

# Linear polyenes: models for the spectroscopy and photophysics of carotenoids

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## Abstract

We have developed procedures for synthesizing dimethyl polyenes using living polymerization techniques and have initiated investigations of the spectroscopic properties of these molecules. Purification using high-performance liquid chromatography (HPLC) of the polyene mixtures resulting from the syntheses promises to provide *all-trans* polyenes with a wide range in the number of conjugated double bonds. Low temperature optical measurements on these model systems, both in glasses and in *n*-alkane mixed crystals, yield absorption and fluorescence spectra with considerably higher vibronic resolution than the spectra currently available for carotenoids with comparable conjugation lengths. The dimethyl polyenes thus allow a more precise exploration of the electronic properties of long, linearly conjugated systems. These studies can be used to verify the existence of low-lying singlet states predicted by theory and recently invoked to explain low-resolution fluorescence, Raman excitation spectra, and the transient absorption spectroscopy of carotenoids. Steady state and time-resolved optical studies of the dimethyl series will be used to better understand the energies and dynamics of the low energy electronic states relevant to the photochemistry and photobiology of all linearly conjugated systems. © 2004 Elsevier Inc. All rights reserved.

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In the early 1970s, Kohler and co-workers [1–6] observed features in the electronic spectra of linear conjugated polyenes that were interpreted in terms of an excited singlet state lying at lower energy than the state responsible for the characteristic strong visible absorption. Theoretical analysis by Schulten and Karplus [7] explained the phenomenon in terms of configuration interaction between singly and multiply excited singlet states with the same symmetry. One consequence of these interactions is the occurrence of a low-lying state into which absorption from the ground state is forbidden by symmetry. This elegant interpretation, summarized by the energy level diagram presented in Fig. 1, explained several distinctive features of polyene spec-

troscopy. These included the large difference in the energies of the onsets of the absorption and fluorescence spectra, the contrasting dynamics of the excited states, and the disparate solvent effects observed for the absorption and fluorescence bands. Three states are depicted in the figure: The ground state,  $S_0$ , designated as  $1^1A_g^-$  according to the idealized  $C_{2h}$  point group;  $S_1$ , designated as  $2^1A_g^-$ ; and, the  $1^1B_u^+$  state. The  $1^1B_u^+$  state, frequently denoted as  $S_2$ , is associated with the HOMO  $\rightarrow$  LUMO transition in simple versions of molecular orbital theory. The  $1^1A_g^- \rightarrow 1^1B_u^+$  transition is strongly allowed and dominates the absorption spectra of polyenes and carotenoids. As will be discussed below, for longer polyenes and carotenoids, other excited states probably lie between the  $2^1A_g^-$  and  $1^1B_u^+$  states, rendering the  $S_0$ ,  $S_1$  and  $S_2$  designations problematic.

The seminal papers of Tavan and Schulten [8–10] offered a detailed theoretical description of the electronic states of polyenes (Fig. 2). Their model included

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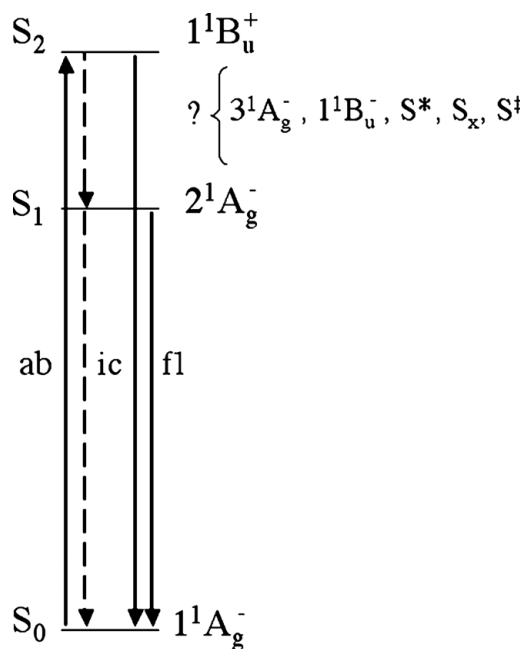


Fig. 1. Energy level diagram for low-lying singlet states of polyene hydrocarbons.

