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 cm⁻¹.

which the $2 {}^{1}A_{g} \leftarrow 1 {}^{1}A_{g}$ transition is symmetry forbidden.¹ Analogous observation of parallel bands in the $2 {}^{1}A_{g} \leftarrow 1 {}^{1}A_{g}$ spectrum of diphenylbutadiene also has been ascribed to mixing between the $2 {}^{1}A_{g}$ and $1 {}^{1}B_{u}$ states.²⁰ The ratio of the FE spectrum intensity relative to the REMPI spectrum¹⁸ drops rapidly between the peaks at

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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

		welcomed below			
the highest energy peaks which could be detected at at			0 (33 046 cm)	17.T 2 A	55 40
247–263 cm ^{-1} (not shown). However, the REMPI spec-			22	3.4	00 54
trum 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			57	8.5	50
			82	1.5	50
			89	20.7	J9 42
			96	3.9	03 70
			107	0.1	70 57
			114	42.0	51
TABLE I The frequencie	e relative integrated intens		121	11.7	00
ABLE I. The frequencies, relative integrated intensities for the major neaks in			124	7 4	75
of FE to PEMPI (Paf 1)	s, relative integrated intensities for	the major peaks in	134	7.4	75
of FE to REMPI (Ref. 1) the $2^{1}A = 1^{1}A$ fluoresce	8) integrated intensities for	the major peaks in bexatrience. All in-	134 136	7.4 7.2	75 66
of FE to REMPI (Ref. 1) the $2^{1}A \leftarrow 1^{1}A$ fluoresce	8) integrated intensities for nce excitation spectrum of	thes, and the ratios the major peaks in hexatriene. All in-	134 136	7.4 7.2	75 66 59
of FE to REMPI (Ref. 1) the $2^{1}A \leftarrow 1^{1}A$ fluoresce	8) integrated intensities for nce excitation spectrum of	the major peaks in hexatriene. All in-	134 136	7.4 7.2	75 66 59
of FE to REMPI (Ref. 1) the $2^{-1}A \leftarrow 1^{-1}A$ fluoresce Frequency (cm ⁻¹)	8) integrated intensities for nee excitation spectrum of Relative intensity	the major peaks in hexatriene. All in-	134 136 141 158	7.4 7.2 100.0 45.1	75 66 59 57
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of FE to REMPI (Ref. 1) the $2^{-1}A = 1^{-1}A$ fluoresce Frequency (cm ⁻¹) 0 (34 384.7 cm ⁻¹) ^a	Relative integrated intensities for Relative intensity 49.7	The major peaks in hexatriene. All in- FE/REMPI 0.94	134 136 141 158 163 164	7.4 7.2 100.0 45.1 60.7 45.3	75 66 59 57 63 66
of FE to REMPI (Ref. 1) the $2^{-1}A = 1^{-1}A$ fluoresce Frequency (cm ⁻¹) 0 (34 384.7 cm ⁻¹) ^a 5.7	Relative integrated intensities for Relative intensity 49.7 100.0	The major peaks in hexatriene. All in- FE/REMPI 0.94 1.00 0.96	134 136 141 158 163 164 168	7.4 7.2 100.0 45.1 60.7 45.3 16.3	75 66 59 57 63 66 71
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of FE to REMPI (Ref. 1) the $2^{+1}A = 1^{+1}A$ fluoresce Frequency (cm ⁻¹) 0 (34 384.7 cm ⁻¹) ^a 5.7 71.3 157.7 247.262 ^b	49.7 100.0 11.5 5.5 2.2	Ities, and the ratios the major peaks in hexatriene. All in- FE/REMP1 0.94 1.00 0.96 0.45 0.2	134 136 141 158 163 164 168 184 197	7.4 7.2 100.0 45.1 60.7 45.3 16.3 7.4 14.1	75 66 59 57 63 66 71 56 51
of FE to REMPI (Ref. 1) the $2^{-1}A = 1^{-1}A$ fluoresce Frequency (cm ⁻¹) 0 (34 384.7 cm ⁻¹) * 5.7 71.3 157.7 247-263 b	(Kelative integrated intensities for Relative intensity 49.7 100.0 11.5 5.5 2.2	Thes, and the ratios the major peaks in hexatriene. All in- FE/REMP1 0.94 1.00 0.96 0.45 0.2	134 136 141 158 163 164 168 184 197 211	7.4 7.2 100.0 45.1 60.7 45.3 16.3 7.4 14.1 23.4	75 66 59 57 63 66 71 56 51 51
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of FE to REMPI (Ref. 1) the $2^{-1}A \leftarrow 1^{-1}A$ fluoresce Frequency (cm ⁻¹) 0 (34 384.7 cm ⁻¹) ^a 5.7 71.3 157.7 247-263 ^b The origin is assigned to intense neak of the doub	(k) relative integrated intensities for nec excitation spectrum of Relative intensity 49.7 100.0 11.5 5.5 2.2 the lowest energy peak, as of let at the origin as in Ref.	Thes, and the ratios the major peaks in hexatriene. All in- FE/REMP1 0.94 1.00 0.96 0.45 0.2 oppposed to the more 8.	134 136 141 158 163 164 168 184 197 211 219 234	7.4 7.2 100.0 45.1 60.7 45.3 16.3 7.4 14.1 23.4 21.3 7.2	75 66 59 57 63 66 71 56 51 51 51 50 45

