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S_1 and S_2 States of Apo- and Diapocarotenes

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A series of apocarotenes with 5 to 11 conjugated double bonds were synthesized and all-trans isomers were isolated using HPLC techniques. Absorption, fluorescence, and fluorescence excitation spectra were obtained in 77 K glasses. As previously noted for other polyenes and carotenoids, fluorescence spectra of the apocarotenes exhibit a systematic crossover from $S_1(2^1A_g) \rightarrow S_0(1^1A_g)$ to $S_2(2^1A_g) \rightarrow S_0(1^1A_g)$ emissions and a sharp decrease in fluorescence yields with increasing conjugation. The apocarotene spectra have sufficient resolution to accurately locate the dominant vibronic bands of the $S_0(1^1A_g) \rightarrow S_2(1^1B_u)$ and $S_1(2^1A_g) \rightarrow S_0(1^1A_g)$ transitions, thus leading to an accurate catalog of S_1 and S_2 electronic energies as a function of conjugation length. We also have obtained the low-temperature absorption and fluorescence spectra of several model polyenes and diapocarotenes. Comparisons between these series allow a systematic exploration of the influence of terminal cyclohexenyl rings on the energies of carotenoid S_1 and S_2 states. In addition, these preliminary studies indicate that the nature of the terminal double bond has a significant influence on nonradiative decay processes in longer carotenoid systems. Implications regarding the use of energy gap law extrapolations to estimate the 2^1A_g energies of long carotenoids are discussed.

Introduction

The low-lying excited states of linear polyenes continue to be the subjects of considerable experimental and theoretical interest.[1,2] Efforts to better describe these states stem in part from a longstanding interest in improving theoretical descriptions of one-dimensional, conjugated π-electron systems. Polyenes provide many examples where the interplay between theory and experiment has resulted in a deeper understanding of excited state electronic structures and chemical dynamics.[1,2] Improvements in computational technologies have led to increasingly more accurate calculations on the excited states of simple, relatively short polyenes such as octatetraene, a molecule which has been subjected to particularly intense experimental scrutiny. These studies have contributed toward a better understanding of polyene excited state potential energy surfaces and plausible mechanisms for photochemical processes such as cis−trans isomerizations.[3]

Experimental efforts on longer polyenes largely have been motivated by their roles in converting light into chemical energy in visual receptors and in photosynthesis. For example, the cis−trans isomerizations of retinal Schiff bases are responsible for the initial photochemical events in all visual systems and in certain light-harvesting bacteria.[4] Molecules such as β-carotene and spheroidene (Figure 1) enhance the light-capturing ability of chlorophylls in antenna pigment−protein complexes of photosynthetic organisms by collecting light at wavelengths (∼450−550 nm) where chlorophylls and bacteriochlorophylls are inefficient absorbers.[5−7] Their energy of excitation then is transferred to the chlorophylls, ultimately reaching reaction centers where it is converted via electron transfer into transmembrane potentials.[8] The energies and dynamics of the electronic states of carotenoids thus are of fundamental interest in understanding energy transfer to chlorophylls in the antenna complexes of photosynthetic systems.

Our current understanding of the low-energy electronic states of carotenoids is largely based on optical studies of short model polyenes.[9−24] Early experimental studies of simple polyenes exploited their relatively high fluorescence yields and geometries that allow their incorporation into low-temperature mixed crystals. Electronic spectra of these samples possess sufficient resolution to allow the detailed analysis of vibronic interactions between the lowest lying singlet electronic states. The 1972 experimental observations by Hudson and Kohler[22] on diphenyloctatetraene and theoretical calculations by Shulten, Ohmine, and Karplus[23,24] established that the lowest excited state of linear polyenes is a highly correlated 2^1A_g state rather than the HOMO to LUMO, ππ* (1^1B_u) state predicted by simple molecular orbital theories.[25] The correct energy ordering of the 2^1A_g (S_1) and 1^1B_u (S_2) states had not previously been understood, in large part because the $2^1A_g \leftarrow 1^1A_g$ transitions generally are too weak to observe by standard absorption techniques. Furthermore, the effects of π-electron correlation had not been sufficiently appreciated in earlier theoretical treatments of linearly conjugated systems. Subsequent studies by Kohler and his collaborators on short, model polyenes firmly established that the strong, symmetry-allowed $S_0 \rightarrow S_2$ absorption is accompanied by a Stokes-shifted, symmetry-forbidden $S_1 \rightarrow S_0$ emission, with fluorescence yields depending on temperature, the solvent environment, the length of conjugation, and the extent of substitution.[1,2,9−21]

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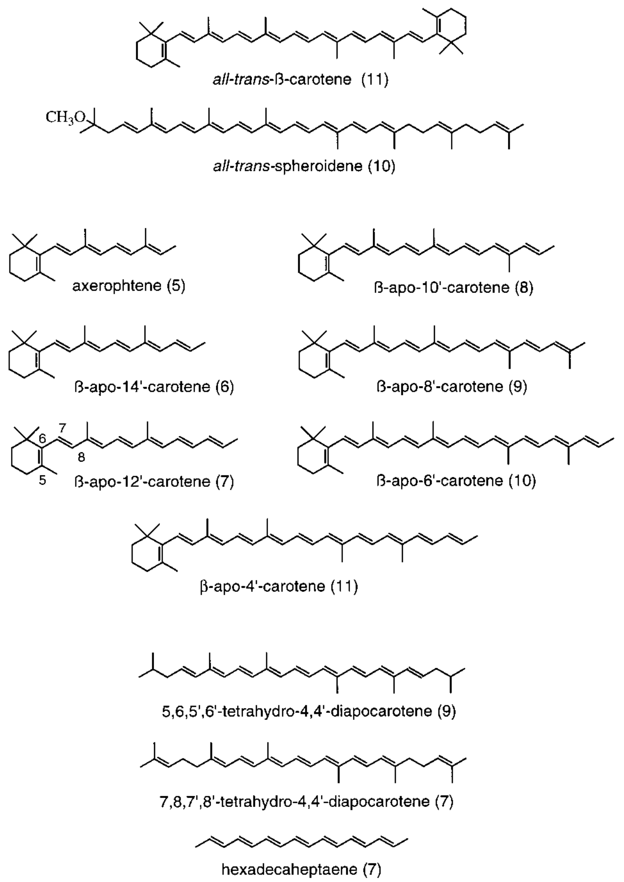

Figure 1. Carotenoids, apocarotenes, and diapocarotenes. Numbers of conjugated double bonds (N) are given in parentheses.