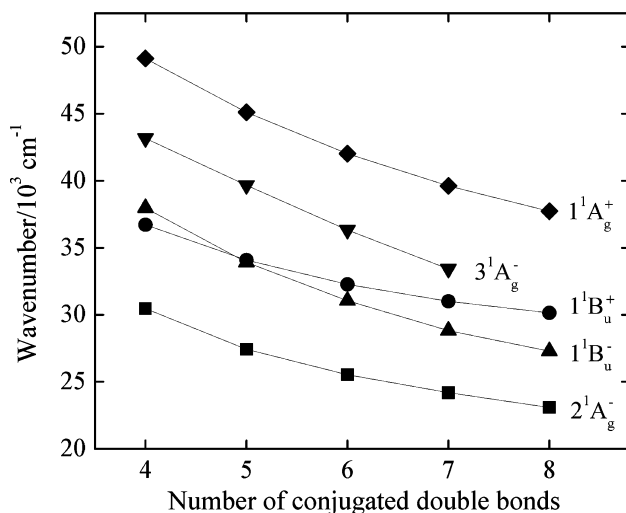


Fig. 2. Tavan and Schulten [8–10] predictions of singlet electronic state energies of unsubstituted polyenes as a function of number of conjugated double bonds ( $N$ ).

predictions for the energies of additional low-lying  $1^1A_g^-$  and  $1^1B_u^-$  excited states not easily detected spectroscopically, especially in longer polyenes, which have extremely low fluorescence yields ( $<10^{-4}$ ), even at low temperature. This model has persisted as the state-of-the-art analysis of polyene photophysics, and several investigators have embraced the predictions, extended the conclusions to more complex systems, and reported evidence for additional states in the vicinity of  $S_1$  and  $S_2$  (Fig. 1). For example, Koyama et al. [11–15] have hy-

pothesized that the spectroscopy, dynamics, and photochemistry of carotenoids are affected by the presence of a low-lying  $1^1B_u^-$  state. They have assigned features in the resonance Raman excitation profiles and in the fluorescence spectra of long carotenoids to low-lying  $1^1B_u^-$  states. Other work from this group has used ultrafast optical spectroscopy to detect spectral features attributed to excited state absorption, not only from  $1^1B_u^+$ , but also from  $1^1B_u^-$ , which may mediate nonradiative relaxation from the  $1^1B_u^+$  state [16,17]. Fujii et al. [18] also have assigned excited state absorption in the longer carotenoids ( $N=11,12,13$ ) to a low-lying  $3^1A_g^-$  state. Cerullo et al. [19] have presented ultrafast spectroscopic evidence for the presence of an intermediate singlet state in lycopene, denoted  $S_x$ , theorized to facilitate internal conversion between the  $S_2$  ( $1^1B_u^+$ ) and  $S_1$  ( $2^1A_g^-$ ) states. Van Grondelle and coworkers [20] have observed a wavelength dependence of the dynamics of spirilloxanthin in solution that was interpreted in terms of yet another singlet state lying between  $S_1$  and  $S_2$ . This state, denoted  $S^*$ , is thought to be an intermediate in the depopulation of  $S_2$  and, additionally in various light-harvesting complexes [21–23], a pathway for the formation of carotenoid triplet states via singlet–triplet homofission. Sophisticated pump–repump–probe and pump–dump–probe fast transient optical absorption spectroscopic techniques have been applied to  $\beta$ -carotene in hexane solution by Larsen et al. [24]. The data have been interpreted in terms of another carotenoid excited state formed directly from  $S_2$ . This state, denoted  $S^\ddagger$ , has a blue-shifted excited state absorption and a longer lifetime than  $S_1$ . Independent assessments of all of these assignments are both necessary and forthcoming.

Recent advances in synthetic procedures coupled with improved purification (HPLC)<sup>1</sup> and analytical techniques (LC-MS and MALDI-MS) promise to provide a wide range of simple, *all-trans* polyenes. New sophisticated spectroscopic technologies offer the opportunity for experimentalists and theorists to carefully re-examine the validity and completeness of the Tavan and Schulten models. Major unanswered questions include: What are the energies and identities of the low-lying excited states of long polyenes? How are the electronic and vibronic states spectroscopically and kinetically coupled to control photochemical behavior? What effect do methyl groups, cyclic end groups, and other substituents have on the spectroscopic and dynamic properties of polyenes? What are the spectroscopic and photochemical effects of solvents and biological matrices? How are the results on simple polyenes relevant to

<sup>1</sup> Abbreviations used: HPLC, high-performance liquid chromatography; MALDI, matrix-assisted laser desorption ionization; LC-MS, liquid chromatography-mass spectrometry;  $N$ , number of conjugated  $\pi$  bonds in polyene.

the photophysics and photochemistry of carotenoids in biological systems?

