Electronic Energy Levels in a Homologous Series of Unsubstituted Linear Polyenes

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Abstract: Absorption, emission, and excitation spectra of 1,3,5,7-octatetraene, 1,3,5,7,9-decapentaene, and 1,3,5,7,9,11-dodecahexaene have been obtained in room temperature solutions and 77 K glasses. All spectra exhibit the characteristic gap between the origin of the strongly allowed absorption ($^1A_g \rightarrow {}^1B_u$) and the origin of fluorescence ($^1A_g{}^* \rightarrow {}^1A_g$). Comparison with results previously obtained for methyl-substituted polyenes shows that the ^1B_u-$^1A_g{}^*$ energy gap is a sensitive function of the degree of substitution. Solvent-effect studies have been used to extrapolate transition energies of the unsubstituted polyenes to gas-phase conditions. For the tetraene, pentaene, and hexaene the ^1B_u-$^1A_g{}^*$ energy differences are 6380, 7050, and 7420 cm^{-1}, respectively. These results are discussed in terms of current theoretical descriptions of polyene electronic states.

I. Introduction

Linearly conjugated π electron systems have been subject to renewed experimental and theoretical interest in recent years. This interest in large part has been stimulated by the important roles played by polyene electronic states in several important photobiological processes. For long polyenes (those with more than three double bonds) in condensed phases there now is a great deal of evidence which indicates the existence of low-lying, $^1A_g{}^*$ excited states below the ^1B_u states responsible for the strong absorptions in these molecules. The positions of the $^1A_g{}^*$ states are not accounted for in simple molecular orbital treatments. It thus is important to obtain more detailed experimental data which can guide the development of more appropriate theoretical models.

Experiments pointing to the existence in long polyenes of the low-lying $^1A_g{}^*$ state can be summarized as follows: (1) observations of large differences between the origins of the strongly allowed absorption ($^1A_g \rightarrow {}^1B_u$) and the origins of fluorescence ($^1A_g{}^* \rightarrow {}^1A_g$);[1-3] (2) different solvent effects for absorption and fluorescence spectra;[1] (3) fluorescent lifetimes which would be anomalously long if the emissions were from the ^1B_u state;[1] (4) direct observation of the $^1A_g \rightarrow {}^1A_g{}^*$ transition in absorption;[2,4,5] (5) detailed excitation, absorption, and emission spectra and photoselection experiments which rule out that the $^1A_g{}^* \rightarrow {}^1A_g$ emission are due to impurities;[4,5] (6) high-resolution optical spectra which indicate that the weak, forbidden transition is vibronically rather than electronically allowed;[4,6] (7) high-resolution one- and two-photon spectra of octatetraene in octane, a crystal lattice which rigorously preserves the tetraene's inversion center. These experiments provide unambiguous proof of the symmetry-forbidden nature of the fluorescent transition.[7]

It must be emphasized that the above criteria do not apply to the shorter polyenes. For example, in substituted trienes the $^1A_g{}^*$ and ^1B_u states are apparently of comparable energy with a relative ordering depending on steric effects.[8] It also should be noted that previous experiments on octatetraene in the gas phase were unable to confirm the $^1A_g{}^*$ as the lowest excited singlet state even though this is clearly the case in solutions.[9]

The present study focuses on the longer polyenes in condensed phases. For these systems the criteria listed above clearly point to a $^1A_g{}^*$ assignment for the lowest excited singlet. We now have extended this conclusion to a more quantitative one, i.e., how do the energies of polyene excited states vary with the number of conjugated double bonds? To answer this question we have studied the simple, unsubstituted tetraene, pentaene, and hexaene. These molecules offer several theoretical and experimental advantages.

The simple polyenes possess the ideal C_{2h} symmetry which is used to describe the electronic states of the entire polyene family, e.g., retinals. Furthermore, as we will show below, the energy levels of substituted polyenes are nonuniformly shifted from the energy levels of the simple systems. Present calculations[10-12] do not consider these complications. The symmetric, unsubstituted compounds thus represent the obvious source for "zero-order" data against which accurate theoretical descriptions might be developed. Previous experimental work on the substituted polyenes was dictated mainly by their availability and the thought that the unsubstituted systems would be considerably less stable. The present work shows this last consideration to be unfounded.

Another important feature of these simple systems is that they all possess appreciable fluorescent quantum yields. This is of critical importance in locating the $^1A_g{}^*$ state since it is only very weakly seen in absorption and is easily masked by the strongly allowed transition to the ^1B_u excited state. The use of fluorescence excitation spectra to confirm that the fluorescences observed are a direct consequence of excitation into the ^1B_u state is crucial to our assignments. Another advantage of the unsubstituted polyenes is that their optical spectra show vibronic structure even in room temperature solutions. This permits the accurate location of electronic origins in a range of solvents and the extrapolation of transition energies to gas-phase conditions.

The low-lying $^1A_g{}^*$ states in the long polyenes can be accounted for by adding doubly excited configurations to the standard SCF theory.[10-12] Such calculations, however, do not account for even general, qualitative trends in the excitation energies of the polyene series. This shortcoming is rooted in the "independent particle" approach of the theory and its general inability to deal with correlation effects in these π-electron systems.[13] Considerable improvement was obtained in the recent triple and quadruple CI calculations of Tavan and Schulten.[12] However, the computational demands of such extended CI treatments become increasingly prohibitive, especially for long polyenes where correlation effects are the most pronounced. In view of these problems, an effort has been made to isolate and treat only that part of electron correlation which changes with electronic state.[13] Such an approach combined with extended CI techniques should provide more quantitative results. The success of these calculations can be measured against the data presented in this paper. Such a tested theory then might be used as a reliable predictor of molecular properties which are not as experimentally accessible as the measurements discussed here. Examples include the energy levels of nonfluorescent polyenes (e.g., hexatriene and β-carotene) as well as other excited-state parameters (electron

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densities and bond orders) which bear on the important photochemistries of the polyene family.