More recently, the relatively high vapor pressures of small polyenes have allowed their study as isolated molecules in supersonic molecular beams.[26−29] These experiments have provided an unprecedented view of the electronic, vibrational, and rotational states of cold, isolated polyenes. However, neither mixed crystal nor jet experiments are yet feasible for carotenoids, and the high-resolution results from model polyenes thus have been critical for interpreting the relatively broad optical spectra of carotenoids in solutions and glasses. Indeed, the rather slow rate of progress in extending the early work of Kohler et al. to the more highly conjugated systems (it has taken an additional 25 years to establish the 2^1A_g energies of β-carotene and spheroidene) can be traced to the need for systematic spectroscopic investigations of polyenes of intermediate conjugation length. These studies have provided critical navigational aids in locating the 2^1A_g states in carotenoids of biological relevance.

Spectroscopic investigations of the carotenoids employed in photobiology have been hampered by several "deficiencies" of longer, more highly substituted conjugated systems. Foremost is the marked decrease in fluorescence quantum yields with increasing conjugation ($<10^{-4}$ for β-carotene and spheroidene).[30,31] The dominance of nonradiative decay processes makes it increasingly difficult to detect the symmetry-forbidden, $S_1(2^1A_g) \rightarrow S_0(1^1A_g)$ transitions, let alone to confirm their identity using standard fluorescence excitation techniques. Furthermore, increasing the conjugation length leads to a predominance of higher energy, $S_2(1^1B_u) \rightarrow S_0(1^1A_g)$ emissions with low-energy vibronic tails that mask the $S_1 \rightarrow S_0$ fluorescence. In addition to minuscule fluorescence intensities, the electronic spectra of naturally occurring carotenoids tend to be significantly broadened, making it even more difficult to observe and identify the weak fluorescence signals from these systems. These problems often are exacerbated by interferences from shorter, more fluorescent polyene degradation products, putting stringent demands on sample purities.

In this paper we investigate the low-temperature absorption and fluorescence spectra of a series of analogous carotenoids (Figure 1). These "apocarotenes" and "diapocarotenes" bridge the gap between molecules with terminal rings such as β-carotene and the open-chained spheroidenes and provide insights into the energetic and kinetic consequences of extending conjugation into the terminal rings. The apocarotenes also offer two critical experimental advantages: the entire series is relatively simple to synthesize from commercially available precursors, and low-temperature absorption and emission spectra have sufficient vibronic resolution to allow the unambiguous identification and measurement of electronic origins ((0−0) bands). This allows for the accurate measurement of S_2 and S_1 energies as a function of conjugation length for $N = 5-11$. We also have made systematic comparisons with two synthetic C_{30} diapocarotenes and previously studied model polyenes. These comparisons provide further insights into how details of molecular structure, including the length of conjugation and the presence or absence of terminal cyclohexenylidene rings, control the rates of radiative and nonradiative decay from the S_1 and S_2 states of carotenoids.

Materials and Methods

2,4,6,8,10,12,14-Hexadecaheptaene was synthesized from dodecapentaenal and crotyltriphenylphosphonium bromide (Instant Ylid, Fluka) as described previously.[21]

The C_{30} diapocarotene with seven conjugated double bonds (7,8,7′,8′-tetrahydro-4,4′-diapocarotene or *all-trans*-2,6,10,15,-19,23-hexamethyl-2,6,8,10,12,14,16,18,22-tetracosanonaene) was synthesized in a double Wittig reaction between a C_{10} dialdehyde and a C_{10} triphenylphosphonium salt prepared by reacting geraniol with triphenylphosphonium hydrobromide. To prepare the C_{30} diapocarotene with nine conjugated bonds (5,6,5′,6′-tetrahydro-4,4′-diapocarotene or *all-trans*-2,6,10,15,19,23-hexamethyl-4,6,8,10,12,14,16,18,20-tetracosanonaene), isovalderaldehyde (3-methylbutanal) was coupled to a C_5-phosphonate ester in a Horner−Wadsworth−Emmons reaction. The resulting ester then was reduced to the corresponding C_{10}-alcohol with Dibal-H. The C_{10} alcohol then was converted into a phosphonium salt and coupled to the C_{10} dialdehyde as described above. The syntheses of the C_{10} dialdehyde and the C_5-phosphonate ester have been described previously.[32,33] Initial purification of the diapocarotenes was accomplished by column chromatography and repeated crystallizations.

β-Apo-16′-carotene (axerophtene) was a obtained as a gift from BASF. The other apocarotenes were synthesized from *all-trans*-retinal (Aldrich) and β-apo-12′-carotenal (a gift from Dr. Percy Manchand of Hoffman-Laroch), and β-apo-8′-carotenal (Fluka) using Wittig reactions. Ethyltriphenylphosphonium bromide, crotyltriphenylphosphonium bromide (both from Fluka), or 2,4-hexadienyltriphenyl phosphonium bromide were reacted with appropriate polyene aldehydes in dry THF as described previously.[17,18,21] The hexadienyl ylide was prepared by adding PPh_3 to the allylic bromide formed from PBr_3 and 2,4-hexadien-1-ol (Aldrich)).

After preliminary workup of reaction mixtures, all-trans isomers were isolated by reversed-phase HPLC, using a Phenomenex ODS column and a mobile phase of methanol or methanol/water (95/5, v/v). HPLC fractions were evaporated or extracted into isopentane and then reconstituted into EPA