overlap of spectra belonging to two distinct cis-isomers ob-

below this energy. Thus in hexatriene there are at least two

est energy feature in FE spectrum, i.e., at 33 648 cm⁻¹. Further differences arise at the high energy end where the TE 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 constraint function $f_{\rm excess}$ energy show a reproducible

tion in the REMPI spectrum.¹⁰ This continuum may be due to a rapid increase in the density of vibrational states due to the annarmomenty of the S_1 state surface, of 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 tetreenee)⁶ and the variation in lifetimes in the < 200cm⁻¹ energy region may be due to nonradiative decay

tatriene isomers. The marked decrease in the hubble rescence 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 remark- able different. The hexatriene encourse is simpler, but	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 mech- anisms.
more peaks, indicates that the S_1 state surface has some complex features. Buma <i>et al.</i> made a proposal supported by <i>ub initio</i> 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	decatetraene and <i>all-trans</i> -nonatetraene show rich progres- sions 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 chose that the polyene back bone is easily distorted in the bending and torsional coor-
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°	tion. 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 magni-
Parge number of times observed in the first 200 cm - of the	FOLTED REDENTIONS TO BUS EVICENCE TO ALL TIME DECKY AND-
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groups. In addition, torsion of the C=C bonds and out-of-	trienes to torsion around the central C—C bond, which has
groups. In addition, torsion of the C=C bonds and out-of- ogous to the hydrogen bending proposed for hexatriene, also may contribute. ^{11,12,18} The 15 ns upper limit for the <i>cis</i> -hexatriene S_1 state lifetime is considerably shorter than the ~350 ns decays observed for isolated <i>all-trans</i> -decatetraene and <i>all-trans</i> -nonatetraene. ⁶ This indicates that, even at the or- igin, the fluorescence quantum yield of hexatriene is signif- icantly 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 factor than the mean diction does not east that the $S_1 \leftarrow S_0$ transition is not saturated). Whereas the FE spec- tra are controlled by the product of the absorption cross	trienes to torsion around the central C—C bond, which has theoretical calculations. ^{2,10,11,13,14} Another important issue is the identification of the iso- meric species responsible for the spectra. Despite having sufficient sensitivity to detect fluorescence from one <i>cis</i> - octatriene and one <i>cis</i> -hexatriene isomers, we could find no features due to the <i>all-trans</i> -octatriene, other <i>cis</i> -isomers, or <i>trans</i> -hexatriene, which show vibrational features in the REMPI spectra. ^{18,19} Based on the strength of <i>all-trans</i> - decatetraene and nonatetraene $S_1 \leftarrow S_0$ spectra, the absorp- tion strength of <i>all-trans</i> -trienes should be sufficient for the detection of an FE spectrum provided that the <i>trans</i> -iso- mers are fluorescent. Therefore, the species not observed in FE to the the <i>all-trans</i> -isomers in the S_1 state, which is

	structures of the fluorescent energies determined by rote	20 Oslandi E. Techetta and M. T. Teiserlii Ohen Der Of 967
	tionally resolving and analyzing the spectra. In conclusion, fluorescence has been observed for the first time from hexatriene and octatriene. The spectra and	(1991). ³ M. Mimuro and T. Katoh, Pure Appl. Chem. 63 , 123 (1991). ⁴ R. R. Birge, Biochim. Biophys. Acta 1016 , 293 (1990).
	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 <i>cis-trans</i> -isomer- ization. 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	 Grosjean (Wiley, New York, 1979), pp. 305-374. ⁶H. Petek, A. J. Bell, K. Yoshihara, and R. L. Christensen, J. Chem. Phys. 95, 4739 (1991); H. Petek, A. J. Bell, K. Yoshihara, and R. L. Christensen (in preparation); H. Petek, A. J. Bell, H. Kandori, K. Yoshihara, and R. L. Christensen, <i>Time Resolved Vibrational Spectroscopy V</i> edited by H. Takahashi (Springer-Verlag, Berlin, in press) ⁷R. M. Gavin, C. Weisman, J. K. McVey, and S. A. Rice, J. Chem. Phys. 68, 522 (1978). ⁸B. F. Kohler, P. Mitra, and P. West, J. Chem. Phys. 85, 4436 (1986).
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