II. Experimental Section

Syntheses of 1,3,5,7-Octatetraene and 1,3,5,7,9,11-Dodecahexaene. The reaction strategy followed was based on the work of Evans[14] and Kuhn, Grundmann, and Hoffer.[15-17] Self-condensation of crotonaldehyde (2-buten-1-al) yields 2,4,6-octatrienal and small quantities of 2,4,6,8,10-dodecapentaenal. These aldehydes are reduced to their corresponding primary alcohols which are then catalytically dehydrated to give the desired polyene hydrocarbons. The advantage of our synthetic route is not that it gives high yields (see below) but that it provides access to both of the hydrocarbons as well as the corresponding alcohols and aldehydes. The electronic states of these latter compounds are also being studied and will be reported elsewhere.

Dry (stored over molecular sieves) crotonaldehyde (200 g) (Eastman, practical grade) was distilled at room temperature and 5 Torr pressure and then deaerated with nitrogen. A mixture of 2 mL of piperidine (Fisher Scientific) and 2 mL of glacial acetic acid was added dropwise with stirring. After refluxing over a steam bath for 15 min, the reaction mixture was cooled with an ice bath, diluted with 800 mL of ether, and washed several times with water. After being dried with sodium sulfate, the ether and unreacted crotonaldehyde (~100 mL) were removed by rotary evaporation. To the remaining dark brown oil was added about one-third its volume of an 80/20 methanol-water mixture. This solution, upon standing at −15 °C for 12 h, yielded about 2 g of crude dodecapentaenal. The dodecapentaenal was recrystallized from ethanol to yield an orange-yellow powder with a melting point of 166-167 °C. This is in good agreement with that reported in the literature.[18]

The filtrate was distilled under vacuum and gave four distinct fractions. The first fraction came off at room temperature and at a pressure of 10 Torr and contained methanol, water, and unreacted crotonaldehyde. The second fraction came off at 65 °C and 10 Torr and contained small amounts of crotonaldehyde and a cyclic side product which has been identified[18-20] as 6-methyl-1,3-cyclohexadiene-1-carboxaldehyde. Fraction 3 was the octatrienal. It came over at 0.2 Torr and 65-72 °C and solidified in the 0 °C receiving flask. The initial yield of octatrienal was about 25 g (25%). Recrystallization of the octatrienal from pentane gave a faintly yellow powder which melted at 56-57 °C, in agreement with that previously reported.[20] The fourth fraction from the vacuum distillation contained small amounts of dodecapentaenal as well as even longer condensation products. Distillation of this fraction required temperatures greater than 80 °C at 0.2 Torr. It proved impossible to isolate pure dodecapentaenal in this manner. The high temperature seems to degrade this final fraction and it is much more convenient to isolate the pentaenal by recrystallization from the original reaction mixture as described above.

Both the octatrienal and the dodecapentaenal are easily reduced to their corresponding alcohols. Following Hubbard[21] a twofold molar excess of $NaBH_4$ was added to 1 g of octatrienal dissolved in 100 mL of methanol. The reaction mixture was stirred for 15 min and the methanol then removed by rotary evaporation. The remaining solid was taken up in ether, washed with water, and dried, and the ether was removed. Two recrystallizations of the octatrienol from petroleum ether (bp 30-60 °C) gave white needles which melted at 101-102 °C, in agreement with previous workers.[22] Dodecapentaenal is much less soluble in methanol and its reduction was carried out under more dilute conditions (100 mg of aldehyde in 500 mL of methanol). Otherwise the procedure was exactly that described above. Two recrystallizations from ethanol gave yellow crystals with a melting point of 203-205 °C in agreement with Fischer et al.[19] Both reductions of the aldehydes to their alcohols gave yields greater than 90%.

Octatetraene and dodecahexaene were obtained by passing their corresponding alcohols through a 10 cm × 10 mm column of 8-14 mesh activated alumina. The temperature of the column was maintained at 270 °C and the alcohol was carried through the column by a stream of nitrogen sufficient to maintain the system at 50 Torr against a standard rotary vacuum pump. Reaction products were collected in a liquid nitrogen trap.

For octatetraene the contents of the trap were dissolved in isopentane and cooled to −78 °C. The white crystals formed were filtered and washed with cold isopentaene. Yields of the dehydration step were about 5%. The octatetraene crystals were stored either at dry ice temperature in evacuated tubes or as dilute hexane solutions. The ultraviolet spectrum of a hexane solution of octatetraene was in excellent agreement with those reported by Lippincott[23] and by Woods and Schwartzman.[24]

Dehydration of the dodecapentaenol gave in the liquid nitrogen trap a mixture of several products. This mixture was purified by chromatography on Woelm neutral alumina, activity grade II. Elution with hexane first gave a fraction containing polyenes which the UV spectrum indicated had fewer than six double bonds. The second fraction gave a spectrum which we have tentatively identified as due to a *cis*-dodecahexaene. The final fraction gave a spectrum which compares well with that reported by Sondheimer et al.[25] for *all-trans*-dodecahexaene. The net yield of the hexaene (about 1%) was considerably less than that of the tetraene. The longer, less volatile pentaenol and the hexaene product apparently spend more time in contact with the hot alumina and are thus subject to significant degradation. Milder methods of dehydration, especially for polyenes longer than the hexaene, are being pursued.