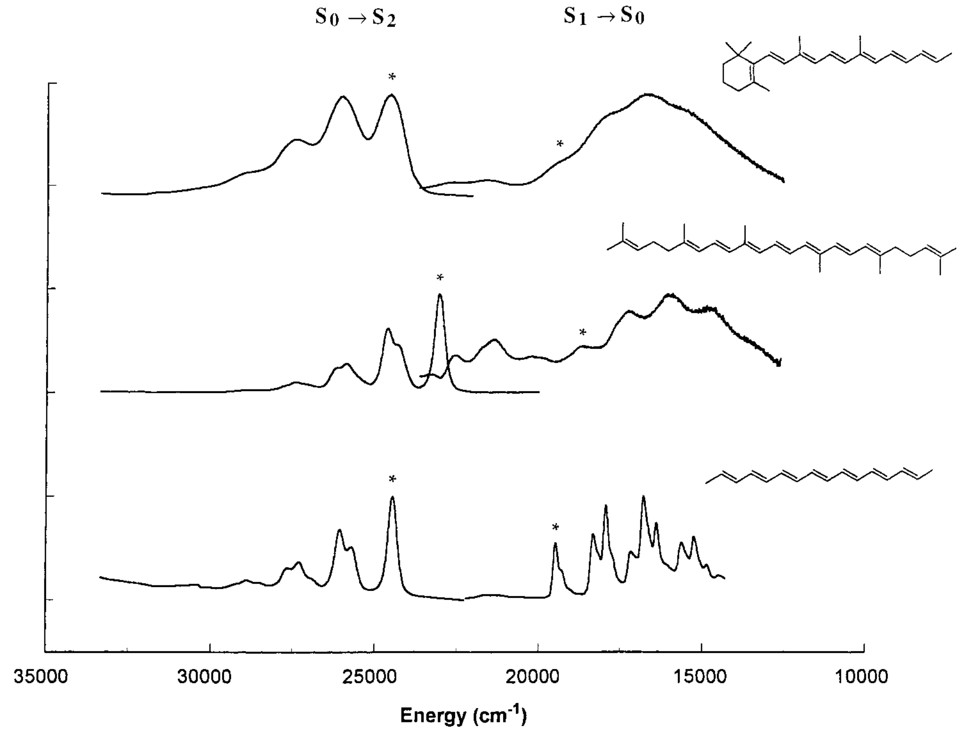

Figure 2. Comparison of absorption and fluorescence spectra of *all-trans*-heptaenes: hexadecaheptaene (bottom), 7,8,7′,8′-tetrahydro-4,4′-diapocarotene (middle), and β-apo-12′-carotene (top). Spectra were obtained at 77 K in an EPA glass (ether/isopentane/ethanol, 5/5/2, v/v/v). Electronic origins are indicated by asterisks.

(ether/isopentane/ethanol, 5/5/2, v/v/v) for low-temperature optical studies. Samples were reinjected into the HPLC before and after exposure to light to ensure that the spectra obtained were those of the all-trans isomers.

Absorption spectra of room temperature solutions and 77 K glasses were acquired on a Shimadzu UV240 spectrophotometer interfaced to a microcomputer. Low-temperature absorption spectra were obtained using a square quartz cuvette and a liquid nitrogen cryostat with flat Suprasil windows. Fluorescence and fluorescence excitation spectra were obtained using a cylindrical Suprasil cryostat and cell on a SPEX Model 212 spectrofluorimeter. All spectra were corrected for the wavelength dependencies of optical components. In converting spectra from wavelength to frequency (cm^{-1}) scales, the data also were corrected for the differences between band-passes at constant wavelength vs constant wavenumber resolution, i.e., $I(\tilde{\nu})/\mathrm{d}\tilde{\nu}) = \lambda^2 I(\lambda)/\mathrm{d}\lambda$. In some cases spectra also were subjected to mild smoothing[34,35] to reduce the noise inherent in these weakly emitting systems. These procedures only minimally distorted the rather broad spectral details of these spectra. The positions of vibronic bands in emission and absorption were determined by fitting spectra to sums of a small number (3−7) of Gaussian-shaped bands using Square Tools, a utility operating within SpectraCalc (Galactic Software). Peak positions of prominent bands and shoulders were averages obtained from a range of fits using different numbers of Gaussians and different approximations for baselines.

Results and Discussion

Major differences between the electronic spectroscopy of simple polyenes and carotenoids are illustrated in Figure 2 which compares the low-temperature absorption and fluorescence spectra of three *all-trans*-heptaenes (Figure 1): hexadecaheptaene, 7,8,7′,8′-tetrahydro-4,4′-diapocarotene, and β-apo-12′-apocarotene. Spectra of hexadecaheptaene are well resolved with well-defined electronic origins, allowing the accurate measurement of $S_1(2^1A_g)$ and $S_2(1^1B_u)$ electronic energies. The addition of methyl substituents and alkyl end groups to form the isoprenoid diapocarotene broadens the vibronic bands and shifts the electronic transitions to lower energy. The $S_0(1^1A_g) \rightarrow S_2(1^1B_u)$ transition energy is considerably more sensitive to alkyl substitution than the $S_0(1^1A_g) \rightarrow S_1(2^1A_g)$ transition. This is a common feature of polyene/carotenoid spectroscopy and mimics the relative sensitivities of the 2^1A_g and 1^1B_u energies to solvent perturbations.[1] Introduction of the terminal β-ionylidene ring in the apocarotene further broadens the spectra and shifts the $S_0(1^1A_g) \rightarrow S_2(1^1B_u)$ transition to substantially higher energy relative to the absorption spectrum of the corresponding diapo compound. The apocarotene $S_1(1^1A_g) \rightarrow S_0(2^1A_g)$ bands experience a significantly smaller blue shift relative to the diapo analogue.

The blue shifts and the loss of resolution in spectra of the apocarotene can be traced to the repulsions between methyl groups on the β-ionylidene ring and the hydrogen atom at the end of the C_{7-8} double bond (Figure 1) in the polyene chain.[36,37] These interactions twist the C_{6-7} single bond, forcing the double bond in the ring (C_{5-6}) out of the plane formed by the other carbon−carbon double bonds. The potential energy along the 5−6−7−8 dihedral angle apparently is both shallow and flat, resulting in a distribution of conformations in solutions and glasses.[36,37] As a result, solutions of apocarotenes, β-carotene, etc. typically contain a distribution of conformers with a range of effective conjugation lengths and transition energies. This simple model also explains the significant blue shift in the apocarotene relative to the diapocarotene. The open-chain diapocarotene enjoys the full effect of conjugation, while the broader apocarotene spectra are due to a superposition of spectra of species with conjugation lengths that average between six (90° rotation about C_{6-7}) and seven (no rotation) conjugated bonds.

