Fluorescence excitation spectra of the S_1 states of isolated trienes

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The study of the low lying states of linear polyenes is vitally important for the understanding of photobiological processes, including energy transfer in photosynthesis, *cis-trans* photoisomerization in visual systems and photosynthetic bacteria, and the photochemistry of vitamin D.[1-5] The complexity of the naturally occurring polyenes inhibits both computational and experimental investigations of these molecules. The research emphasis thus has moved towards model systems with similar but simpler chromophores and analogous photochemical behaviors.[1,2] The relative simplicity and availability of dienes, trienes, and tetraenes has meant that they have received much attention from experimentalists and theoreticians. Tetraenes have yielded a considerable amount of experimental data on the structure and dynamics of linear polyenes in the S_1 and S_2 states in solution and under isolated conditions.[1,6-9] However, theoretical calculations on tetraenes and longer polyenes are limited by the unusually large amount of electron correlation required to describe accurately the S_1 states.[1,2] Higher level calculations have been applied to dienes and trienes,[2,10-15] but theoretical predictions of S_1 state structure and dynamics have been difficult to verify. The weak, symmetry forbidden $S_1 \leftarrow S_0$ ($2\,^1A_g \leftarrow 1\,^1A_g$) transition is not easily detected in absorption, and, in contrast to tetraenes and longer polyenes, the apparent lack of emission in dienes and trienes prevents the study of their S_1 states by more sensitive fluorescence techniques.[16] The fast nonradiative decay in dienes and trienes has been attributed to enhancement of coupling between the S_1 and S_0 states by distortions of the S_1 states from their planar ground state geometries.[2,10,11,13] Current experimental and theoretical evidence for fast nonradiative decay in trienes has led to the consensus that triene S_1 states do not fluoresce.[1,2,17]

Encouraged by the recent observation of fluorescence from the S_1 states of tetraenes and pentaenes,[6,9] and the measurement of the resonance enhanced multiphoton ionization (REMPI) $S_1 \leftarrow S_0$ spectra of several trienes by Buma *et al.*,[18,19] we have attempted to observe fluorescence from several trienes under isolated conditions. We report here the successful observation of the fluorescence excitation (FE) spectra of the S_1 state of hexatriene and ocatriene. The FE spectra, emission lifetimes, and relative emission quantum yields for trienes and tetraenes allow some preliminary conjectures on the dynamics of the S_1 states in short, isolated polyenes.

The experimental setup used to measure fluorescence excitation spectra under collision free conditions has been described previously.[6] The apparatus consists of (i) a vacuum chamber equipped with a pulsed valve, for production of the molecular beam, (ii) an excimer-pumped dye laser for excitation of the molecule under study, and (iii) emission collection optics and detection electronics.

Hexatriene (Aldrich) contained a mixture of *cis-* and *trans-*isomers and was used as received. The octatriene sample was prepared by the Wittig reaction between hexadienal (Aldrich) and ethyltriphenylphosphonium bromide (Fluka) using a method similar to that described previously for the synthesis of *all-trans*-decatetraene.[6] Analysis of the sample by GC/MS and HPLC showed it to contain an isomeric mixture which was ~90% *all-trans*-octatriene together with at least two *cis*-isomers. The trienes were coexpanded with He carrier gas through the 500 μm orifice of the pulsed valve into the vacuum chamber. The sample reservoir was maintained at room temperature, which gave sufficient vapor pressures of both trienes to observe FE spectra in a molecular beam.

The excitation source was an excimer-pumped dye laser system. The frequency-doubled output of a rhodamine 6G dye was used to excite the S_1 states of the trienes. The frequency and time resolution was limited by the ~0.3 cm^{-1} band width and ~15 ns pulse width of the laser. The data were acquired for 10 laser shots for each frequency interval of ~0.3 cm^{-1}. The dye laser wavelength was calibrated against the optogalvanic spectrum of neon. The laser and molecular beams crossed 15 mm from the nozzle orifice. The laser beam was gently focused so as to maximize the signal without saturating the transitions. The fluorescence was collected by an $f/1$ quartz lens and detected by a PMT tube. The signal was gated and integrated with a boxcar and then passed to a microcomputer along with a monitor of the laser intensity for normalization and signal averaging. Fluorescence decays traces were recorded and averaged 200 times using a digital oscilloscope and transferred to a computer for analysis.

