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been applied to our results. It is found that this model in both the short- and long-time domains cannot explain all the observed results. We have tried to show the importance of considering the role of the solvent acceptor molecules. Both mechanisms of the Coulomb cage effect and acceptor properties seem to contribute to the decay of HOPTS in water/alcohol mixtures.

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Fluorescence of Gaseous Tetraenes and Pentaenes

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Fluorescence, fluorescence excitation, and absorption spectra of room temperature vapors of 1,3,5,7-octatetraene, 1,3,5,7-nonatetraene, 2,4,6,8-decatetraene, and 2,4,6,8,10-dodecapentaene have been obtained. All four polyenes show dual ($S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$) fluorescences with the ratios of the two emissions ($2^1A_g \rightarrow 1^1A_g$ and $1^1B_u \rightarrow 1^1A_g$) being sensitive to the extent of substitution. For example, the $(S_1 \rightarrow S_0)/(S_2 \rightarrow S_0)$ fluorescence yield ratio increases from 0.06 to 0.7 when terminal methyl groups are added to octatetraene. The gas-phase S_2–S_1 energy gaps are almost identical for these two molecules (6600 cm^{-1} for octatetraene versus 6300 cm^{-1} for decatetraene), suggesting that the apparent difference in internal conversion efficiencies is due to the larger density of vibronic states in the methyl-substituted compounds. This is supported by an even larger $(S_1 \rightarrow S_0)/(S_2 \rightarrow S_0)$ yield ratio (1.4) in dodecapentaene, for which the gas-phase S_2–S_1 energy difference is 7200 cm^{-1}. The fluorescence excitation spectrum of decatetraene has been measured in the 34 600–37 450-cm^{-1} region ($S_0 \rightarrow S_2$) in a supersonic expansion. Vibronic line widths have been used to estimate a lifetime of 0.25 ps for the zero-point level of 1^1B_u and indicate coupling between the 1^1B_u and 2^1A_g manifolds in the statistical limit. These results are discussed in relation to the previous gas-phase spectroscopy of octatetraene and shorter polyenes.

Introduction

Linear polyenes have received experimental and theoretical attention for several decades because of their relevance in several photobiological processes, such as vision and photosynthesis, and their usefulness as models for developing descriptions of the electronic states of conjugated π-electron systems.[1] The optical spectroscopy of simple, unsubstiuted polyenes in low-temperature solutions[1-3] and mixed crystals[1,4-6] has established (for simple, unsubstituted polyenes with four or more double bonds) the presence of a 2^1A_g (S_1) state between the ground 1^1A_g (S_0) and first one-photon-allowed excited state 1^1B_u (S_2). Absorption into S_2 typically is followed by a Stokes-shifted emission from S_1, though the fluorescence yields are sensitive to details of molecular structure. For example, the high emission yields of certain long polyenes (~0.6 in frozen solutions of octatetraene)[7] contrast the absence of fluorescence in shorter analogues such as hexatriene under identical experimental conditions.

Low-temperature optical measurements in glasses and mixed crystals have been supplemented by recent studies of polyenes in supersonic jets.[8-11] Most of this work has focused on the spectroscopy of diphenyl-substituted compounds.[12-19] These compounds not only are commercially available but also are both highly fluorescent and relatively stable. Absorption, fluorescence, and fluorescence excitation spectra have provided additional information on the electronic structures and dynamics of these polyene systems and for diphenylhexatriene and diphenylbutadiene suggest intermediate case coupling between the 2^1A_g and 1^1B_u excited states.

The high fluorescence quantum yields of the diphenylpolyenes contrast the immeasurably weak fluorescences of butadiene and hexatriene, indicating that the results obtained for the short diphenylpolyenes are not applicable to polyenes without phenyl substituents. Octatetraene is the shortest unsubstituted polyene with detectable fluorescence and thus has been the subject of a

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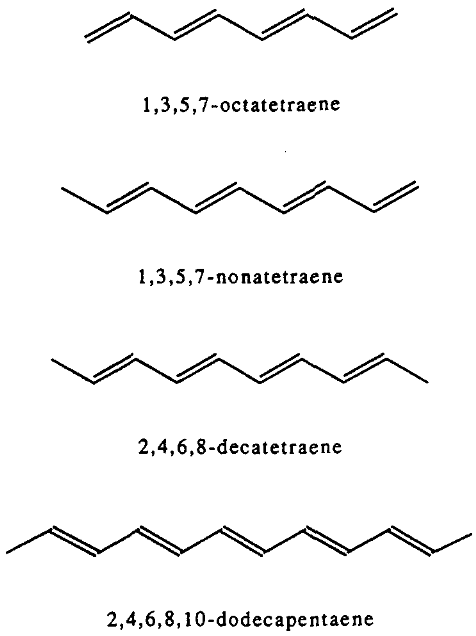