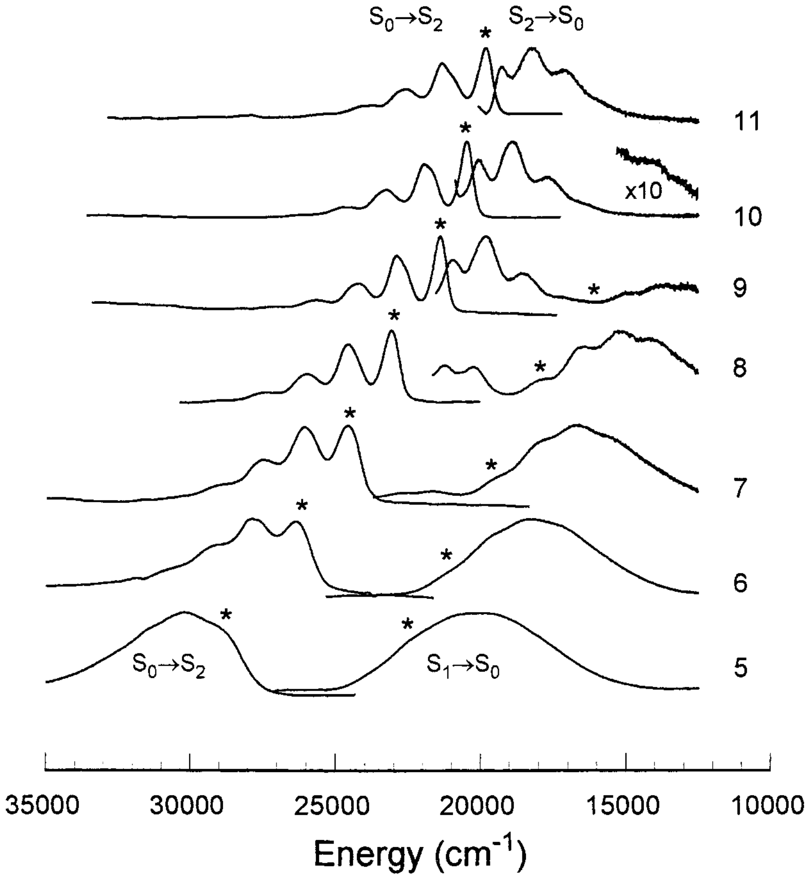

Figure 3. Absorption and fluorescence spectra of *all-trans*-apocarotenes. Spectra were obtained at 77 K in EPA glasses and electronic origins are designated by asterisks. The number given to the right of the spectra indicates the number of conjugated double bonds (N), e.g., β-apo-4′-carotene ($N = 11$), β-apo-6′-carotene ($N = 10$), etc. (See Figure 1 for apocarotene structures.)

Comparison of the spectra of hexadecaheptaene and β-apo-12′-apocarotene show fortuitous agreements in $S_0(1^1A_g) \rightarrow S_2(1^1B_u)$ and $S_1(2^1A_g) \rightarrow S_0(1^1A_g)$ transition energies. For heptaenes the red shifts induced by methyl substituents are offset by the blue shifts due to nonplanarities and the resulting loss in effective conjugation length due to the presence of the ring. This suggests that model polyenes may provide reasonable models for estimating the excited-state energies of apocarotenes (including molecules such as β-carotene) with the same formal number of double bonds. However, more work is needed to quantify the counterbalancing effects of alkyl substitution and nonplanarities on the 2^1A_g and 1^1B_u energies of longer carotenoids.

A systematic comparison of the absorption and emission spectra of the apocarotene series is presented in Figure 3. One striking feature is the crossover from the $S_1(2^1A_g) \rightarrow S_0(1^1A_g)$ emissions observed for the shorter apocarotenes ($N \leq 8$) to the dominant $S_2(1^1B_u) \rightarrow S_0(1^1A_g)$ fluorescence of more extensively conjugated molecules. Similar changes from $S_1 \rightarrow S_0$ to $S_2 \rightarrow S_0$ emissions have been noted in simple polyenes,[17] apocarotenols,[21] spheroidenes,[38] and analogues of β-carotene.[31,39] Relative ($S_2 \rightarrow S_0/S_1 \rightarrow S_0$) fluorescence quantum yields are sensitive to structural details (e.g., see Figure 2), though the relatively abrupt change to $S_2 \rightarrow S_0$ emissions invariably occurs for molecules with seven or eight conjugated bonds. This has the important practical consequence for photobiology that the 2^1A_g states of molecules such as spheroidene ($N = 10$) and β-carotene ($N = 11$) are difficult to study using routine fluorescence techniques.

The characteristic change from $S_1 \rightarrow S_0$ to $S_2 \rightarrow S_0$ emissions in longer polyenes and carotenoids originally was attributed to the increase in the S_2-S_1 energy difference with increasing conjugation length.[17,21] This should result in a decrease in the rate of $S_2 \rightarrow S_1$ internal conversion following the well-known energy gap law.[40] For large energy gaps, internal conversion rates become sufficiently small to allow the strongly allowed $S_2 \rightarrow S_0$ fluorescence to compete with radiationless decay processes, leading to violations of Kasha's rule.[41] The energy gap model accounts for $S_2 \rightarrow S_0$ emissions in several aromatic molecules that are characterized by large S_2-S_1 energy differences.[40] However, recent investigations of $S_2 \rightarrow S_0$ fluorescence quantum yields in carotenes[31] and spheroidenes[42,43] indicate $S_2 \rightarrow S_1$ internal conversion rates that are relatively insensitive to conjugation length over the range $N = 5$ to $N = 13$. The "crossover" to $S_2 \rightarrow S_0$ fluorescence in the longer apocarotenes (Figure 3) thus is most easily explained by increases in the rates of $S_1 \rightarrow S_0$ nonradiative decay due to a combination of smaller S_1-S_0 energy gaps and the increased density of S_0 accepting modes in larger molecules. This leads to the disappearance of $S_1 \rightarrow S_0$ fluorescence, allowing the weak, residual $S_2 \rightarrow S_0$ fluorescence to dominate the emissions of longer carotenoids.

The spectra presented in Figure 3 exhibit systematic increases in resolution with increasing conjugation length. This can be explained by the "distribution of conformers" model discussed above.[36,37] The leveling-off of $S_0 \rightarrow S_2$ transition energies for large N implies that the nonplanarity between the cyclohexenylidene double bond (Figure 1) and the rest of the polyene chain has a decreasing impact on the spread in transition energies. Optical excitation of longer carotenes thus selects conformers with a less heterogeneous distribution of $S_0 \rightarrow S_2$ transition energies. This process of photoselection appears to be preserved in the $S_2 \rightarrow S_0$ and $S_1 \rightarrow S_0$ emission spectra. The

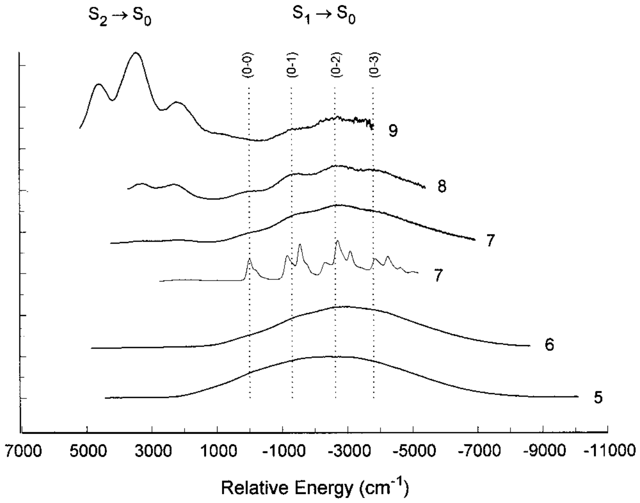

Figure 4. Comparison of the fluorescence spectra of *all-trans*-apocarotenes. Spectra have been shifted so that the $S_1 \rightarrow S_0$ electronic origins ((0−0)'s) share a common zero of energy. The number given to the right of the spectra indicates the number of conjugated double bonds (*N*) as in Figure 3. The spectral intensities are normalized to give the same maximum intensities for the $S_1 \rightarrow S_0$ transitions. Vertical lines are based on the vibronic spacings observed for β-apo-10′-carotene ($N = 8$).

modest increase in resolution partially offsets lower fluorescence yields, allowing the detection and identification of $S_1 \rightarrow S_0$ vibronic bands in longer apocarotenes and other carotenoids.