In this mini-review, the synthesis, purification, and spectroscopic analysis of dimethyl polyenes are described. Preliminary experiments illustrate the promise of this approach to test the validity of the Tavan and Schulten predictions and to confirm the recent experimental sightings of additional low-lying electronic states in carotenoid spectroscopy. The dimethyl polyene series combines the advantages of relatively straightforward synthetic access to a broad range of polyene conjugation lengths, the potential for considerably higher resolution spectroscopy than is possible for corresponding carotenoids, and the important theoretical advantage of their unsubstituted, symmetric structures. It is important to note that the Tavan and Schulten results apply to simple, symmetric polyenes and do not consider the effects of methyl substitutions, cyclic end groups, nonplanarities, and other distortions from the idealized  $C_{2h}$  geometry. Furthermore, solvent effects are not accounted for in the calculations. For example, preferential stabilization of the  $1^1B_u^+$  state ( $\sim 3000\text{ cm}^{-1}$  in standard organic solvents) will significantly modify the data presented in Fig. 2 and, in particular, insure that  $E(1^1B_u^+) < E(1^1B_u^-)$  for shorter polyenes. These important details not only will impact the energies of the excited states, but also will affect the oscillator strengths and vibronic interactions between the electronic states, which must be considered when extending the theoretical models to carotenoids employed in photobiology. The electron correlation problem described by Tavan

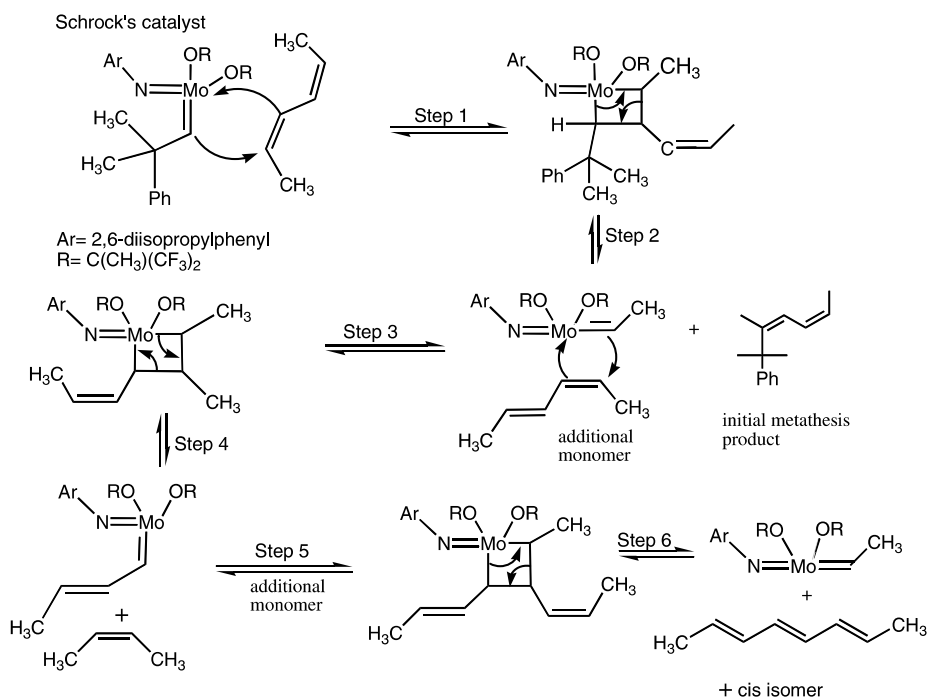
and Schulten is sufficiently complicated and computationally unwieldy, that it is appropriate to revisit the validity of the early calculations on the simple polyenes, which in fact were the objects of the theory.