Figure 1. Polyenes studied.

great deal of experimental and theoretical interest. Gavin et al.[7] were the first to report its gas-phase emission and the absence of a Stokes shift leads to a $S_2 \rightarrow S_0$ assignment for the fluorescence. Heimbrook et al.[11] later measured the $S_2 \rightarrow S_0$ emission in a supersonic expansion and estimated an S_2 lifetime of 100–300 ps. Neither group was able to detect $S_1 \rightarrow S_0$ ($2^1A_g \rightarrow 1^1A_g$) fluorescence in octatetraene, and it is interesting to note that the 2^1A_g state of this archetypical polyene has not been observed in the gas phase. In fact Heimbrook et al.[11] were unable to detect any emission from octatetraene in the static gas, and all the free jet work on octatetraene has been on the 1^1B_u fluorescence. In contrast, recent work on gaseous diphenyloctatetraene[20] showed fluorescence solely from S_1 (2^1A_g) as in solutions and mixed crystals.

The striking differences between diphenyloctatetraene and unsubstituted octatetraene as well as the abrupt changes in fluorescence yields ($\sim$0.6 for octatetraene, $<10^{-4}$ for hexatriene) with polyene length pose some fundamental questions concerning the relaxation of polyene excited states. These issues have received little attention, however, due to the relative inaccessibility and fragility of the longer unsubstituted systems. Octatetraene and its longer analogues are not commercially available and are difficult to synthesize in the quantities required for jet experiments. In addition, simple, unsubstituted polyenes tend to oxidize, isomerize, and polymerize even when stored in dilute solution. In an effort to expand upon the experiments on octatetraene and the phenyl-substituted polyenes, we have developed new synthetic routes to several unsubstituted and methyl-substituted tetraenes, pentaenes, and hexaenes. We initially investigated the fluorescence properties of octatetraene, nonatetraene, decatetraene, and dodecapentaene (Figure 1) as static, room-temperature vapors. The multigram quantities available from improved synthetic procedures also have allowed us to extend these measurements to supersonic jets. We report here our preliminary results on the free-jet spectroscopy of decatetraene and compare with spectra previously obtained for octatetraene.[8,10]

Experimental Section

Octatetraene was prepared as reported previously.[3] Decatetraene was synthesized, employing the Wittig reaction between hexadienal (Aldrich) and crotyltriphenylphosphonium bromide ("instant ylide", Fluka). Nonatetraene was synthesized by a similar reaction between hexadienal and allyltriphenylphosphonium bromide (Fluka). Dodecapentaene was obtained from the reaction between crotyltriphenylphosphonium bromide and octatrienal, which had been obtained from the acid-catalyzed self-condensation of crotonaldehyde.[3] All samples were purified by multiple recrystallizations. Ultraviolet spectra and HPLC analyses showed that these samples were dominated by all-trans isomers. Further details of the syntheses and purification of these and several other simple polyenes will be described separately.[21]

Absorption spectra of static vapor samples were measured on a Shimadzu UV240 spectrophotometer interfaced to a microcomputer. Fluorescence and fluorescence excitation spectra were obtained 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 main-frame computer for subsequent analysis and display. Comparison of corrected excitation and emission spectra of standard samples such as naphthalene and anthracene showed that the correction procedures were valid over the wavelength range of interest (250–500 nm). Relative fluorescence yields from the S_1 and S_2 states were obtained by integrating the spectral bands with respect to frequency by using the trapezoidal method. The photolability and thermal lability of these compounds required repeated measurements on several (5–10) polyene samples to achieve accurate estimates of the fluorescence ratios.

Crystalline tetraenes or pentaenes were placed in a nonfluorescent, 1-cm quartz cell equipped with a stopcock to allow evacuation. The samples were repeatedly pumped on and degassed and then allowed to reach their equilibrium vapor pressures (a few Torr). Sample quality was monitored by comparing excitation spectra with gas-phase absorption spectra of fresh samples, and the spectra presented in this paper are representative of fresh, unexposed polyene samples. Spectra also were taken of polyene vapors in the presence of an atmosphere of air. These samples appeared to deteriorate more quickly than those studied in the absence of air and had to be replenished periodically to obtain spectra that could be identified with those of pure polyene samples.

The supersonic jet apparatus has been described elsewhere.[22] Sample vapor, produced by heating the crystals in an oven at 70 °C, was mixed with helium carrier gas, at a stagnation pressure of 3.5 bar, and expanded through a continuous flow nozzle of diameter 100 μm. The excitation source was a frequency-doubled excimer-pumped dye laser (Lambda Physik 103MSC/FL2002) with a band width of 0.2 cm^{-1}. The dye laser grating was calibrated with a hollow cathode lamp by using the optogalvanic effect. The laser beam was softly focused in the supersonic expansion to avoid saturation.