The vibronic structure observed in the low-temperature spectra of the apocarotene series proves to be sufficient to accurately locate $S_0 \rightarrow S_2$ and $S_1 \rightarrow S_0$ vibronic bands, including the electronic origins. The spectra presented in Figure 3 were fit to a superposition of Gaussian-shaped bands using standard least-squares procedures. The number of Gaussians (and their widths and amplitudes) used for relatively unresolved spectra (e.g., $N = 5$) was compared with those obtained from similar fits of more resolved spectra of apocarotenes (e.g., $N = 8$). Spectra such as those of hexadecaheptaene (Figure 2) also were used as templates to ensure that the least-squares fits on the apocarotenes were consistent with the vibronic patterns observed for simple polyenes. Peak positions obtained by varying the number of Gaussians (3−8) and the nature of the baselines were averaged to estimate the positions of the dominant vibronic bands and shoulders of the spectra presented in Figure 3. The results of these fits (and their estimated errors) are presented in Table 1. We also have detected in β-apo-6′-carotene ($N = 10$) a weak, partially resolved $S_1 \rightarrow S_0$ emission on the tail of the dominant $S_2 \rightarrow S_0$ transition (Figure 3). However, the spectrum is not of sufficient quality to allow accurate deconvolution into its vibronic components.

Figure 4 compares the apocarotene emission spectra on a scale on which the emission spectra have been shifted to force the $S_1 \rightarrow S_0$ (0−0)'s (Table 1) to share a common zero of energy. The remarkable similarities between these spectra provide strong confirmation that our deconvolution of vibronic components gives an accurate account of the energies of electronic origins as well as other prominent vibronic features. (It should be noted that the consequences of conformational disorder make it difficult to unambiguously assign the vibronic bands in the broad spectra of axerophtene ($N = 5$). In this instance, we also have been guided by the vibronic energies of longer members of the apocarotene series; see Figure 5.) Comparisons with the $S_1 \rightarrow S_0$ spectrum of the simple heptaene provide further support for the results given in Table 1. The Franck−Condon envelopes show a consistent pattern of vibronic intensities with the primary differences being traced to differences in resolution. The emission spectra presented in Figure 4 are dominated by combinations of totally symmetric (a_g) C−C and C═C stretching modes with vibrational frequencies of ∼1200 and ∼1600 cm^{-1}. These details are more easily identified in the $S_1(2^1A_g) \rightarrow S_0(1^1A_g)$ fluorescence spectrum of the simple heptaene which shows Franck−Condon maxima that characteristically involve at least one quantum of the double bond stretch. In the broader apocarotene spectra, vibronic features corresponding to single and double bond stretches coalesce into progressions in what appears to be a single, intermediate frequency of 1300−1400 cm^{-1}. Bands designated as (0−1), (0−2), and (0−3) in Table 1 and Figure 4 thus refer to overtones of this "hybrid" frequency which is a common signature of carotenoid absorption and emission spectra. Note (Figure 4) that the (0−1) hybrid essentially bisects the C−C and C═C fundamentals seen in the well-resolved $S_1 \rightarrow S_0$ emission spectrum of the simple heptaene.

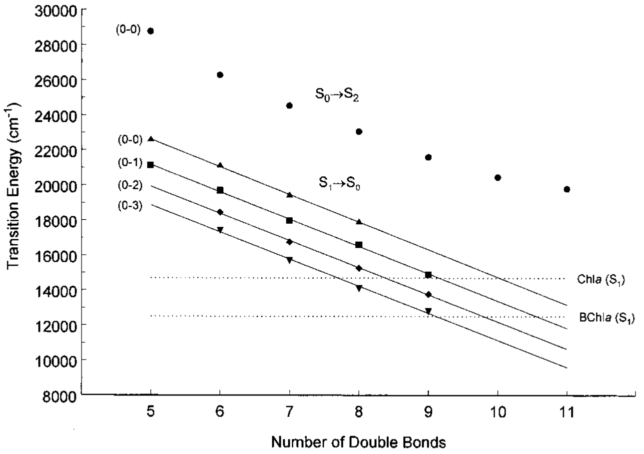

Figure 5. $S_1 \rightarrow S_0$ ($1^1A_g \rightarrow 2^1A_g$) and $S_0 \rightarrow S_2$ ($1^1A_g \rightarrow 1^1B_u$) vibronic transition energies for apocarotenes as a function of conjugation length (data from Table 1). The S_1 (Q_y) energy of bacteriochlorophyll *a* (12 500 cm^{-1}) is for the B800 monomer of the light-harvesting complex (LH2) of *Rhodobacter sphaeroides*.[47] The S_1 (Q_y) energy of chlorophyll *a* (∼14 700 cm^{-1}) is for the light-harvesting complex of photosystem II.[48]

It is important to comment on why the (0−0) bands tend to be so prominent for supposedly forbidden $S_1(2^1A_g) \rightarrow S_0(1^1A_g)$ transitions. The forbidden nature of the $S_0 \rightarrow S_1$ transition is confirmed by the difficulty in detecting it in standard absorption experiments, e.g., the $S_0 \rightarrow S_1$ transition dipole moment of spheroidene has been estimated to be $<10^{-3}$ that observed for the $S_0 \rightarrow S_2$ absorption.[44] The selection rules imply that the (0−0) band should be weak (or nonexistent) with the major part of the spectral intensity built on nontotally symmetric (b_u), Herzberg−Teller "promoting" modes that mix the 2^1A_g and 1^1B_u electronic states.[45] Under isolated-molecule conditions (e.g., supersonic jets) or in the small number of cases where polyenes have been incorporated into crystals that rigorously retain their inversion centers, the $S_0 \leftrightarrow S_1$ (0−0)'s are indeed missing with transitions being built on b_u false origins.[28] However, the most prominent b_u promoting vibrations are in-plane bending modes of very low frequency, <100 cm^{-1} in long polyenes. Therefore, even for polyenes or carotenoids that retain idealized C_{2h} symmetries (e.g., hexadecaheptaene), (0−0) bands and b_u false origins will not be readily distinguishable, especially for the low-resolution spectra $S_1 \rightarrow S_0$ spectra presented in this paper. In addition, small distortions from C_{2h} symmetry, either due to asymmetric substitutions or solvent perturbations, tend to give the (0−0) bands intensities that are comparable to those of false

