TABLE IV: Experimental and Calculated Values of the g Tensor of Cu(II)-Doped Single Crystals of α-Glycylglycine at 4.2 K

	calculated	experimental	
g_{xx}	2.040	2.033[a]	2.022[b]
g_{yy}	2.083	2.085[a]	2.059[b]
g_{zz}	2.236	2.236[a]	2.273[b]

[a] This work. [b] Fujimoto et al.[12]

were assumed. To evaluate the energy matrix the AOM orbital parameters given in refs 43 and 44 were used. The total energy matrix consisting of the ligand field and the spin-orbit coupling (there is no electron-electron repulsion to consider in the d^1 and d^9 cases) was diagonalized to yield eigenvalues and eigenvectors. The spin-orbit interaction matrix is given in Table I of ref 43.

The g-tensor principal values were calculated from the equations

$$g_{zz} = 2\sum c_i c_j \langle \psi_i | l_z + 2s_z | \psi_i \rangle \tag{5a}$$

$$g_{xx} = 2\sum c_i c_j \langle \psi_i | l_x + 2s_x | \psi_j \rangle \tag{5b}$$

$$g_{yy} = 2\sum c_i c_j \langle \psi_i | l_y + 2s_y | \psi_j \rangle \tag{5c}$$

The calculated principal values of the **g** tensor are compared with our experimental data in Table IV. There is very good agreement between the experimental values and those calculated from the modified Lin method[42] which we adapted to encompass the AOM approximations in our earlier work.[27] The coefficients of the eigenfunctions of the Kramers doublet showed that the free electron in the complex is mainly in a $d_{x^2-y^2}$ orbital. This agrees with the original assignment proposed by Fujimoto et al.[12]

Acknowledgment. We thank the National Sciences and Engineering Research Council of Canada for grants to C.A.M. to support this research. K.S. and Y.C. thank Jilin University and Nankai University, respectively, for leaves of absence.

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(43) Lever, B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; pp 53, 67.

(44) Gerlock, M.; Slade, R. C. *Ligand-Field Parameters*; Cambridge University Press: Cambridge, U.K.; 1973.

Electronic Relaxation in Long Polyenes

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A series of carotenols with from 7 to 11 conjugated double bonds have been synthesized and purified by using HPLC techniques. Absorption, fluorescence, and fluorescence excitation spectra have been obtained in 77 K glasses. The shorter members of this series exhibit the Stokes-shifted, $S_1 \rightarrow S_0$ emissions seen in previous studies of model polyenes. For carotenols with more than eight conjugated double bonds, however, the fluorescence is dominated by "anti-Kasha", $S_2 \rightarrow S_0$ fluorescence. These findings in part can be attributed to a larger S_2-S_1 energy difference and the resultant decrease in $S_2 \rightarrow S_1$ radiationless decay rates in longer polyenes. The precipitous crossover from $S_1 \rightarrow S_0$ to $S_2 \rightarrow S_0$ emission, however, cannot be fully accounted for by the energy gap law, which predicts only modest changes in radiative and nonradiative decay rates with increasing polyene length. The lack of S_1 fluorescence prohibits the direct observation of the S_1 state in the longer carotenols. Nevertheless, trends noted in the shorter polyenes indicate a 5500-6500-cm^{-1} S_2-S_1 energy difference for polyenes such as β-carotene (11 conjugated double bonds). The implications of large S_2-S_1 energy gaps for the spectroscopy and photochemistry of β-carotene and other long polyenes also are discussed.

Introduction

The electronic spectroscopy and excited-state dynamics of linear polyenes continue to be topics of considerable interest. Recent experiments range from time-resolved studies of cis-trans isomerization in substituted butadienes,[1] to transient Raman spectroscopy of carotenoids bound to membranes of photosynthetic bacteria,[2] to investigations of the electronic properties of polyacetylenes.[3] These studies encompass a wide range of experimental techniques and theoretical models, and it is not surprising that the relationships between polyenes of different conjugated lengths largely remain unexplored. A common understanding of linearly conjugated systems remains a goal of active interest. This investigation contributes toward this effort by establishing links between the electronic properties of short, model polyenes and the carotenoids, which play important roles in photobiology.

A brief review of previous work on polyenes establishes several distinct areas of interest. Spectroscopic and kinetic investigations of short diphenylpolyenes (from stilbene to diphenyloctatetraene)[4-11] have exploited their commercial availability, stability, high fluorescence yields and relative ease of placement in supersonic jets. Short, unsubstituted polyenes, on the other hand, are not as stable and most notably are nonfluorescent. This has severely hampered their study, and considerably more attention has been focused on unsubstituted or methyl-substituted polyenes of intermediate length.[12-23] These compounds combine at least

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(1) Lee, M.; Haseltine, J. N.; Smith III, A. B.; Hochstrasser, R. M. *J. Am. Chem. Soc.* **1989**, *11*, 5044.

(2) Kuki, M.; Hashimoto, H.; Koyama, Y. *Chem. Phys. Lett.* **1990**, *165*, 417-421.

(3) Yoshizawa, M.; Kobayashi, T.; Fujimoto, H.; Tanaka, J.; Shirakawa, H. *J. Lumin.* **1987**, *38*, 300-304.

(4) Shepanski, J. F.; Keelan, B. W.; Zewail, A. H. *Chem. Phys. Lett.* **1983**, *103*, 9.

(5) Kohler, B. E.; Spiglanin, T. A. *J. Chem. Phys.* **1984**, *80*, 5465-5471.

(6) Kohler, B. E.; Spiglanin, T. A. *J. Chem. Phys.* **1985**, *82*, 2939.

(7) Troe, J.; Amirav, A.; Jortner, J. *Chem. Phys. Lett.* **1985**, *115*, 245.

(8) Horwitz, J. S.; Kohler, B. E.; Spiglanin, T. A. *J. Chem. Phys.* **1985**, *83*, 2186.

(9) Horwitz, J. S.; Kohler, B. E.; Spiglanin, T. A. *J. Phys. Chem.* **1985**, *89*, 1574-1576.

(10) Amirav, A.; Sonnenschein, M.; Jortner, J. *J. Chem. Phys.* **1986**, *102*, 305.

(11) Itoh, T.; Kohler, B. E. *J. Phys. Chem.* **1988**, *92*, 1807-1813.

(12) Gavin, Jr., R. M.; Weisman, C.; McVey, J. K.; Rice, S. A. *J. Chem. Phys.* **1978**, *68*, 522-529.

(13) Granville, M. F.; Holton, G. R.; Kohler, B. E.; Christensen, R. L.; D'Amico, K. L. *J. Chem. Phys.* **1979**, *70*, 593.

(14) D'Amico, K. L.; Manos, C.; Christensen, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1777.

(15) Heimbrook, L. A.; Kenny, J. E.; Kohler, B. E.; Scott, G. W. *J. Chem. Phys.* **1981**, *75*, 4338-4342.

(16) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E.C., Ed.; Academic Press: New York, 1982; Vol. 6, pp 1-95.