## Results and discussion

### Synthesis of dimethyl polyenes

Simple polyenes have been synthesized through reactions between polyenals and vinyl Grignard reagents followed by dehydration [25,26] or by Wittig-type reactions between polyenals and vinyl phosphonium ylides [27,28]. Species with up to 8 conjugated double bonds capped by a variety of functional groups have been achieved through the use of palladium catalyzed coupling of silyl-substituted polyenes [29]. Mixtures of methyl [30] and *t*-butyl substituted [31] polyenes have been synthesized through the molybdenum-catalyzed metathesis of acyclic dienes via a living polymerization sequence. This method produces mixtures of different conjugation lengths governed by relative rates of insertion of various polyenes in the polymerization reaction.

In the initial communication reporting the synthesis of  $\alpha,\omega$ -dimethyl capped polyenes, Tao and Wagener [30] used a Mo-carbene species to polymerize 2,4-hexadiene providing polyenes with up to 20 conjugated bonds as identified by mass spectral and UV-visible analysis. The reaction mechanism for the overall transformation is given in Scheme 1. The reaction mixture was exposed to



Scheme 1.

high vacuum periodically during the metathesis to remove the butene formed as a by-product of the polymerization to help drive the equilibrium toward higher conjugation lengths.

This synthetic method has several advantages over the stepwise syntheses leading to polyenes. It provides a variety of different size conjugated polyenes in a single reaction, which under appropriate conditions can be isolated as pure materials. Also, since the reaction is a living polymerization, the amount of material isolated, and the conjugation lengths, depend on the amount and timing of added additional monomer. The catalyst and the monomer both are commercially available, obviating the need to synthesize complicated intermediates.

There also are several drawbacks to this synthesis. There is little or no stereoselectivity in the metathesis step leading to initial materials that not only have multiple conjugation lengths but also have nearly random *cis/trans*  $\pi$  bond geometries. Furthermore, the conjugation length depends not only on the relative amount of the butene produced (Step 4, see Scheme 1), but also on the solubility of the intermediate polyenes. For instance, the conditions described by Tao and Wagener produce isolable quantities of polyenes only up to nine conjugated  $\pi$  bonds, along with a substantial amount of insoluble red-colored material. The Mo-carbene catalyst is also air and moisture sensitive, requiring the reaction to be done using inert atmosphere techniques with rigorously dried and degassed starting materials.

We have modified the reaction taking advantage of recent advances in metathesis catalyst design to provide similar products under experimentally more accommodating conditions. Polymerization of 2,4-hexadiene with Grubbs' second-generation carbene catalyst {[1, 3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium} [32] not only provides longer isolable conjugation lengths, but also has the added benefit of being less sensitive to air and moisture. Under the modified conditions, polyenes with up to 11 conjugated bonds were observed using UV-visible spectroscopy, and polyenes containing up to 15  $\pi$  bonds were observed by MALDI-FT-MS. We note however that Grubbs' catalyst produces more of the *cis* isomers for a given conjugation length, which helps with the solubility, but makes separation more difficult.

#### Purification of dimethyl polyenes

Current synthetic and purification capacities are summarized in Figs. 3 and 4. Fig. 3 shows the HPLC separation of a typical sample prepared by the living polymerization of hexadiene using the Schrock catalyst. The array of chromatographic peaks detected at wavelengths sensitive to polyenes with specific conjugation lengths illustrates the broad distributions of conjugation