TABLE 1: Vibronic Energies (in cm^{-1}) of Apocarotenes in 77 K EPA[a]

N	$1^1B_u(0-0)$	$2^1A_g(0-0)$	$2^1A_g(0-1)$	$2^1A_g(0-2)$	$2^1A_g(0-3)$
5	28 750 (60)	22 590 (90)	21 120 (200)		
6	26 260 (5)	21 110 (40)	19 700 (50)	18 490 (40)	17 410 (130)
7	24 530 (20)	19 420 (15)	17 960 (40)	16 749 (20)	15 690 (80)
8	23 050 (10)	17 900 (20)	16 590 (20)	15 270 (40)	14 110 (90)
9	21 590 (30)	16 310* (100)	14 860 (130)	13 780 (500)	12 790 (110)
10	20 450 (15)				
11	19 790 (10)				

[a] Numbers in parentheses refer to uncertainties (±1σ). (* Estimated by extrapolation from shorter apocarotenes and the energies of other N = 9 vibronic bands.)

origins.[28,46,47] Furthermore, these bands undergo inhomogeneous solvent shifts due to the distribution of local solvent environments.[46] As a result, the electronic origins of $S_0 \leftrightarrow S_1$ spectra of polyenes and carotenoids in solutions and glasses should be viewed as due to a complicated, unresolved collection of distorted and undistorted molecules all of which contribute to the "(0−0)" band shapes in Figures 3 and 4.

Figure 5 summarizes the $S_0 \rightarrow S_2$ (0−0) energies and the energies of the dominant vibronic components of the $S_1 \rightarrow S_0$ transitions as a function of the number of conjugated double bonds. The $S_1 \rightarrow S_0$ vibronic energies vary almost linearly with N, and we have included best fit lines as a guide for summarizing the data. (Theory suggests that $E = A - B/N$ for large N, but plots of the apocarotene energies versus $1/N$ show large curvatures over the limited range of conjugation (N = 5−9 for the $S_1 \rightarrow S_0$ vibronic bands) for which we have reliable data.) In spite of the inherent limitations of extrapolations, such plots naturally encourage speculation on the S_1 energies of slightly longer apocarotenes. Given their connections with the naturally occurring carotenoids employed in photosynthetic antenna, namely spheroidene and β-carotene (Figure 1), it is particularly interesting to extrapolate to the S_1 energies of the apocarotenes with N = 10 and N = 11. To this end, we have superimposed on the graph of apocarotene electronic energies the S_1 energies of chlorophylls found in the antenna of plants (Chl*a* (Q_y)) and bacteria (BChl*a* (Q_y)). Regardless of the details of the extrapolation, Figure 5 indicates that the 2^1A_g state of spheroidene must lie well above the $S_1(Q_y)$ state of bacteriochlorophyll *a* (e.g., $E \sim$ 12 500 cm^{-1} in the B800 monomer of the light harvesting complex (LH2) of *Rhodobacter sphaeroides*),[48] allowing efficient spheroidene (S_1) → bacteriochlorophyll *a* (S_1) energy transfer in the antenna complexes of typical photosynthetic bacteria. This conclusion has been substantiated by the recent direct detection of the $S_1 \rightarrow S_0$ emission spectrum of *all-trans*-spheroidene[50] and the independent use of the energy gap law to estimate the S_1 energy of spheroidene from its lifetime.[51,52] These experiments all converge on a spheroidene S_1 energy of ~14 200 cm^{-1} (cf. ~14 700 cm^{-1} for β-apo-6′-carotene (N = 10), estimated by linear extrapolation of the data summarized in Figure 5.)

Establishing that S_1(spheroidene) is substantially more energetic than S_1(BChl*a*) is relatively straightforward, even allowing for the differences between the apocarotenes and corresponding spheroidenes, different solvent shifts between in vitro and in vivo environments, etc. However, Figure 5 suggests that the S_1 energies of β-carotene and Chl*a* may be quite comparable, as originally suggested by Christensen et al.[17,21] This might then require energy transfer from the S_2 state of β-carotene to chlorophyll. This idea has been supported by the recent detection of $S_1 \rightarrow S_0$ emission in β-carotene, placing the 2^1A_g state at ~14 500 cm^{-1} in *n*-hexane.[30,31] The 2^1A_g state of β-carotene thus appears to be almost isoenergetic with the S_1-(Q_y) state of chlorophyll a (e.g., 14 700 cm^{-1} in the light-harvesting complex of photosystem II).[49] The energetic consequences of extending conjugation into terminal rings thus require careful consideration. In an effort to better understand the differences in the excited state energies of spheroidenes, apocarotenes, and the analogues of β-carotene, we thus have extended our measurements on the apocarotenes to include systematic comparisons with comparable diapo- analogues. Preliminary results for N = 7 and 9 (see Figure 1 for structures) are presented in Figure 6.

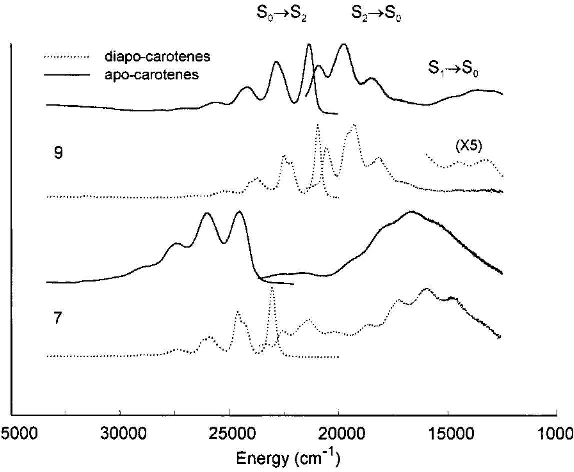

Figure 6. Comparison of the 77 K absorption and fluorescence spectra of apocarotenes and corresponding diapocarotenes. The number given to the left of the spectra indicates the number of conjugated double bonds (N) (see Figure 1).