It also should be mentioned that, if one were interested solely in obtaining octatetraene, better yields (about 10%) were obtained via the catalytic dehydration of the secondary alcohol, 2,4,7-octatrien-6-ol. This compound was synthesized by reacting 2,4-hexadienal (Aldrich) with vinylmagnesium bromide by procedures strictly analogous to those outlined below for the synthesis of the decapentaene.

Synthesis of 1,3,5,7,9-Decapentaene. The pentaene was synthesized by an extension of the procedure given by Woods and Schwartzman[24] for octatetraene. Starting materials were vinylmagnesium bromide and 2,4,6-octatrienal, which was obtained from crotonaldehyde as described above. Reaction of these materials gave 2,4,6,10-decatetraen-8-ol, which was then catalytically dehydrated to give the desired product.

Vinylmagnesium bromide was formed by the slow addition of vinyl bromide (Aldrich) to a flask containing a molar excess magnesium powder covered by tetrahydrofuran. The reaction flask was maintained at 0 °C. Because of the volatility of vinyl bromide it was necessary to carry out this reaction under two cooled water condensers packed with glass beads. All glassware was carefully dried and air was excluded by maintaining a positive pressure of nitrogen over the reaction vessel. After the vinyl bromide was added, a few drops of methyl iodide were introduced to initiate the reaction. The reaction then proceeded at 0 °C until refluxing caused by the heat of reaction subsided. The Grignard was obtained in about 90% yield and no effort was made to separate it from the excess magnesium powder.

About 20 g of octatrienal was slowly added with stirring at 0 °C to an equimolar amount of the vinyl bromide mixture from above. The reaction was finished within 10 min. Excess Grignard reagent was decomposed by washing the THF solution with saturated aqueous ammonium chloride followed by washings with aqueous sodium bicarbonate. Addition of 25-30 mL of diethyl ether helped clear the turbidity and hastened the separation of the aqueous and organic layers. The ether fraction was subjected to rotary evaporation giving 2,4,6,10-decatetraen-8-ol in about 80% yield. This structure was confirmed by UV and NMR.

Dehydration of this secondary alcohol was carried out as described above for 2,4,6-octatrienol and 2,4,6,8,10-dodecapentaenol; 15 g of alcohol gave about 1 g of material in the liquid nitrogen trap. Crystallization of these solids from hexane at −20 °C gave pale yellow crystals of decapentaene. The decapentaene was recrystallized from cold isopentaene and then redissolved in isopentane for storage. The ultraviolet spectrum of our product in hexane compared very well with that given by Sondheimer[25] for the all-trans isomer.

Spectra. Absorption spectra were obtained on a Perkin-Elmer Model 356 absorption spectrometer which had been modified for 77 K operation. Typical operating conditions provided 0.1-nm resolution, which was well within the narrowest line widths of our spectra.

Corrected excitation and emission spectra were obtained on a Perkin-Elmer Model MPF-44A fluorescence spectrophotometer kindly made available to us by Professor Rex Pratt. This instrument provides spectra which are corrected for the spectral responses of the optics and photomultiplier.

Room temperature emission spectra were measured with a ¼-m Jarrell-Ash monochromator. The excitation source was a 100-W mercury lamp which was filtered by 313- or 365-nm interference filters (Ditric Optics) and additional glass and solution filters suitable for these wavelengths. The emitted light was picked up at right angles to the exciting light and filtered before being focused on the entrance slit of the monochromator. Typical slit widths of 150 μ provided

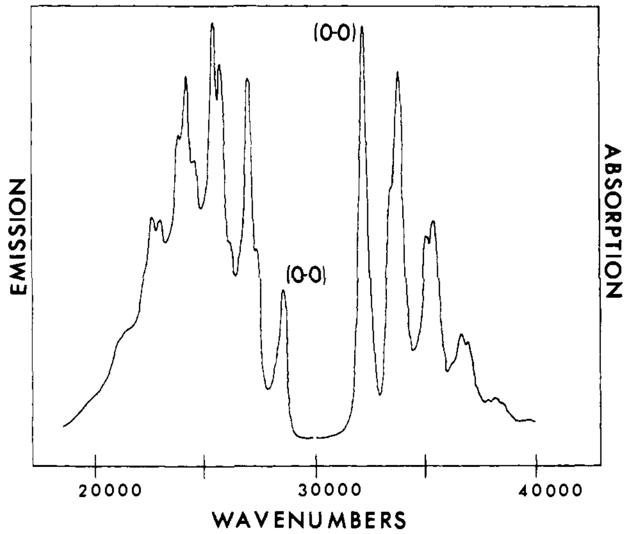

Figure 1. Corrected fluorescence and fluorescence excitation spectra of 1,3,5,7-octatetraene in 77 K, 3-methylpentane. Fluorescence: excited at 310 nm (20-nm bandwidth), detected with 1-nm bandwidth. Fluorescence excitation: monitored at 390 nm (20-nm bandwidth), excitation scanned with 1-nm bandwidth.