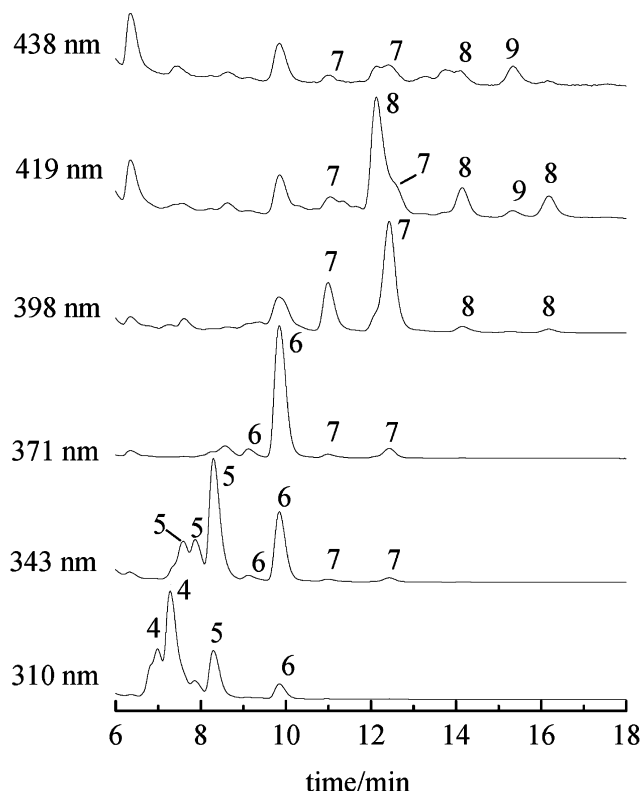


Fig. 3. HPLC of a typical dimethyl polyene reaction mixture. Reverse-phase separations were achieved using a  $3.9 \times 300$  mm C18 column (60 Å, 4  $\mu$ m spherical amorphous silica). The run used an isocratic mobile phase (90:5:5% v/v/v  $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2:\text{H}_2\text{O}$ ) flowing at 0.5 mL/min. Chromatograms are presented at wavelengths that optimize detection of polyenes with a given conjugation length ( $N=4-9$ ) [31]. Integers indicate conjugation length ( $N$ ) of primary component peaks.

lengths and isomers in these samples. These mixtures provide significant challenges in isolating *all-trans* isomers for detailed spectroscopic investigations. The distinctive shift in the strongly allowed  $1^1A_g^- \rightarrow 1^1B_u^+$  absorption as a function of conjugation length provides the means for monitoring the course of the reactions as well as identifying products. In addition, the intensity of the “*cis*-bands” ( $1^1A_g^- \rightarrow 1^1A_g^+$ ) and the relative retention times for polyenes with a given  $N$  prove useful in the preliminary identification of the *all-trans* isomers.

The series of spectra of dimethyl polyenes presented in Fig. 4 illustrate the potential for isolating dimethyl polyenes with a given conjugation length. The synthetic conditions (ratio of catalyst to monomer, reaction times, temperature, etc.) control the distribution of conjugation lengths in a given reaction. Whereas it proves relatively simple to isolate and identify the *all-trans* isomers of the shorter polyenes, the propagation of *cis* bonds in these polymerizations provides a wider range of isomers with increasing  $N$ . Previous work by Knoll and Schrock [31] indicates that for shorter polyenes ( $N=5-9$ ), standard photochemical isomerization techniques (with or without iodine catalysis) can tilt the distribution of

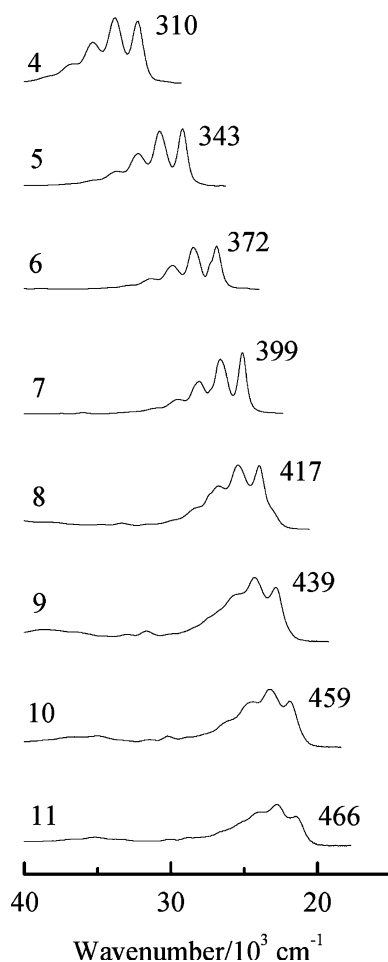


Fig. 4. Absorption spectra ( $1^1A_g^- \rightarrow 1^1B_u^+$ ) of peaks from HPLC (in 90:5:5% v/v/v  $CH_3CN:CH_2Cl_2:H_2O$ ). Integers indicate conjugation length ( $N$ ) of primary component. Wavelengths (in nm) indicate position of (0–0) bands.

isomers toward the thermodynamically favored *all-trans* isomers. For longer polyenes, thermal isomerizations were more successful. In all cases, the significantly lower solubilities of the *trans* isomers can be exploited to crystallize the *all-trans* components out of concentrated solutions [31]. The longer *all-trans* isomers should have sufficient residual solubility ( $>10^{-6}$  M) for fluorescence, fluorescence excitation, resonance Raman, and other optical experiments. It also should be pointed out that thermal, photochemical, and catalytic oxidative isomerizations have been used for decades to change isomer distributions in carotenoids [33].