For measurements of excitation spectra, fluorescence was collected with an $f/1$ lens, passed through a Schott WG295 or WG345 cutoff filter and focused onto a photomultiplier tube (EMI XP2020Q). The photomultiplier output was processed by a Stanford Research Systems boxcar averager interfaced to a microcomputer. Spectra were corrected for variations in laser intensity by dividing the photomultiplier tube signal by the laser power measured with a photodiode (Hamamatsu S1722-02). The observed band shapes were fit to Gaussian and Lorentzian functions by using a nonlinear least-squares fitting program that employed the Marquardt algorithm.[23,24]

Results

Spectra of Static Gases. Absorption and fluorescence spectra of the three gas-phase tetraenes are compared in Figure 2. The fluorescence and fluorescence excitation spectra of the vapors of room-temperature crystals of dodecapentaene are given in Figure 3. Each of these polyenes show two distinct fluorescence bands, a structured fluorescence with an electronic origin coincident with that of the strongly allowed $S_0(1^1A_g) \rightarrow S_2(1^1B_u)$ absorption and a broad, unstructured emission at longer wavelengths. It is im-

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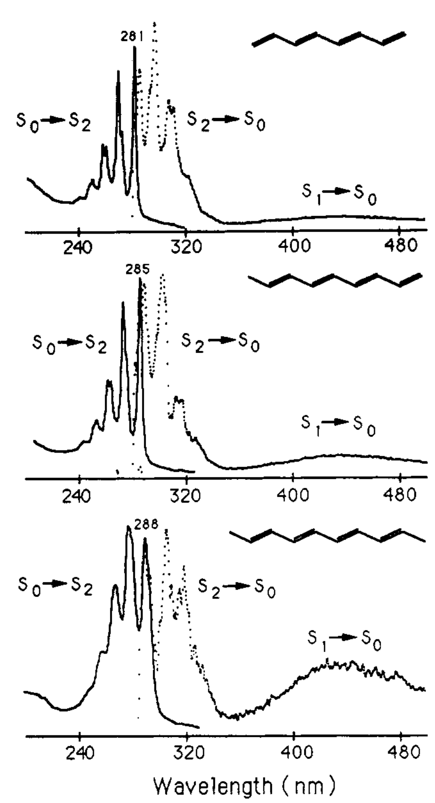

Figure 2. Absorption and fluorescence spectra of the vapors in equilibrium with room-temperature crystals of octatetraene, nonatetraene, and decatetraene. Absorption spectra were obtained at 0.5-nm resolution. Fluorescence spectra were obtained by exciting into the strong absorption features (269, 273, and 275 nm, respectively) lying ~1600 cm^{-1} above the electronic origins of the three polyenes. Excitation and emission bandwidths were set at 3.6 and 1.8 nm for all fluorescence spectra. The spectra of octatetraene (obtained with no external buffer gas) were identical with those measured in the presence of ambient air. The spectra of nonatetraene and decatetraene were obtained in air.

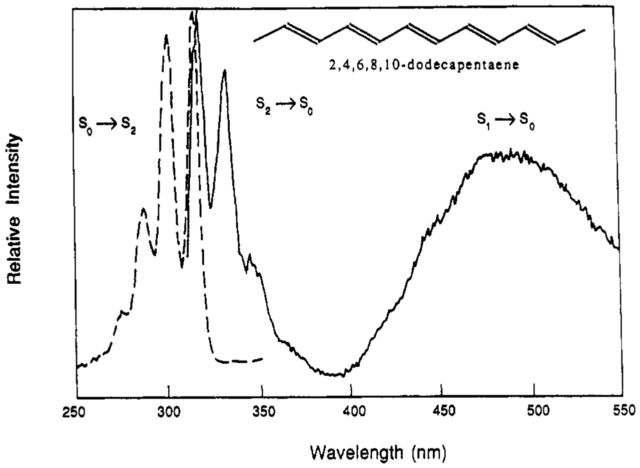

Figure 3. Fluorescence and fluorescence excitation spectra of the vapors in equilibrium with room-temperature crystals of dodecapentaene in the presence of an atmosphere of air. The fluorescence spectrum was obtained by exciting at 300 nm, and the excitation spectrum was analyzed at 477 nm. The excitation and emission bandpasses were both 2.7 nm. The fluorescence excitation spectrum is in excellent agreement with the absorption spectrum obtained under identical conditions.