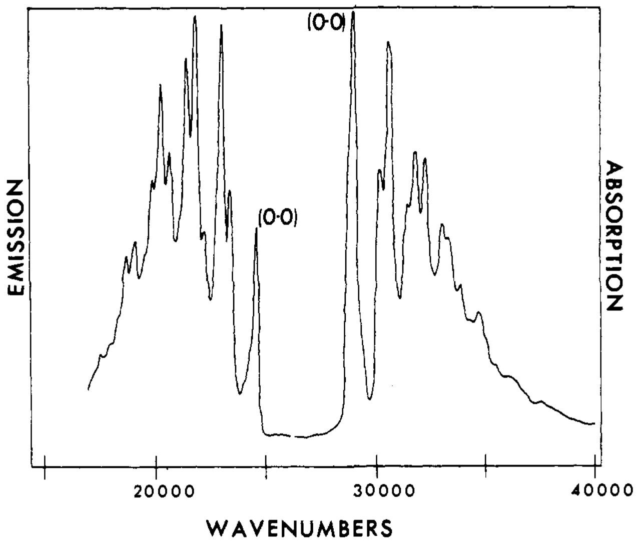

Figure 2. Corrected fluorescence and fluorescence excitation spectra of 1,3,5,7,9-decapentaene in 77 K, 3-methylpentane. Fluorescence: excited at 345 nm (20-nm bandwidth), detected with 1-nm bandwidth. Fluorescence excitation: monitored at 490 nm (20-nm bandwidth), excitation scanned with 1-nm bandwidth.

0.4-nm resolution, which was more than sufficient for our room temperature samples. The fluorescence was detected by a Hamamatsu 1P28 photomultiplier, the current from which was monitored by a Keithly Model 610C electrometer and then presented on a chart recorder.

All spectra were digitized, rescaled, and then replotted as relative absorption or relative fluorescence intensity as a function of the energy in wavenumbers.

III. Results

Fluorescence and fluorescence excitation spectra at 77 K of octatetraene and decapentaene are presented in Figures 1 and 2. For these molecules the excitation spectra were in excellent agreement with the absorption spectra and, in addition, the fluorescence spectra were independent of the wavelength of excitation. These observations confirm that we are dealing with pure samples and that the emissions observed occur as a consequence of absorption into the ^1B_u state. The spectra of octatetraene are consistent with those previously reported by Gavin et al.,[9] although these workers did not present corrected excitation and emission at 77 K. For the dodecahexaene we had considerable difficulty in achieving low-temperature excitation spectra which were in good agreement with absorption. We thus have presented room temperature data for the hexaene (Figure 3). Under these conditions the interpretation of spectra is much more straightforward (see below).

We have noted a marked decrease in fluorescence efficiency in going from the tetraene to the pentaene to the hexaene. We estimate that the hexaene's fluorescence quantum yield is at least 50 times smaller than that of the tetraene, given by Gavin et al.[9] as 0.02 ± 0.01 in hexane at room temperature (0.58 ± 0.15 at 77 K). In addition, we have observed that in hydrocarbon solvents the hexaene tends to precipitate out of solution during cooling to 77 K. The net result of these two effects is that short polyene impurities are greatly favored in low-temperature measurements of hexaene fluorescence. Thus, even though our room temperature hexaene samples showed reasonable absorption, emission, and excitation spectra, at 77 K the emission is dominated by blue-shifted impurities. In spite of several attempts to further purify our samples we have not been able to improve on this situation and thus have reported our more reliable, room temperature results in Figure 3. These spectra are seen to be more than adequate for the accurate location of electronic origins.

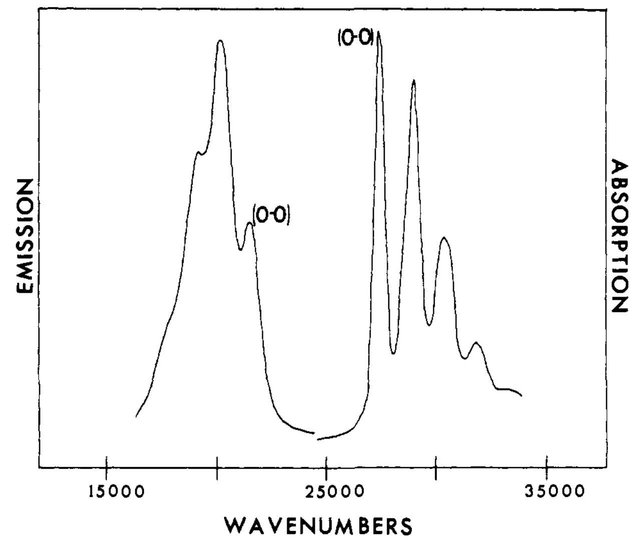

Figure 3. Absorption and uncorrected fluorescence spectra of 1,3,5,7,9,11-dodecahexaene in hexane at 25 °C. Fluorescence: excited at 365 nm (10-nm bandwidth), fluorescence detected with 10-nm bandwidth. Absorption taken with 0.1-nm bandwidth.

In Figure 4 we present a summary of the (0–0) transitions in absorption ($^1A_g \rightarrow {}^1B_u$) and emission ($^1A_g{}^* \rightarrow {}^1A_g$) for the tetraene, pentaene, and hexaene. We also have included in this figure the transition energies for three methyl-substituted polyenes: 1,8-dimethyloctatetraene,[6] 2,10-dimethylundecapentaene,[2,4] and 2,12-dimethyltridecahexaene.[3] Methyl substitution induces an almost uniform 1000 ± 100 cm^{-1} red shift in the $^1A_g \rightarrow {}^1B_u$ transition. The $^1A_g{}^* \rightarrow {}^1A_g$ transition is almost unaffected by these substitutions.