The FE spectrum of isolated hexatriene is shown in Fig. 1. The positions and relative intensities of the peaks are given in Table I. Based on the assignment of the REMPI spectrum, the FE spectrum is due to the *cis*-isomer.[18] The origin region consists of two major peaks separated by ~5.7 cm^{-1}. This doublet shows further structure due to partially resolved rotational features. Changing the expansion conditions affects the rotational structure, however, the relative integrated intensities of the two bands are not affected. The rotational line shapes of the origin bands are consistent with a predominantly parallel transition of *cis*-hexatriene. The $^1A_1 \leftarrow \,^1A_1$ transition is allowed for a molecule with a C_{2v} symmetry, however, a perpendicular band is expected. This spectrum appears to be deriving strength by intensity borrowing from the $S_2 \leftarrow S_0$ transition as is the case for *all-trans* polyenes for
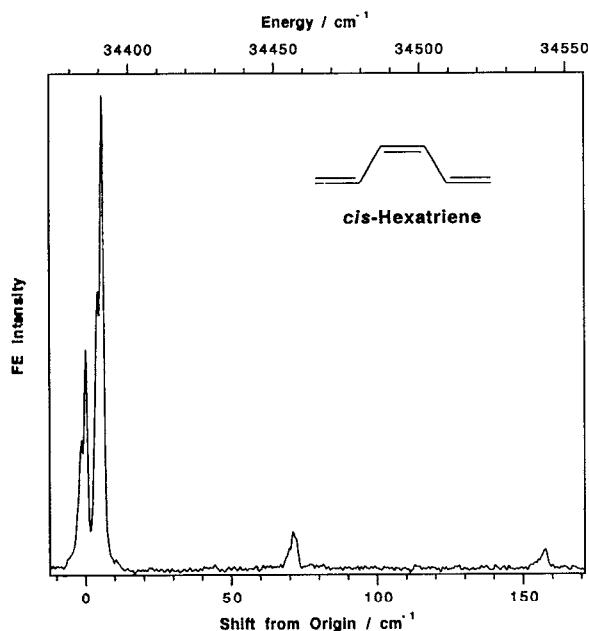
FIG. 1. The fluorescence excitation spectrum of hexatriene. The abscissa shows both absolute energy and energy shift from the origin. The molecular beam was formed by coexpanding hexatriene with helium at a pressure of 575 Torr. The origin is at 34 384 cm^{-1}.

which the $2\,^1A_g \leftarrow 1\,^1A_g$ transition is symmetry forbidden.[1] Analogous observation of parallel bands in the $2\,^1A_g \leftarrow 1\,^1A_g$ spectrum of diphenylbutadiene also has been ascribed to mixing between the $2\,^1A_g$ and $1\,^1B_u$ states.[20]

The ratio of the FE spectrum intensity relative to the REMPI spectrum[18] drops rapidly between the peaks at 71.3 and 157.7 cm^{-1} (Table I). Since the hexatriene lifetimes are shorter than the experimental time resolution, these intensity ratios provide indirect evidence of a nonradiative decay channel that requires an activation energy between 71.3 and 157.7 cm^{-1}, as will be explained below. Due to a rapid decrease in the fluorescence quantum yields, the highest energy peaks which could be detected are at 247–263 cm^{-1} (not shown). However, the REMPI spectrum is seen to increase in intensity for >4000 cm^{-1} above the origin.[18]

The fluorescence excitation spectrum of octatriene, as well as the fluorescence lifetimes measured at several peaks

TABLE I. The frequencies, relative integrated intensities, and the ratios of FE to REMPI (Ref. 18) integrated intensities for the major peaks in the $2\,^1A_g \leftarrow 1\,^1A_g$ fluorescence excitation spectrum of hexatriene. All intensity measurements are relative to the peak at 5.7 cm^{-1}.

Frequency (cm^{-1})	Relative intensity	FE/REMPI
0 (34 384.7 cm^{-1}) [a]	49.7	0.94
5.7	100.0	1.00
71.3	11.5	0.96
157.7	5.5	0.45
247–263 [b]	2.2	0.2

[a] The origin is assigned to the lowest energy peak, as opposed to the more intense peak of the doublet at the origin as in Ref. 18.
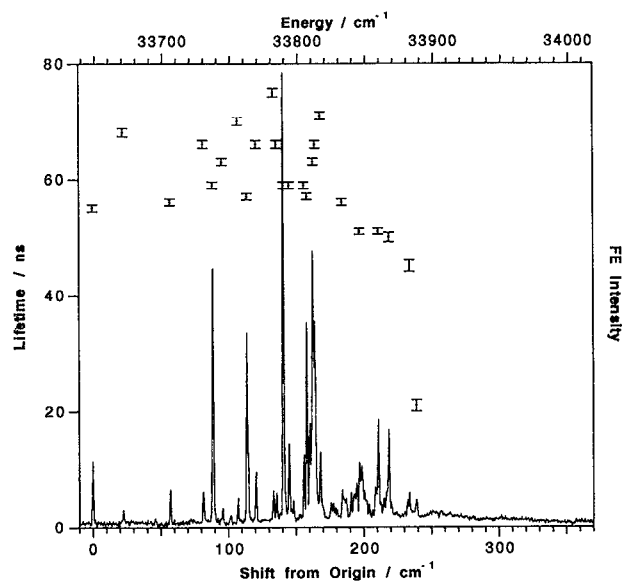[b] Due to low intensity of the FE spectrum, the peaks in this region are considered as a group.

