Qualitatively similar to the case of 12'-apo-β-caroten-12'-al, the $\tau_1$ values for 12'-apo-β-carotenoic-12'-acid show a pronounced dependence on the solvent polarity (see below).

Additional time-resolved absorption traces at 850, 860 or 890 nm have been obtained using a different setup at corresponding pump wavelengths of 425, 430 or 445 nm. Fig. 5 shows representative absorption/stimulated emission signals observed at 860 nm for 12'-CA in $i$-octane and in methanol. A strong ultrafast initial spike is due to $S_2 \rightarrow S_0$ absorption, which is followed by formation of stimulated emission (SE). Such an SE feature was not reported in the previous studies of 12'-CA.25,26 We assign the SE to a low-lying electronic state with intramolecular charge transfer character ($S_1$/ICT $\rightarrow S_0$). The dynamics of 12'-CA showed a strong dependence on the solvent environment. For instance, the transients decayed with time constants $\tau_1(S_1$/ICT $\rightarrow S_0) = 203$ and 49 ps for $i$-octane and methanol, respectively. These $\tau_1$ values were obtained from simple monoexponential fits to the final well-separated decay of the SE. Except for THF, the lifetimes extracted from the SE decays are systematically shorter by ~10% than those extracted from the GSR (at 390 nm) and ESA (at 575 nm) profiles in nonpolar and polar solvents (see Table 1). We postpone a detailed global analysis of the traces to a future.

Fig. 4 Representative TA signals for 12'-apo-β-carotenoic-12'-acid in tetrahydrofuran after excitation to the $S_2$ state at 390 nm. Open squares: $S_1$/ICT $\rightarrow S_0$ absorption at 575 nm. Open circles: $S_0 \rightarrow S_2$ absorption at 390 nm. Solid lines are fits using the model from ref. 5. Time constants $\tau_1$ for the $S_1$/ICT $\rightarrow S_0$ IC process can be found in Table 1.

Fig. 5 Examples of time-resolved transient absorption/stimulated emission signals of 12'-apo-β-carotenoic-12'-acid in $i$-octane (○) and methanol (+). $\lambda_{\text{pump}} = 430$ nm and $\lambda_{\text{probe}} = 860$ nm. Signals are normalized to the maximum of the $S_2 \rightarrow S_0$ absorption. The evolution of the signals at early times is shown in the inset. Lines are intended only as a guide for the eye and have no further significance. $\tau_1$ values obtained from a monoexponential fit to the final SE decay are summarized in Table 1.
publication, where we will present a refined model based on results from broadband absorption spectroscopy employing supercontinuum probing in the range 350–800 nm.

We also note that the SE feature exhibits a delayed appearance in all solvents (see the inset in Fig. 5), similar to our previous study of the corresponding apocarotenals and earlier studies on peridinin. Similarly, the ESA signals at 575 nm show an analogous weak “rise component”. In the previous paper, we proposed a simple model, which accounted for the observed dynamics: It features excited state branching from $S_2$ to populate separate $S_1$ and ICT states, which are connected by an equilibrium. Only the latter state emits in the near IR, and the delayed appearance of part of the SE is then due to formation of ICT population from the $S_1$ state. Correspondingly, the rise in the Vis region is due to formation of transient absorption from the ICT part. Preliminary fitting of the 12′/ICT transients provides solvent dependent time constants for this “delay” between 0.6–3.0 ps, which is in the same range as for the related aldehyde 12′-apo-β-caroten-12′-al (0.9–2.5 ps). Broadband probing in combination with a global kinetic analysis will be required for an accurate analysis of this additional component and a complete deconvolution of the transient ESA band in the visible region.