0022-3654/90/2094-8118$02.50/0

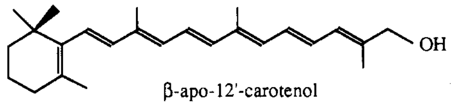
modest fluorescence yields with the ability to be placed in low-temperature mixed crystals as well as supersonic jets. The spectroscopy of these model systems has established (for polyenes with four or more conjugated bonds) the presence of a 2^1A_g (S_1) state between the ground state (1^1A_g (S_0)) and lowest one-photon-allowed excited state (1^1B_u (S_2)).[16] Absorption into S_2 typically is followed by a Stokes-shifted emission from S_1 with fluorescence yields being sensitive to molecular structure. Spectra of intermediate length systems also indicate an increase in the S_2–S_1 energy difference with increasing conjugated length.[14,16,21,23] This raises some interesting questions on the energy and properties of the 2^1A_g state in long conjugated systems such as β-carotene and polyacetylene.

Another focus of experimental effort has been on the excited states of carotenoids. This has been motivated in large part by the important roles played by carotenoids in photosynthesis both as antennae pigments[24–26] and as photoprotectors.[27] The relationships between these important functions and the properties of carotenoid excited states remain to be worked out. β-Carotene (11 conjugated double bonds) has been a particularly popular subject of investigation. Its strong, broad absorption provides a good target for laser excitation, and fluorescence measurements,[28–34] transient absorption experiments,[35,36] and Raman[37–39] and resonance Raman[40,41] spectroscopy have provided many important details of excited-state structure and dynamics.

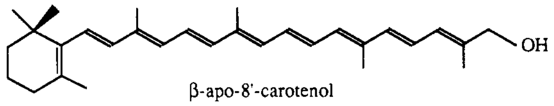
Earlier reports of β-carotene's fluorescence[28] have been confirmed by several groups.[29–34] However, the fluorescence origin is not shifted from the origin of the strongly allowed $1^1A_g \rightarrow 1^1B_u$ absorption, indicating that emissions in β-carotene and related molecules originate from the S_2 state. The absence of detectable $S_1 \rightarrow S_0$ emissions leaves the location of the 2^1A_g state open to question. Previous investigation of resonance Raman profiles in β-carotene led to the suggestion[37,38] that the 2^1A_g state lies $\sim$3500 cm^{-1} below 1^1B_u, and this has been widely cited in discussions of the antennae function of carotenoids in photosynthesis.[26] (The 3500-cm^{-1} energy gap puts the carotene S_1 level well above the lowest singlet state of chlorophyll.) Recent picosecond transient absorption studies on β-carotene also have been interpreted in support of a relatively small S_2–S_1 energy difference.[35,36]

1,3,5,7,9,11,13-tetradecaheptaene

2,4,6,8,10,12,14-hexadecaheptaene



β-apo-12'-carotenol



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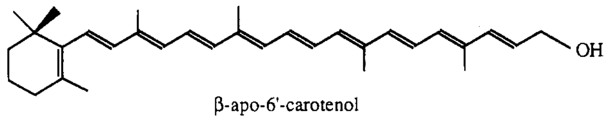
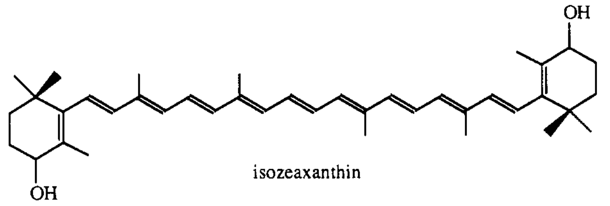


β-apo-6'-carotenol



isozeaxanthin

Figure 1. Molecules studied.

A relatively small S_2–S_1 energy difference (ΔE) in the carotenoids, however, is not consistent with trends noted in shorter polyenes.[14,16,21,23] For example, octatetraene, decapentaene, dodecahexaene, and tetradecaheptaene in *n*-hexane at room temperature show a 1^1B_u–2^1A_g energy difference that systematically increases from 4900 to 6300 cm^{-1} in this series.[21] The α,ω-methyl-substituted series shows slightly smaller energy gaps (ΔE increases from 4600 to 5800 cm^{-1} in going from decatetraene to hexadecaheptaene).[42] The more highly substituted isoprenoid structures of carotenoids may lead to somewhat smaller energy differences, but extrapolation of the trends noted above to carotenoids with 10 or 11 conjugated double bonds is not easily reconciled with the $\leq$3500-cm^{-1} energy gap suggested for β-carotene.[37,38]

In an effort to link the previous spectroscopic work on shorter, model polyenes with the experiments on the carotenoids, we have carried out a systematic investigation of the fluorescence properties of the molecules indicated in Figure 1. The carotenols were chosen in part because of the availability of precursors that considerably reduced the synthetic effort in obtaining polyenes with 7–11 conjugated double bonds. The alcohols proved to be particularly well suited for purification by reversed-phase HPLC procedures and also are considerably more soluble in low-temperature glasses than their hydrocarbon counterparts. We thus were able to obtain low-temperature absorption, fluorescence, and fluorescence excitation spectra of isomerically pure samples. The spectra obtained were of sufficient quality to allow the unambiguous assignment of electronic origins and have extended our understanding of the energies and decay patterns of low-lying electronic states in longer polyenes.

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(17) Heimbrook, L. A.; Kohler, B. E.; Spiglanin, T. A. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 4580–4584.

(18) Leopold, D. G.; Vaida, V.; Granville, M. F. *J. Chem. Phys.* **1984**, *81*, 4210–4217.

(19) Leopold, D. G.; Pendley, R. D.; Roebber, J. L.; Hemley, R. J.; Vaida, V. *J. Chem. Phys.* **1984**, *81*, 4218–4229.

(20) Heimbrook, L. A.; Kohler, B. E.; Levy, I. J. *J. Chem. Phys.* **1984**, *81*, 1592–1597.

(21) Snyder, R.; Arvidson, E.; Foote, C.; Harrigan, L.; Christensen, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 4117–4122.

(22) Simpson, J. H.; McLaughlin, L.; Smith, D. S.; Christensen, R. L. *J. Chem. Phys.* **1987**, *87*, 3360–3365.

(23) Kohler, B.; Spangler, C.; Westerfield, C. *J. Chem. Phys.* **1988**, *89*, 5422–5428.

(24) Sauer, K. *Acc. Chem. Rev.* **1978**, *11*, 257–264.

(25) Cogdell, R. J.; Hipkins, M. F.; MacDonald, W.; Truscott, T. G. *Biochim. Biophys. Acta* **1981**, *634*, 191–202.

(26) Siefermans-Harms, D. *Biochim. Biophys. Acta* **1985**, *811*, 325.

(27) Cogdell, R. J.; Frank, H. A. *Biochim. Biophys. Acta* **1988**, *895*, 63.

(28) Cherry, R. J.; Chapman, D.; Langelaar, J. *Trans. Faraday Soc.* **1968**, *64*, 2304.

(29) van Riel, M.; Kleinen-Hammans, J.; van de Ven, M.; Verwer, W.; Levine, Y. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 102–107.