The data presented in Figure 4 is of some practical use in predicting the transition energies of related polyenes in hydrocarbon environments. However, in order to compare these results with present theoretical treatments, we need to correct the data for the effect of the solvents. Since the molecules considered have no dipole moment, the major solute–solvent interactions are due to dispersion forces.[26-28] The transition energy is given then by

$$\nu(\text{solvent}) = \nu(\text{gas}) - k\alpha \tag{1}$$

where k is constant for a given transition and α is the solvent

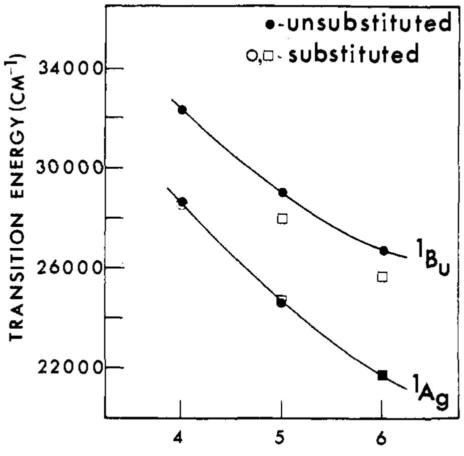

Figure 4. Comparison of $^1A_g \rightarrow {}^1A_g{}^*$ and $^1A_g \rightarrow {}^1B_u$ transition energies of substituted and unsubstituted tetraenes, pentaenes, and hexaenes: (●) unsubstituted polyenes in 77 K, 3-methylpentane (present work); (○) 1,8-dimethyloctatetraene in 4.2 K *n*-nonane (ref 25); (□) 2,10-dimethylundecapentaene in 4.2 K *n*-nonane (ref 4); 2,12-dimethyltridecahexaene in 4.2 K *n*-undecane (ref 3).

polarizibility = $(n^2 - 1)/(n^2 + 2)$, where n is the index of refraction.[26-28] We have obtained spectra of the decapentaene and the dodecahexaene in a variety of room temperature solvents and in Table I present least-squares fits of our data along with those of Gavin et al.[9] for octatetraene. The simple solvent model fits the observed transition energies rather well. A summary of the extrapolated gas-phase energy differences between the ^1B_u and $^1A_g{}^*$ states is given in Figure 5.

It should be noted that for both the tetraene and pentaene the $^1A_g \rightarrow {}^1B_u$ (0-0)'s can be measured directly on gas-phase samples. For octatetraene the direct measurement gives 35 523 cm^{-1} (cf. an extrapolated value of 35 350 ± 250 cm^{-1}),[9] while for decapentaene the direct measurement gives 32 415 cm^{-1} (cf. an extrapolated value of 32 075 ± 334 cm^{-1}). In both instances the extrapolated and directly measured values coincide to within the precision of the extrapolation. Since we do not have direct gas-phase information for the hexaene we compare extrapolated values in Figure 5. The rather good agreement between the differently obtained values for the tetraene and trapolated values in Figure 5. The rather good agreement between the differently obtained values for the tetraene and pentaene leaves us with considerable confidence that the true "gap" for the hexaene also lies within the deviations represented in Figure 5.

The main results of our work, i.e., the data presented in Figure 5, show that the $^1A_g{}^*$ and ^1B_u states diverge with increasing polyene length in going from the tetraene to the hexaene. Whether or not the difference in energy between these two states is approaching some constant value for long polyenes is not possible to judge from this data. It should be noted that the 300-400-cm^{-1} deviations in the measurements of the ^1B_u-$^1A_g{}^*$ energy differences are not unreasonable when one considers the problems in locating the (0-0)'s in the spectra. We have seen in previous high-resolution studies[3] that even in the same solvent (alkane crystals) there often exist several well-defined sites with origins differing by 100-200 cm^{-1}. Because of the forbidden nature of the $^1A_g{}^* \rightarrow {}^1A_g$ transition these sites can exhibit a distribution of vibronically and electronically allowed spectra depending on solvent-induced distortions of the polyenes. The present data would thus appear to be near the limit where the ^1B_u-$^1A_g{}^*$ splittings are determined by specific solvent-solute interactions as well as general polarizability effects.

The simple solvent model not only yields gas-phase transition energies, but provides additional information in the constant k. This constant is proportional to $(M_{ge}{}^2 + \epsilon\Delta\alpha)$ where M_{ge} is the transition dipole between the ground and excited states, $\Delta\alpha = \alpha_g - \alpha_e$ is the difference in the polarizibilities of the two states, and ϵ is the average excitation energy of the molecule in question.[27,28] For linear polyenes k is thought to be dominated by the transition dipole term.[1] This can be seen in the data presented in Table I. The strongly allowed $^1A_g \rightarrow {}^1B_u$ absorptions have k's (~10 000 cm^{-1}) five to six times larger than the k's (~1500-2000 cm^{-1}) associated with the forbidden $^1A_g{}^* \rightarrow {}^1A_g$ emissions.

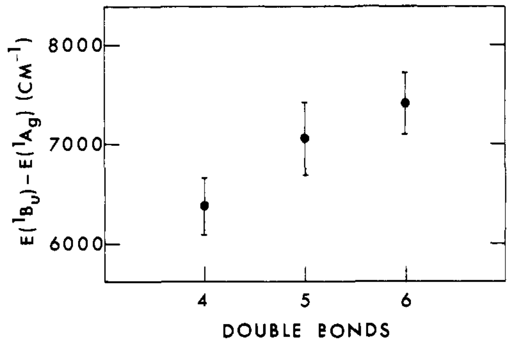

Figure 5. Gas-phase energy differences between ^1B_u and $^1A_g{}^*$ states in the unsubstituted tetraene, pentaene, and hexaene. Error bars represent 1σ. (Data from Table I.)