The amplitude ratio of $S_1$/ICT $\rightarrow$ $S_0$ stimulated emission relative to $S_2$ $\rightarrow$ $S_n$ absorption was smaller in nonpolar solvents than in polar solvents. Similar to our previous study of 12′-apo-β-caroten-12′-al and 8′-apo-β-caroten-8′-al stimulated emission of 12′CA was observed in all solvents: strong in polar media and much weaker in nonpolar ones. The results indicate the involvement of intramolecular charge transfer (ICT) character in the excited state dynamics, regardless of solvent polarity.

**3.2.2 10′-Apo-β-carotenoid-10′-acid.** We have also obtained transient absorption signals for 10′CA in n-hexane, tetrahydrofuran, acetone and methanol (not shown here). The carotenoid was excited at 390 nm (blue edge of the $S_0$ $\rightarrow$ $S_2$ transition), and the subsequent dynamics were probed at the wavelengths 390 nm (GSR) and 575 nm (ESA). Time constants $\tau_1$ are also summarized in Table 1. Upon 390 nm excitation of 10′CA in n-hexane and tetrahydrofuran, a variation of the time constants with probe wavelength was observed in the range $\tau_1 = 67–79$ ps. In acetone, slightly smaller time constants (62–66 ps) were obtained. On the other hand, we observed an almost twice as fast decay kinetics of 10′CA in methanol ($\tau_1 = 33–34$ ps).

**3.2.3 8′-Apo-β-carotenoid-8′-acid.** In the case of 8′CA, $\tau_1$ was practically insensitive to the change of the excitation wavelength, probe wavelength and the solvent polarity. On the other hand, we observed an almost twice as fast decay kinetics of 10′CA in methanol ($\tau_1 = 33–34$ ps).

where values for the dielectric constant $\varepsilon$ and index of refraction $n$ were taken from the literature. A pronounced decrease of $\tau_1$ was observed in 12′CA for $\Delta \varepsilon > 0.5$ (~218 ps in n-hexane and ~55 ps in methanol). In the case of 10′CA, $\tau_1$ values were insensitive to the polarity change in the range $\Delta \varepsilon = 0.0$ (~75 ps), but a pronounced drop of $\tau_1$ was observed in methanol ($\Delta \varepsilon = 0.71$, $\tau_1 = 34$ ps). For 8′CA, we did not observe any systematic change of $\tau_1$ with solvent polarity over the range $\Delta \varepsilon = 0$–0.7. Apparently, there are characteristic differences regarding the onset and the strength of the solvent dependence of $\tau_1$ between the different apocarotenoid acids. Fig. 6 summarizes these findings.

Similar observations of different solvent polarity dependences of $\tau_1$ for different conjugation lengths were made in the case of the n′-apo-β-caroten-n′-als ($n = 4, 8, 12$). For instance, in the case of 12′-apo-β-caroten-12′-al, time-resolved transient absorption data recorded in the $S_0$ $\rightarrow$ $S_2$ and $S_1$/ICT $\rightarrow$ $S_n$ absorption bands and pump–probe measurements in the near infrared region suggested that in the lower polarity range ($\Delta \varepsilon = 0$–0.3) the $\tau_1$ values are not particularly sensitive to the solvent polarity and are very similar to that of 12′CA. However, $\tau_1$ values were almost linearly correlated with $\Delta \varepsilon$ over the range 0.3–0.7. While a qualitatively similar effect is also seen for 12′CA, the onset of solvent polarity dependence of $\tau_1$
This change is however still much weaker than for the even smaller time constant (largest IC rate constant) for the $S_{1}/ICT$ state, and in this case $\tau_1$ polarity dependence appears at a considerably higher $\Delta f$ value ($\sim 0.5$) compared to the aldehyde. For 8'apo-β-caroten-8'-al, the $\tau_1$ values decreased only at the highest $\Delta f$ values, whereas for 8'CA such a decrease was not observed.