(30) Haley, L. V.; Koningstein, J. A. *J. Phys. Chem.* **1983**, *87*, 621.

(31) Watanabe, J.; Kinoshita, S.; Kushida, T. *Chem. Phys. Lett.* **1986**, *126*, 197–200.

(32) Gillbro, T.; Cogdell, R. J. *Chem. Phys. Lett.* **1989**, *158*, 312–316.

(33) Bondarev, S. L.; Dvornikov, S. S.; Bachilo, S. M. *Opt. Spectrosc. (USSR)* **1988**, *64*(2), 268–270.

(34) Bondarev, S. L.; Bachilo, S. M.; Dvornikov, S. S.; Tikhomorov, S. A. *J. Photochem. Photobiol., A: Chem.* **1989**, *46*, 315–322.

(35) Wasielewski, M. R.; Kispert, L. W. *Chem. Phys. Lett.* **1986**, *128*, 238–243.

(36) Hashimoto, H.; Koyama, Y. *Chem. Phys. Lett.* **1989**, *154*, 321–325.

(37) Thrash, R. J.; Fang, H.; Leroi, G. E. *J. Chem. Phys.* **1977**, *67*, 5930–5933.

(38) Thrash, R. J.; Fang, H.; Leroi, G. E. *Photochem. Photobiol.* **1979**, *29*, 1049–1050.

(39) Binnie, N. E.; Haley, L. V.; Koningstein, J. A. *Chem. Phys. Lett.* **1985**, *120*, 564–568.

(40) Hashimoto, H.; Koyama, Y. *Chem. Phys. Lett.* **1989**, *162*, 523–527.

(41) Hashimoto, H.; Koyama, Y. *Chem. Phys. Lett.* **1989**, *163*, 251–256.

(42) Morey, T.; Klein, D.; Guite, M.; Howard, J.; Christensen, R., to be published.

Experimental Section

Synthesis and Purification. 1,3,5,7,9,11,13-Tetradecaheptaene was synthesized as described previously.[21] Reaction mixtures initially were purified by chromatography on Woelm neutral alumina (activity grade II) to separate the heptaene isomers from reactants and shorter polyene impurities. *all-trans*-Tetradecaheptaene was obtained by reversed-phase HPLC using a Altex Ultrasphere-ODS column and a mobile phase of methanol/water (4/1 v/v). Samples for spectroscopy were collected in the absence of the UV light normally used for detection and extracted into *n*-pentane. The *n*-pentane solution was evaporated in a stream of nitrogen, and the residue redissolved in EPA (ether/isopentane/ethanol, 5/5/2 v/v/v). The procedure by which an HPLC peak was collected and converted into a 77 K glass sample was carried out as rapidly as possible under subdued lights to minimize interferences from heptaene degradation products. Sample purities were monitored by reinjection of samples after spectroscopic measurements. Tetradecaheptaene proved the most fragile of the molecules given in Figure 1, and certain of our sample handling procedures (e.g., collection of HPLC samples in the dark and the rapid conversion into low-temperature glasses) were not required to obtain reproducible spectra of the other compounds.

2,4,6,8,10,12,14-Hexadecaheptaene was synthesized from decapentaenal[14] and crotyltriphenylphosphonium bromide (Instant Ylid, Fluka).[22] The all-trans isomer was obtained by reversed-phase HPLC using an Altex Ultrasphere-ODS column and a mobile phase of methanol/water (95/5 v/v). This fraction was extracted into *n*-hexane for storage at −20 °C. Dilute samples retained their isomeric purity for several days. However, these procedures did not completely eliminate the presence of less conjugated polyene impurities which could be detected by their low-temperature fluorescence under certain excitation conditions.

β-Apo-12′-carotenol was synthesized by $NaBH_4$ reduction of β-apo-12′-carotenal, which was a gift from Dr. Percy Manchand of Hoffman-Laroche. After initial recrystallization from ether the alcohol was purified by reversed-phase HPLC (Altex, ODS column) using a mobile phase of methanol/water (95/5 v/v). Due to the low purity (10–20%) of the starting aldehyde, the reaction products contained many visible absorbing components, but the HPLC procedures allowed the isolation of a fraction that could be identified from room-temperature absorption measurements (e.g., wavelength of absorption and the lack of cis peaks) as the all-trans isomer.

β-Apo-8′-carotenol was synthesized by $NaBH_4$ reduction of β-apo-8′-carotenal (Fluka). Crystallization from ether followed by HPLC (Altex-ODS, 95% methanol/water) allowed the isolation of the predominant all-trans isomer.

β-Apo-6′-carotenol was synthesized by $LiAlH_4$ reduction of methyl β-apo-6′-carotenoate which was obtained by a Wittig reaction between β-apo-8′-carotenal and trimethyl phosphonoacetate. Trimethyl phosphonoacetate (Aldrich, 110 mg) and NaH (15 mg) were dissolved in 20 mL of anhydrous DMF and stirred under argon gas in the presence of molecular sieves. After 30 min, 250 mg of β-apo-8′-carotenal (Fluka) in 2 mL of DMF was added, and the solution stirred for 15 h at room temperature. The reaction mixture was then diluted with water, and the organic components were extracted into ether, which was then washed and evaporated to yield the ester. Reduction of the ester was carried out at −30 °C in a closed argon system. After 90 min the reaction was quenched by the addition of ethyl acetate. Workup of the organic fractions gave crude β-apo-6′-carotenol in 90% overall yield. The all-trans isomer was isolated by reversed-phase HPLC (Altex, ODS column) using a mobile phase of 100% methanol.

Isozeaxanthin was obtained by $LiAlH_4$ reduction of canthaxanthin (Fluka). After recrystallization from methanol the crude product was purified on an ODS column using 100% methanol as the mobile phase. Due to the high purity of the starting materials, the chromatograms showed a dominant component that could be identified as *all-trans*-isozeaxanthin.

Spectral Measurements. Absorption spectra of room-temperature solutions and 77 K glasses were obtained on a Shimadzu UV240 spectrophotometer interfaced to a microcomputer. Low-temperature absorption spectra were obtained by using a square quartz cuvette and a flat window, suprasil liquid nitrogen dewar. Fluorescence and fluorescence excitation spectra were obtained by using a cylindrical suprasil dewar and cell on a SPEX Model 212 spectrofluorimeter equipped with a SPEX DM1B data station. All spectra were corrected for the wavelength dependencies of optical components and then transferred to a mainframe computer for subsequent analysis and display. In some cases spectra were subjected to mild smoothing[43,44] to reduce the noise inherent in these weakly emitting systems. These procedures only minimally distorted the rather broad spectral details of these spectra.