FIG. 2. The fluorescence excitation spectrum of octatriene. The abscissa shows both absolute energy and energy shift from the origin. Also shown are lifetimes for the major peaks. The error bars correspond to one standard deviation determined from the fit of the fluorescence decays to single exponentials. The origin is at 33 648 cm^{-1}.

are shown in Fig. 2. The frequencies, intensities, and lifetimes of stronger peaks are given in Table II. Qualitatively, the FE spectrum is similar to the REMPI spectrum of a cis-octatriene isomer.[19] The smaller fluorescence yields of other isomers that are present in the sample precludes their detection in our experiments. In the REMPI study, the

TABLE II. The frequencies, relative peak intensities, and lifetimes of major peaks in the $2\,^1A_g$ fluorescence excitation spectrum of octatriene. All intensity measurements are relative to the peak at 141 cm^{-1} above the origin.

Frequency (cm^{-1})	Relative intensity	Lifetime (ns)
0 (33 648 cm^{-1})	14.4	55
22	3.4	68
57	8.3	56
82	7.5	66
89	56.7	59
96	3.9	63
107	6.1	70
114	42.6	57
121	11.7	66
134	7.4	75
136	7.2	66
141	100.0	59
145	17.8	59
156	15.8	59
158	45.1	57
163	60.7	63
164	45.3	66
168	16.3	71
184	7.4	56
197	14.1	51
211	23.4	51
219	21.3	50
234	7.2	45
239	5.7	21

overlap of spectra belonging to two distinct *cis*-isomers obscures the origin of the spectrum belonging to the fluorescent isomer observed in the FE spectrum. The origin which Buma *et al.* assigned to this spectrum at 33 562 cm^{-1} is not observed,[19] therefore, we reassign the origin to the lowest energy feature in FE spectrum, i.e., at 33 648 cm^{-1}. Further differences arise at the high energy end, where the FE spectrum rapidly drops in intensity to below the detection limit, while the REMPI spectrum has further vibrational structure followed by a rising continuous absorption.[19]

The octatriene fluorescence lifetimes measured for states with < 200 cm^{-1} excess energy show a reproducible scatter about an average of 63 ns. This may be due the vibrational dependence of radiative and nonradiative decay rates, or possibly due to the presence of two or more octatriene isomers. The marked decrease in the fluorescence lifetimes shown in Fig. 2 coincides with the drop in FE spectral intensity relative to the REMPI spectrum.[19] This implies a sudden decrease in the fluorescence quantum yields as in hexatriene.

Even though the S_1 states of hexatriene and octatriene have similar electronic structures, their spectra are remarkably different. The hexatriene spectrum is simpler, but splitting of most lines, including the origin, into two or more peaks, indicates that the S_1 state surface has some complex features. Buma *et al.* made a proposal supported by *ab initio* calculations that this splitting is due to out-of-plane distortion of the terminal hydrogens which give rise to two distinct geometries in the S_1 state.[18]

The presence of the methyl groups make the spectrum of octatriene significantly more complex than that of hexatriene. This difference is reminiscent of the differences between the $T_1 \leftarrow S_0$ spectra of glyoxal and biacetyl. It was proposed that the methyl groups in biacetyl undergo a 60° torsion upon the $T_1 \leftarrow S_0$ excitation.[21] The phenomenally large number of lines observed in the first 250 cm^{-1} of the octatriene spectrum implies a large geometrical change upon $S_1 \leftarrow S_0$ excitation, most likely torsion of the methyl groups. In addition, torsion of the C=C bonds and out-of-plane bending distortions of methyl groups, that are analogous to the hydrogen bending proposed for hexatriene, also may contribute.[11,12,18]