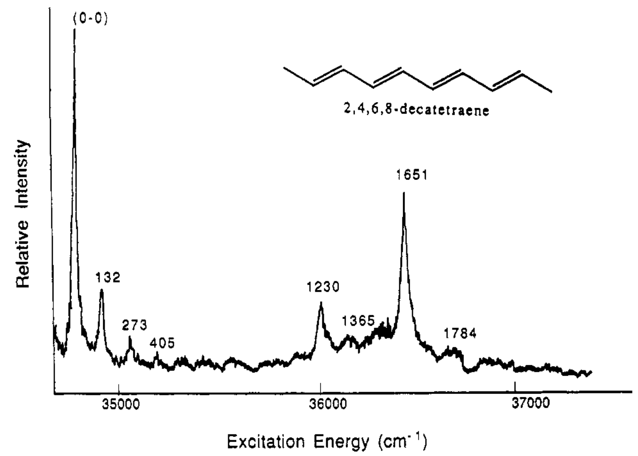

Figure 4. Fluorescence excitation spectrum of the $1^1A_g \rightarrow 1^1B_u$ transition in jet-cooled decatetraene. The numbers indicate the shift from the origin in wavenumbers.

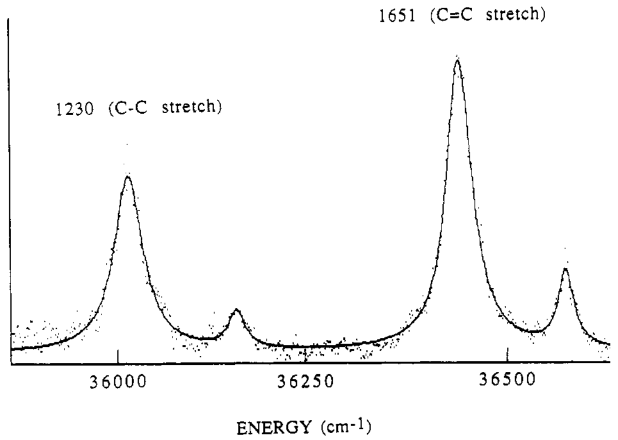

Figure 5. Points are the measured $1^1A_g \rightarrow 1^1B_u$ excitation spectrum of jet-cooled decatetraene in the C–C and C=C stretching region. The solid line is the best fit of four Lorentzian functions to the observed spectrum.

portant to note that both emissions give rise to the same structured fluorescence excitation spectra and that the corrected excitation spectra are in good agreement with the gas-phase absorption spectra in terms of both the wavelengths and the relative intensities of the $S_0 \rightarrow S_2$ vibronic bands. Fluorescence and fluorescence excitation spectra obtained at the low vapor pressures (<1 Torr) of the polyene crystals were identical with those measured in an atmosphere of air. Spectra taken as a function of time showed evidence of photodegradation, and the spectra presented here are typical of fresh, unexposed samples.

The fluorescence spectra given in Figures 2 and 3 were obtained by excitation into the prominent absorption band (0–1) lying ~1600 cm^{-1} above the $S_0 \rightarrow S_2$ electronic origins. Other excitation conditions, e.g., pumping the (0–0), gave similar emission spectra with the ratio between the structured and the broad fluorescences not being sensitive to the S_2 vibronic level excited. Emission spectra obtained exciting different vibronic levels of S_2 showed small (15–20%), systematic differences in relative vibronic intensities of the structured fluorescences. Excitation spectra monitoring different features of the structured emission showed similar systematic differences.

The structured fluorescences are similar to those previously reported for room-temperature octatetraene vapors by Gavin and Rice[7] and can be assigned as $S_0 \rightarrow S_2$ emissions. The longer wavelength, unstructured emissions have not previously been observed in the gas-phase spectra of simple polyenes. Comparison with the Stokes-shifted fluorescences of polyenes in condensed phases leads to an $S_1 \rightarrow S_0$ assignment for these broad emissions with the ratio $(S_1 \rightarrow S_0)/(S_2 \rightarrow S_0)$ of the integrated fluorescence intensities as follows: octatetraene (0.06 ± 0.01), nonatetraene (0.25 ± 0.04), decatetraene (0.7 ± 0.2), and dodecapentaene (1.4 ± 0.4).