The reason for the different behavior regarding the onset and the strength of polarity dependence for apocarotenoic acids and apocarotenals is not yet clear, but can be probably rationalized in terms of the varying $S_{1}/ICT$--$S_0$ energy gap. Several effects might play a role: (1) Steric effects (worse conjugation for the bulky acid group) or (2) differences in the electronic properties of terminal –COOH and –CHO groups with respect to stabilizing charge separation, and therefore ICT formation, in the excited state. For larger conjugation lengths the $S_{1}/ICT$ state might be already energetically so low that solvent dependent ICT stabilization has only a minor influence on the rate constant of internal conversion to $S_0$.

4. Conclusions

We have employed femtosecond pump–probe transient absorption spectroscopy to characterize the solvent dependence of the IC processes of a series of $n'$-apo-β-carotenonic-$n'$-acids (with $n = 8$, 10 and 12). 8'-Apo-β-carotenonic-8'-acid, having the largest number of conjugated double bonds, shows the smallest time constant (largest IC rate constant) for the $S_{1}/ICT \rightarrow S_0$ transition, and in this case $\tau_1$ is almost independent of solvent polarity ($\sim 24$ ps). For the shorter 10'-apo-β-carotenonic-10'-acid a pronounced reduction of $\tau_1$ from ca. 71 to 34 ps was observed when changing from $n$-hexane to methanol. This change is however much weaker than for the even shorter 12'-apo-β-carotenonic-12'-acid ($\sim 218$ and 55 ps, respectively). The conjugation length dependence of $\tau_1$ in the nonpolar medium $n$-hexane can be qualitatively rationalized in terms of an energy gap law approach based on energy differences between the ground and first excited electronic state. The values are comparable with the corresponding 12'- and 8'-aldehydes studies previously in our groups.5,7 In highly polar solvents like methanol the IC process is in all cases not as strongly accelerated as in the aldehydes.

For apocarotenoic acids with shorter conjugation length (and thus a long $S_1$ lifetime in nonpolar solvents), an “$S_1/ICT$” state is stabilized in highly polar solvents, which leads to the pronounced reduction of the lifetime. A characteristic signature of this state is its stimulated emission in the near IR. For apocarotenoic acids with longer conjugation length, the lifetime of the $S_1$ state is already short in nonpolar solvents, so the influence of ICT character on the lifetime appears to become less and less important with increasing conjugation length.

The differences between the 12'-species with terminal aldehyde and carboxyl groups are particularly interesting. In the latter case, the onset of the $\tau_1$ polarity dependence appears at markedly higher $\Delta f$ values, and is also less pronounced. Two effects could be responsible for such a behavior: The incremental stabilization of the ICT region of the “$S_{1}/ICT$” state with increasing polarity could be weaker for the acid than for the aldehyde. In addition, even for comparable incremental stabilization of the ICT part with increasing $\Delta f$ for both types of substituents, the ICT region of 12'-apo-β-carotenonic-12'-acid in nonpolar solvents might be located higher above the $S_1$ part, so that it falls energetically below the $S_1$ part only at considerably larger $\Delta f$, consistent with the experimental observation of the shifted onset of the $\tau_1$ decay. Clearly, at least some information on the energetic positions of the $S_0$ and “$S_{1}/ICT$” states (and thus the energy gap, which probably controls $\tau_1$) will be required for further interpretation. We have therefore very recently launched quantum mechanical calculations for the electronically excited states of carbonyl substituted carotenoids. Together with ongoing pump–supercontinuum probe measurements in our group we plan to obtain a complete view of the excited state dynamics of low-lying electronic states of the apocarotenonic acids and related compounds.

Acknowledgements

Financial support by the German Science Foundation is gratefully acknowledged. We would like to thank J. Troe, J. Schroeder, and T. Polivka for stimulating discussions and S. Druzhinin for his advice during the steady-state fluorescence measurements. Special thanks go to the BASF AG, and here especially H. Ernst, for generously providing the all-trans-$n'$-apo-β-carotenonic-$n'$-acid samples and extensive support. Sample purification was performed by J. Bienert and J. Schimpfhauser.

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