As previously discussed, the twisting of the C_{6-7} bonds (Figure 1) to relieve steric strain results in blue shifts of the apocarotene $S_0 \rightarrow S_2$ and $S_1 \rightarrow S_0$ transition energies as well as broadening of the spectra. The nature of the terminal double bond has a smaller effect on the $S_1 \rightarrow S_0$ transition energies than on $S_0 \rightarrow S_2$ energies. These effects are further mitigated by an increase in conjugation length (Table 2). This trend is not unexpected, given the expected decrease in influence of the terminal double bonds as $N \rightarrow \infty$. There appears to be a rather rapid convergence toward comparable transition energies for diapo- and apocarotenes with differences (Δ's in Table 2) approximately halving for $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_2$ transition energies in increasing N from seven to nine conjugated bonds. These trends also are consistent with the 500 cm^{-1} difference between the S_1 energy estimated for β-apo-6′-carotene (N = 10) relative to that of spheroidene (see above).

The data summarized in Table 2 can be linked with observed differences in the $S_0 \rightarrow S_2$ transition energies in N = 11 molecules such as β-carotene (λ(0−0) = 478 nm in hexane) and its open-chain analogue, lycopene (λ(0−0) = 503 nm).[53] The intermediate transition energies of γ-carotene (λ(0−0) = 493 nm)[53] and gazaniaxanthin (λ(0−0) = 491 nm),[54] both N = 11 systems with apocarotene-like, single ring structures, support the notion that the spectral shifts due to terminal rings are

TABLE 2: Comparison of the Electronic Transition Energies (in cm^{-1}) of Apocarotenes and Corresponding Diapocarotenes in 77 K EPA[a]

	N	apocarotenes	diapocarotenes	Δ
$S_0 \rightarrow S_2$ (0−0)	7	24 530 (20)	23 045 (15)	1485 (25)
$S_0 \rightarrow S_2$ (0−0)	9	21 590 (30)	20 960 (20)	630 (35)
$S_1 \rightarrow S_0$ (0−1)	7	17 960 (40)	17 240 (30)	720 (50)
$S_1 \rightarrow S_0$ (0−1)	9	14 860 (130)	14 500 (150)	360 (200)

[a] Δ refers to the increase in transition energy (in cm^{-1}) due to the presence of a cyclohexenyl ring. Numbers in parentheses refer to uncertainties ($\pm 1\sigma$).

approximately additive. $S_0 \rightarrow S_2$ shifts of ~500 cm^{-1}/ring in these $N = 11$ systems are quite consistent with the trends summarized in Table 2. In addition, the data indicates that the shifts in $S_1 \rightarrow S_0$ transitions are about half as large as the shifts in corresponding $S_0 \rightarrow S_2$ transitions, suggesting, for example, that the 2^1A_g state of lycopene should lie ~500 cm^{-1} below the ~14 500 cm^{-1} 2^1A_g state of β-carotene.[30,31]

In spite of the paucity of data, Table 2 represents the first systematic attempt to catalog the effects of terminal rings on the 1^1B_u and 2^1A_g energies of carotenoids. Previous confusion in relating the transition energies of β-carotene and related compounds to open-chained carotenoids can be illustrated by the relatively recent assertion that β-carotene should be considered to possess nine conjugated double bonds due to the twisting of the terminal double bonds out of the plane of the central double bonds.[55] Kohler later developed the concept of an "effective" length of conjugation ($N_{\mathrm{eff}} = N \pm \delta N_{\mathrm{substituent}}$) to rationalize the shifts observed in the spectra of β-carotene and its shorter analogues.[2,56] However, the shortcomings of this approach are illustrated in the difference between $N_{\mathrm{eff}} = N - 0.3$ for the 1^1B_u energies and $N_{\mathrm{eff}} = N + 0.5$ for the 2^1A_g energies. While it is reasonable that the effective conjugation length may not be the same for every electronic transition, an *increase* in the effective conjugation length of 2^1A_g due to nonplanarity has no physical basis. These problems most likely can be traced to the experimental difficulties in accurately locating vibronic origins in β-carotene and its shorter analogues,[39] a problem overcome in our investigation of the better resolved apocarotene series. The extension of the comparisons summarized in Table 2 to a wider range of conjugation lengths promises to give a much better accounting of the effects of cyclohexenyl rings on the 2^1A_g and 1^1B_u energies of β-carotene and other carotenoids employed in photobiological processes.

In addition to modifying electronic transition energies, the presence or absence of terminal cyclohexenyl rings appears to have an important influence on the dynamics of carotenoid excited states. This is most easily seen by comparing the emission spectra of the apo- and diapocarotenes with $N = 9$ (Figure 6). $S_1 \rightarrow S_0$ emission is significantly reduced in the open-chain, diapocarotene. Although we have not measured fluorescence quantum yields, the absolute $S_1 \rightarrow S_0$ emission intensity appears to be reduced by at least a factor of 3 in going from the apocarotene to the open-chained diapocarotene. Given the extremely low fluorescence yields of these molecules, this should translate into a parallel reduction in the fluorescence lifetime and parallel increase in the $S_1 \rightarrow S_0$ nonradiative decay rate. A similar sensitivity of $S_1 \rightarrow S_0$ fluorescence yields to relatively subtle structural effects has been observed in simple heptaenes where the addition of terminal methyl groups in converting tetradecaheptaene to hexadecaheptaene changes a molecule with relatively strong $S_2 \rightarrow S_0$ fluorescence into a species dominated by $S_1 \rightarrow S_0$ emission.[21] Comparable effects have been observed in the gas phase spectra of model tetraenes where the addition of methyl substituents again appears to activate $S_1 \rightarrow S_0$ fluorescence.[20] In all of these cases, the S_1 energies remain relatively constant (e.g., $\Delta \approx 400$ cm^{-1} for the nonaenes (Table 2)) while $S_1 \rightarrow S_0$ quantum yields (and lifetimes) appear to be much more sensitive to substitution.

One practical consequence of the effects noted in Figure 6 is that $S_1 \rightarrow S_0$ transitions may be more easily detected in long carotenoids containing terminal rings, e.g., β-carotene should be a stronger S_1 emitter than lycopene. The apparent sensitivity of $S_1 \rightarrow S_0$ emission yields to subtle structural details also has implications for understanding the factors controlling nonradiative decay processes in excited carotenoids. As previously noted, the crossover from $S_1 \rightarrow S_0$ to $S_2 \rightarrow S_0$ emission in Figure 3 largely can be related to the acceleration of $S_1 \rightarrow S_0$ nonradiative decay due to the decrease in S_1 energy with increasing conjugation. The kinetics of the S_1 state appears to follow the energy gap law:[40]

$$k_{\mathrm{ic}} = A \exp(-\Delta E/B) \tag{1}$$

where k_{ic} is the rate of $S_1 \rightarrow S_0$ internal conversion (≈ the reciprocal of the S_1 lifetime for these weakly fluorescent molecules) and ΔE is the electronic energy difference between the S_0 and S_1 states, i.e., the energy of the (0−0) transition.