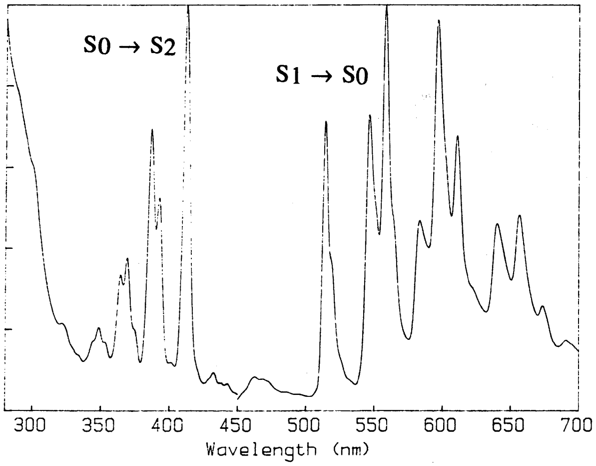

Figure 2. Fluorescence and fluorescence excitation spectra of *all-trans*-2,4,6,8,10,12,14-hexadecaheptaene in 77 K *n*-pentadecane. The fluorescence spectrum was obtained by exciting at 414 nm. The fluorescence excitation spectrum was obtained by monitoring the emission intensity at 558 nm.

The fluorescence quantum yield of isozeaxanthin was obtained by comparing its fluorescence intensity (integrated with respect to frequency) with that of fluorescein ($\Phi_f = 0.90$ in 0.1 N sodium hydroxide).[45] Although isozeaxanthin and fluorescein have comparable absorption and emission spectra, the large disparity between their emission yields required the use of dilute fluorescein solutions to obtain emission spectra of isozeaxanthin and the standard under the same electronic and optical conditions.

Results

Spectra of the two simple heptaenes provide the link between the present study and the previous work on shorter model polyenes. The 77 K fluorescence and fluorescence excitation spectra of hexadecaheptaene are given in Figure 2. The corrected excitation spectrum is in excellent agreement with the absorption spectrum, and the fluorescence spectrum is independent of excitation wavelength. These observations confirm that the HPLC procedures have resulted in a single-component sample. The hexadecaheptaene spectra are very similar to 77 K spectra obtained for shorter hexaenes, pentaenes, and tetraenes,[14] showing the classic Stokes shift between the electronic origins of absorption ($\lambda = 414$ nm) and emission ($\lambda = 514$ nm). The 4700-cm^{-1} gap between the origins in Figure 2 thus corresponds to the energy difference between the 1^1B_u and 2^1A_g excited states.

The 77 K absorption and fluorescence spectra of tetradecaheptaene are given in Figure 3.[46] Comparison of the corrected excitation spectrum with the absorption spectrum and the ob-

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[43] Savitsky, A.; Golay, M. J. E. *Anal. Chem.* **1964**, *36*, 1727.

[44] Steiner, J.; Termonia, Y.; Deltour, J. *Anal. Chem.* **1972**, *44*, 1906.

[45] Rabek, J. F. *Experimental Methods in Photochemistry and Photophysics*; Wiley: New York, 1982; pp 750–752.

[46] The absorption spectrum of tetradecaheptaene given in Figure 3 of ref 21 was plotted incorrectly. This error has been corrected in Figure 3 of this paper. We thank Dr. Leonard Doub for pointing out discrepancies between the original figure and absorption wavelengths referred to in the text. The discussion of the absorption spectrum (e.g., (0–0) at 402 nm) is correct, but the original figure[21] should be replaced by Figure 3 of this paper.

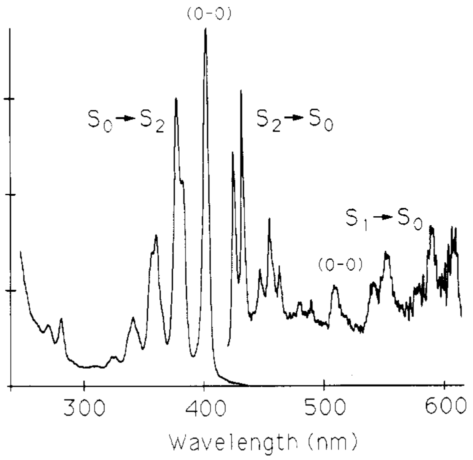

Figure 3. Absorption and fluorescence spectra of *all-trans*-1,3,5,7,9,11,13-tetradecaheptaene in 77 K EPA. The absorption spectrum was obtained with a 2-nm bandpass. The fluorescence spectrum was excited by using the 405.4-nm line from a Hg lamp and detected with a 1-nm bandpass through a Schott KV-418 filter (see footnote 46).

servation that the fluorescence spectrum is not strictly independent of the excitation wavelength indicate the presence of shorter polyenes, even in these highly purified samples. In spite of these interferences, the heptaene fluorescence can be isolated by excitation into the absorption origin at 402 nm. This results in the well-resolved fluorescence spectrum given in Figure 3. Excitation into higher energy vibronic levels (e.g., the strong vibronic band at 383 nm) gives emissions with decreased resolution and increased intensity at shorter wavelengths. A series of fluorescence spectra taken over a range of excitation wavelengths establish the emission origin at 408 nm and eliminate the possibility that the short-wavelength emissions are due to Raman or resonance Raman scattering. Similarly, a series of excitation spectra taken at different monitoring wavelengths gave spectra that reproduce all the vibronic features of the tetraene absorption.

The 77 K spectra of hexadecaheptaene and tetradecaheptaene offer some interesting contrasts. Most obvious is the absence of an energy gap between the $1^1A_g \rightarrow 1^1B_u$ absorption and the onset of the fluorescence, suggesting $1^1B_u \rightarrow 1^1A_g$ emission. In addition to the relatively strong fluorescence in the 410–500-nm region, tetradecaheptaene also shows some weak but reproducible vibronic features at $\lambda \geq 511$ nm. Excitation spectra monitored on these bands also closely correspond with the absorption spectrum. These weak emissions are almost identical to the $2^1A_g \rightarrow 1^1A_g$ fluorescence observed for hexadecaheptaene. We thus must conclude that in tetradecaheptaene emission occurs from both $1^1B_u(S_2)$ and $2^1A_g(S_1)$ with $S_2 \rightarrow S_0$ emission dominating.

Previous solvent-shift studies on room-temperature absorption and fluorescence spectra confirm the assignment of dual emissions in tetradecaheptaene.[21] The 402-nm absorption band and the 410–500-nm emission features exhibit comparable shifts in a series of hydrocarbon solvents. The dependence of these shifts on solvent polarizability also is typical of shifts obtained for the strongly allowed $1^1A_g \rightarrow 1^1B_u$ transition in shorter polyenes. In contrast, the longer wavelength emissions at $\lambda \geq 511$ nm show a much weaker dependence on solvent polarizability, comparable to solvent shifts previously observed for forbidden $2^1A_g \rightarrow 1^1A_g$ transitions.[14,21] The solvent studies also help in identifying the $2^1A_g \rightarrow 1^1A_g$ (0–0) at 511 nm, since all the vibronic features at shorter wavelengths exhibit the polarizability dependences of allowed transitions. In addition, the 514 nm $S_1 \rightarrow S_0$ electronic origin in hexadecaheptaene (Figure 2) strongly supports our assignment.