### Optical spectroscopy of dimethyl polyenes

The low temperature absorption and fluorescence spectra of *all-trans*-2,4,6,8,10,12-tetradecaheptaene are presented in Fig. 5. These spectra indicate the potential for isolating and studying *all-trans* polyenes from the HPLC-purified products of the living polymerizations.

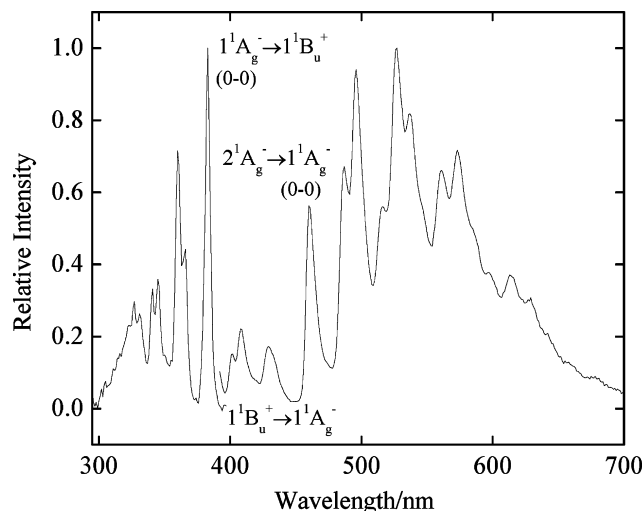


Fig. 5. Absorption and fluorescence spectra of *all-trans*-2,4,6,8,10,12-tetradecaheptaene in 77 K EPA (5/5/2, ether/isopentane/ethanol, v/v/v). Fluorescence spectrum was obtained by exciting the ( $1^1A_g^- \rightarrow 1^1B_u^+$ ) (0–0) band at 382 nm.

Furthermore, the relatively well-resolved absorption and emission spectra illustrate a critical advantage of the simple polyenes. The vibronic details, invariably broadened in the spectra of more highly substituted carotenoids, facilitate the unambiguous identification of the electronic origins and other vibronic bands. We can precisely determine the (0–0) bands of the  $1^1A_g^- \rightarrow 1^1B_u^+$  and  $2^1A_g^- \rightarrow 1^1A_g^-$  transitions at 382 nm ( $26,180\text{ cm}^{-1}$ ) and 460 nm ( $21,740\text{ cm}^{-1}$ ), giving a  $1^1B_u^+ - 2^1A_g^-$  energy difference of  $4440\text{ cm}^{-1}$  at 77 K in EPA (5/5/2, ether/isopentane/ethanol, v/v/v) solvent. This compares with the  $6750\text{ cm}^{-1}$  band gap predicted by Tavan and Schulten [9]. However, these calculations do not account for the preferential stabilization of the  $1^1B_u^+$  state by the solvent environment. Analysis of solvent effects on the  $1^1A_g^- \rightarrow 1^1B_u^+$  and  $2^1A_g^- \rightarrow 1^1A_g^-$  transitions energies [34] leads to an experimental gas phase gap of  $\sim 7500\text{ cm}^{-1}$ , in much better agreement with theory. This reminds us that the theoretical calculations presented in Fig. 2 apply to unsubstituted polyenes in the gas phase. Solvent effects preferentially stabilize the  $1^1B_u^+$  state, due to the large  $1^1A_g^- \rightarrow 1^1B_u^+$  transition dipole [34]. This results in a red shift of  $\sim 3000\text{ cm}^{-1}$  for the  $1^1A_g^- \rightarrow 1^1B_u^+$  transition when gaseous tetradecaheptaene is solvated in 77 K EPA. Additional stabilization due to methyl groups results in even lower  $1^1B_u^+$  energies in comparable carotenoids in solution. The crossing of the  $1^1B_u^-$  and  $1^1B_u^+$  states thus will occur at significantly longer conjugation lengths than indicated in Fig. 2. For example, the calculations predict that  $1^1B_u^+$  lies  $\sim 2000\text{ cm}^{-1}$  above  $1^1B_u^-$  for  $N=8$ . This ordering most likely is reversed in solution, even for simple polyenes.