Fluorescence Excitation Spectra of Jet-Cooled Decatetraene. The fluorescence excitation spectrum of the $1^1A_g \rightarrow 1^1B_u$ transition in jet-cooled decatetraene was measured between 34 600 and 37 450 cm^{-1} (289–267 nm). The excitation spectrum (Figure 4) is characterized by an intense (0–0) transition at 34 784 cm^{-1}, a number of weak, low-frequency transitions, and two moderately

TABLE I: Band Positions and Bandwidths Observed in the $1^1A_g \rightarrow 1^1B_u$ Fluorescence Excitation Spectrum of *all-trans*-2,4,6,8-Decatetraene

freq,[a] cm^{-1}	shift,[b] cm^{-1}	bandwidth,[c] cm^{-1}	height[d]	assignment[e]
34780	(0)	22 (2)	100	0–0
34916	132	24 (4)	20	
35057	273		8	
35189	405		5	
36014	1230	43 (3)	20	
36149	1365		5	1230 + 132
36435	1651	40 (3)	52	
36568	1784		10	1651 + 132

[a] Uncertainties of 2 cm^{-1}. [b] Uncertainties of 3 cm^{-1}. [c] Uncertainties in parentheses were determined from least-squares fits to Lorentzian band shapes. [d] Relative heights are accurate to within 30%. Errors are due to fluctuations in the laser intensity and oven temperature. [e] All transitions originate in zero-point level of the ground state.

intense higher frequency features at 1230 and 1651 cm^{-1}. The band contours of the peaks were independent of both the expansion conditions and the laser power. Fits to the band contours using Gaussian and Lorentzian functions showed that the peaks are better described by the Lorentzian line shapes shown in Figure 5. Transition frequencies and associated fwhm Lorentzian band widths are listed in Table I.

To estimate the relative intensities of fluorescence emanating from the S_2 and S_1 states, excitation spectra were obtained by monitoring the emission through two different long-pass filters (WG 295 and WG 345). Monitoring the emission at emission wavelengths >345 nm resulted in a decrease in the fluorescence intensity but no discernible change in the excitation profile. The fraction of emission occurring at wavelengths greater than 345 nm ($S_1 \rightarrow S_0$ emission) was found to be comparable to the fraction of S_1 emission (30–50% of the total fluorescence intensity) observed for decatetraene as a static, room-temperature vapor.

Discussion

Our experiments on gaseous tetraenes and pentaenes indicate an increase in the $(S_2 \rightarrow S_0)/(S_1 \rightarrow S_0)$ emission ratio both with the addition of methyl substituents and with increasing polyene length. Previous workers[7,11] had indicated substantial (quantum yields of 0.10 ± 0.05) S_2 emission from gaseous octatetraene but were unable to detect the S_1 fluorescence. This now can be attributed to its lack of structure and relatively low intensity compared with the S_1 emissions of methyl-substituted systems such as decatetraene and dodecapentaene (Figures 2 and 3).

A review of previous work on octatetraene points to other, less easily resolved discrepancies with regard to fluorescence yields and lifetimes. The initial report[7] of a 14.8-ns fluorescence lifetime for octatetraene cannot be reconciled with the intrinsic lifetime of 2.0 ns calculated from the $S_0 \rightarrow S_2$ integrated absorption intensity.[1] Heimbrook et al.[11] later used the saturation behavior of the S_2 fluorescence intensity in jet-cooled octatetraene to estimate an S_2 lieftime of 100–300 ps, which would be consistent with the 0.05–0.15 fluorescence quantum yield.[7,11] However, these workers were unable to detect emission from the room-temperature vapor and concluded that the fluorescence yield must be $<10^{-4}$. Our own work suggests that the static gas yield is on the order of 10^{-4}, though absolute fluorescence quantum yields of these gaseous samples are extremely difficult to measure. Experimental problems include the variability of the vapor pressures of the unstable crystalline samples and the thermal and photochemical instabilities of the polyenes once placed in the gas phase. The wide variations between different studies[7,11] might be attributed to differences between static gases and supersonic jets, though it seems unlikely that octatetraene's fluorescence quantum yield and lifetime change by 3 orders of magnitude in going from a room-temperature vapor into a supersonic expansion. In addition, the lack of agreement between various measurements on the static gas samples cannot be overlooked.

One issue that deserves careful exploration is whether the $S_1 \rightarrow S_0$ emissions we have observed might be due the presence of cis isomer impurities in our samples. The $S_1 \rightarrow S_0$ transition in cis polyenes is not symmetry forbidden and thus might be preferentially observed. However, there are several reasons why *cis*-decatetraenes cannot be implicated in our spectra: The room-temperature, static gas fluorescence excitation spectrum obtained by monitoring the broad $S_1 \rightarrow S_0$ emission is identical with the excitation spectrum obtained by monitoring the $S_2 \rightarrow S_0$ emission. Both of these spectra are in good agreement with the static gas $S_0 \rightarrow S_2$ absorption spectrum, which shows no evidence of interference from cis isomers. Similarly, in the free jet the same $S_0 \rightarrow S_2$ excitation spectrum is obtained when separately monitoring the two emissions with no evidence for features that might be attributed to more than one tetraene component. The excitation spectra do not eliminate the possibility of the photochemical conversion of *trans*- into *cis*-decatetraene during $S_2 \rightarrow S_1$ internal conversion. However, recent lifetime measurements of the $S_1 \rightarrow S_0$ emission[38] show a long-lived, single-exponential decay as expected for the symmetry-forbidden transition of an *all-trans*-polyene.