The 77 K excitation and emission spectra of β-apo-12′-carotenol are compared with spectra of hexadecaheptaene in Figure 4. Spectra of the carotenol are noticeably broader due to well-understood complications brought about by the cyclohexenylidene ring.[47,48] Nevertheless, there is sufficient resolution in the carotenol spectra to allow the identification of the electronic origins in both emission and excitation. The spectra of β-apo-12′-carotenol and hexadecaheptaene are then seen to be quite similar with almost identical electronic energies and a clear indication of $2^1A_g \rightarrow 1^1A_g$ ($S_1 \rightarrow S_0$) fluorescence.

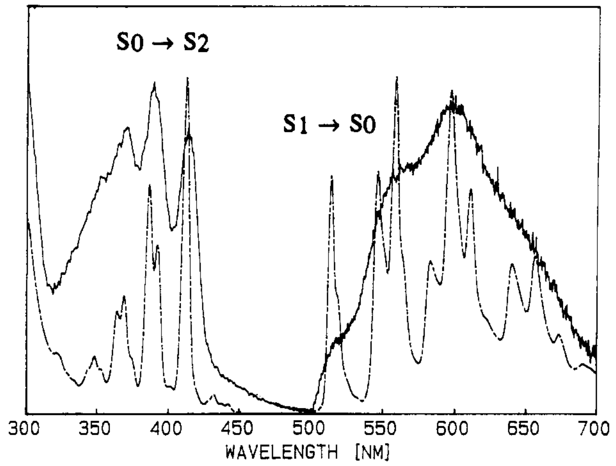

Figure 4. Comparison of fluorescence and fluorescence excitation spectra of *all-trans*-2,4,6,8,10,12,14-hexadecaheptaene (dashed lines) and *all-trans*-β-apo-12′-carotenol (solid lines). Spectra of hexadecaheptaene were obtained as described in Figure 2. The fluorescence spectrum of β-apo-12′-carotenol in 77 K EPA was obtained by exciting at 413 nm. The excitation spectrum was obtained by monitoring the fluorescence intensity at 650 nm.

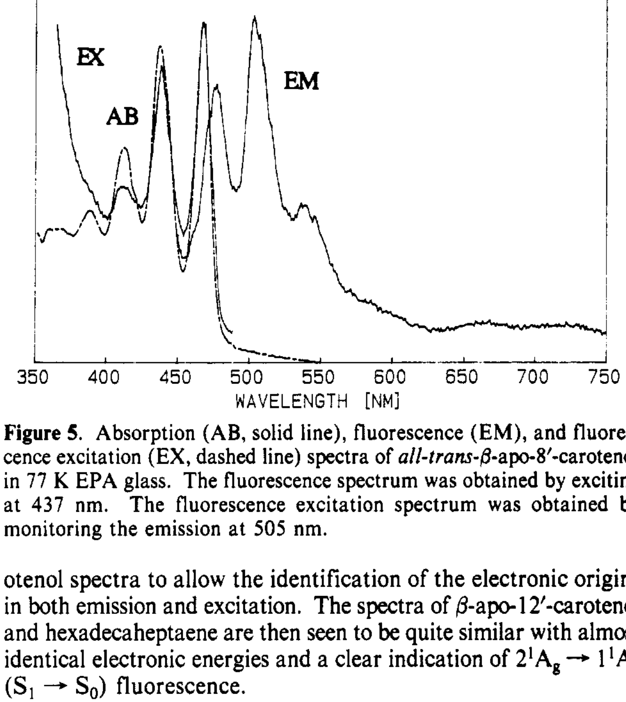

Figure 5. Absorption (AB, solid line), fluorescence (EM), and fluorescence excitation (EX, dashed line) spectra of *all-trans*-β-apo-8′-carotenol in 77 K EPA glass. The fluorescence spectrum was obtained by exciting at 437 nm. The fluorescence excitation spectrum was obtained by monitoring the emission at 505 nm.

In contrast to β-apo-12′-carotenol, the low-temperature fluorescence from β-apo-8′-carotenol is dominated by $1^1B_u \rightarrow 1^1A_g$ ($S_2 \rightarrow S_0$) emission (see Figure 5). The long wavelength region (600–700 nm) of the fluorescence spectrum is perhaps suggestive of weak $S_1 \rightarrow S_0$ emission (compare with Figure 3), but the broad, unresolved spectral tail does not allow identification of vibronic features similar to those seen in tetradecaheptaene. The fluorescence characteristics of β-apo-6′-carotenol (Figure 6) are almost identical with those exhibited by β-apo-8′-carotenol. For both of these molecules the fluorescence excitation spectra are in excellent agreement with the well-resolved $1^1A_g \rightarrow 1^1B_u$ absorption, and the fluorescence spectra are independent of the wavelength of excitation. These features plus the good overlap between absorption and emission origins strongly support the assignment of "anti-Kasha", $S_2 \rightarrow S_0$ emission in these systems.

Isozeaxanthin also emits from its S_2 state (Figure 7). The 77 K absorption and excitation spectra are in excellent agreement,

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(47) Christensen, R. L.; Kohler, B. E. *Photochem. Photobiol.* **1973**, *18*, 293.

(48) Hemley, R.; Kohler, B. *Biophys. J.* **1977**, *20*, 377.

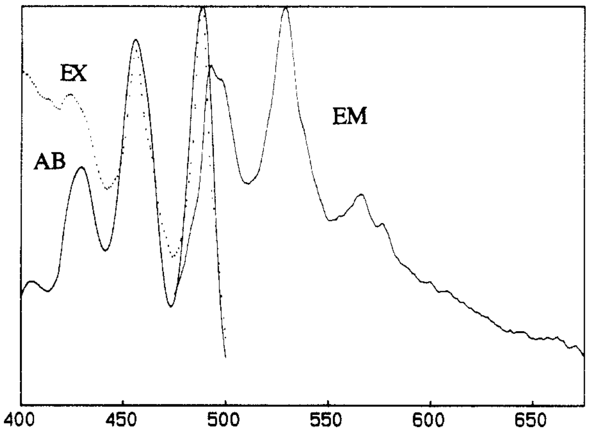

Figure 6. Absorption (AB, solid line), fluorescence (EM), and fluorescence excitation (EX, dotted line) spectra of *all-trans*-β-apo-6′-carotenol in 77 K EPA glass. The fluorescence spectrum was obtained by monitoring the emission at 529 nm.

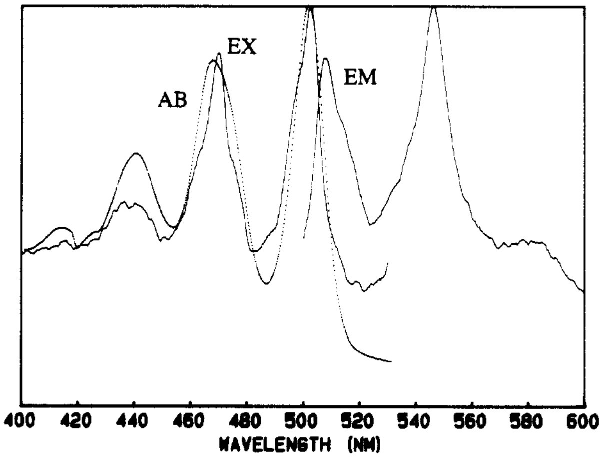

Figure 7. Absorption (AB, dotted line), fluorescence (EM), and fluorescence excitation (EX, solid line) spectra of *all-trans*-isozeaxanthin in 77 K EPA glass. The fluorescence spectrum was obtained by exciting at 470 nm. The fluorescence excitation spectrum was obtained by monitoring the emission at 547 nm.

indicating high sample purity. We also have measured the fluorescence quantum yield of isozeaxanthin. Comparison of its integrated fluorescence intensity with that of a fluorescein standard gives a $S_2 \rightarrow S_0$ fluorescence yield in a 77 K EPA glass of $(2.3 \pm 0.4) \times 10^{-4}$.