The vibronic signatures of these spectra are worth noting. The emission spectrum is dominated by combinations of totally symmetric C–C and C=C stretches

with frequencies of  $\sim 1200$  and  $\sim 1600\text{ cm}^{-1}$ . In the less-resolved emission spectra of carotenoids these vibronic features often coalesce into progression of what appears to be an intermediate frequency of  $\sim 1400\text{ cm}^{-1}$ . Further analysis of the tetradecaheptaene spectra (Christensen, Broene, and Frank, unpublished) facilitates the assignment of the weak vibronic features from 400 to 440 nm as vibronic progressions of the  $1^1\text{B}_u^+ \rightarrow 1^1\text{A}_g^-$  emission, and we thus are able to confirm dual emission in this relatively short polyene.

Another crucial advantage of this series of dimethyl polyenes is that their simple geometries allow their incorporation into low temperature *n*-alkane mixed crystals, giving optical spectra that are even more highly resolved [28,35–39]. Under these conditions, the vibronic lines are sufficiently narrow to allow the detection of the weak,  $1^1\text{A}_g^- \rightarrow 2^1\text{A}_g^-$  absorption (and other transitions) using fluorescence excitation techniques. This is illustrated in Fig. 6 for *all-trans*-2,4,6,8,10,12,14-hexadecaheptaene in a 10 K matrix of *n*-pentadecane. Simpson et al. [28] have presented the full analysis of this spectrum as well as that of the  $2^1\text{A}_g^- \rightarrow 1^1\text{A}_g^-$  emission. Suffice it to say that the  $\sim 4700\text{ cm}^{-1}$  gap between the  $2^1\text{A}_g^-$  and  $1^1\text{B}_u^+$  states affords a relatively wide and clear window to look for evidence of additional low-lying electronic states (e.g.,  $1^1\text{B}_u^-$ ) in this molecule. The detailed analysis of this spectrum offers no evidence for any of the additional states indicated in Fig. 1. However, the systematic extension of high-resolution techniques to both shorter and longer dimethyl polyenes should provide important links with the wealth of low-resolution spectroscopic data now available for carotenoids of photobiological relevance. Further work on “high-res-

olution” model systems also should lead to refined theoretical descriptions of polyene and carotenoid excited states for both gaseous and solvated molecules.

## Summary/conclusions

New options for polyene synthesis, combined with improved HPLC separation techniques and high-resolution spectroscopy will allow a more systematic investigation of the influence of additional low-lying singlet electronic states on the photophysics and photochemistry of simple polyenes. The extension of this approach to longer dimethyl polyenes and ultimately to carotenoids is well within reach and will improve our theoretical understanding of the excited states of these systems.

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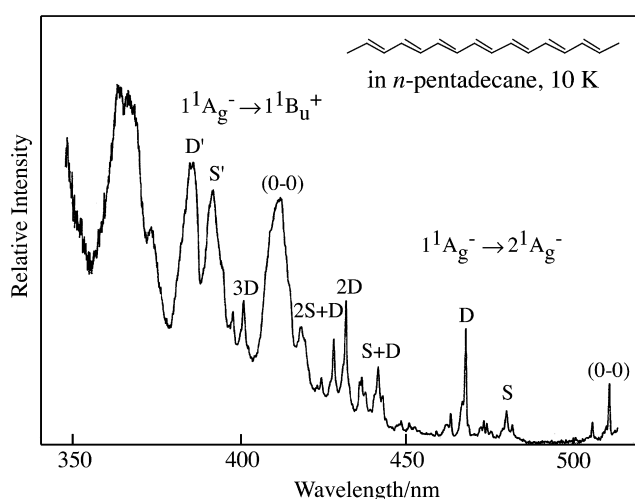


Fig. 6. Fluorescence excitation spectra ( $1^1\text{A}_g^- \rightarrow 2^1\text{A}_g^-$  and  $1^1\text{A}_g^- \rightarrow 1^1\text{B}_u^+$ ) of *all-trans*-2,4,6,8,10,12,14-hexadecaheptaene in 10 K *n*-pentadecane. Fluorescence was detected at 560 nm. The excitation spectrum is not corrected for the wavelength dependence of the excitation system. (Figure adapted by the author, RLC, from his own Fig. 3 of [28].)

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