Recent work on gaseous diphenylpolyenes also bears on our results.[20] Both diphenylhexatriene and diphenyloctatetraene are dominated by S_1 fluorescence in the low-pressure (isolated molecule) limit. This has been attributed to the relatively large S_2–S_1 energy gaps (3400 and 5600 cm^{-1}, respectively) in these compounds.[20] However, unsubstituted octatetraene has an even larger S_2–S_1 energy separation (6600 cm^{-1}) but is dominated by S_2 emission in the low-pressure limit. The striking contrast between the static gas fluorescence properties of hexatriene (no emission) and diphenylhexatriene also reminds us that phenyl groups have a dramatic effect on the photodynamics of these molecules.

The earlier experiments on the $S_2 \rightarrow S_0$ emission of octatetraene in a jet indicated that a dispersed spectrum could be obtained only by excitation into the electronic origin.[11] Excitation of higher vibronic levels of S_2 was assumed to result in greatly reduced emission yields or a diffuse, unstructured spectrum. This contrasts the original report of $S_2 \rightarrow S_0$ emission in gaseous octatetraene[7] and the static gas spectra presented here. A comparison of absorption spectra and the fluorescence excitation spectra given in Figure 2 shows systematic but small (15–20%) falloffs in the fluorescence yields when levels above the S_2 zero-point level are excited. Similar patterns are observed in the gas-phase emissions of diphenylhexatriene and diphenyloctatetraene.[20] In addition, the fluorescence excitation spectrum of gaseous dodecapentaene (Figure 3) is in excellent agreement with its absorption spectrum, indicating an emission yield independent of the vibronic level excited. The apparently unique behavior of octatetraene in the free jet may in part be attributed to differences in the excited-state vibronic levels accessed in jet and static vapor measurements. Further understanding of these effects as well as the role of molecular structure in determining relaxation pathways clearly will require additional experimental attention.

The excitation spectrum of the 1^1B_u state of jet-cooled decatetraene closely resembles the excitation[10] and absorption[8] spectra of octatetraene obtained under similar conditions. Our assignments of the vibronic bands (Table I) follow those of Leopold et al.[8] for octatetraene. The a_g (symmetry allowed) in-plane angle deformations[25] at 132, 273, and 405 cm^{-1} occur at 197, 348, and 547 cm^{-1} in octatetraene. The decrease in frequency can be explained by the added reduced mass of the methyl groups in decatetraene. The dominant 1230- and 1651-cm^{-1} modes are assigned to totally symmetric carbon–carbon single- and double-bond stretches.[1,4] The high relative intensity of the (0–0) transition indicates that, as in octatetraene and other long polyenes, the geometry of the 1^1B_u state must be very similar to that of the 1^1A_g ground state.

The observation of discrete but broad single vibronic transitions that can be fit by Lorentzian functions is characteristic of homogeneous broadening due to S_2/S_1 interstate coupling in the

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statistical limit.[26,27] Similar statistical limit behavior has been observed previously for the S_2 state of a number of large organic molecules such as phenanthrene,[28] porphyrins,[29,30] and free-base porphine.[31] In each of these molecules the S_2–S_1 energy difference is greater than 4000 cm^{-1} and the Lorentzian absorption line shapes have widths in the range 1.5–20 cm^{-1}.

For decatetraene the contribution of laser line width (~0.35 cm^{-1} for the second harmonic) and of the rotational contour (<2–3 cm^{-1} under these expansion conditions) to the observed profiles can be neglected. In addition, great care has been taken to avoid saturation effects. Sequence congestion can be ruled out in this ultracold environment as shown by the independence of the line shapes on the expansion conditions. The (0–0) band has a Lorentzian fwhm of 22 cm^{-1}. In the statistical limit the homogeneous line width is given by[26,27]

$$\Gamma_\nu = 1/2\pi c\tau \qquad (1)$$

where Γ_ν is the line width in cm^{-1}, c is the speed of light in cm s^{-1}, and τ is the nonradiative decay time in seconds. This gives a nonradiative decay time of ~0.25 ps for the zero-point level of the 1^1B_u state of decatetraene.