Discussion of Results

The spectra presented in the previous section clearly indicate a cross-over from the Stokes-shifted $2^1A_g \rightarrow 1^1A_g$ ($S_1 \rightarrow S_0$) fluorescences of short polyenes to the "anti-Kasha", $1^1B_u \rightarrow 1^1A_g$ ($S_2 \rightarrow S_0$) emissions of longer conjugated systems. For simple, unsubstituted polyenes, $S_2 \rightarrow S_0$ emissions are observed in molecules with more than six conjugated double bonds. For methyl-substituted polyenes and carotenoids, however, the conversion between S_1 and S_2 emission occurs for polyenes with more than seven or eight conjugated bonds with the ratio of the two emission intensities also being sensitive to substitution and other details of molecular structure.

The general pattern we have observed, i.e., the changeover to $S_2 \rightarrow S_0$ emissions in longer polyenes, can in part be attributed to the large S_2–S_1 energy differences in these systems. $S_2 \rightarrow S_0$ emission from a large molecule in solution (conditions for which Kasha's rule generally works quite well) first was observed for azulene by Beer and Longuet-Higgins.[49] This was attributed to the usually large spacing (14 000 cm^{-1}) between azulene's first and second excited singlets. Similar violations of Kasha's rule subsequently were observed for derivatives of azulene,[50,51] metalloporphyrins,[52,53] and several polyacenes.[54,55] All of these molecules are characterized by large S_2–S_1 energy differences, e.g., 6900 cm^{-1} in zinc tetrabenzoporphyrin[52] and 7000 cm^{-1} in aceanthrylene.[55]

The theoretical basis for the $S_2 \rightarrow S_0$ emissions in azulene and other cyclic aromatics was provided by Robinson and Frosch[56] and by Englman and Jortner[57] in their general treatments of radiationless transitions in large molecules. These molecules can be described in the "weak coupling limit" in which the displacement between the potential energy surfaces of different electronic states is relatively small. This leads to the well-known energy gap law, which predicts an exponential decrease of the internal conversion rate with increasing energy difference between electronic states. The energy gap law has been used to analyze radiationless decay processes in a wide variety of organic[53,57] and inorganic[58] molecules and appears to give a good account of the violations of Kasha's rule cited above.

Long polyenes are, at first glance, well-suited for exhibiting $S_2 \rightarrow S_0$ fluorescence. The increase in the S_2–S_1 energy gap (ΔE) with increasing conjugation thus should be accompanied by a decrease in the rate of $S_2 \rightarrow S_1$ internal conversion (k_{21}). For polyenes with seven or eight double bonds k_{21} apparently becomes small enough to allow the detection of S_2 fluorescence (recall that the $S_2 \rightarrow S_0$ fluorescence quantum yield $= k_{2r}/(k_{2r} + k_{21})$, where k_{2r} is the rate of radiative decay from S_2). S_2 emission also is favored by the relatively large k_{2r} provided by the symmetry-allowed $S_0 \rightarrow S_2$ ($1^1A_g \rightarrow 1^1B_u$) transition. It is interesting to note that S_2 emission in polyenes makes its appearance at energy differences ($\Delta E > 5000$ cm^{-1}) comparable to those required to observe S_2 emissions in aromatic systems.[52-55] This suggests that many of the parameters contained in the energy gap law (the changes in molecular geometry, the energies and number of C–H "acceptor models", vibronic coupling parameters, etc.)[57] are similar for polyene and aromatic systems.

While the energy gap law gives a qualitative explanation for the appearance of S_2 emission in longer polyenes, the crossover from the Stokes-shifted S_1 emissions of shorter polyenes to the dominant S_2 emissions of longer polyenes is quite abrupt given the rather gradual increase in the S_2–S_1 energy gap. This can be seen in the comparison of the fluorescence spectra of β-apo-12′-carotenol (Figure 4) and β-apo-8′-carotenol (Figure 5). The S_2–S_1 energy difference (ΔE) in the shorter carotenoid is similar to that of hexadecapentaene ($\sim$4700 cm^{-1}). On the basis of our work on shorter unsubstituted[14] and α,ω-substituted polyenes,[21,23] we estimate $\Delta E = 5500 \pm 200$ cm^{-1} for β-apo-8′-carotenol in a 77 K EPA glass. Substituting these ΔE's into the weak-coupling limit equation given by Englman and Jortner[57] (and assuming that the parameters used for azulene and several aromatic systems also are appropriate for the polyenes) gives an $S_2 \rightarrow S_1$ internal conversion rate that is reduced by no more than a factor of 2 in changing from β-apo-12′-carotenol to β-apo-8′-carotenol.

A more detailed analysis of the radiative and nonradiative processes connecting S_2, S_1, and S_0 leads to the following equation:

$$\Phi_1/\Phi_2 = (k_{21}/k_1)(k_{1r}/k_{2r}) \qquad (1)$$

where Φ_1 and Φ_2 are the fluorescence yields from S_1 and S_2

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(49) Beer, M.; Longuet-Higgins, H. C. *J. Chem. Phys.* **1955**, *23*, 1390.

(50) Maurata, S.; Iwanaga, C.; Toda, T.; Kokubun, H. *Chem. Phys. Lett.* **1972**, *13*, 101.

(51) Eber, G.; Schneider, S.; Dörr, F. *Chem. Phys. Lett.* **1977**, *52*, 59.

(52) Bajema, K.; Gouterman, M.; Rose, C. B. *J. Mol. Spectrosc.* **1971**, *39*, 421.

(53) Kurabayashi, Y.; Kikuchi, K.; Kokubun, H.; Kaizu, T.; Kobayashi, H. *J. Phys. Chem.* **1984**, *88*, 1308.

(54) Leupin, W.; Berens, S.; Magde, D.; Wirz, J. *J. Phys. Chem.* **1984**, *88*, 1376.

(55) Plummer, B.; Al-Saigh, Z.; Arfan, M. *Chem. Phys. Lett.* **1984**, *104*, 389.

(56) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962; **1963**, *38*, 1187.

(57) Englman, R.; Jortner, J. *J. Mol. Phys.* **1970**, *18*, 145.

(58) Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 5307–5312.

following $S_0 \rightarrow S_2$ absorption, k_{21} is the rate of conversion between S_2 and S_1, k_1 is the rate of depopulation of S_1 ($=k_{1r} + k_{1nr}$), k_{1r} is the radiative decay rate from S_1, and k_{2r} is the radiative decay rate from S_2. This model assumes that S_1 is populated only via S_2. Also, the extremely low fluorescence yields means that $k_1 \approx k_{1nr}$ for the longer polyenes considered in this paper.