The 15 ns upper limit for the *cis*-hexatriene S_1 state lifetime is considerably shorter than the ~350 ns decays observed for isolated *all-trans*-decatetraene and *all-trans*-nonatetraene.[6] This indicates that, even at the origin, the fluorescence quantum yield of hexatriene is significantly less than unity. Relative lifetimes as a function of vibronic energy can be deduced from ratios of relative FE to REMPI integrated intensities in Table I. The intensity of lines in the REMPI spectra mainly are dictated by the absorption of the species (assuming that the ionization rate is faster than the nonradiative decay rate and that the $S_1 \leftarrow S_0$ transition is not saturated),[18] whereas the FE spectra are controlled by the product of the absorption cross section and fluorescence quantum yield. The decrease of the intensity ratios from unity starting with peak at 157.7 cm^{-1}, implies that a nonradiative decay channel opens up

below this energy. Thus in hexatriene there are at least two processes which lead to nonradiative decay: One appears to be energy independent, and the other has an activation energy of < 157.7 cm^{-1}. Further evidence for a low barrier on the S_1 state surface may be the continuous absorption in the REMPI spectrum.[18] This continuum may be due to a rapid increase in the density of vibrational states due to the anharmonicity of the S_1 state surface, or due to the coupling between the S_1 and another dark state.

Although the octatriene lifetimes are significantly longer than those of hexatriene, their shortness (relative to the tetraenes)[6] and the variation in lifetimes in the < 200 cm^{-1} energy region may be due to nonradiative decay processes that have a weak dependence on energy and quantum state. The decrease in octatriene lifetimes and the loss of the FE spectrum intensity above 200 cm^{-1} from the origin both are indicative of nonradiative decay by barrier crossing. The transition from discrete vibrational structure to the continuous absorption seen in the REMPI spectrum at higher energies probably implies an abrupt increase in the density of states above the barrier. As in hexatriene, there is evidence for two distinct nonradiative decay mechanisms.

It is useful to compare the $S_1 \leftarrow S_0$ spectra and dynamics of the trienes and tetraenes. The FE spectra of *all-trans*-decatetraene and *all-trans*-nonatetraene show rich progressions in low frequency skeletal distortions, and carbon-carbon stretching modes, and are consistent with planar structures in their S_1 state.[6] However, the presence of many low frequency modes shows that the polyene backbone is easily distorted in the bending and torsional coordinates, as would be required for facile *trans-cis* isomerizattion. The fluorescence lifetimes of both tetraenes decrease above ~2000 cm^{-1} due to the opening of a nonradiative decay channels, with barriers that are an order of magnitude higher in energy than those observed for the trienes. For tetraenes there is strong evidence that this decay process is *trans-cis* isomerization.[6] By analogy, we tentatively assign the energy activated nonradiative decay process in trienes to torsion around the central C=C bond, which has a low barrier or no barrier in the S_1 state according to theoretical calculations.[2,10,11,13,14]

Another important issue is the identification of the isomeric species responsible for the spectra. Despite having sufficient sensitivity to detect fluorescence from one *cis*-octatriene and one *cis*-hexatriene isomers, we could find no features due to the *all-trans*-octatriene, other *cis*-isomers, or *trans*-hexatriene, which show vibrational features in the REMPI spectra.[18,19] Based on the strength of *all-trans*-decatetraene and nonatetraene $S_1 \leftarrow S_0$ spectra, the absorption strength of *all-trans*-trienes should be sufficient for the detection of an FE spectrum provided that the *trans*-isomers are fluorescent. Therefore, the species not observed in FE spectra must have significantly smaller fluorescence quantum yields, implying that *cis*-triene isomers are more stable than the *all-trans*-isomers in the S_1 state, which is contrary to what is observed for octatetraene.[8] The reason for greater stability of *cis*-trienes in the S_1 states should be investigated by theoretical calculations and the precise

structures of the fluorescent species determined by rotationally resolving and analyzing the spectra.

In conclusion, fluorescence has been observed for the first time from hexatriene and octatriene. The spectra and lifetimes provide evidence for nonradiative decay by at least two processes, one of which is independent of energy, and another which requires an activation energy of < 157.7 cm^{-1} for hexatriene and ~ 200 cm^{-1} for octatriene. We propose that this second process involves *cis-trans*-isomerization. Low barriers for nonradiative decay explain why fluorescence from trienes can only be observed when low energy vibronic levels of the S_1 state are excited under low temperature, isolated conditions. The relative stability of *cis*-trienes compared to *all-trans*-isomers in the S_1 state requires further study by high level theoretical calculations of the excited state equilibrium structures and nonradiative decay rates. The detection of fluorescence from isolated trienes significantly expands the repertoire of experimental techniques available for the study of the excited state structures and dynamics of this important family of molecules.

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