Lorentzian line shapes also have been observed in the excitation[10] and absorption spectra[8] of the $1^1A_g \rightarrow 1^1B_u$ transition of jet-cooled octatetraene and can be interpreted similarly in terms of statistical limit behavior. Leopold et al.[8] reported a line width of 18 cm^{-1} for the (0–0) transition, giving a nonradiative lifetime of 0.3 ps. The 35-cm^{-1} bandwidth in the fluorescence excitation spectrum reported by Heimbrook et al.[10] subsequently[11] was found to be an overestimate of the homogeneous line width due to the effects of saturation broadening. The fwhm of the (0–0) was found to be 12 cm^{-1}, corresponding to a nonradiative lifetime of 0.4 ps. From the integrated absorption intensity, the intrinsic radiative lifetime of the 1^1B_u states of decatetraene and octatetraene have been estimated to be 1.8 (ref 32) and 1.5 ns,[11] respectively. This indicates $S_2 \rightarrow S_0$ fluorescence quantum yields of $<10^{-4}$. For both molecules the line widths increase with increasing excitation energy, suggesting an increase in the rate of internal conversion from S_2 to S_1 with excess vibrational energy, though the broadening also may be due to intrastate anharmonic coupling (intramolecular vibrational redistribution).

It is tempting to extend our analysis of vibronic bandwidths to the free-jet absorption spectra of hexatriene and butadiene.[9] The width of the $1^1A_g \rightarrow 1^1B_u$ electronic origin increases from 18 cm^{-1} in octatetraene to 155 cm^{-1} in hexatriene to ~1000 cm^{-1} in butadiene. Various mechanisms for this broadening have been discussed by Leopold et al.,[9] including the possibility that the observed line widths may be related to the excited-state lifetimes. In the statistical limit the bandwidths would correspond to 2^1B_u lifetimes of 80 fs for hexatriene and 5 fs for butadiene. These short lifetimes clearly are consistent with the lack of detectable S_2 emissions in shorter polyene systems and presumably are due to rapid internal conversion processes.[33] If the internal conversion were from S_2 to S_1, then the vibronic states thus populated must also undergo rapid nonradiative decay, since S_1 emission is not observed either. Alternatively, as suggested by Leopold et al.,[9] fast $S_2 \rightarrow S_0$ internal conversion may be the dominant nonradiative channel.

It is important to point out that the expected lowering of the S_2–S_1 energy gap in the shorter polyenes may mean that their behavior is better described in terms of intermediate case coupling[17,19,34-36] between the S_2 and S_1 states. This also would account for the wide vibronic bands in the absorption spectra of shorter polyenes and would imply that the absence of fluorescence is due to rapid nonradiative decay of the mixed S_2/S_1 state. However, intermediate case coupling should give rise to irregular, closely spaced spectral structure on top of a broad background. This was not observed in the spectra reported by Leopold et al.,[9] though the resolution employed in their studies (~10 cm^{-1} for butadiene) may have been insufficient to observe such details.

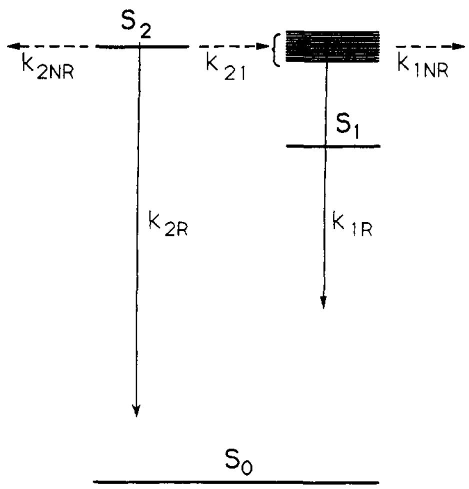

Figure 6. Energy levels and relaxation pathways for gaseous tetraenes and pentaenes. The S_2 level indicated represents any of the (1^1B_u) vibronic levels (including the zero-point level) shown in Figure 4.

We now must try to relate the free-jet experiments on octatetraene and decatetraene to the trends observed in the static gas emissions of hexatriene (emission from neither S_1 or S_2), octatetraene (emission from S_2), decatetraene (emission from both S_1 and S_2), and diphenyloctatetraene (emission from S_1). The kinetic scheme summarized in Figure 6 leads to the following expression:

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

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

The increase in the quantum yield ratio in going from octatetraene to decatetraene is most likely related to an increase in k_{21}, assuming that k_1 and k_{1r}/k_{2r} should be about the same for octatetraene, nonatetraene, and decatetraene. Given the almost identical S_2–S_1 energy gaps for the three tetraenes (6300–6600 cm^{-1}), the increase in k_{21} then might be ascribed to the larger density of S_1 vibronic states in the methyl-substituted systems. This model also accounts for the even larger increase in the quantum yield ratio in dodecapentaene and the complete dominance of S_1 emission in gaseous diphenyloctatetraene.[20] The phenyl-substituted compound has a much larger density S_1 vibronic states that are isoenergetic with low-energy vibronic levels of S_2, and the smaller energy gap ($E(S_2) - E(S_1) = 5600 \pm 300$ cm^{-1})[37] should make k_{21} even larger.[27] Given the rather high densities of S_1 vibronic states in all of these molecules, the density of states argument may be plausible if only a fraction of the isoenergetic S_1 levels are effectively coupled to S_2. Methyl or phenyl groups thus might play specific roles in interstate coupling in addition to simply increasing the density of vibronic levels.