Increasing the length of conjugation will change all of the rate constants indicated in eq 1. The lowering of the S_1–S_0 energy gap will increase k_{1nr}, again following the energy gap law. In addition the larger S_2–S_1 gap should reduce k_{1r} due to the decrease in mixing between S_1 (2^1A_g) and S_2 (1^1B_u). This mixing provides oscillator strength to the symmetry-forbidden $2^1A_g \rightarrow 1^1A_g$ transition and should vary inverse quadratically with the S_2–S_1 energy difference.[16] Finally, k_{2r} should show a mild increase with polyene length.[59] It is interesting to note that the four rate constants change "constructively", i.e., k_{21} and k_{1r} decrease and k_1 and k_{2r} increase with increasing polyene length. This accounts for the general trend from S_1 emission in short polyenes to S_2 emission in long polyenes. On the other hand, even with the most extreme (but still physically reasonable) choices for energy differences and parameters, we can account for no more than a factor of 5 change in Φ_1/Φ_2 in changing from β-apo-12′-carotenol ($\Phi_1/\Phi_2 > 10$) to β-apo-8′-carotenol ($\Phi_1/\Phi_2 < 10$). We must conclude either that nonradiative processes in polyenes are governed by parameters of different magnitudes (giving a steeper dependence on energy gap) than those that apply to aromatic systems or that there are additional effects (other than those considered in the energy gap model) that control electronic relaxation in polyenes.

Comparison of the fluorescence spectra of hexadecaheptaene (Figure 2) and tetradecaheptaene (Figure 3) shows that the extent of substitution also may change the rate constants of eq 1. The two heptaenes have comparable S_2–S_1 energy differences (4700 cm^{-1} for hexadecaheptaene and 5300 cm^{-1} for tetradecaheptaene) but large differences in the ratio of their $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$ emissions. We recently have observed a similar pattern in the gas-phase fluorescence of tetraenes.[60] The emission spectrum of the unsubstituted octatetraene (ΔE = 6600 cm^{-1}) exhibits $S_2 \rightarrow S_1$ fluorescence ($\Phi_1/\Phi_2 = 0.06$) whereas α,ω-dimethyl-substituted decatetraene (ΔE = 6300 cm^{-1}) has $\Phi_1/\Phi_2 = 0.70$. This suggests that the methyl groups play specific roles in influencing radiationless decay processes in polyenes and that similar effects may operate in the highly substituted carotenoids. It clearly would be useful to measure the various constants indicated in eq 1 to evaluate the relative influence of the energy gap and substituents on the kinetics of these systems. This would be particularly interesting for dual emitting systems such as tetradecaheptaene where the energy gap could be "tuned" by changing the solvent.

Regardless of the reasons for the large sensitivity of the fluorescence yield ratio to conjugated length, the trends we have observed have important implications for longer polyenes such as β-carotene. Our experiments indicate that 2^1A_g states in polyenes with more than eight or nine double bonds will not be easily detected in standard fluorescence or absorption experiments. Nevertheless, in β-carotene and related compounds the 2^1A_g state lives long enough to be characterized by transient absorption[35,36] and resonance Raman experiments.[40,41] These measurements indicate ~10^{-11}-s S_1 lifetimes, which are in good agreement with ground-state depletion studies on these molecules.[32] The 2 × 10^{-4} $S_2 \rightarrow S_0$ fluorescence yield for 77 K isozeaxanthin is comparable to that of β-carotene.[32] Our inability to detect S_1 emission in isozeaxanthin suggests a $S_1 \rightarrow S_0$ fluorescence yield of <10^{-5}. This combined with the 10^{-11}-s lifetime indicates an S_1 intrinsic lifetime of >10^{-6} s and a $S_0 \rightarrow S_1$ oscillator strength that is at least 10^3 times smaller than that of the $S_0 \rightarrow S_2$ absorption (10^{-9}-s intrinsic lifetime).

The lack of $S_1 \rightarrow S_0$ emission and the forbidden (or at least extremely weak) nature of the $S_0 \rightarrow S_1$ absorption means that the S_1 state in β-carotene, isozeaxanthin, and other long polyenes must be detected by other than conventional optical techniques. For example, the Raman excitation profile of β-carotene in the preresonance region revealed some weak spectral features ~18 000 cm^{-1}, which were identified as vibronic bands of 2^1A_g.[37,38] This leads to an ~3500-cm^{-1} S_2–S_1 energy gap and placement of 2^1A_g well above the ~15 000-cm^{-1} origin of the lowest energy absorption in chlorophyll, an assignment widely cited in discussions of energy transfer between carotenoids and chlorophylls in photosynthesis.[25,26,39] The Raman excitation results have received support from recent transient absorption measurements that detect a strong $S_1 \rightarrow S_n$ absorption in β-carotene at 555 nm.[34,36,41] Identification of S_n as the same state responsible for the moderately strong $S_0 \rightarrow S_n$ absorption at 275 nm leads to an S_1 energy of ~18 500 cm^{-1}.[34] The Raman excitation and transient absorption experiments thus seem to lead to the same conclusion, i.e., the S_2–S_1 energy difference in β-carotene is ≤3500 cm^{-1}.

Placement of the 2^1A_g state of β-carotene in the 17 000–18 500-cm^{-1} (540–590-nm) range,[34,37] however, is not consistent with energy trends observed in shorter polyenes. The $2^1A_g \rightarrow 1^1A_g$ transitions of shorter polyenes show a smooth progression toward longer wavelengths as a function of polyene length. For example, the α,ω-dimethyl polyenes have $S_1 \rightarrow S_0$ electronic origins at the following wavelengths: tetraene (361 nm), pentaene (412 nm), hexaene (468 nm), heptaene (514 nm), and octaene (560 nm).[42] Unlike the symmetry-allowed $1^1A_g \rightarrow 1^1B_u$ transitions, the $2^1A_g \rightarrow 1^1A_g$ origins are quite insensitive to solvent environment, temperature, or details of substitution. This is best illustrated by comparing (Figures 2 and 3) the $S_1 \rightarrow S_0$ emissions of tetradecaheptaene, hexadecaheptaene, and β-apo-12′-carotenol. The three heptaenes have almost identical $S_1 \rightarrow S_0$ emission origins. This is somewhat surprising in the case of the carotenol since the nonplanarity between the ring double bond and the polyene side chain generally is considered to lower the effective length of conjugation.[61] Nevertheless, β-apo-12′-carotenol behaves (at least in terms of the energy of the 2^1A_g state) as a normal heptaene. We recently have detected the $S_1 \rightarrow S_0$ emission in a carotenoid with eight conjugated double bonds.[62] The electronic origin occurs at 565 nm, in good agreement with the 560-nm origin observed for the simple, α,ω-methyl-substituted octadecaoctaene.[23] We therefore conclude that 2^1A_g energies observed for model polyenes provide good estimates of 2^1A_g energies in carotenoids of the same conjugated length. Extrapolation of data on the shorter model polyenes listed above indicates an $S_1 \leftrightarrow S_0$ electronic origin of ~700 nm for isozeaxanthin and β-carotene, putting the 2^1A_g state at a substantially lower energy than suggested by the Raman excitation and transient absorption measurements.