In the simplest applications of the energy gap law, A and B (which depend on the energy and number of accepting modes, the displacement between S_0 and S_1 potential energy surfaces, etc.)[40] are treated as constants. Frank et al. applied the energy gap law to a series of spheroidenes,[51,52] Andersson et al. carried out a similar study on β-carotene and its analogues,[31] and Bachilo et al. studied internal conversion rates in diphenylpolyenes.[57] The rates of S_1 nonradiative decay (determined from fluorescence lifetimes or transient absorption measurements) and the ΔE's (with (0−0) bands determined or estimated from fluorescence spectra) can be fit to eq 1, giving $A = 10^{15}-10^{17}$ and $B = 1100-1500$ cm^{-1}. These parameters combined with S_1 lifetimes obtained from transient absorption experiments then can be used to estimate ΔE ($=E(2^1A_g)$ for longer carotenoids ($N > 9$) for which the weak $S_1 \rightarrow S_0$ (0−0)'s are difficult, if not impossible, to observe using standard fluorescence techniques. This approach has been used to estimate the 2^1A_g energies of several carotenoids that play important roles in biological systems.[43,51,52,58]

The comparison between the $S_1 \rightarrow S_0$ emission intensities of the $N = 9$ apo- and diapocarotenes and the earlier work on the effect of methyl groups on the fluorescence spectra of simple tetraenes[20] and heptaenes[21] reminds us that the S_1-S_0 energy gap is not the sole determinant of the rates of $S_1 \rightarrow S_0$ internal conversion in polyenes and carotenoids. The frequencies and number of accepting modes, density of vibronic states, etc. will be sensitive to structural details such as methyl substitution and whether terminal double bonds are included in cyclohexenyl rings. Energy gap law fits to spheroidenes, minicarotenes, and diphenyl polyenes shows systematic differences in the parameters (A and B) extracted from different series.[31,52,57] This argues for caution in applying the energy gap law to a wide range of polyenes and carotenoids, even if both k_{ic} and ΔE can be accurately determined. These issues are amplified by comparisons of the fluorescence lifetimes of three algal carotenoids, fucoxanthin, siphonaxanthin, and peridinin.[59,60] These highly substituted systems have almost identical S_1 energies, as determined from their relatively strong and partially resolved fluorescence spectra. Their fluorescence lifetimes vary from 40 to 100 ps. Typical parameters from energy gap law fits indicate that a 2-fold change in the S_1 lifetime ($\approx 1/k_{\mathrm{ic}}$) requires a 750−

1000 cm^{-1} change in ΔE which clearly is not the case for these molecules. This analysis and the comparisons provided by Figure 6 reinforce the notion that, in spite of the great usefulness of eq 1 in rationalizing fluorescence yields and lifetimes,[51,52] the dynamics of carotenoid S_1 states depend on the details of molecular structure as well as the S_1-S_0 energy gap. Energy gap law extrapolations thus will be most accurate when comparing molecules with similar structures and conjugation lengths.

Conclusions

The apocarotene series bridges the gap between molecules such as β-carotene and open-chain carotenoids such as lycopene and spheroidene. Unlike β-carotene and its analogues, the low-temperature absorption and emission spectra of the apocarotenes are sufficiently resolved to allow the identification and accurate measurement of $S_0 \leftrightarrow S_2$ and $S_1 \rightarrow S_0$ vibronic bands, including the energies of electronic origins. The apocarotene spectra presented in this paper provide a considerably more accurate catalog of 2^1A_g and 1^1B_u energies as a function of conjugation length than those obtained from previous studies of synthetic carotenoids and spheroidenes.

Comparisons with comparable diapocarotenes provide quantitative measures of the increases in $S_0 \rightarrow S_2$ and $S_1 \rightarrow S_0$ transition energies when terminal double bonds are embedded in cyclohexenyl rings. Differences in transition energies decrease with increasing conjugation, and $S_1 \rightarrow S_0$ transitions are significantly less sensitive to structural differences than $S_0 \rightarrow S_2$ transitions. The presence or absence of terminal rings appears to have a much more significant impact on the dynamics of carotenoid excited states. These results echo earlier observations on model tetraenes and heptaenes which indicate the important role of terminal methyl substituents in controlling $S_2 \rightarrow S_0$ and $S_1 \rightarrow S_0$ fluorescence yields.[20,21] In addition, carotenoids containing keto and allenic or acetylenic groups show significant variations in $S_1 \rightarrow S_0$ lifetimes that are not accompanied by corresponding changes in the $S_1 \rightarrow S_0$ transition energies.[59,60] These results suggest that some caution should be used in applying "universal" energy gap law expressions to a wide range of polyenes and carotenoids, particularly in estimating S_1 energies from the S_1 lifetimes of species with significant variations in molecular structure.

Given their relative ease of synthesis and the tabulations of S_1 and S_2 energies provided by this study, the apocarotenes should be viewed as attractive targets for calibrating new spectroscopic techniques before extending these approaches to longer, nonfluorescent polyenes and carotenoids. Due to its photobiological importance and the commercial availability of high-purity samples, β-carotene has been the almost exclusive target for the initial application of a wide variety of spectroscopic techniques to elucidate energies and properties of "long carotenoid" 2^1A_g states. Recent publications claiming the detection of the 2^1A_g state in β-carotene include the use of reflectance spectroscopy in zeolite[61] and 4.2 K single crystals[55] and the electric-field-induced change in the absorption (electroabsorption) in polystyrene matrices.[62] Another intriguing result is the observation of a weak absorption background in the inverse Raman (Raman loss) spectrum of a related carotenoid, canthaxanthin.[63] By far the most promising of recent experiments on longer carotenoids are the reports of the detection of 2^1A_g states in the resonance Raman excitation spectra of 4.2 K single crystals of β-carotene[55] and in solid *all-trans*-spheroidene.[64] The potential of resonance Raman excitation techniques to detect $S_0 \rightarrow S_1$ absorptions in long carotenoids provides a tantalizing alternative to the detection of extremely weak fluorescence signals and/or the use of energy gap and other extrapolation techniques. However, the use of resonance Raman excitation techniques to uncover 2^1A_g states in carotenoids has a troubled past.[21,65,66] Resonance Raman and other techniques thus would benefit from systematic calibration on shorter polyenes and carotenoids whose 2^1A_g energies can be unambiguously established by detection of vibronically resolved, $S_1 \rightarrow S_0$ fluorescence. This would allow the straightforward evaluation of the ability of these alternate techniques to detect $1^1A_g \rightarrow 2^1A_g$ transitions in spheroidene, β-carotene and other carotenoids of biological interest.

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