Our analysis of vibronic line widths indicates similar subpicosecond S_2 lifetimes for octatetraene and decatetraene, suggesting

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that these molecules have comparable k_{21} values, at least in supersonic jets. It thus is not obvious from the lifetimes why the methyl-substituted compounds show such a significantly larger proportion of S_1 emission (Φ_1/Φ_2 increases by an order of magnitude in adding two methyl groups). This in part might be attributed to the differences between the vibronic states accessed in exciting room-temperature gases compared with supersonic jets, though our experiments indicate that Φ_1/Φ_2 is comparable for the two experiments. Another way to explain these effects is to assume that k_{1nr}, k_{2nr}, and/or k_{1r}/k_{2r} change systematically upon methyl or phenyl substitution. However, the fluorescence yield and lifetime data currently available (mainly obtained on polyene solutions[1]) are not of sufficient accuracy to evaluate such trends.

In addition to the obvious pitfalls in interchanging data from free jets, static gases, and solutions, we also must stress that the wide variation in polyene quantum yields and lifetimes, even for similar conditions, awaits further experimental attention. The discrepancies between previous studies would very much benefit from direct measurements of S_1 lifetimes and quantum yields in both static gases and free jets. These numbers also should indicate whether the relative increase in S_1 fluorescence in the methyl-substituted and longer polyenes is due to enhanced $S_2 \rightarrow S_1$ internal conversion, changes in the rates of S_1 and S_1 nonradiative decays, or unexpected changes in the ratio of radiative rate constants. Measurement of S_2 lifetimes, while considerably more difficult, would provide the crucial test of the line-width analysis presented above.

Conclusions

The work described here provides the first evidence for the existence of the low lying 2^1A_g state in unsubstituted, gaseous tetraenes and pentaenes. In addition, we have shown that the $S_2 \rightarrow S_0$ and $S_1 \rightarrow S_0$ emission intensities exhibit systematic dependences both on the extent of substitution and on polyene length. The free-jet spectra of decatetraene suggest that the interaction between S_2 and S_1 states in longer polyenes can be treated in the statistical limit. However, the limited, and in some cases conflicting, gas-phase data now available do not allow us to draw a simple picture of the mechanisms by which simple polyenes undergo electronic relaxation. Further work is required to provide reliable lifetime and quantum yield data on unsubstituted and methyl-substituted polyenes under similar experimental conditions.

A review of previous work points to the difficulty in obtaining accurate values for absolute quantum yields, especially in the gas phase. It thus is important to stress that the *dual* fluorescences of the tetraenes and pentaenes offer some critical advantages in unraveling the kinetics and mechanisms of excited-state relaxation. As shown by eq 2, the fluorescence lifetime and quantum yield *ratio* can be used to calculate the rate of internal conversion between S_2 and S_1. Lifetimes and quantum yield ratios both can be measured very accurately, even for polyenes in gases and jets. The observation of two emitting states thus avoids the formidable problems in measuring the absolute fluorescence yields of unstable vapors.

The discovery of $2^1A_g \rightarrow 1^1A_g$ emission in gaseous tetraenes and pentaenes means that the 2^1A_g states of these polyenes now can be studied under isolated molecule conditions. One- and two-photon fluorescence excitation spectroscopy, single vibronic level fluorescence spectroscopy, and fluorescence lifetime measurements in supersonic jets should provide considerable information on the excited-state structures and dynamics of simple polyene systems. We recently have extended the free-jet experiments described here to obtain the one-photon $1^1A_g \rightarrow 2^1A_g$ fluorescence excitation spectrum and single vibronic level decay kinetics of isolated decatetraene.[38] After submission of this paper, we learned of Buma et al.'s detection of the $1^1A_g \rightarrow 2^1A_g$ transition in *cis*-hexatriene using multiphoton ionization techniques.[39] The fluorescence and ionization techniques clearly are complementary and together should lead to a better understanding of excited electronic states and the relaxation dynamics (including photoisomerization pathways) of model polyenes.

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Registry No. 1,3,5,7-Octatetraene, 1482-91-3; 1,3,5,7-nonatetraene, 31699-36-2; 2,4,6,8-decatetraene, 2423-96-3; 2,4,6,8,10-dodecapentaene, 2423-78-1.

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