

Fluorescence excitation spectra of the S_1 states of isolated trienes

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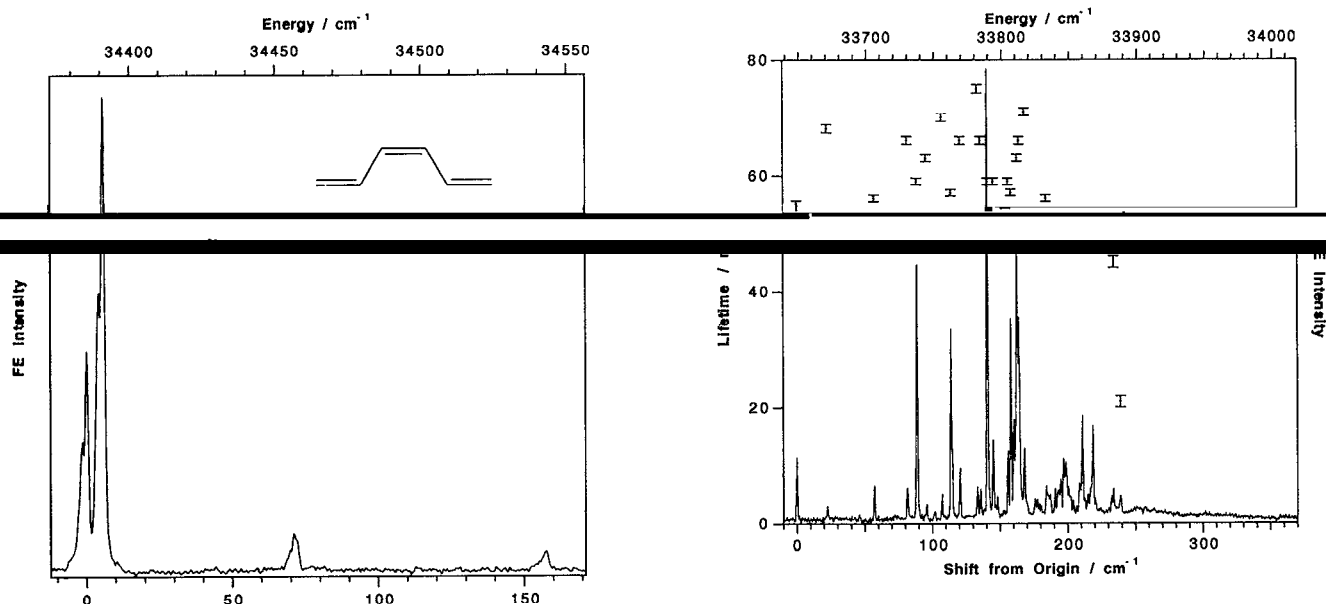


FIG. 1. The fluorescence excitation spectrum of hexatriene. The abscissa shows both absolute energy and energy shift from the origin. The molecular beam was formed by coexpanding hexatriene with helium at a pressure of 575 Torr. The origin is at $34\,384\text{ cm}^{-1}$.

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 spectrum¹⁸ drops rapidly between the peaks at

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 $33\,648\text{ cm}^{-1}$.

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

the highest energy peaks which could be detected are at $247\text{--}263\text{ cm}^{-1}$ (not shown). However, the REMPI spectrum is seen to increase in intensity for $>4000\text{ cm}^{-1}$ 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 in-

Frequency (cm^{-1})	Relative intensity	FE/REMPI
0 ($34\,384.7\text{ cm}^{-1}$) ^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

^aThe 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.

^bDue to low intensity of the FE spectrum, the peaks in this region are considered as a group.

major peaks in the $2^1A_g \leftarrow 1^1A_g$ fluorescence excitation spectrum

0 ($33\,648\text{ cm}^{-1}$)	14.7	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
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 observed. The most prominent feature in the FE spectrum is the most intense 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 $< 200 \text{ cm}^{-1}$ excess energy show a reproducible

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

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 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°

large number of lines observed in the first 2000 cm^{-1} of the open S_1 by excitation, most likely torsion of the methyl groups. In addition, torsion of the C=C bonds and out-of-plane bending distortions of the terminal hydrogens are expected to be important for the hydrogen bending proposed for hexatriene.

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

$S_1 \leftarrow S_0$ transition is not saturated), 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 nonradiative decay channels. The origin of the continuum in the REMPI spectrum.¹⁹ 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 $< 200 \text{ cm}^{-1}$ energy region may be due to nonradiative decay

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

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 coordi-

tion. The fluorescence lifetimes of both tetraenes decrease above $\sim 2000 \text{ cm}^{-1}$ due to the opening of a nonradiative decay channels, with barriers that are an order of magni-

For tetraenes there is strong evidence that this decay originates from the energy activated nonradiative decay process in trienes to torsion around the central C=C bond, which has been investigated by theoretical calculations.^{2,10,11,13,14}

meric 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

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 main

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

at least two processes, one of which is independent of energy, and another which requires an activation energy of $< 157.7 \text{ cm}^{-1}$ for hexatriene and $\sim 200 \text{ cm}^{-1}$ 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

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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