We might extend these comparisons and analyze how k's for a given transition depend on polyene length. The general rise in $^1A_g \rightarrow {}^1B_u$ oscillator strength with increasing polyene length[29] should be accompanied by parallel increases in k. Likewise, the $^1A_g{}^* \rightarrow {}^1A_g$ oscillator strengths (and hence k's) might be expected to decrease with increasing length since the larger ^1B_u-$^1A_g{}^*$ energy gaps (Table I) should lead to a reduction in ^1B_u, ^1A_g vibronic mixing.[27] However, neither of these a priori generalizations is supported by the data. This, in large part, may be due to the experimental uncertainties associated with the k's. We also may be seeing manifestations of polarizability differences between the ground and excited states (this should be more significant for the weak $^1A_g{}^* \rightarrow {}^1A_g$ transition) and/or the quantitative shortcomings of the simple solvent model.

IV. Discussion of Results

The spectra presented in Figures 1-3 exhibit several common features. Foremost for the purposes of this paper are the characteristic gaps between the origins of absorption and emission. This fact along with the arguments outlined in the Introduction leads us to assign the absorptions as $^1A_g \rightarrow {}^1B_u$ and the emissions as $^1A_g{}^* \rightarrow {}^1A_g$.

The $^1A_g{}^* \rightarrow {}^1A_g$ fluorescence transitions are formally forbidden. However, these transitions generally show allowed origins, especially in low-resolution spectra such as those presented here. This is because of the asymmetric nature of sites in these glassy solvent systems[3] and the fact that, even for molecules which retain their ideal symmetry, intensity is borrowed by promoting modes of rather low frequency (~100 cm^{-1}).[4,6,7] The broad (~200-300 cm^{-1}) vibronic features of our spectra thus represent a distribution of solvent distorted and vibronically coupled polyenes. For both kinds of molecules the origins appear "allowed".

The fluorescence origins increase in relative intensity (i.e., relative to other vibronic bands) in going from the tetraene to the hexaene. This should prove quite helpful in identifying origins in the spectra of longer molecules. The general rise in the relative intensities of the $^1A_g{}^* \rightarrow {}^1A_g$ origins is accompanied by a sharp decrease in absolute fluorescence yield in the longer polyenes. This latter trend points to increased challenges in extending the present work to heptaene, octaene, etc. Such

Table I. Solvent Effects on Polyene Transition Energies: $\nu(\text{solvent}) = \nu(\text{gas}) - k(n^2 - 1)/(n^2 + 2)$

	absorption (${}^1B_u \leftarrow {}^1A_g$)			emission (${}^1A_g^* \rightarrow {}^1A_g$)			measured
	ν(gas),[c] cm^{-1}	k, cm^{-1}	r[d]	ν(gas), cm^{-1}	k, cm^{-1}	r	energy gap,[e] cm^{-1}
octatetraene[a]	35 350 ± 250	10 909 ± 1000	0.96	28 970 ± 100	1690 ± 400	0.84	6380 ± 270
decapentaene[b]	32 075 ± 334	9639 ± 1287	0.97	25 019 ± 160	2156 ± 340	0.99	7056 ± 366[f]
dodecahexaene[b]	29 449 ± 302	9264 ± 1141	0.98	22 034 ± 90	1572 ± 359	0.93	7415 ± 315[f]

[a] Data of Gavin et al., ref. 9. [b] Solvents used: methanol, hexane, isooctane, chloroform, and benzene. [c] ν's refer to transition energies of (0–0)'s. [d] r = correlation coefficient. [e] Measured energy gap = ν(gas) absorption − ν(gas) emission = energy (${}^1B_u$) − energy (${}^1A_g^*$). [f] Errors are given as ± 1 σ.

investigations will require more stringent purification procedures to ensure that the weak emissions are not overwhelmed by those from shorter, more fluorescent impurities. In view of the trend in emission yields, it is surprising that no emission has been reported for hexatriene. One possibility is that the ${}^1B_u$ state is the lowest excited state in the triene. However, as shown by the data presented in Figure 5, this would require a change of over 0.80 eV in the relative energies of the ${}^1B_u$ and ${}^1A_g^*$ states with respect to those observed in the tetraene. There do exist calculations with ${}^1B_u$ lower than ${}^1A_g^*$ on hexatriene[30] and with ${}^1A_g^*$ lower than ${}^1B_u$ in octatetraene.[12] However, neither of these calculations taken alone predicts a crossing of ${}^1A_g^*$ and ${}^1B_u$ states between the tetraene and triene. The striking differences in fluorescence characteristics of these molecules and the relative ordering of electronic states in hexatriene remain matters of conjecture.

Comparison of the energy levels of substituted vs. unsubstituted polyenes (Figure 4) shows that methyl groups give rise to substantial red shifts in the ${}^1A_g \rightarrow {}^1B_u$ absorption while having negligible effect on the fluorescence (${}^1A_g^* \rightarrow {}^1A_g$). A general, position-independent energy lowering of the ${}^1B_u$ state has been noted before on methyl-substituted polyenes (Woodward's rules[31]). Our data indicate that such lowerings are not to be expected for the ${}^1A_g^*$ state. These generalizations should be useful in predicting the transition energies of the highly substituted retinyl polyenes and indicate a smaller ${}^1B_u$–${}^1A_g^*$ energy gap in these systems. This supports state assignments based on recent two-photon spectra of retinol and retinal by Birge et al.[32,33] In retinol (five double bonds) in EPA glass, the ${}^1B_u$–${}^1A_g^*$ states are reported[32] to be separated by 1600 cm^{-1}. This finding is not inconsistent with ${}^1B_u$–${}^1A_g^*$ gaps of 3250 cm^{-1} in 2,10-dimethylundecapentaene[2] and 4400 cm^{-1} in the unsubstituted pentaene. Similarly, the 1900-cm^{-1} gap[33] for retinal (six double bonds) compares with gaps of 4000 cm^{-1} in 2,12-dimethyldodecahexaene[3] and 5000 cm^{-1} in the unsubstituted hexaene. Accurate location of retinyl electronic states is hampered by the lack of vibronic resolution. Nevertheless, the two-photon results seem quite reasonable in light of the data presented in Figure 4.