The lack of $S_1 \rightarrow S_0$ emission in longer carotenoids also is not consistent with a small (i.e., $\Delta E \leq$ 3500 cm^{-1}) S_2–S_1 energy difference. Examination of room-temperature n-hexane solutions of the α,ω-dimethyl series shows the following ΔE's: tetraene (4600 cm^{-1}), pentaene (5000 cm^{-1}), hexaene (5600 cm^{-1}), and heptaene (5900 cm^{-1}).[42] These energy differences are lower for carotenoids in low-temperature glasses due to stabilization of 1^1B_u relative to 2^1A_g. Thus ΔE for β-apo-12′-carotenol in 77 K EPA (Figure 3) falls from 5900 to 4700 cm^{-1}. In any event the energy gap, like the wavelength of the $S_0 \leftrightarrow S_1$ electronic origin, clearly increases with increasing conjugation and does not point to a substantially reduced ΔE in β-carotene. If the S_2–S_1 energy difference were smaller in β-carotene, then it would be difficult to explain the lack of $S_1 \rightarrow S_0$ fluorescence. There certainly are examples of anti-Kasha emission in systems with small energy gaps,[63] but these tend to be accompanied by substantial S_1

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[59] Murrell, J. N. *The Electronic Spectroscopy of Organic Molecules*; Wiley: New York, 1963; pp 63–77.

[60] Bouwman, W.; Jones, A. C.; Phillips, D.; Thibodeau, P.; Friel, C.; Christensen, R. L. *J. Phys. Chem.* **1990**, *94*, 7429.

[61] Vetter, W.; Englert, G.; Rigassi, N.; Schweiter, U. In *Carotenoids*; Isler, O., Ed.; Birkhäuser Verlag: Basel, 1971; pp 189–202.

[62] Cosgrove, S.; Smith, G. S.; Christensen, R. L., to be published.

[63] Bark, K. M.; Forcé, R. K. *J. Phys. Chem.* **1989**, *93*, 7985–7988.

[64] Arabei, S. M.; Solovev, K. N.; Kachura, T. F. *Opt. Spectrosc. (USSR)* **1988**, *65*, 213–215.

emission. *Quenching of S_1 emission requires a large ΔE.*

Consideration of polyene S_1 energies and S_2–S_1 energy differences thus requires a reevaluation of the Raman excitation and transient absorption experiments. Of particular significance is a more recent investigation of the Raman excitation profile of β-carotene. Watanabe et al. investigated the preresonance region and found no evidence for the 2^1A_g state.[31] These experiments indicate that this technique (like standard absorption measurements) is not capable of detecting the weak $1^1A_g \rightarrow 2^1A_g$ transition on top of the strong $1^1A_g \rightarrow 1^1B_u$ absorption tail. The transient absorption measurements appeared to support an even smaller 1^1B_u–2^1A_g energy difference (~2400 cm^{-1}).[34] However, such experiments are difficult to interpret. Connecting the $S_1 \rightarrow S_n$ and $S_0 \rightarrow S_m$ absorption spectra is fraught with the obvious difficulty in identifying a common final state ($n = m$), especially for a large molecule such as β-carotene where there are many electronic states in the neighborhood of S_n and S_m. Theory is of little or no help in assigning transitions for a polyene of this size. The problems in assigning excited state spectra are best illustrated by the transient absorption spectrum of diphenyloctatetraene. Initial assignments of nanosecond time-scale $S_1 \rightarrow S_n$ spectral features were based on an apparently reasonable theoretical model.[65] However, recent picosecond $S_1 \rightarrow S_n$ measurements[66] lead to a revision in the original assignments and cast doubt on the model's ability to distinguish between transitions of comparable energy and oscillator strength. We therefore suggest that the 555-nm transient absorption in *all-trans-β*-carotene does not terminate in the state responsible for the 275-nm absorption. The *results* of the Raman excitation experiments and the *interpretation* of the transient absorption experiments thus are very much open to question.

Replacing the previous picture of a relatively narrow S_2–S_1 energy gap in long carotenoids opens up some interesting possibilities for energy transfer between molecules such as β-carotene and various chlorophylls. If our extrapolation of the 2^1A_g state to 650–700 nm is correct, then β-carotene and chlorophyll would have S_1 states of comparable energies. On the other hand, the S_1 state of β-carotene and longer carotenoids (e.g., spirilloxanthin, with 13 conjugated double bonds) may indeed be lower than the lowest energy singlet in certain chlorophylls. One then might need to invoke higher energy electronic states (e.g., S_2) in the energy transfer mechanism. It also should be noted that our rather limited experimental and theoretical understanding of the electronic levels in long polyenes does not preclude the existence of additional ^1A_g states lying below 1^1B_u. This complication might explain the abrupt changeover to 1^1B_u emission in the longer polyenes and account for the transient absorption experiments discussed above while also providing additional mechanisms for energy transfer between carotenoids and chlorophylls.

Refinement of these speculations awaits experiments that more accurately locate low-lying ^1A_g states in long polyenes. Particularly promising in this regard would be the direct measurement of the S_1–S_2 energy gap in $S_1 \rightarrow S_2$ absorption experiments. Bachilo and Bondarev recently reported transient absorption in the near IR (1000–1650 nm) for excited diphenyloctatetraene and assigned this to a high-energy vibronic band of the $2^1A_g \rightarrow 1^1B_u$ transition.[67] The energy of this transition and its sensitivity to solvent changes appear to conform to S_1–S_2 energy differences obtained from the Stokes shift between the absorption and emission in room-temperature solutions. However, the low ΔE (~3000 cm^{-1}) for diphenyloctatetraene prevented the direct observation of the $S_1 \rightarrow S_2$ (0–0) and other vibronic bands. For polyenes of conjugated lengths comparable to β-carotene we estimate a considerably larger ΔE, ~5500–6500 cm^{-1}. The electronic origin of $2^1A_g \rightarrow 1^1B_u$ thus should occur at 1500–1800 nm with vibronic structure extending toward the visible. Extension of the previous $S_1 \rightarrow S_n$ measurements on β-carotene into the near IR thus should accurately locate the 2^1A_g state in this important molecule. Application of this technique to longer and shorter polyenes also would provide a much better indication of the energy of 2^1A_g in the long polyene limit.

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(65) Goldbeck, R. A.; Twarowski, A. J.; Russel, E. L.; Rice, J. K.; Birge, R. R.; Switkes, E.; Kliger, D. S. *J. Chem. Phys.* **1982**, *77*, 3319–3328.

(66) Rullière, C.; Declémy, A. *Chem. Phys. Lett.* **1987**, *135*, 213–218.

(67) Bachilo, S. M.; Bondarev, S. L. *Opt. Spectrosc.* (*USSR*) **1988**, *65*, 177–180.