Recent theoretical work on methyl-substituted butadienes indicates that the shifts in the ${}^1A_g \rightarrow {}^1B_u$ transition energies involve both hyperconjugative and inductive effects.[34] Which of these two factors pertains depends on the position of substitution. This suggests that, in our long polyenes, substitution on inner carbons (the examples shown in Figure 4 have methyl groups on either terminal or next to terminal carbons) might lead to shifts in the fluorescence spectra. We therefore must exercise some caution in applying our results to all methyl-substituted polyenes.

Our most significant finding is that for the polyenes studied the ${}^1B_u$ and ${}^1A_g^*$ states diverge with increasing numbers of double bonds (Figure 5). The ${}^1B_u$ state energy approaches a finite limit for long polyenes.[29] Explanation of this fact in terms of bond alternation is a cornerstone of molecular orbital theory. The long polyene behavior of the ${}^1A_g^*$ state poses another interesting question.

Table II. Energy Differences between the Lowest Excited Electronic States (${}^1A_g^*$ and ${}^1B_u$) in Unsubstituted Linear Polyenes

	calcd differences, eV[a]			exptl
	D	T	Q	differences, eV
octatetraene	0.285	0.371	0.560	0.791 ± 0.033[b]
decapentaene	0.231	0.290	0.595	0.874 ± 0.045[c]
dodecahexaene	0.162	0.153		0.920 ± 0.039[c]

[a] From Tavan and Schulten, ref 12. D, T, and Q refer to CI calculations which include all single and double excitations (D), all single, double, and triple excitations (T), and all single, double, triple, and quadruple excitations (Q). [b] From Gavin et al., ref 9. [c] This work.

The relative ordering of the low-lying ${}^1A_g^*$ and ${}^1B_u$ states is explained by the inclusion of both singly and double excited configurations in the SCF–PPP treatment.[10] As indicated in Table II, however, these calculations underestimate (by >0.5 eV) the ${}^1B_u$–${}^1A_g$ gaps. Moreover, the double CI treatment predicts a convergence of the long polyene gap rather than the observed divergence. Tavan and Schulten[12] have shown that much better agreement is obtained when all excitations up to quadruple are included in the theory (see Table II). These calculations place severe demands on computer time, but are required in order to correct the "independent particle" PPP description for correlation effects. Other approaches to the correlation problem have been considered.[13] Combination of these with moderately extensive CI should provide an even more quantitative account of the ${}^1B_u$–${}^1A_g^*$ differences presented here.

It obviously would be useful to extend our work to achieve a better understanding of long polyene trends. The rather sharp drop in emission yields, however, suggests that fluorescence and fluorescence excitation techniques will not be useful beyond heptaenes or possibly octaenes. Other techniques such as two-photon spectroscopy and Raman excitation spectroscopy will be needed. In this regard the Raman excitation spectra of β-carotene, a nonfluorescent polyene with 11 double bonds, deserves special mention. Excitation profiles indicate a weak absorption ~3470 cm^{-1} below the strongly allowed ${}^1A_g \rightarrow {}^1B_u$ transition.[35] The weak absorption is assigned to ${}^1A_g \rightarrow {}^1A_g^*$. It should be pointed out, however, that as in conventional absorption spectroscopy it is difficult to eliminate the possibility that the weak absorption is due to impurities or to something other than the lowest vibronic level of the lowest excited singlet. These kinds of ambiguities are not present in our results since the fluorescence and fluorescence excitation spectra show a one-to-one correspondence between the well-characterized ${}^1A_g \rightarrow {}^1B_u$ absorptions and the emissions (from the lowest excited singlet state). It is clear, nevertheless, that fluorescent techniques are limited and a combination of techniques, preferably with overlaps on mutually accessible molecules, will be required to provide a more complete catalog of polyene energy levels.

The primary goal of this paper has been to determine the location of spectral origins and the energies of the ${}^1A_g^*$ and ${}^1B_u$ states. Additional information is contained in other vibronic details, specifically the characteristic progressions in the single ($\nu \sim 1200$ cm^{-1}) and double ($\nu \sim 1600$ cm^{-1}) bond stretching vibrations. A detailed analysis of the Franck-Condon factors associated with these bands and their dependence on the extent of conjugation would provide insights on the excited-state geometries in the polyene series. Thus, for example, the increase in relative intensity of the fluorescence origins in the longer polyenes is consistent with the notion that the $^1A_g{}^*$ potential energy surfaces are not as greatly distorted from ground-state geometries. These and other trends in spectral intensities could be put on a more quantitative footing. This, however, is outside the scope of the present study.

V. Summary and Conclusions

Low-resolution optical spectra of simple polyenes with four, five, and six conjugated double bonds lead to $^1A_g{}^*$ assignments for the lowest $^1\pi\pi^*$ states. The $^1A_g{}^*$ energy is relatively insensitive to terminal methyl substitution as well as to changes in solvent polarizibility. The higher energy ^1B_u state, however, is shifted to lower energy both by substituents and by polarizible environments. The net effect of solvents and substituents is thus a substantial lowering of the ^1B_u-$^1A_g{}^*$ energy differences from those observed for unsubstituted polyenes in the gas phase. Both of these effects should be accounted for in evaluating calculations and in comparing spectra of different polyenes.

We have applied a simple solvent model to extract gas-phase values for the $^1A_g \rightarrow {}^1A_g{}^*$ and $^1A_g \rightarrow {}^1B_u$ transition energies. The ^1B_u-$^1A_g{}^*$ energy difference increases with increasing polyene length. Molecular orbital calculations which include all single and double excited configurations[10] underestimate the ^1B_u-$^1A_g{}^*$ gap and do not account for its dependence on polyene length. Recent, more extensive CI treatments of Tavan and Schulten[12] provide a more quantitative accounting of our data. Further extension of the CI calculations coupled with more direct approaches to the electron correlation problem[13] should give even better agreement between theory and experiment.

The present study indicates the need for additional experiments on both longer and shorter polyenes. Work on the longer systems would more firmly establish whether the $^1A_g{}^*$ energy approaches a nonzero limit. The increasingly smaller fluorescent yields for the longer molecules most likely will require the use of other than fluorescence techniques (e.g., two-photon absorption and Raman excitation spectra) to locate the $^1A_g{}^*$ state. The gradual decrease in fluorescence in the long polyenes contrasts the abrupt disappearance in fluorescence in going from octatetraene to hexatriene. This cannot be due to a reordering of the ^1B_u and $^1A_g{}^*$ states unless these states undergo a 0.70-0.80-eV change in their relative energies in these two molecules. The ordering of the lowest electronic levels in hexatriene remains a mystery, and more work is needed to link the present results to those obtained on shorter polyenes.

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References and Notes

(1) B. S. Hudson and B. E. Kohler, *Annu. Rev. Phys. Chem.*, **25**, 437 (1974).
(2) R. L. Christensen and B. E. Kohler, *Photochem. Photobiol.*, **18**, 293 (1973).
(3) R. L. Christensen and B. E. Kohler, *J. Phys. Chem.*, **80**, 2197 (1976).
(4) R. L. Christensen and B. E. Kohler, *J. Chem. Phys.*, **63**, 1837 (1975).
(5) B. S. Hudson and B. E. Kohler, *J. Chem. Phys.*, **59**, 4984 (1973).
(6) J. R. Andrews and B. S. Hudson, *Chem. Phys. Lett.*, **57**, 600 (1978).
(7) M. F. Granville, G. R. Holtom, B. E. Kohler, R. L. Christensen, and K. L. D'Amico, *J. Chem. Phys.*, **70**, 593 (1979).
(8) J. R. Andrews and B. S. Hudson, *Chem. Phys. Lett.*, **60**, 380 (1979).
(9) R. M. Gavin, Jr., C. Weisman, J. K. McVey, and S. A. Rice, *J. Chem. Phys.*, **68**, 522 (1978).
(10) K. Schulten and M. Karplus, *Chem. Phys. Lett.*, **14**, 305 (1972).
(11) K. Schulten, I. Ohmine, and M. Karplus, *J. Chem. Phys.*, **64**, 4422 (1976).
(12) P. Tavan and K. Schulten, *J. Chem. Phys.*, **70**, 5407 (1979).
(13) I. Ohmine, K. Schulten, and M. Karplus, *J. Chem. Phys.*, **68**, 2298 (1978).
(14) D. F. Evans, *J. Chem. Soc.*, 2566 (1961).
(15) R. Kuhn and M. Hoffer, *Ber.*, **63**, 2164 (1930).
(16) R. Kuhn and C. Grundmann, *Ber.*, **71**, 2274 (1938).
(17) R. Kuhn and C. Grundmann, *Ber.*, **70**, 1318 (1937).
(18) H. L. duMont and H. Fleischauer, *Ber.*, **71**, 1958 (1938).
(19) F. G. Fischer, K. Hultzch, and W. Flaig, *Ber.*, **70**, 370 (1937).
(20) I. N. Nazarov and Zh. A. Krasnaia, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 224 (1958).
(21) R. Hubbard, *J. Am. Chem. Soc.*, **78**, 4662 (1956).
(22) T. Reichstein, C. Ammann, and G. Trivelli, *Helv. Chim. Acta*, **15**, 261 (1932).
(23) E. R. Lippincott, W. R. Feairheller, Jr., and C. E. White, *J. Am. Chem. Soc.*, **81**, 1316 (1959).
(24) G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, **71**, 1396 (1949).
(25) F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).
(26) S. Basu, *Adv. Quantum Chem.*, 1, 145 (1964).
(27) J. R. Andrews and B. S. Hudson, *J. Chem. Phys.*, **68**, 4587 (1978).
(28) A. T. Amos and B. L. Burrows, *Adv. Quantum Chem.*, **7**, 289 (1973).
(29) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules", Wiley, New York, 1963, pp 67-77.
(30) M. Nascimento and W. Goddard III, *Chem. Phys. Lett.*, **60**, 197 (1979).
(31) R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72 (1942).
(32) R. R. Birge, J. A. Bennett, B. M. Pierce, and T. M. Thomas, *J. Am. Chem. Soc.*, **100**, 1533 (1978).
(33) R. R. Birge, J. A. Bennett, H. L. B. Fang, and G. E. Leroi, "Advances in Laser Chemistry", A. H. Zewail, Ed., Springer Series in Chemical Physics, Vol. 3, Springer-Verlag, New York, 1978, pp 347-354.
(34) U. Dinur and B. Honig, *J. Am. Chem. Soc.*, **101**, 4453 (1979).
(35) R. J. Thrash, H. Fang, and G. E. Leroi, *J. Chem. Phys.*, **67**, 5930 (1977).